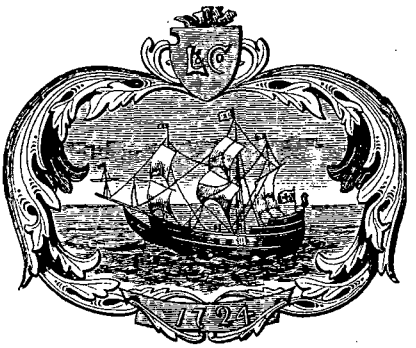
# A COMPREHENSIVE TREATISE ON INORGANIC AND THEORETICAL CHEMISTRY

BY
J. W. MELLOR, D.Sc.

VOLUME VI




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# PREFACE

THE greater part of this volume is devoted to the silicates which, in turn, are closely connected with mineralogy. In the original design of this work—many years backwards—it was not intended to devote so much space to the minerals, but no sound reason could be found for excluding the purer minerals from inorganic chemistry. It is merely an *accidental* circumstance that the majority of the silicates has been made in Nature's laboratory where she is continually carrying on an endless variety of chemical operations, the results of which, like those which obtain in our own laboratories, belong to the domain of chemistry. No one doubts that the minerals have been formed by the operations of the very same laws as those which are recognized in general chemistry. On its chemical side, therefore, mineralogy is a subordinate branch of inorganic chemistry.

In many of the legal cases tried in the courts in connection with the so-called "mineral rights," it has been instructive to see how difficult it has been to get a definition of a mineral which can hold its own against the cross-examination of the opposing counsel. Those accustomed to declaim only before passive listeners-in are sometimes bewildered by the conflict of testimony which is more or less dominated by training, temperament, interests, and desires. From the chemical side, the definition is neither more nor less difficult than is the definition of a chemical compound discussed in the second chapter of this work.

An appalling number of analyses have been reported for many minerals. As a result, the chemist can regard most minerals only as more or less "dirty compounds." To continue the language of the laboratory, Nature has used dirty beakers and dirty solvents in the production of minerals, and she has not always preserved her products from contamination after they have been made. These "dirty compounds" have often received different names, and even different names with different degrees of contamination. It is therefore a problem for the mineralogist to select a kind of representative or idealized mineral from a mass of analyses of contaminated products.

The difficulties which have attended the efforts to find the essential *composition* of a mineral have been accentuated when the attempt has been made to elucidate its *constitution*. In particular cases, owing to the paucity of relevant facts, quite a number of opposing hypotheses has been defended. There is a temptation to solve or perhaps evade many of the difficult problems by regarding the untractable minerals as solid solutions of a number of simpler components. So long as the constitution of a mineral has not been completely elucidated, it is better to employ the mineralogist's term in place of a systematic name; otherwise, as in the case of some compounds in organic chemistry, the name adopted will depend on the particular hypothesis which happens to be in fashion at the time. I cannot help taking the opportunity of expressing my appreciation of the valuable work being done under Dr. A. L. Day at the Geophysical Laboratory, Carnegie Institution of Washington. Here a good start has been made in introducing order in the mineralogical chaos.

The chapter on carbon does not include those hydrocarbons, and their derivatives commonly but arbitrarily admitted into inorganic chemistry; the cyanides and

complex cyanides; nor does it include the combustion of the hydrocarbons. These subjects may later be discussed in a supplementary volume.

I greatly appreciate the kindness of my colleagues—Dr. A. Scott, Mr. H. V. Thompson, and Mr. A. T. Green—who have read the proofs of this and the previous volumes; of Mr. A. Rigby, who has also read all the volumes; of Mr. F. H. Clews, who has read from Vol. III; of Mr. L. S. Theobald, from Vol. IV; and of Mr. A. J. Dale, from Vol. V.

J. W. M.

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# ABBREVIATIONS

aq. = aqueous

atm. = atmospheric or atmosphere(s)

at. vol. = atomic volume(s)

at. wt. = atomic weight(s)

T° or °K = absolute degrees of temperature

b.p. = boiling point(s)

$\theta$° = centigrade degrees of temperature

coeff. = coefficient

conc. = concentrated or concentration

dil. = dilute

eq. = equivalent(s)

f.p. = freezing point(s)

m.p. = melting point(s)

mol(s) = {gram-molecule(s) / gram-molecular

mol(s). = {molecule(s) / molecular

mol. ht. = molecular heat(s)

mol. vol. = molecular volume(s)

mol. wt. = molecular weight(s)

press. = pressure(s)

sat. = saturated

soln. = solution(s)

sp. gr. = specific gravity (gravities

sp. ht. = specific heat(s)

sp. vol. = specific volume(s)

temp. = temperature(s)

vap. = vapour

In the **cross references** the first number in clarendon type is the number of the volume; the second number refers to the chapter; and the succeeding number refers to the "§," section. Thus **5**. 38, 24 refers to § 24, chapter 38, volume 5.

The *oxides, hydrides, halides, sulphides, sulphates, carbonates, nitrates, and phosphates* are considered with the basic elements; the other compounds are taken in connection with the acidic element. The double or complex salts in connection with a given element include those associated with elements previously discussed. The carbides, silicides, titanides, phosphides, arsenides, etc., are considered in connection with carbon, silicon, titanium, etc. The intermetallic compounds of a given element include those associated with elements previously considered.

The use of **triangular diagrams** for representing the properties of three-component systems was suggested by G. G. Stokes (*Proc. Roy. Soc.*, **49**. 174, 1891). The method was immediately taken up in many directions and it has proved of great value. With practice it becomes as useful for representing the properties of ternary mixtures as squared paper is for binary mixtures. The principle of triangular diagrams is based on the fact that in an equilateral triangle the sum of the perpendicular distances of any point from the three sides is a constant. Given any three substances *A*, *B*, and *C*, the composition of any possible combination of these can be represented by a point in or on the triangle. The apices of the

triangle represent the single components $A$, $B$, and $C$, the sides of the triangle represent binary mixtures of $A$ and $B$, $B$ and $C$, or $C$ and $A$; and points within the triangle ternary mixture. The compositions of the mixtures can be represented in percentages, or referred to unity, 10, etc. In Fig. 1, pure $A$ will be represented by a point at the apex marked $A$. If 100 be the

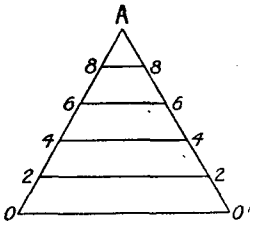



FIG. 1.

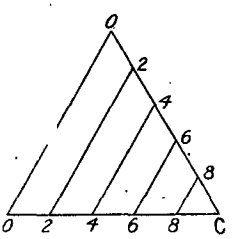



FIG. 2.

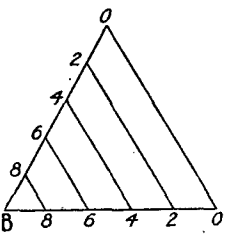



FIG. 3.

standard of reference, the point $A$ represents 100 per cent. of $A$ and nothing else; mixtures containing 80 per cent. of $A$ are represented by a point on the line 88, 60 per cent. of $A$ by a point on the line 66, etc. Similarly with $B$ and $C$—Figs. 3 and 2 respectively. Combine Figs. 1, 2, and 3 into one diagram by superposition, and Fig. 4 results. Any point in this

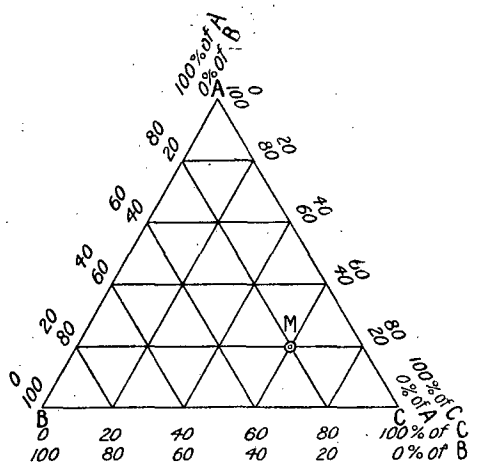



FIG. 4.—Standard Reference. Triangle.

diagram, Fig. 4, thus represents a ternary mixture. For instance, the point $M$ represents a mixture containing 20 per cent. of $A$, 20 per cent. of $B$, and 60 per cent. of $C$.

# CHAPTER XXXIX (*continued*)

## *CARBON* (*continued*)

### § 30. The History of Carbon Dioxide

In the first century of our era, Pliny[1] mentioned the exhalation of lethal vapours —*spiritus lethales*—from caverns, like the Grotto del Cane, etc. It was also known that the mild alkalies gave off a gas with effervescence when treated with acetic acid or vinegar—*vide* **2**. 20, 1 No one, however, recognized that these phenomena were produced by specific gases. A. Libavius, in 1597, also noted the acidic qualities of certain mineral waters which he attributed to the presence of an imponderable *spiritus* of great volatility. Shortly afterwards, J. B. van Helmont, who had *l'immortelle gloire de révéler scientifiquement l'existence de corps invisible et impalpables—les gaz,* pointed out that:

> Carbon, and, in general, bodies which cannot be immediately resolved into water necessarily give off, during combustion, *spiritus sylvestris—vide* **1**. 3, 1. Sixty-two parts of oak-charcoal leave one part of ash, and the remaining sixty-one parts produce the *spiritus sylvestris*.

In addition to the formation of *gas sylvestre* (i) by the combustion of carbon, and (ii) during fermentations, J. B. van Helmont showed that (iii) it is also formed when calcareous stones are treated with distilled vinegar; and (iv) it is found in the air of caverns, mines, and cellars. (v) Mineral waters like those of Spa disengage the gas sylvestre when exposed to the air; and (vi) the flatus produced by the digestion of food and by the excrement is gas sylvestre: J. B. van Helmont called gas sylvestre many names—*gas carbonum, gas vinorum, gas uvarum, gas musti,* etc. C. Wren, and J. Bernoulli made some confirmatory observations, and F. Hoffmann in his work on mineral waters often alludes to this gas as the *principium spirituosum, spiritus mineralis,* and less frequently as the *spiritus sulphureus, spiritus æthereus,* and *spiritus elasticus.* He discovered that when charcoal is burnt it dissolves in the atmosphere producing choke-damp; and he noted that like acids, the soln. of the gas in water reddens blue-coloured extracts of plants. The subject was discussed by F. Venel, J. F. Demachy, etc. R. Boyle noted the evolution of an air—*factitious air*—when corals or oyster shells are treated with vinegar, and in fermentations. S. Hales made some observations on this gas in 1727; H. Boerhaave, in 1732, emphasized the suffocating effects of gas sylvestre, although this quality had been noted by J. B. van Helmont.

J. Black's work in 1757 on the mild and caustic alkalies—*i.e.* alkali carbonates and hydroxides—showed that the causticity of quicklime was not due to the union of phlogiston with elemental chalk, but rather is chalk produced by the union of quicklime with what J. Black called *fixed air—vide* **2**. 20, 11. In 1764, D. McBride studied the formation of fixed air in fermentation and putrefaction, and its presence in blood, and in atm. air. In 1766, H. Cavendish made a number of observations on fixed air, and found that fixed air precipitates chalk from a soln. of lime-water, and that the precipitate is redissolved by the continued action of fixed air. T. Lane also examined the action of an aq. soln. of fixed air on iron and zinc. J. Priestley made some observations on the gas in 1767. Then followed, in 1774, T. Bergman's classical dissertation on the gas which he called *aerial acid*—the acid of the air. He showed that the gas behaves like acids in uniting

with bases like lime; that the gas is soluble in water, and the soln., like acids, reddens litmus; and that the gas is heavier than atm. air. He further proved that the presence of water is necessary for the union of the gas with quicklime, for, quoting an experiment by J. B. Bucquet (1773), "quicklime does not slake in fixed air but it may be instantly slaked in aerated water." J. B. M. Bucquet called the gas *acide à la craie*; J. Keir (1777), *calcareous gas*; and L. B. G. de Morveau (1782), *acide mephitique*, and the salts, *mephites—e.g.* mephite de potasse; mephite d'ammoniaque; etc. The term *gas mephitique* was elsewhere used for nitrogen, so that L. B. G. de Morveau's term was not adopted.

J. B. van Helmont assumed that the gas sylvestre in mineral water was derived from sulphur, and hence F. Hoffmann's term *spiritus sulphureus*; but G. E. Stahl (1702) did not accept this view. B. G. Sage regarded it as a kind of phlogisticated hydrochloric acid; and J. R. Deiman and P. van Troostwijk, P. J. Macquer, J. Priestley, C. W. Scheele, R. Kirwan, etc., made various suggestions in which fixed air was regarded as a combination of phlogiston with oxygen, nitrogen, or an acid. A. L. Lavoisier then showed that just as mercuric oxide is formed when mercury is heated in oxygen, so is fixed air formed when carbon is heated in that gas; and he re-christened fixed air, *acide carbonique* in harmony with the antiphlogistian's views on combustion. A. L. Lavoisier, alone, and also in conjunction with P. S. de Laplace, showed that *acide carbonique* is a compound of 23·5 to 28·9 parts of carbon with 71·1 to 76·5 parts of oxygen. A. L. Lavoisier obtained the gas by the combustion of the diamond in oxygen, and S. Tennant analyzed it in 1797. Subsequent observations are indicated in connection with the at. wt. of carbon (*q.v.*). The gas now called *carbon dioxide* was liquefied by M. Faraday in 1823, and solidified by M. Thilorier in 1835.


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## § 31. The Occurrence of Carbon Dioxide

Carbon dioxide is one of the most important of the accessory constituents of air. In 1796, H. B. de Saussure [1] directed special attention to the carbon dioxide content of the atm., and he established its presence in the mountain air of Switzerland as well as in the air of the plains. His son, N. T. de Saussure, followed up the inquiry in 1828–30, and concluded:

The quantity of carbon dioxide in the open air in the same place is subject to almost continual changes equally with the temp., the winds, the rain, and atm. press. . . . The augmentation of the average quantity of carbon dioxide in summer and its diminution in winter are manifested at different stations—in the country as in the city, upon the Lake of Geneva and upon a hill, and in calm and in disturbed air. . . . The ratio is not constant throughout the year. There are times which form exceptions, and in which the quantity of carbon dioxide in summer is inferior to that in winter, or *vice versa*. . . . The difference in the quantities of carbon dioxide contained in the atm. in calm weather, during day and night is one of the most remarkable results of my late observations—more is present during the night than during the day. . . . The air of Geneva contains more carbon dioxide than the air of a meadow at Chambeiry.

At first, N. T. de Saussure believed that rain increased the proportion of carbon dioxide, but later found that a greater proportion was present in dry weather. A few analyses are quoted in Table XXI. Collections of data have been compiled by R. A. Smith, and by E. A. Letts and R. F. Blake. According to E. L. Moss, arctic air is richer in carbon dioxide than the air of England; A. Krogh found the proportion in Greenland to vary from 2·5 to 7·0 parts per 10,000; and R. Legendre found 3·5 parts in 10,000 in ocean air off Western France. In general, however, the proportion of carbon dioxide in the atm. is very nearly constant. Atm. air contains about 3 vols. of carbon dioxide per 10,000 vols. *i.e.* 0·046 per cent. by weight. These figures may be regarded as a norm or standard of reference. According to F. W. Clarke, this norm corresponds with about 2,200,000,000,000 tons of carbon dioxide, or 600,000,000,000 tons of carbon. A. Krogh estimated the total carbon dioxide in the atm. to be $2{\cdot}4 \times 10^{12}$ tons; and C. R. van Hise, and W. Dittmar obtained similar estimates, while T. C. Chamberlin made a rather higher estimate. There are moderate variations above and below the standard. In towns, for example, the proportion is greater, and in the open country it is less; but the excessive accumulation of this gas in any one locality is prevented by the circulation induced by winds and atm. currents, *vide* atmospheric air.

TABLE XXI.—DETERMINATIONS OF THE AMOUNT OF CARBON DIOXIDE IN ATMOSPHERIC AIR.

| Locality. | Vols. of $CO_2$ per 10,000 vols. of air. | Observer. |
|---|---|---|
| Paris | 3·027 | J. A. Reiset |
| Dieppe | 2·942 | J. A. Reiset |
| Bloomington, Ind. | 2·816 | T. C. van Nüys and B. F. Adams |
| Country of Belgium | 2·944 | A. Petermann and J. Graftiau |
| Gembloux | 3·70 | A. Petermann and J. Graftiau |
| Sheffield | 3·90 | W. C. Williams |
| 1½ miles west of Sheffield | 3·27 | W. C. Williams |
| Mont Blanc, 1080 m. | 2·62 | M. de Thierry |
| Mont Blanc, 3050 m. | 2·69 | M. de Thierry |
| Belfast | 2·91 | E. A. Letts and R. F. Blake |
| Kew (max. and min.) | 2·43 to 3·60 | H. T. Brown and F. Escombe |

The chief sources of the carbon dioxide in the atm. are (i) the evolution of carbon dioxide from mineral springs, volcanoes, etc.; (ii) the combustion of fuels, thus, in 1844, J. B. J. D. Boussingault estimated that about 3,000,000 cub. metres of this gas were generated daily by the combustion of fuel, and by life in Paris, and A. Krogh estimated that about one-thousandth of its present content in carbon dioxide was added yearly to the atm. by the combustion of coal; (iii) the respiration of animals; (iv) the decay of organic matter; and (v), added F. W. Clarke, perhaps the majority of shooting stars represents the combustion of carbonaceous meteorites in the upper regions of the atm., and the consequent addition of carbon dioxide to the air. Few such meteors reach the earth. The main counterbalancing influences are (i) the decomposition of carbon dioxide by plants. H. T. Brown found that the air before passing through a vessel containing the leaves of a growing plant contained

2·80 parts of carbon dioxide per 10,000, and on leaving 1·74 parts per 10,000; the loss, 1·06, corresponded with an assimilation of 412 c.c. of carbon dioxide at n.$\theta$.p., per sq. metre of leaf surface per hour. Under constant illumination, the intake was directly proportional to the partial press. of the gas. E. H. Cook estimated that the leaf action alone more than compensates for the increase in the carbon dioxide in the atm., and without this influence, the amount of carbon dioxide in the atm. would double itself in a century. A part of the carbon dioxide withdrawn by plants is restored when the leaves decay in autumn, but a portion is withdrawn permanently. (ii) Carbon dioxide is consumed in the weathering of rocks. T. S. Hunt attempted to estimate the amount of carbon dioxide consumed in the production of china clay from orthoclase; and added that the carbon dioxide now represented by the carbonates of the earth's crust must have equalled two hundred times the entire amount in the present atm. The carbon of the coal measures and of the sedimentary rocks has all been directly or indirectly obtained from the atm. The soluble carbonates produced by weathering are washed into the ocean, and there transformed with sediments, shells, coral reefs, etc. The carbon of sedimentary rocks is estimated by F. W. Clarke to be about 30,000 times that contained in the atm., and T. C. Chamberlin estimated that 1,620,000,000 tons of carbon dioxide are annually withdrawn from the atm. in the formation of sedimentary rocks.

In 1848, T. J. Pelouze and E. Frémy pointed out that although no appreciable variation in the proportions of oxygen and nitrogen had been detected by analyses of atm. air, yet the methods of analysis are not exact, and that it is quite possible that the composition of the atm. is undergoing very slight variations which will become appreciable only after the lapse of a great number of years. J. B. A. Dumas, and J. von Liebig seem to have regarded the composition of the atm. as a fixed constant which is maintained by the mutual action of the animal and vegetable kingdoms whereby the former introduces carbon dioxide and the latter removes that gas and introduces oxygen. C. Martins, however, has shown that the supposed compensations must be fallacious when it is remembered that the quantity of oxygen consumed by the entire animal kingdom is out of all proportion to that contained in the entire globe—some 0·011 per cent. per century.

The comparatively large proportion of free oxygen in the atm. is remarkable when it is remembered what a strong affinity oxygen has for other substances—*e.g.* graphite, sulphur, pyrites, and other sulphides which occur in primitive rocks in an unoxidized state. These facts have been cited to support the thesis that *the primitive atmosphere of the earth contained no free oxygen.* It is agreed that the later deposits of coal and of the carbonate rocks were derived from the carbon dioxide formerly diffused in air and sea; and the great extent of coal deposits as contrasted with the more recent deposits of lignite and peat, has been cited to support the thesis that *a considerably larger proportion of carbon dioxide must have been present in the atmosphere during the period of the coal flora than now.* There is, however, nothing to show that this stored carbon was ever all present in the atm. at one time. It is further supposed that during this period, an evolution of oxygen from the vegetation must have occurred simultaneously with the absorption of oxygen. C. J. Koene, J. Lemberg, T. L. Phipson, Lord Kelvin, J. Stevenson, etc., argue that the earth's primitive atm. contained very little oxygen, large quantities of carbon dioxide, and possibly appreciable quantities of hydrogen, carbon monoxide, and hydrocarbon gases. In further support of the argument, it is said that no oxygen is found in the gases extracted from rocks.

According to the nebular hypothesis, the temp. of the earth was once above the dissociation point of most oxides or oxygen compounds, and therefore the earth's supply of oxygen may have been free. On cooling, the oxygen united with the elements for which it had a sufficient affinity, first with the lighter and more oxidizable elements—silicon, carbon, aluminium, calcium, magnesium, potassium, and sodium—and a large quantity of silica or silicate would be formed as a thick

surface layer hindering the passage of the remaining oxygen to the still oxidizable elements lower down. Otherwise, the graphite and sulphides found in the oldest rocks would have been oxidized. It happens that there is about 6000 times more combined than free oxygen ; so that the earth's supply has combined to the extent of 99·98 per cent. of the total, and it seems likely that all the oxygen would have so combined were it not for counteracting influences. Naturally, after the oxygen had been all consumed a considerable excess of hydrogen and hydrocarbon gases remained. This is evidenced by the spectra of the sun and stars, by the presence of metal carbides, and of occluded hydrogen in meteorites. It is then assumed that vegetation appeared—more or less anærobic—and as the vegetation increased the proportion of oxygen in the atm. likewise increased, and the proportion of carbon dioxide diminished. As time went on, the amount of oxygen increased until animal life became possible and animals appeared. Animals take in oxygen and give off carbon dioxide. The two types of organism developed until a state of equilibrium was attained. According to this hypothesis nearly all the free oxygen at present in the atm. has been derived from carbon dioxide, and has been produced by the action of sunlight on vegetation growing in an atm. of this gas.

While the cooling earth was at a high temp. no carbonates could be present ; they must have been formed after the earth had cooled. As indicated above, T. S. Hunt estimated that if all the carbon dioxide at present in the earth as carbonates were set free, the atm. would have 200 times its present amount. Such an atm. would have a much greater solvent action on silicate rocks, so that the rates of formation of carbonates and of the denudation of silicates would be greater than now. The effect of the weathering of silicate rocks is to decrease the amount of carbon dioxide and of water in air and sea. It is estimated that the water at present combined in terrestrial rocks amounts to about one-third or one-fourth of that contained in the ocean. W. Ostwald considers it probable that more carbon dioxide is withdrawn from the atm. than is restored ; as a result, there is a slow diminution of the floating carbon-capital taking place on the surface of the earth. That change must be very slow, as is exemplified by the fact that analyses extending over a century show no definite alteration.

The premises from which this story has been elaborated are not unimpeachable. The observations which have been made at high temp. in electric furnaces have shown that the oxidized compounds were not necessarily formed first. The first compounds were probably carbides, silicides, etc., and in that case, all the oxygen would be atmospheric. As illustrating the extreme case, H. Lenicque argues that the great masses of limestone were formed by the atm. oxidation of the primitive carbides. In any case, it will be evident that two equally plausible lines of argument furnish opposing conclusions—one that the primitive atm. was rich in oxygen, and the other that it was free from oxygen.

There are other hypotheses. T. S. Hunt, and A. Winchell argued in favour of an atm. of carbon dioxide drawn from celestial sources ; but there is no satisfactory evidence of this. S. Meunier combatted this hypothesis, and he favoured the assumption that the carbon dioxide was added to the primitive atm. by volcanic agencies. T. C. Chamberlin, and E. H. L. Schwarz favour the view that the planet was built up by accretion or the slow aggregation of small meteorites carrying occluded gases which formed the earth's atmosphere.

The carbon dioxide present in sea-water has been (i) absorbed from the atm. or brought down with the rain ; (ii) carried in as hydrocarbonates by river-water ; (iii) produced from decaying organic matter ; (iv) produced by the respiration of aquatic animals; and (v) derived in part from submarine volcanic springs. The gas is liberated from the hydrocarbonates when coral and shell-building organisms assimilate the normal carbonate. Carbon dioxide is therefore continuously being added to sea-water, and it is continually being lost ; it is either given up directly to the atm., or consumed in the maintenance of marine plants. T. Schlösing [2] has estimated that the ocean holds in soln. 18–27 times as much carbon dioxide as does the atm., and he regarded

the ocean as the great regulative reservoir of this gas. There is a continuous interchange of carbon dioxide between the ocean and the atm.; the gas is released from the waters in warm climates, and absorbed in cold regions. Hence the atm. supply is alternately being enriched and impoverished. The regulating action of water in maintaining the state of equilibrium necessary for the welfare of animals and plants was first pointed out by E. Péligot in his *Études sur la composition des eaux*, in 1855. The rain-water absorbs some gas from the atm., and still more on coming in contact with the soil; then carbonates are dissolved as hydrocarbonates, which eventually make their way to the ocean. C. F. Tolman has discussed the conditions of equilibrium. Analyses of the gases in sea-water have been made by O. Jacobsen, H. Tornöe, K. Natterer, etc. Usually, there is not sufficient to transform all the calcium carbonate into the hydrocarbonate. J. Y. Buchanan, and W. Dittmar found the amount of carbon dioxide in sea-water in excess of that required for the formation of normal calcium carbonate in mgrms. per litre to be, at different temp.

| | 25°–28·7° | 20°–25° | 15°–20° | 10°–15° | 5°–10° | −1·4–3·2° |
|---|---|---|---|---|---|---|
| $CO_2$ . . . | 35·88 | 37·18 | 42·68 | 43·50 | 47·21 | 53·31 |

Hence, the ocean contains less carbon dioxide in warm than in cold latitudes —the average may be taken as 45 mgrms. per litre. The variations at different depths are less marked:

| | Surface | 100 fath. | 400 fath. | 800 fath. | Over 800 fath. | Bottom |
|---|---|---|---|---|---|---|
| $CO_2$ . . . . | 42·6 | 43·6 | 41·1 | 42·2 | 44·6 | 47·4 |

G. Linck found the maximum solubility of calcium carbonate in sea-water to be 0·191 grm. per litre at 17°–18°; and W. Dittmar found the average sea-water to contain 0·121 grm. per litre. J. Johnston and E. D. Williamson considered the warm surface layers of the ocean to be practically sat. with carbonates which are subject to precipitation by changes of temp., and by fluctuations in the proportion of carbon dioxide in the atm. above. J. Y. Buchanan found that the carbon dioxide was sometimes in excess of that necessary to form hydrocarbonates, and sometimes just sufficient to convert the normal carbonates into the acid salt.

Carbon dioxide is found free or combined in mineral and spring waters [3]—*e.g.* Carlsbad, Seltzer, etc. The original *Apollinaris* is a natural water from a spring in the Valley of Aar, near the Rhine, which has carbon dioxide in soln., and an acid reaction, while the waters of Vichy, Neuenahr, etc., have an alkaline reaction although the same gas is in soln. Apollinaris and other natural waters are bottled and exported, and they are imitated artificially and sold as "mineral waters." The acidity of water containing carbonic acid plays a great part in geological changes—*vide* the weathering of silicates.

Carbon dioxide issues as a gas from many parts of the earth. C. St. C. Deville and F. le Blanc's analysis [4] of the air in the Grotta del Cane gave 70·35 per cent. $CO_2$, 23·7 per cent. $N_2$, and 6·0 per cent. $O_2$. A stratum of *spiritus lethales* is said to occupy the lower portion of the cave to a depth of about 18 inches on the floor, so that dogs, whose nostrils are near the ground, are suffocated, while men are safe. During the 1869 eruption of Vesuvius, F. Gorceix said the gas which escaped was virtually pure carbon dioxide. Pliny said that some persons call vents emitting mephitic fumes, *Charoneas scrobes*—Charon's sewers. The Poison Valley or the Valley of Death in Java is an old volcanic crater with fissures from which are evolved large quantities of carbon dioxide which fill the valley as water fills a lake. The flow is apparently intermittent because sometimes scarce a trace of gas can be found, at other times it fills the valley. A. Loudon thus describes his observations:

> We took with us two dogs and some fowls to try experiments in this poisonous hollow. On arriving at the foot of the mountain we dismounted and scrambled up the side about a quarter of a mile, holding on by the branches of trees. When within a few yards of the valley we experienced a strong nauseous suffocating smell, but on coming close to its edge

this disagreeable odour left us. The valley appeared to be about half a mile in circumference, oval, and the depth from thirty to thirty-five feet, the bottom quite flat; no vegetation; strewed with some very large (apparently) river stones; and the whole covered with the skeletons of human beings, tigers, pigs, deer, peacocks, and all sorts of birds. We could not perceive any vap. or any opening in the ground, which last appeared to us to be of a hard sandy substance. It was now proposed by one of the party to enter the valley; but at the spot where we were this was difficult at least for me, as one false step would have brought us to eternity, seeing no assistance could be given. We lighted our cigars, and, with the assistance of a bamboo, we went down within eighteen feet of the bottom. Here we did not experience any difficulty in breathing, but an offensive nauseous smell annoyed us. We now fastened a dog to the end of a bamboo eighteen feet long, and sent him in: we had our watches in our hands, and in fourteen seconds he fell on his back, did not move his limbs or look round, but continued to breathe eighteen minutes. We then sent in another, or rather he got loose, and walked in to where the other dog was lying. He then stood quite still, and in ten minutes fell on his face, and never afterwards moved his limbs: he continued to breathe seven minutes. We now tried a fowl, which died in a minute and a half. We threw in another, which died before touching the ground. During these experiments we experienced a heavy shower of rain; but we were so interested by the awful sight before us that we did not care for getting wet. On the opposite side, near a large stone, was the skeleton of a human being, who must have perished on his back, with his right hand under his head. From being exposed to the weather the bones were bleached as white as ivory. I was anxious to procure this skeleton, but any attempt to get it would have been madness.

The Death Gulch of the Yellowstone Park, Cal., is another such valley, where it is said that grizzly bears are sometimes found suffocated to death by the carbon dioxide which issues from the ground. The Laacher Sea is the water-filled crater of a prehistoric volcano, and near by is a depression filled with this gas. Birds and insects flying in this region are suffocated. The gas, issuing from outlets in the vicinity, tends to collect in the cellars of houses, where it has caused many tragedies by suffocating those who incautiously enter. The gas is also emitted from numerous fumeroles and rents in the ground in the old lavas at Brohl in the Eifel; in the caves at Pyrmont; at Lahntal near Ems; Taunus; near Driburg in Westphalia, Sondro in Thuringia, Montpensier, etc. In Auvergne in the neighbourhood of Vichy and Hauterive, the gas has been utilized in the manufacture of white-lead. The presence of carbon dioxide has been recorded in volcanic gases.[5] After an eruption at Vesuvius, the carbon dioxide has been reported to come from the ground, in the vicinity (*vide supra*), in such quantities as to asphyxiate numerous small animals and to fill the cellars of the houses. Torrents of the gas are evolved from the craters in South America. J. B. J. D. Boussingault estimated that Cotopaxi emitted more carbon dioxide annually than was produced by combustion and respiration in the city of Paris. The 1783 eruption at Skaptar Jokull, Iceland, is said to have suffocated thousands of men and hundreds of thousands of cattle. Carbon dioxide has been reported in the gases from the salt deposits at Stassfurt,[6] and in the gases from coal,[7] and soils.[8] Processes of oxidation in the soil impoverish the oxygen in the air of wells, and mines, and form carbon dioxide. It has been estimated that an acre of good garden land in summer evolves more than six tons of carbon dioxide derived from the oxidation of the organic matter in the soil. Again, the oxidation of iron pyrites furnishes sulphuric acid which coming in contact with the carbonates yields carbon dioxide. The so-called *choke-damp*, or *black-damp*, contains 85 to 95 per cent. of nitrogen and 5 to 15 per cent. of carbon dioxide. According to C. le Neve Foster and J. S. Haldane, an enormous quantity of black-damp is formed in mines: 2000–5000 c. ft. per minute is a common quantity; and the oxidation process which produces it is the chief source of heat in mines. Choke-damp issues from soils into mines or wells when the barometric column is falling. Meteorites[9] may contain carbonates; and carbon dioxide has been reported to occur in blood,[10] urine,[11] muscles,[12] etc. Carbon dioxide occurs as an inclusion in cavities in many minerals.[13] Numerous metal carbonates occur in nature; they are discussed in connection with the respective metals.

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## § 32. The Metabolism of Animals and Plants

Two chemical individuals stand alone in importance for the great biological cycle upon earth. The one is water, the other carbon dioxide. . . . These two simple substances are the common source of every one of the complicated substances which are produced by living beings, and they are the common end products of the wearing away of all the constituents of protoplasm, and of the destruction of those materials which yield energy to the body.—L. J. Henderson (1913).

In 1674, John Mayow [1] demonstrated that the respiration of animals is a process of oxidation analogous with combustion. J. Mayow placed a mouse in a cage under a vessel standing over water—Fig. 42—and noticed that the water rose in the jar as respiration continued just as if a burning candle had been placed under the jar, owing to the withdrawal of " nitroaërial particles " (oxygen). He found that the mouse died after a time, and it was impossible to ignite a combustible body in the residual " aërial " gas (nitrogen).

**Metabolism of animals.**—Organisms are continually wasting tissue as a result of muscular or other forms of work. Those constructive processes by which sub-

stances taken in as food by living organisms are converted into protoplasm are said to be **anabolic**—from *ἀνά*, anew; *βάλλειν*, to throw. Those destructive processes by which the protoplasm, etc., breaks down into simpler products are termed **katabolic**—from *κατά*, down. The two phenomena are included under the term **metabolism**—*μετά*, about. The air during respiration loses about 4 to 5 per cent. of oxygen, and gains 3 to 4 per cent. of carbon dioxide. Oxygen, taken in by the lungs, is absorbed by the blood. The blood contains **hæmoglobin**; this unites with oxygen, forming **oxyhæmoglobin**—the former is present in blue venous blood; the latter is red arterial blood. The oxyhæmoglobin gives up to its oxygen very readily, and it thus oxidizes the waste products—partly to carbon dioxide. The carbon dioxide held in soln. by the venous blood is pumped by the heart to the lungs, and the gas is finally exhaled in the breath.

By breathing into a beaker, and then adding clear lime-water; or better, by blowing through a glass tube into a beaker containing clear lime-water, it is easy to demonstrate the presence of carbon dioxide in the breath. The precipitation of calcium carbonate causes the clear lime-water to become turbid, etc. The experiment can be modified by drawing a stream of air through pieces of soda-lime in a tower, *A*, Fig. 43, to remove carbon dioxide

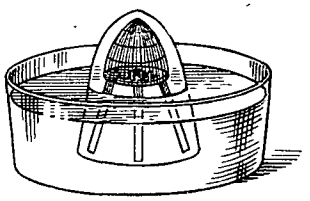


FIG. 42.—J. Mayow's Experiment on Respiration.

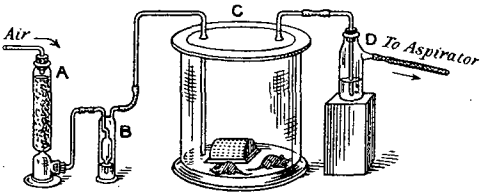



FIG. 43.—Exhalation of Carbon Dioxide by Animals.

from the air: then through a wash-bottle, *B*, with clear lime-water. The clarity of the lime-water demonstrates the absence of carbon dioxide in the stream of air. The air after passing the *temoin* (witness) tube, *B*, enters a glass chamber, *C*, which holds a mouse or a couple of mice, and then passes through another wash-bottle, *D*, containing clear lime-water. The turbidity of the lime-water in *D*, and the clarity of the lime-water in *B*, can be explained only by assuming that the mice are giving off carbon dioxide during respiration.

Less carbon dioxide is exhaled during sleep because less waste products are formed. The heat evolved during the oxidation processes in the body maintains the the body at the necessary temp. In the case of plants, most of this work is done by the leaves. The respiration of animals and plants goes on continuously, night and day—oxygen (air) is taken in, and returned to the air as carbon dioxide and water. The consequent loss in weight in both animals and plants is made good by assimilation or feeding. Fish abstract dissolved oxygen from water by means of their gills. Fish quickly die for want of oxygen when placed in cold water which has been deprived of dissolved air by boiling. Aërated water furnishes the oxygen necessary for their sustenance.

**Assimilation by plants.**—The respiration of plants must not be confused with the process of assimilation. In daylight, green plants absorb carbon dioxide from the air, fix the carbon, and give off oxygen. In sunlight, the process is very active, so that the respiration process, though at work, is masked because more carbon dioxide is taken in and oxygen given out by assimilation (feeding) than oxygen is taken in and carbon dioxide given out by respiration (breathing). The decomposition of the carbon dioxide (feeding) occurs only in daylight, and plant life is thus dependent upon this process for nourishment.

This action of light may be readily shown by modifying an old experiment due to J. Ingenhouz.[2] A two-litre flask is loosely packed with green leaves, and filled up with water through which carbon dioxide has been allowed to bubble. Fit the flask with a stopper, and

funnel as shown in the diagram, Fig. 44. Also fill the flask and part of the funnel with water. A test-tube inverted over the funnel will collect sufficient oxygen to allow the usual tests being made. Carbon dioxide can be removed from the gas by a soln. of potassium hydroxide.



FIG. 44.—Assimilation of Carbon Dioxide by Plants.

In 1774, J. Priestley observed that air spoilt by mice so that it is rendered incapable of supporting animal life, can be made good by allowing green plants to remain in it for some time. Six years later, J. Ingenhousz found that this action occurs only in light. He said that

> The light of the sun is alone capable of producing in the leaves that movement which can develop dephlogisticated air (oxygen) . . . as soon as the light ceases to act on the leaves, the operation ceases at the same time, and another of a different nature commences.

In 1783, J. Senebier showed that the chemical changes which occur result in transforming fixed air (carbon dioxide) into dephlogisticated air (oxygen). N. T. de Saussure, in 1804, also investigated the phenomenon. Only the green parts of plants are able to decompose atm. carbon dioxide in the presence of sunlight. In plants, the green pigment, **chlorophyll**, is associated with living protoplasm, forming granular masses called **chloroplasts**—studied by C. Timiriazeff. The nature of the green pigment has been discussed by R. Willstätter and A. Stoll. The absorption spectrum of chlorophyll has bands in the red and blue, practically none in the ultra-red or in the yellowish-green, but there is a faint one in the ultra-violet. The most striking feature is the dark band in practically the position of the maximum energy of the solar spectrum. T. W. Engelmann, H. Kniep and F. Minder, and C. Timiriazeff have demonstrated that the maximum evolution of oxygen occurs where there is the greatest absorption of light.

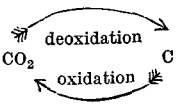
Radiant energy is stored up by the insolated chlorophyll. The decomposition of the carbon dioxide at ordinary temp. requires the expenditure of energy. The process is not catalytic. F. Weigert explains this by assuming that the chlorophyll itself takes part in the reaction, and that the increase in potential is due to the physiological processes in the protoplasm of the chloroplasts.

According to M. Trautz, the process is accompanied by chemi-luminescence so that the reddish light emitted has the same wave-length as the main absorption band of the chlorophyll. Starting then from the energy stored by the chlorophyll and carbon dioxide, A. von Baeyer suggested that formaldehyde, H.CO.H, is the first product of the reaction: $CO_2+H_2O=H.CO.H+O_2$, and that the end-product of the photosynthesis is a polymer of formaldehyde: $6(H.CO.H)=C_6H_{12}O_6$. He assumed that the carbon dioxide breaks down: $CO_2=CO+O$, and the product reacts: $CO+H_2O+O=O_2+H.CO.H$; E. Erlenmeyer, however, assumes that formic acid, H.COOH, and hydrogen dioxide are first produced: $CO_2+2H_2O=H.COOH+H_2O_2$, and that these products interact, giving formaldehyde: $H.COOH+H_2O_2=H.CO.H+H_2O+O_2$. A. Bach, indeed, obtained formic acid by the action of light on carbon dioxide in the presence of a soln. of a uranium salt, and assumed that the first stage of the reaction involves the formation of percarbonic acid and formaldehyde: $3CO_2+3H_2O=2H_2CO_4+H.COH$, followed by $H_2CO_4=CO_2+H_2O_2$. F. L. Usher and J. H. Priestley have studied the mechanism of the carbon assimilation; they found an aldehyde and hydrogen dioxide among the products of the action of light on films of chlorophyll in the presence of moist carbon dioxide. The work of S. B. Schryver, H. Wager, and C. H. Warner makes it doubtful if an aldehyde can be produced from carbon dioxide and water by chlorophyll alone without the intervention of protoplasm. The production of formaldehyde from carbon dioxide has been studied by F. Hoppe-Seyler, F. L. Usher and J. H. Priestley, T. Curtius and H. Franzen, F. Weigert, B. Moore, S. M. Baker, R. Willstätter and A. Stoll, O. Warburg and E. Negelein, etc.—*vide* chemical properties of carbon dioxide.

The energy required for the decomposition of the carbon dioxide is derived mainly from the radiant energy of the sun. There is thus a transformation of the sun's radiant energy into chemical energy which is stored up as vegetable tissue. The heat of combustion of burning wood is believed to be eq. to the solar energy used in its formation (Hess' law). At night, *i.e.* in darkness, feeding stops, but breathing—the absorption of oxygen and the evolution of carbon dioxide—continues. The net result of both processes—assimilation and respiration—is to remove carbon dioxide from the air, and restore oxygen. There is probably a kind of equilibrium press. between plants and the carbon dioxide of the air. If the amount of carbon dioxide exceeds a certain limit, this would be followed by greater activity in vegetable life, and thus the normal proportion of carbon dioxide would be restored. Similarly, if the amount of carbon dioxide were reduced below the normal, vegetable life would be impoverished until equilibrium was restored. The proportion of carbon dioxide present in the gases dissolved by sea-water is about 27 times as great as the proportion of this gas in air. Since carbon dioxide is fairly soluble in water, it follows that if a large surplus of carbon dioxide were introduced into the atm., say, from volcanic sources, the sea would dissolve a still greater proportion. Hence, as indicated above, *the sea must be an important means of regulating the amount of carbon dioxide in the atm.*

It will be noticed that all animal and vegetable life is dependent upon the carbon dioxide⇒carbon reaction, which in turn is dependent upon the sun's energy. There is a kind of closed cycle, an alternation of oxidations and deoxidations :

Sun's energy stored—plants feed




Energy dissipated—animals and plants breathe, etc.

maintained by a continuous supply of energy from the sun. If the supply should cease, the deoxidation of carbon dioxide would stop and the present conditions of life on the earth would come to an end because the available carbon would be transformed into unavailable carbon dioxide.

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## § 33. The Formation and Preparation of Carbon Dioxide

In some districts carbon dioxide is collected from springs—*e.g.* the natural waters from the Saratoga Springs (New York), and in South Germany. Borings are made, and a basin is excavated about each bore-hole. The basin is filled with water from the bore-hole, and the excess is allowed to escape by an overflow channel. A kind of gasometer is placed over the bore-hole so as to collect the gas. The gas is led from the gas-holder, and purified by passing through a spraying apparatus. A little potassium permanganate may be added to oxidize such impurities as hydrogen sulphide.[1]

Carbon dioxide is the end-product of the combustion of carbon in its various forms—*vide* carbon. In technical work, when contamination with nitrogen is of no moment, carbon dioxide is obtained by passing air over heated carbon—charcoal, coke, etc. Furnace gases resulting from the combustion of coke, charcoal, etc., may have up to 20 per cent. by vol. of carbon dioxide. The carbon dioxide so formed can be isolated by passing the gas into a soln. of potassium or sodium carbonate, so as to form the hydrocarbonate: $K_2CO_3+H_2O+CO_2=2KHCO_3$; the gas can be recovered by heating the hydrocarbonate. Many modifications of this process have been suggested.[2] The exhaust gas from gas-engines has also been employed. The sulphur dioxide and dust are removed by passing the gas through scrubbers containing limestone over which water trickles. L. Hackspill and A. Couder noted the formation of nitrates and nitrites in the preparation of carbon dioxide by the combustion of coke. The formation of carbon dioxide in the combustion of carbon monoxide has been treated in connection with the latter gas. The preparation of carbon dioxide from water-gas has been treated by C. Arnais,[3] and J. Pullman and H. S. Elworthy.

The slow oxidation of hydrocarbons, said F. C. Phillips,[4] always yields carbon dioxide; ethylene is oxidized by a soln. of potassium permanganate in sulphuric acid below 100°; and acetylene is oxidized by the same soln. cold, as well as by calcium hypobromite, or by osmic acid. O. Angelucci found that when acetylene is heated with oxygen and nitrogen in the presence of platinum sponge: $2C_2H_2+5O_2(+5N_2)=4CO_2+2H_2O(+5N_2)$, or $C_2H_2+2O_2(+2N_2)=CO_2+CO+H_2O(+2N_2)$. J. Coquillion and J. Henrivaux passed ethylene and water vap. through a red-hot porcelain tube packed with bits of porcelain, or pumice-stone, and, at a bright red heat, the product contained 15·7 per cent. of carbon dioxide and 24·7 per cent. of ethylene; at a higher temp. a larger proportion of ethylene and carbon dioxide was formed. The fractional oxidation of the hydrocarbons has been discussed in connection with carbon monoxide. R. Pippig and O. Trachmann discussed the purification of coal gas, and the subsequent formation of carbon dioxide from the products of combustion. C. G. P. de Laval obtained carbon dioxide from the products of combustion of petroleum. Carbon dioxide is produced by the action of steam on heated carbon (*q.v.*). E. E. Arnold obtained it by the action of air on molten pig iron.

The carbon in organic substances furnishes carbon dioxide during oxidation partly by air and partly by the contained oxygen, at ordinary temp. or when warm. The gas, for example, is produced during fermentation.[5] Enormous quantities are evolved as a by-product during the manufacture of beers, wines, etc., in the alcoholic fermentations of sugar: $C_6H_{12}O_6=2C_2H_5OH+2CO_2$. The gas so produced has a flavour like that of fusel oil, but it can be used for some purposes as discussed by H. Kerr-Thomas, J. C. Stead and T. C. Palmer, R. Thalwitzer, J. L. Seyboth, C. Dörries, etc. None of the proposed methods has been successful from an industrial point of view. F. Stolba obtained a very slow current of carbon dioxide from a mixture of 5 vols. of yeast with 1000 vols. of a soln. of one part of sugar in four parts of water. Carbon dioxide is formed during the putrefaction and decay of organic matter.[6] It is formed during respiration,[7] during muscular work,[8] and during the germination of plants.[9]

H. Karsten[10] found that various organic substances furnish carbon dioxide

when exposed to ozonized air. Carbon, and various organic substances evolve carbon dioxide in contact with oxygenated compounds at ordinary or at elevated temp., thus, A. F. Fol, and E. Moride observed that many soln. of the metal salts are reduced by carbon with the formation of carbon dioxide. Several other reactions have been indicated in connection with the chemical activity of carbon, carbon monoxide, oxychloride, oxysulphide, and disulphide. P. Schützenberger [11] found that when carbon tetrachloride is heated many hours with zinc oxide, at 200°, carbon dioxide is formed. H. St. C. Deville and H. Debray found that powdered rhodium converts formic acid into carbon dioxide. A. Richardson found an aq. soln. of oxalic acid in light furnishes carbon dioxide and water, and may be hydrogen dioxide. According to C. Wilde, fuming sulphuric acid and citraconic anhydride give carbon dioxide at 150°–160°, and carbon monoxide at 220°. A. Bouvier patented a process for the preparation of a mixture of carbon dioxide and acetylene by the action of water on a fused mixture of powdered calcium carbonate and carbide, and sodium hydrosulphate, $NaHSO_4$.

Carbon dioxide is obtained by heating various carbonates to suitable temp.—*e.g.* dolomite, limestone, magnesite, sodium hydrocarbonate, barium carbonate, manganese carbonate, etc. The gas is a by-product in the burning of limestone and marble for lime, or magnesite for making magnesia bricks. The evolved gas contains about 30 per cent. of carbon dioxide; the remainder is nitrogen and carbon monoxide. Some of the carbon dioxide is derived from the fuel. Many processes have been devised for collecting and purifying the gases from lime-kilns or magnesite-kilns—*vide supra* on the recovery of carbon dioxide from flue gases.[12] The gas can be purified from nitrogen, etc., by passing it into a soln. of alkali carbonate as indicated above. G. Bischof [13] decomposed magnesium carbonate by steam; and V. A. Jacquelain showed that the carbonates of sodium, silver, calcium, barium, magnesium, and lead are decomposed, when heated in steam. M. Meschelynck and J. F. Lionnet found calcium carbonate is decomposed by steam at a dull red heat. The manufacture of carbon dioxide by the action of steam on limestone has been treated by J. Dauglish, H. Blair, G. M. Westmann, E. Luhmann and G. A. Schütz, etc. The decomposition of the sodium hydrocarbonate by steam has been investigated by J. Young, and A. Campbell and co-workers. L. A. Staub [14] discussed the decomposition of sodium hydrocarbonate by ammonia; H. Howard, its decomposition by sodium hydrosulphite; H. Grimshaw, and E. Sandow, its decomposition by sodium hydrosulphate; H. G. Elledge, by calcium chloride; H. and J. F. Beins, its decomposition by ammonia-alum, or potash-alum; C. Löwig, the decomposition of carbonates by heating them with ferric oxide; and J. L. W. Thudichum and J. A. Wanklyn, by potassium dichromate.

Carbon dioxide is usually prepared in the laboratory by the action of different acids on various carbonates. For example, magnesite, limestone, and marble may be decomposed with dil. nitric acid as recommended by J. G. Bogusky,[15] J. G. Bogusky and N. Kajander, and I. Langmuir; with dil. hydrochloric acid, or hydrobromic acid as recommended by N. N. Beketoff. Sodium carbonate or hydrocarbonate may be decomposed with sulphuric, or hydrochloric acid, with tartaric acid as recommended by W. B. Dick; or with sodium hydrosulphate as recommended by H. Bornträger, H. Grimshaw, and E. Sandow. J. A. Ageron and B. J. M. Remy heated a mixture of magnesium sulphate and sodium sulphate or hydrosulphate with sulphuric acid, and used the product as a substitute for acids in liberating carbon dioxide from carbonates. F. Menter and W. A. Sedlitzky added to water a mixture of a carbonate or hydrocarbonate with a readily hydrolysable salt—*e.g.* alum, aluminium sulphate, or ferrous sulphate. J. H. Niemann decomposed ammonium carbonate with dil. sulphuric acid. R. C. Farmer described an apparatus for preparing carbon dioxide free from measurable quantities of air from a soln. of potassium hydrocarbonate (300 grms. per litre) and dil. sulphuric acid (1 : 8). L. Moser discussed the purification of the gas, using a paste of chromous acetate, and a 15 per cent. soln. of titanous chloride in hydrochloric acid to remove oxygen; heated cuprous oxide to remove

carbon monoxide; cupric sulphate on pumice to remove hydrogen sulphide; and a soln. of potassium permanganate to remove sulphur dioxide.

The acid process is used industrially, but not nearly so much now as formerly. The carbonate in the generator is mixed with water. The generator is cylindrical and constructed of lead, or of cast iron lined with lead. A safety-valve and an agitator are provided. The conc. acid is run from an acid-tank into the generator usually in quantities not sufficient to neutralize the carbonate. Sulphuric acid is preferred to hydrochloric acid because the volatile impurities in the gas from the last-named acid render the purification of the final product more costly. The sulphuric acid should be free from appreciable amounts of arsenic if the gas is to be used for mineral waters. If sulphuric acid were to be used with marble or whiting, a troublesome mass of sparingly soluble calcium sulphate would be left in the generator. Sodium hydrocarbonate with sulphuric acid is expensive; marble frequently contains bituminous impurities which contaminate the gas with substances difficult to remove. Whiting requires to be mixed with more water than does marble before the addition of the acid. This makes a proportionally larger generator necessary. Magnesite can be used with sulphuric acid: it gives a high yield of gas (52 per cent. by weight), and the mother-liquor can be worked for magnesium sulphate.

The gas usually needs purification. A certain amount of purification is effected on a large scale by passing the gas through water-scrubbers. If the gas still possesses an unpleasant odour, it is purified by passing it through a soln. of potassium permanganate which destroys the organic compounds and hydrogen sulphide; and through a soln. of sodium hydrocarbonate, which retains acid fumes. Sometimes manganese dioxide or potassium permanganate is added directly to the generator when sulphuric acid, but not hydrochloric acid, is used. J. Stenhouse,[16] and J. Förster recommended purifying the gas from objectionable odours by passing it over pieces of wood charcoal. To remove hydrogen sulphide, when working on a small scale, H. Hager passed the gas through an acid soln. of ferric sulphate, then through a dil. soln. of iodine, then through two wash-bottles containing an aq. soln. of potassium permanganate, and finally through water. N. Gräger said that potassium permanganate, or other oxidizing agents does not always remove the objectionable odour from the gas. E. Pfeiffer recommended scrubbing the gas with olive oil to get rid of the odour. H. Reinsch said that it is simplest to destroy the bituminous matters by pre-heating the limestone or dolomite to a low temp. The impurities in liquefied carbon dioxide were discussed by O. Wentzky, H. Lange, J. C. A. S. Thomas, R. Woy, H. Thiele and H. Deckert, and J. Werder. V. Cremieu and A. Lepape purified the gas by the solidification of the carbon dioxide, and pumping off the less condensable gases; and A. A. Backhaus, by passing it over activated carbon.

I. Langmuir recommended preparing carbon dioxide from marble and purified 50 per cent. nitric acid. The marble was boiled several times with weakly acidulated water to free it from air, and the acid was freed from air by a stream of carbon dioxide. The gas was purified by passing it through a sat. soln. of sodium hydrocarbonate, then through conc. sulphuric acid, and finally dried by passing the gas through a long tube containing phosphorus pentoxide. Numerous varieties of apparatus[17] have been devised for the intermittent supply of carbon dioxide by the action of acid on a carbonate. Many of these are also used for hydrogen sulphide, etc. F. Küspert obtained small quantities of the gas from a syphon of soda water.

On an industrial scale carbon dioxide may be obtained from lime-kilns;[18] from producer gas, combustion gases;[19] from fermentation processes and other processes[20] in which the gases are absorbed by a soln. of sodium carbonate, and the soln. of hydrocarbonate heated to drive off the absorbed gas. L. Hackspill and A. Couder found nitric acid in the gas derived from potassium hydrocarbonate. This salt was made from carbon dioxide obtained from coke, and the nitric acid was derived from the nitrous acid formed during the oxidation of the nitrogen compounds when the coke was converted into carbon dioxide.

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## § 34. The Physical Properties of Carbon Dioxide

Carbon dioxide is an invisible, colourless, and odourless gas at ordinary temp. A. L. Lavoisier's [1] statement that the gas has a feeble odour shows that his product was probably impure, but when breathed through the nostrils it does give a tingling sensation, due, probably, to its forming carbonic acid with the moisture; this also accounts for its having an acid taste. Liquid carbon dioxide was found by M. Faraday, J. H. Niemann, L. P. Cailletet, and B. Schwalbe to be a water-clear, colourless, very mobile liquid. M. Thilorier stated that the solid is a white flocculent mass resembling snow, and, like snow, is readily compressed. H. Landolt obtained dense hard cylinders of the compound by compressing the snow. M. Faraday, and A. Loir and

C. Drion obtained the solid as a colourless mass resembling ice, which, when fractured furnished small cubes. The ice-like form is obtained by cooling the liquid *en masse*; or, according to U. Behn, by cooling the vap. in a chamber below −79°. A. Liversidge said that the crystals resemble those of gold, iron, or ammonium chloride, and belong to the cubic system, although they volatilized before measurements could be made. P. Villard and R. Jarry said that the crystals do not act on polarized light. A. Liversidge, and H. E. Behnken found that the clear optically isotropic **crystals** belonged to the cubic system, and showed both cubes and octahedra. The sharpest and best formed crystals were liable to explosive rupture owing to contraction strains. According to W. Wahl, when carbon dioxide is cooled by liquid air, it condenses in the form of small cubes which are quite isotropic. No polymorphic change was observed above −210°. H. Mark and E. Pohland obtained **X-radiograms** in agreement with an elementary cube of side 5·62A. M. Thilorier said: When the solid is exposed to air it disappears insensibly by slow evaporation, without melting. A fragment of the solid, slightly touched by the finger, glides rapidly over a polished surface, as if it were sustained by the gaseous atm. with which it is constantly surrounded. The vaporization of solid carbon dioxide is complete; it leaves but rarely a slight humidity which may be attributed to the action of air on a cold body, the temp. of which is far below that of freezing mercury. The snow can be handled without harm, but when pressed on the skin for a few seconds or more, it produces blisters.

The gas is about one and a half times as heavy as air, and this explains its tendency to accumulate in low-lying places—valleys, cellars, etc.—*vide* the occurrence of this gas.

The invisibility of the gas, its heaviness compared with air, and its property of quenching flame, enable many pleasing and attractive experiments to be arranged; their variety is limited only by the ingenuity and skill of the experimenter. Thus: (1) a long cardboard gutter leading into a glass trough in which a number of candles are burning can be arranged. The invisible gas, carbon dioxide, can then be poured from a large beaker down the gutter, when the candles will be extinguished just as if water had been poured down the gutter. (2) A cylinder can be arranged with candles at different levels; the gas when led into the cylinder, extinguishes the candles one by one as the gas rises in the jar. (3) A wheel of stiff cardboard can be mounted upon two corks on a knitting needle journalled into a wooden standard; paper buckets can be attached to the periphery of the disc by joining the edges of the paper so as to form a hollow cone. When carbon dioxide is poured into the buckets, the wheel will rotate, if properly balanced, as it were a "water wheel," moved by a stream of water. (4) A cardboard box, or a light glass vessel, can be counterpoised on a balance; the beam will be depressed when carbon dioxide is poured into the box, showing that the carbon dioxide is heavier than the air displaced. (5) Soap-bubbles blown with the air can be floated on the carbon dioxide in a large dish. (6) Petroleum burning in a shallow dish can be extinguished by pouring the gas over the dish; and a beaker of the gas poured over a lighted candle will quench the flame. (7) Carbon dioxide can be ladled from a large cylinder by a small beaker tied on to a string. The action is analogous with the method of emptying a well of water by means of a bucket and rope. Finally, a candle will burn in the cylinder, showing that the carbon dioxide has been removed. The beakers of carbon dioxide can be emptied into another cylinder and the presence of carbon dioxide demonstrated in the usual way.

F. Mohr[2] gave 22 for **relative density,** at n.p.t., if H=1; and J. P. Cooke, 21·971. R. F. Marchand gave 1·3819 to 1·3825 if O=1; and P. A. Guye, 1·3833. L. Bleekrode gave 1·529 (air unity) at 15° and 760 mm. With air at n.p.t. unity, R. F. Marchand gave 1·5282; H. V. Regnault, 1·51910; F. J. Wrede, 1·52037; J. J. Berzelius and P. L. Dulong, 1·5245; F. Exner, 1·52; E. Wiedemann, and R. K. McClung, 1·529; J. M. Crafts, 1·52897; J. P. Cooke, 1·52856; A. Leduc, 1·5287; Lord Rayleigh, 1·52909; R. J. Strutt, 1·53; and N. S. Drenteln, 1·50 to 1·52. According to J. P. Cooke, the calculated density is usually smaller than the observed value because the gas under atm. press. is more strongly compressed and much nearer its point of liquefaction, than the standard of comparison. F. Emich found 1·485 at 1000°, 1·497 at 1500°, and 1·527 at 2000°; and with gas dried by sulphuric acid, 1·557 at 19° and 1·550 at 1875°—all referred to nitrogen unity. A. P. Lidoff said that the density of carbon dioxide from various natural sources

is lower than the theoretical. E. Mathias studied the density curves at low temp. and near the critical point.

L. P. Cailletet and E. Mathias, E. H. Amagat, P. Phillips, and U. Behn measured the vap. density of carbon dioxide at different temp.—*vide infra.* According to H. V. Regnault, the **weight of a litre** of the gas at 0° and 760° is 1·9777404 grms. under standard conditions; E. Dietrich, 1·9678; J. M. Crafts gave 1·97772; P. A. Guye, and P. A. Guye and A. Printza, 1·9768; A. Leduc, 1·9763; Lord Rayleigh, 1·9769; and A. Jaquerod and F. L. Perrot, 1·47677, and at 1067·4° and 760 mm., 0·39966 grm. S. W. Parr has calculated a table of values between 10° and 30°, 720 to 770 mm. press., and latitude 41°, and altitude 100 metres.

The **specific gravity** of liquid carbon dioxide was given by M. Thilorier [3] as 0·38 at 0°; 0·90 at −20°; and 0·60 at 30°; E. Andréeff gave 0·9470 at 0°; L. Bleekrode, 0·863 at 15°; L. P. Cailletet and E. Mathias, 1·057 at 34°; 0·910 at −1·6°; and 0·76 at 22·2°; and B. Schwalbe, 0·83 at 0°. E. H. Amagat found the sp. gr. of liquid and gas converged as the temp. approached the critical point, when the two coincided:

| | 0° | 10° | 20° | 30° | 30·5° | 31° | 31·35° |
|---|---|---|---|---|---|---|---|
| Liquid . . . . | 0·914 | 0·856 | 0·766 | 0·589 | 0·574 | 0·536 | 0·464 |
| Gas . . . . . | 0·096 | 0·133 | 0·190 | 0·334 | 0·356 | 0·392 | 0·464 |

J. Timmermans measured the sp. gr. of liquid carbon dioxide between 0° and the b.p. A. Blümcke measured the density of mixtures of sulphur and carbon dioxides. According to P. Villard and R. Jarry, the sp. gr. of the solid is greater than that of the liquid; H. Landolt gave 1·188 to 1·199 for the sp. gr. of the compressed snow; L. Bleekrode gave 1·3 to 1·6; B. Schwalbe, 1·19. By subliming solid carbon dioxide in a vessel cooled below −79°, U. Behn obtained the solid as a clear glass of sp. gr. 1·56; and he obtained 1·53 for the sp. gr. of the snow suspended therein; J. P. Kuenen and W. G. Robson, 1·48; J. Dewar, 1·6267 at −188·8°; and 1·53 at the b.p.

The **molecular volume**, according to L. Meyer,[4] is 26·7; and A. Naumann also gave a value for this constant. D. Berthelot gave 0·99326 for $v_0$ in the equation $v_0=(vp/p_0)\{1+a(p-p_0)\}$, where $a$ is a constant, $v$ the vol. under a very small press. $p$, and $p_0$ is the normal press. P. N. Pavloff discussed the relations $T_c=1{\cdot}6167M/n^{\frac{1}{4}}$, where $n$ denotes the number of atoms per mol. Values for the **specific volume** of carbon dioxide vap. were obtained by L. P. Cailletet and E. Mathias, U. Behn, J. J. van Laar, E. H. Amagat, and C. F. Jenkins and D. R. Pye—*vide* Table XXIII. According to F. G. Keyes and A. W. Kenney, the sp. vols. of the vap. in c.c. per gram are:

| | −50° | −40° | −30° | −20° | 0° | 10° | 20° | 30° | 30·2° |
|---|---|---|---|---|---|---|---|---|---|
| Sp. vol. . . | 57·32 | 38·92 | 27·44 | 19·72 | 14·32 | 10·44 | 7·561 | 5·319 | 3·70 |

The sp. vols. of the liquid in c.c. per gram have been measured by L. P. Cailletet and E. Mathias, U. Behn, and E. H. Amagat. The following data at 10° and downwards are by U. Behn, and those above 10° by E. H. Amagat:

| | −50° | −40° | −30° | −20° | −10° | 0° | 10° | 20° | 30° |
|---|---|---|---|---|---|---|---|---|---|
| Sp. vol. | 0·8665 | 0·8960 | 0·9302 | 0·9699 | 1·019 | 1·081 | 1·163 | 1·305 | 1·672 |
| $a$ . | 308·7 | 313·2 | 319·2 | 320·4 | 323·2 | 325·5 | 326·8 | 324·7 | 315·3 |

F. G. Keyes and A. W. Kenney found that data are then well represented by $v=2{\cdot}7986-\log(a-T)$; and if $D_1$ be the density of the vap., and $D_2$ that of the liquid, the mean density equation is $\frac{1}{2}(D_1+D_2)=0{\cdot}4597+0{\cdot}00179(T_c-T)-0{\cdot}0000041(T_c-T)^2$.

The **molecular weight** calculated by D. Berthelot is 44·000; Lord Rayleigh obtained 44·268 at 0° and atm. press., and 44·014 at small press. (O=32); A. Jaquerod and F. L. Perrot gave 43·992 at 1067°; and L. Löwenstein, 43·8 at 1350°. H. von Jüptner observed no appreciable mol. association in liquid carbon dioxide. H. Kolbe represented the mol. by the formula $(C_2O_2)O_2$; and L. Zeschko made some observations on this subject. J. C. Maxwell gave $9{\cdot}3\times10^{-8}$ mm. for the

**diameter of the molecule**; J. H. Jeans gave $4{\cdot}56\times10^{-8}$ mm.; E. Dorn, and A. von Obermayer made estimates of this constant. C. E. Guye calculated the mol. diameter from the electromagnetic rotation. J. H. Jeans gave $4{\cdot}0\times10^{-6}$ cm. for the **mean free path**. J. C. Maxwell estimated the **collision frequency** to be $97{\cdot}2\times10^{8}$ per sec. P. Blaserna found the **molecular velocity**, $V$, in metres per sec.

| Press. | 0 | 76 | 100 | 500 | 1000 | 1500 | 2000 cms. |
|---|---|---|---|---|---|---|---|
| $V$ at 3·3° . . . | 393·3 | 392·1 | 391·8 | 385·0 | 374·5 | 362·9 | 350·4 |
| $V$ at 100° . . . | 459·7 | 459·2 | 459·0 | 456·4 | 452·8 | 449·4 | 446·2 |

A. Eucken infers that in the mol. of carbon dioxide, the carbon atom lies almost in a line joining the oxygen atoms and that it executes small elastic circular vibrations about them. M. F. Skinker investigated the motion of electrons in carbon dioxide. The **moment of inertia** perpendicular to the line joining the oxygen atoms is about $50\times10^{-40}$ grm. per sq. cm., and the mutual separation of the oxygen atoms is about $2\times10^{-8}$ cm. J. E. Mills studied the **molecular attractions** of liquid carbon dioxide. J. A. Muller estimates the degree of polymerization of carbon dioxide in the critical state to be 1·351. C. Ramsauer estimated the effective diameter of the molecules towards slow electrons. R. Gans discussed the symmetry of the mol. of carbon dioxide; and A. E. Oxley, A. O. Rankine, E. D. Eastman, A. W. C. Menzies, and A. Eucken, the electronic structure of the molecule—*vide* **4**. 27, 4; H. F. Meyer, the action of slowly moving electrons on the carbon dioxide molecule; and L. B. Loeb, the affinity of the mols. for electrons.

According to W. Crookes,[5] the **viscosity** of carbon dioxide decreases very rapidly between 620 mm. and 50 mm. press., and between 760 mm. and 1 mm., the decrease is twice as great as in air. The viscosity, $\eta$, of carbon dioxide has been determined over the range −21·5° and 302° by a number of different investigators—A. Kundt and E. Warburg, E. Warburg and J. Sachs, O. Schumann, S. Pagliani and A. Batelli, Y. Ishida, L. J. Lassalle, O. E. Meyer and F. Springmühl, etc. O. E. Meyer gave 0·000160 to 0·000168 at 0°; A. Klemenc and W. Remi, 0·0001382 at 0°; and A. Wüllner, 0·0001383 at 0° and 0·0001859 at 100°. The values increase with rise of temp.

| | −21·5° | 0° | 15° | 20° | 53·5° | 100° | 182·4° | 240·3° | 302° |
|---|---|---|---|---|---|---|---|---|---|
| $\eta\times10^{7}$ . | 1278 | 1414 | 1488 | 1579 | 1638 | 1916 | 2221 | 2458 | 2682 |

In W. Sutherland's formula $\eta=\eta_0\{(273+T)/(T+C)\}(T/273)^{\frac{3}{2}}$, for the relation between the viscosity of a gas and temp., $C$ has the value 277 for carbon dioxide; P. Breitenbach gave 239·7; and A. Klemenc and W. Remi, 263·4. The effect of air on the density and the viscosity was determined at different temp. and press. by E. Warburg and L. von Babo in 1882. P. Phillips determined the viscosity-press. isothermals at 20°, 30°, 32°, 35°, and 40°. Some of the measurements are shown in Table XXII, and the results are plotted in Fig. 45. The form of the viscosity-

TABLE XXII.—THE EFFECT OF PRESSURE ON THE VISCOSITY AND DENSITY OF CARBON DIOXIDE.

| 20° | | | 32° | | | 40° | | |
|---|---|---|---|---|---|---|---|---|
| Press. $p$ atm. | Viscosity $\eta$. | Density $D$. | Press. $p$ atm. | Viscosity $\eta$. | Density $D$. | Press. $p$ atm. | Viscosity $\eta$. | Density $D$. |
| 83 | 0·000823 | 0·835 | 120 | 0·000788 | 0·790 | 112 | 0·000571 | 0·699 |
| 72 | 771 | 0·812 | 104 | 695 | 0·760 | 100 | 483 | 0·636 |
| 59 | 697 | 0·768 | 93 | 627 | 0·729 | 94 | 414 | 0·582 |
| 56 | 186 | 0·190 | 84 | 560 | 0·682 | 80 | 218 | 0·291 |
| 50 | 177 | 0·145 | 70 | 214 | 0·255 | 70 | 200 | 0·204 |
| 40 | 166 | 0·100 | 60 | 187 | 0·170 | 60 | 187 | 0·153 |
| 20 | 156 | 0·036 | 20 | 162 | 0·0352 | 23·8 | 169 | 0·0408 |
| 1 | 148 | 0·00183 | 1 | 155 | 0·00176 | 1 | 157 | 0·00173 |

press. isothermals is very similar to the density-press. isothermals except that the former cross one another, while the latter do not. This is due to the fact that the viscosity of a gas increases with a rise of temp., whereas the viscosity of a liquid decreases with rising temp. The curves cross before the gas is liquefied, showing that it is beginning to act like a viscous liquid before condensation occurs. The critical viscosity is $0{\cdot}321\times10^{-3}$, and the critical density 0·464. The portions $AB$ and $A'B'$ represent the viscosity of a superheated liquid, while $CD$ and $C'D'$ represent the viscosity of a supercooled vap. By plotting the density-viscosity curves, the points corresponding with different temp. run along curves very close together, showing that in the range of temp., 20°–40°, of these experiments, the viscosity depends almost entirely on the density. By plotting the square of the densities between 0·2 and 0·7, the viscosity is a linear function of the square of the density, meaning that within this region of rapid variation of density with temp. or press., "the change in viscosity is almost entirely due to the change in attraction between two adjacent layers of the fluid, for this would be proportional to the square of density. In other words, the viscosity in this region depends almost entirely on the term $a/v^2$ in J. H. van der Waals' equation. At higher densities, it is probable that the change in the kinetic energy of the mol. begins to play a larger part, and at low densities, the attraction between the mols. becomes quite negligible." The **coefficient of slip**—*vide* hydrogen—is $\gamma=0{\cdot}00000650$. J. Puluj measured the viscosity of mixtures of carbon dioxide and hydrogen, and found a maximum with the mixture $CO_2+0{\cdot}3H$; with $CO_2+6H$ the viscosity is the same as that of pure carbon dioxide; and the values then decrease regularly with increasing proportions of hydrogen. E. Warburg and L. von Babo found the sp. gr., $D$, and viscosity, $\eta$, of liquid carbon dioxide to be:

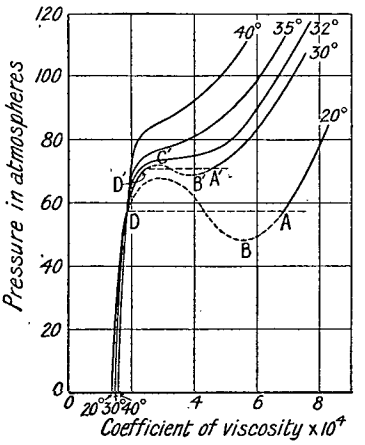



FIG. 45.—Viscosity-Pressure Isothermals of Carbon Dioxide.

| | 5° | 10° | 15° | 20° | 25° | 29° |
|---|---|---|---|---|---|---|
| $D$ | 0·922 | 0·895 | 0·864 | 0·827 | 0·783 | — |
| $\eta\times10^6$ | 925 | 852 | 784 | 712 | 625 | 539 |

C. J. Smith showed that the viscosity of a mixture of nitrous oxide and carbon dioxide in C.G.S. units is 0·0001366 at 0°; 0·0001441 at 15°; and 0·0001845 at 100°. The mean collision area was calculated to be $0{\cdot}834\times10^{-15}$ sq. cm. J. E. Verschaffelt [6] found the **capillary constant**, $a^2$, and the **surface tension**, $\sigma$, of liquid carbon dioxide to be:

| | −24·3 | 8·9 | 15·2 | 20·0 | |
|---|---|---|---|---|---|
| $a^2$ | 1·950 | 0·821 | 0·585 | 0·375 | sq. mm. |
| $\sigma$ | 9·21 | 2·90 | 1·82 | 1·00 | dynes per cm. |

The **velocity of sound** in carbon dioxide at 0° has been measured by W. J. M. Rankine, C. Bender, C. T. Knipp and W. B. Worsham, P. L. Dulong, A. Masson, I. B. Zoch, T. Martini, H. B. Dixon and co-workers, and A. Wüllner; and at 10°–24°, by J. W. Low. According to O. Buckendahl, the velocities in metres per second at different temp. are:

| | 0° | 100° | 300° | 500° | 670° | 945° | 1080° |
|---|---|---|---|---|---|---|---|
| Velocity | 258·04 | 301·54 | 373·74 | 434·06 | 503·28 | 543·29 | 572·45 |

J. L. M. Poiseuille [7] computed the speeds at which water and a sat. aq. soln. of carbon dioxide passed through capillary tubes. T. Graham measured the rate of transpiration of carbon dioxide under similar conditions, and found that if the time

for oxygen be unity, that for carbon dioxide is 0·7272 ; and for the **effusion** of carbon dioxide into a vacuum, 1·1573 when that for oxygen is unity. W. Timofejeff made some measurements on this subject ; and F. G. Donnan found that the rate of effusion of carbon dioxide is about one per cent. in excess of that calculated from T. Graham's law. K. Sameshima and K. Fukaya studied the atmolysis of carbon dioxide. The throttling experiments producing the so-called **Joule-Thomson effect** were found by J. P. Joule and W. Thomson, at about 3 atm., to be 1·34 at 7·4°, 1·03 at 35·6°, 0·89 at 54·0°, and 0·65 at 97·55° ; C. F. Jenkin and D. R. Pye found at 40·8 atm. press., 1·091 at 29·5°, 1·62 at 24·5°, and 1·242 at 20° ; E. Natanson found at 25°, 1·18 at 0 atm., 1·30 at 10 atm., 1·43 at 20 atm., and 1·50 at 25 atm. F. E. Kester represented their results at 22°, by $d\theta/dp=1{\cdot}187°+0{\cdot}0015p$. The variation of $d\theta/dp$ with $p$ is greater than would follow from J. D. van der Waals' equation. W. A. D. Rudge measured the effect at 21° with a difference of press. of 57° to be −1·894° per atm. difference of press. M. Jakob found the press., $p$, and temp., $T$, at which the differential Joule effect is zero, is $(dv/dT)_p=v/T$ ; and that $p=899{\cdot}7-1{\cdot}167T-1102\times10^4T^{-2}$. E. S. Burnett, and F. G. Keyes also studied the effect with carbon dioxide.

J. Loschmidt's values[8] for the **diffusion coefficient**, $k$, per sq. cm. per sec. of carbon dioxide and

| | $N_2O$ | CO | $O_2$ | Air | $CH_4$ | $H_2$ |
|---|---|---|---|---|---|---|
| $k$ . . . . . | 0·09831 | 0·14055 | 0·14095 | 0·14231 | 0·15856 | 0·55585 |

A. von Obermayer gave values for carbon dioxide with nitrous oxide, ethylene, methane, carbon monoxide, air, oxygen, and hydrogen ; A. Lonius, and R. Lorenz and A. Magnus, for hydrogen ; J. Stefan, for water, and alcohol ; A. Winkelmann, and G. Guglielmo, for water vap. ; K. Waitz, V. Hausmaninger, J. C. Maxwell, J. J. Hood, H. T. Brown and F. Escombe, for air ; G. Hüfner, for carbon monoxide ; A. Winkelmann, for alcohol, ether, esters, and fatty acids. A. von Obermayer represented the effect of temp. and press. with air, oxygen, and nitrous oxide by $k_0=k(T_0/T)^{1{\cdot}75}p/76$ ; J. Loschmidt used $k_0=k(T_0/T)^2p/76$ for a number of gases. According to R. Brimmeyr, when carbon dioxide is separated from hydrogen or oxygen by a moist bladder, more carbon dioxide diffuses to the specifically lighter gas than conversely ; and with a dry porous partition, less carbon dioxide diffuses to the specifically lighter gas than conversely. J. Wiesner and H. Molisch also found that carbon dioxide diffuses through vegetable membranes more rapidly than hydrogen, oxygen, or nitrogen. T. Graham, and C. Matteucci studied the rate of diffusion of carbon dioxide through dry plaster of Paris ; H. E. Roscoe, and M. Pettenkofer, through bricks ; and F. Hannen, through soils. L. Pfaundler, and G. Quincke found that carbon dioxide under press. does not diffuse perceptibly through glass walls 1·5 mm. thick. T. Graham. J. Dewar, and E. Obach measured the diffusion of carbon dioxide through caoutchouc or rubber, and the first-named found that the rates with carbon dioxide and monoxide are as 13·585 : 1·113. F. Kolbe found 0·003 c.c. of the gas passes per hour through a sq. cm. of rubber 2 mm. thick ; and H. Kayser found the speed to be much less than that of hydrogen, and to increase proportionally with temp., while the absorption coeff. decreases with temp.—*vide infra.* L. L. Grunmach showed that the increase in the rate of diffusion through rubber is not proportional to the difference of press., and that the decrease in the rate is not proportional to the thickness of the membrane.

R. Fricke[9] investigated the growth in the size of bubbles of carbon dioxide rising in liquids. F. J. Wrede showed that Boyle's law does not describe the behaviour of carbon dioxide at elevated press., and H. V. Regnault found the gas to be more compressible than is represented by the function $(v_0p_0/vp)-1=0$, and he represented the compressibility by an interpolation formula ; so also did A. Avogadro. E. Mascart gave 0·00901 for the **compressibility** at 3° ; D. Berthelot, 0·00688 between 1 atm. and 2 atm., between 1 and 0·5 atm., 0·00676, and between 0·5 and 0·25 atm., 0·00666. P. A. Guye and T. Batuecas gave $0{\cdot}00706\pm0{\cdot}00004$ for the compressibility

coeff. W. H. Kleeson, T. Andrews, and Lord Rayleigh also measured the compressibility of this gas. T. Andrews' observations on the $pT$-curves of carbon dioxide have been discussed previously (**1**. 4, 8); and C. G. Knott has compiled the data from T. Andrews' note-books. E. H. Amagat gave for the change of compressibility $pv/p_1v_1$ with temp., when the value of $pv$ at 0° and 1 atm. press. is unity.

| | | 50° | 100° | 200° | 300° |
|---|---|---|---|---|---|
| Press. | 0·725 atm. | 1·0037 | 1·0021 | 1·0009 | 1·0003 |
| | 1·440 atm. | 1·0075 | 1·0048 | 1·0025 | 1·0015 |
| | 2·850 atm. | 1·0145 | 1·0087 | 1·0040 | 1·0020 |

E. H. Amagat, H. V. Regnault, K. Neumann, and P. Blaserna measured the deviations from Boyle's law exhibited by this gas. E. H. Amagat's results are given in Table XXIII. The results are plotted in Fig. 46, where the inset represents the

TABLE XXIII.—E. H. AMAGAT'S VALUES FOR THE PRODUCT $pv$.
($pv$ = UNITY AT 0° AND 1 ATM. PRESS.)

| Press. atm. | Temperatures. | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | 0° | 10° | 20° | 40° | 60° | 80° | 100° | 137° | 198° | 258° |
| 50 | 0·1050 | 0·1145 | 0·6800 | 0·8500 | 0·9840 | 1·0960 | 1·2065 | 1·3800 | — | — |
| 100 | 0·2020 | 0·2130 | 0·2285 | 0·3090 | 0·6610 | 0·8725 | 0·9535 | 1·2590 | 1·5820 | 1·8470 |
| 150 | 0·2950 | 0·3090 | 0·3260 | 0·3770 | 0·4850 | 0·6805 | 0·8780 | 1·1585 | 1·5295 | 1·8180 |
| 200 | 0·3850 | 0·4010 | 0·4190 | 0·4400 | 0·5425 | 0·6600 | 0·8145 | 1·0960 | 1·4960 | 1·8040 |
| 250 | 0·4740 | 0·4900 | 0·5100 | 0·5580 | 0·6250 | 0·7135 | 0·8355 | 1·0810 | 1·4870 | 1·8060 |
| 300 | 0·5590 | 0·5775 | 0·5985 | 0·6485 | 0·7100 | 0·7900 | 0·8900 | 1·1080 | 1·4935 | 1·8200 |
| 350 | 0·6445 | 0·6640 | 0·6850 | 0·7635 | 0·7980 | 0·8725 | 0·9615 | 1·1565 | 1·5210 | 1·8465 |
| 400 | 0·7280 | 0·7475 | 0·7710 | 0·8320 | 0·8840 | 0·9560 | 1·0385 | 1·2175 | 1·5630 | 1·8830 |
| 450 | 0·8090 | 0·8310 | 0·8550 | 0·9075 | 0·9690 | 1·0400 | 1·1190 | 1·2880 | 1·6160 | 1·9280 |
| 500 | 0·8905 | 0·9130 | 0·9380 | 0·9900 | 1·0540 | 1·1250 | 1·2005 | 1·3620 | 1·6775 | — |
| 550 | 0·9700 | 0·9935 | 1·0200 | 1·0740 | 1·1370 | 1·2085 | 1·2830 | 1·4400 | 1·7450 | — |
| 600 | 1·0495 | 1·0730 | 1·0995 | 1·1270 | 1·2190 | 1·2900 | 1·3655 | 1·5180 | 1·8120 | — |
| 650 | 1·1275 | 1·1530 | 1·1800 | 1·2375 | 1·3010 | 1·3725 | 1·4475 | 1·5960 | 1·8835 | — |
| 700 | 1·2055 | 1·2325 | 1·2590 | 1·3190 | 1·3825 | 1·4535 | 1·5285 | 1·6760 | 1·9560 | — |
| 750 | 1·2815 | 1·3105 | 1·3395 | 1·4000 | 1·4640 | 1·5335 | 1·6100 | 1·7565 | 2·0330 | — |
| 800 | 1·3580 | 1·3870 | 1·4170 | 1·4790 | 1·5435 | 1·6140 | 1·6890 | 1·8355 | 2·1080 | — |
| 850 | 1·4340 | 1·4625 | 1·4935 | 1·5570 | 1·6225 | 1·6925 | 1·7680 | 1·9150 | 2·1860 | — |
| 900 | 1·5090 | 1·5385 | 1·5685 | 1·6325 | 1·6995 | 1·7710 | 1·8460 | 1·9940 | 2·2600 | — |
| 950 | 1·5830 | 1·6115 | 1·6430 | 1·7065 | 1·7745 | 1·8470 | 1·9230 | 2·0720 | 2·3350 | — |
| 1000 | 1·6560 | 1·6850 | 1·7160 | 1·7800 | 1·8475 | 1·9210 | 1·9990 | 2·0720 | — | — |

curves for values of $p$ between 25 and 125 atm. on a magnified scale. It will be observed that the value of $pv$ at a given temp. falls to a minimum and then rises again. The press. $p$ atm. at which $pv$ reaches a minimum at different temp. are

| | 0° | 10° | 20° | 40° | 60° | 80° | 100° | 137° | 198° | 258° |
|---|---|---|---|---|---|---|---|---|---|---|
| $p$ . . | 35 | 45 | 57 | 101 | 143 | 179 | 211 | 247 | 255 | 218 |

These results mean that the compressibility reaches a maximum and then diminishes again. The minimum, Fig. 46, at the higher press. is flatter and less abrupt. The curve at the highest temp. is not parallel to the abscissa-axis as would be the case if $pv$=constant. From the inset of Fig. 46, it follows that below the critical temp. the press. remains constant for certain values of $pv$. This means that the gas has partly liquefied, and the vap. press. of the liquid at the given temp. is being measured. The deviations from Boyle's law have been discussed by J. A. Siljeström, D. I. Mendeléeff, P. Blaserna. T. Batuecas represented the deviation from Avogadro's law by $1+\lambda=1{\cdot}00706$. F. G. Keyes discussed the error in the measurements produced by the adsorption of carbon dioxide by the glass. A. Wohl,

and R. Wegscheider studied the applicability of an amended gas equation. In the vicinity of the critical temp., the values of $pv$ are as follow (when $pv$ at 0° and 1 atm. press. is unity):

| | | 70 | 71 | 72 | 73 | 74 | 75 |
|---|---|---|---|---|---|---|---|
| $p$ | | | | | | | |
| $pv$ | at 30° | 0·470 | 0·230 | 0·223 | — | 0·219 | 0·219 |
| | at 32° | 0·540 | — | 0·491 | 0·460 | 0·405 | 0·268 |
| | at 38° | 0·602 | — | — | — | 0·531 | 0·510 |

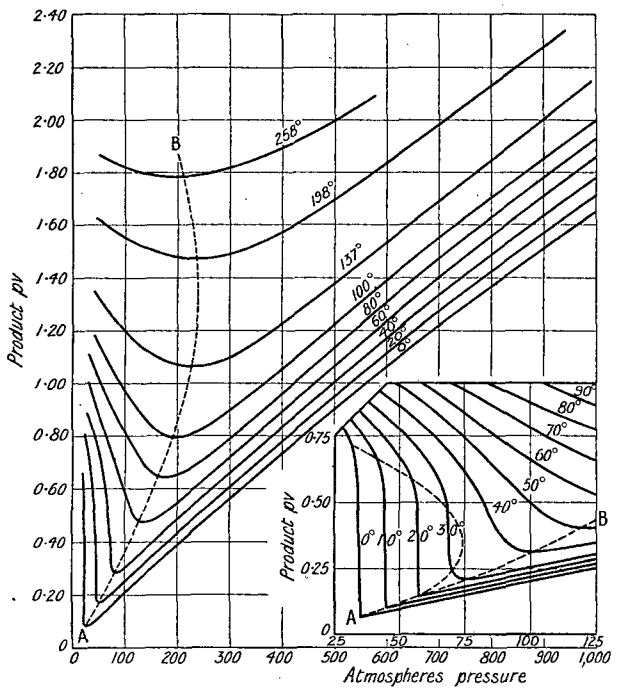



FIG. 46.—Isothermal Pressure and $pv$-curves of Carbon Dioxide at Different Temperatures.

W. H. Keesom measured the compressibility of mixtures of carbon dioxide and oxygen; T. Andrews, of mixtures of carbon dioxide and nitrogen; A. Thiel and E. Schulte, R. Pictet, F. Braun, and A. Blümcke, of mixtures of carbon dioxide and sulphur dioxide; J. P. Kuenen, of mixtures of carbon dioxide and methyl chloride; A. Thiel and E. Schulte, of binary mixtures of carbon dioxide with ethyl chloride, methyl ether, ethyl ether, chlorine, or hydrogen sulphide; and J. Dewar, of binary mixtures of carbon dioxide with bromine, hydrogen chloride, carbon disulphide, chloroform, methyl chloride, carbon tetrachloride, benzene, acetylene, ether, camphor, nitrous oxide, and phosphorous trichloride—*vide* chemical properties of carbon dioxide.

T. Andrews emphasized the high compressibility of liquid carbon dioxide; and J. Natterer said that it has a greater compressibility than that of any other liquid yet tried. C. F. Jenkin investigated the compressibility of liquid carbon dioxide; and C. A. Parsons compressed the liquid one-fifth of its vol. by a press. of 30 tons per sq. in. According to W. P. Bradley, A. W. Browne, and C. F. Hale, when a system containing both liquid and gaseous carbon dioxide between temp. of 29° and 31·2° is subjected to proper mechanical vibration, a peculiar **fog-effect** is produced. This is due not to impurities in the gas, but to a change of state in the liquid and vap. phases, resulting respectively in the formation of minute bubbles and drops. The change of state is produced by alternate compression and dilatation effected by the vibrations of a steel rod clamped to the press. jacket of the apparatus. Under given conditions of temp., press., length of mercury column, and relative vol. of the

press., vibrations of a certain definite pitch are required in order to produce the fog effect.

The **vapour pressure** of liquid carbon dioxide has been measured by M. Faraday,[10] H. V. Regnault, R. Mollier, E. H. Amagat, T. Tate, P. Blaserna, L. P. Cailletet, H. du Bois and A. P. Wills, P. Villard and R. Jarry, J. Verschaffelt, J. Zeleny and R. H. Smith, C. Antoine, A. Jarolimek, etc. H. V. Regnault represented his results at $\theta°$ between $-25°$ and $45°$ by $\log p = 5{\cdot}6771989 - 2{\cdot}2651888\alpha^{\theta+26} + 0{\cdot}6888035\beta^{\theta+26}$, where $\log \alpha = 9{\cdot}9947089 - 10$, and $\log \beta = 9{\cdot}9910406 - 10$. C. Antoine used the formula $\log p = 0{\cdot}8118\{9{\cdot}2615 - 1000(\theta+263)^{-1}\}$; and A. Jarolimek, $\theta = 63p^{0{\cdot}25} - 3{\cdot}5p^{-1} - 154{\cdot}5$. F. Henning and A. Stock gave between 10° and −181°, $\log p = -1279{\cdot}11T^{-1} + 1{\cdot}75 \log T - 0{\cdot}0020757T + 5{\cdot}85242$. F. G. Keyes and A. W. Kenney used $\log_{10} p = 12{\cdot}0722 - 1496{\cdot}7T^{-1} - 0{\cdot}028453T + 0{\cdot}0000364T^2$; and for the rate of change of press. with temp., $dp/dt = p(3446{\cdot}3T^{-2} + 0{\cdot}0001676T - 0{\cdot}065527)$. F. G. Keyes and A. W. Kenney gave:

| | −50° | −40° | −30° | −20° | −10° | 0° | 10° | 20° | 30° |
|---|---|---|---|---|---|---|---|---|---|
| $p$ . . | 6·63 | 9·90 | 14·08 | 19·40 | 26·07 | 34·28 | 44·31 | 57·03 | 71·25 |
| $dp/dT$ . | 0·2726 | 0·3660 | 0·4722 | 0·595 | 0·739 | 0·906 | 1·104 | 1·353 | 1·624 |

E. Falck represented the vap. press., $p$, of the liquid by $\log_{10} p = -4970/4{\cdot}571T + 1{\cdot}75 \log_{10} T - 0{\cdot}03239T/4{\cdot}571 + 3{\cdot}17$. J. P. Kuenen and W. G. Robson's values for the vap. press. of solid and liquid are:

| | 78·32° | −75° | −70° | −60° | −55° | −50° | −40° | −20° | 0° |
|---|---|---|---|---|---|---|---|---|---|
| $p$ (solid) . | 1·00 | 1·28 | 1·88 | 3·97 | — | — | — | — | — |
| $p$ (liquid) . | — | — | — | 4·30 | 5·35 | 6·60 | 9·82 | 19·3 | 34·3 |

H. L. Callendar used $\log_{10} p = 2{\cdot}7033 + 3{\cdot}157/\theta T$ in atm. of 760 mm. (latitude 45°), which is the simplest possible formula; A. Stock and co-workers used $\log p = -1279{\cdot}11T^{-1} + 1{\cdot}75 \log T - 0{\cdot}0020757T + 5{\cdot}85242$ between −78° and −110°. E. Falck represented the vap. press., $p$, of the solid by $\log_{10} p = -6000/4{\cdot}541T + 1{\cdot}75 \log_{10} T - 0{\cdot}009982T/4{\cdot}541 + 3{\cdot}17$. J. Zeleny and R. H. Smith obtained for the vap. press. $p$ cm. of the solid:

| | −56·4° | −57° | −60° | −70° | −80° | −90° | −100° | −120° | −134° |
|---|---|---|---|---|---|---|---|---|---|
| $p$ . . | 391 | 368·5 | 343 | 144 | 65·7 | 28·8 | 11·9 | 1·4 | 0·1 |

H. K. Onnes and S. Weber measured the vap. press. of carbon dioxide down to −183°, and found the results in agreement with E. Falck's formula. A. Stock recommended carbon dioxide as a liquid for thermometers over the range −73° to −100°. R. Lorenz studied the theory of the subject.

The **coefficient of thermal expansion,** $\alpha$, at constant press. has been measured by G. Magnus,[11] who found $\alpha = 0{\cdot}00369087$ between 0° and 100°; H. V. Regnault, $\alpha = 0{\cdot}003710$, and at constant vol., $\beta = 0{\cdot}003688$ between 0° and 100°. Values were also obtained by W. J. M. Rankine, P. von Jolly, T. Andrews, J. Moutier, E. Natanson, A. Cazin, V. Meyer, F. Roth, E. H. Amagat, etc. A. Jaquerod and F. L. Perrot obtained at constant vol. between 1° and 1067°, $\beta = 0{\cdot}0036756$ with the initial press. 240 mm. at 0°; and $\beta = 0{\cdot}0036713$ with the initial press. 170 mm. at 0°. G. Melander found at constant vol., at $p$ mm. press.

| $p$ . | 18·1 | 55·8 | 101·5 | 169·1 | 267 | 347 | 749 |
|---|---|---|---|---|---|---|---|
| $\alpha$ . | 0·0036753 | 0·0036641 | 0·0036657 | 0·0036701 | 0·0036803 | 0·0036856 | 0·0037264 |

A. Leduc gave $\alpha = 0{\cdot}003724$ between 0° and 100° at constant press., and $\beta = 0{\cdot}003713$ at constant vol.; or $\alpha = 0{\cdot}003750$ at 0°, and $\beta = 0{\cdot}003725$ at 0°. P. Chappius found for the coeff. of expansion, $\alpha$, at constant press.:

| | | 0° to 20° | 0° to 40° | 0° to 100° |
|---|---|---|---|---|
| $\alpha$ | 518 mm. . . | 0·0037128 | 0·0037100 | 0·0037073 |
| | 998 mm. . . | 0·0037602 | 0·0037536 | 0·0037410 |
| | 1377 mm. . . | 0·0037972 | 0·0037906 | 0·0037703 |

E. H. Amagat found at constant press., $a \times 10^5$ to have at $p$ atm. press., and between 0° and 258°, the values indicated in Table XXIV. The thermal expansion of

TABLE XXIV.—COEFFICIENTS OF EXPANSION OF CARBON DIOXIDE AT DIFFERENT TEMPERATURES AND PRESSURES.

| Press. atm. | Temperatures. | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | 10° | 20° | 30° | 40° | 50° | 60° | 70° | 80° | 90° | 100° | 137° | 198° | 258° |
| 75 | 654 | 884 | 1437 | 7631 | 7764 | 7487 | 7142 | 6821 | 6524 | 6281 | 5490 | 4766 | 4290 |
| 100 | 544 | 655 | 877 | 1327 | 2867 | 3794 | 4074 | 4189 | 4173 | 4137 | 3933 | 3420 | 3128 |
| 200 | 416 | 422 | 483 | 529 | 597 | 682 | 781 | 893 | 1000 | 1115 | 1349 | 1631 | 1593 |
| 500 | 253 | 267 | 271 | 278 | 292 | 305 | 316 | 327 | 337 | 349 | 387 | 449 | — |
| 1000 | 175 | 181 | 183 | 185 | 189 | 190 | 194 | 198 | 202 | 206 | 226 | — | — |

liquid carbon dioxide is stated by J. H. Niemann to be greater than that of any substance yet observed; B. Schwalbe also emphasized the large coeff. of expansion. J. Dewar found that the coeff. of expansion of the liquid at the b.p. 0·002989 is very nearly five times the value of the coeff. of the solid between —188° and the b.p. E. d'Andréeff found that if the vol. at 0° is unity, the vol. at —10° is 0·9517; at +10°, 1·0585; and at 20°, 1·1457. J. Dewar gave 0·0005704 for the coeff. of expansion of solid carbon dioxide between —188° and the b.p. J. D. van der Waals, R. Clausius, L. Schames, A. Ritter, E. Sarrau, K. Langen, W. Schütt, A. Leduc, B. Leinweber, V. Njegovan, J. B. Goebel, V. Fischer, J. Daclaux, etc., have discussed the **equation of state** of carbon dioxide. R. Clausius' and J. B. Goebel's equations are respectively:

$$p = \frac{0{\cdot}003688T}{v-0{\cdot}000843} - \frac{2{\cdot}0935}{T(v-0{\cdot}000977)}; \quad p = \frac{0{\cdot}0036847T}{v-0{\cdot}00329} - \frac{0{\cdot}00917}{(v-0{\cdot}00068)^2}$$

J. D. van der Waals' equation has been previously discussed:

$$\left(p + \frac{0{\cdot}00894}{v^2}\right)(v-b) = 1{\cdot}00646 + \frac{T}{273}$$

The values from T. Andrews' data are $a$=0·00678 to 0·00717, $b$=0·001807 to 0·001908; from E. H. Amagat's data, $a$=0·00719, and $b$=0·001912; and from J. Dewar's data, $a$=0·00683, and $b$=0·001813. F. B. MacDougall's calculations of the variations in $a$ and $b$ from E. H. Amagat's data have been indicated (**1**. 13, 4). H. von Jüptner found the values of $b$ are variable with temp. and internal press., and possibly also with the attraction of neighbouring mols. From E. H. Amagat's data at 100°:

| $p$ | 50 | 100 | 300 | 500 | 700 | 900 | 1000 |
|---|---|---|---|---|---|---|---|
| $v$ | 0·02413 | 0·01030 | 0·00297 | 0·002401 | 0·002183 | 0·002051 | 0·001990 |
| $b$ | 0·00298 | 0·00276 | 0·00191 | 0·00172 | 0·00164 | 0·00159 | 0·00156 |

A similar variation occurs with T. Andrews' data. The variations in the values of $b$ in the neighbourhood of the critical temp. are considerable; but F. Roth showed that over 100°, $b$ is constant.

The **thermal conductivity** of carbon dioxide has been measured by J. Stefan,[12] A. Winkelmann, A. Wüllner, L. Graetz, G. W. Todd, F. Soddy and A. J. Berry, J. Jamin and F. Richard, A. Oberbeck, F. Narr, A. Kundt and E. Warburg, etc. P. A. Eckerlein found for the coeff. $k$ cals. per cm. for 1°, 0·0002546 at —78·5°; 0·0002824 at —50·5°; and 0·0003434 at 0°; A. Winkelmann found 0·000307 at 0°; and A. Schleiermacher, 0·000327 at 0° and 0·000506 at 100°. E. Pauli found for the ratio $k_{100°}/k_{0°}$ 1·418. S. Weber gave $3{\cdot}393 \times 10^{-5}$. E. Mallard and H. le Chatelier studied the rate of cooling of carbon dioxide.

In 1797, Count Rumford [13] described experiments on the explosion of gunpowder in a cylinder with a capacity equal to the vol. of the explosive, and fitted with a valve. He said :

> What was very remarkable in all these experiments, in which the generated elastic vap. was completely confined, was the small degree of expansive force which this vap. appeared to possess, after it has been suffered to remain a few minutes, or even only a few seconds, confined in the barrel ; for upon raising the weight by means of its lever, and suffering this vap. to escape, instead of escaping with a loud report it rushed out with a hissing noise, hardly so loud or so sharp as the report of a common air-gun, and its effects against the leather stopper, by which it assisted in raising the weight, were so very feeble as not to be sensible.

M. Faraday takes this to mean that the carbon dioxide and other gases were condensed to the liquid state. In 1823, H. Davy said that in attempting to liquefy carbon dioxide by a method analogous to that which he employed for hydrogen chloride, by the action of sulphuric acid on ammonium carbonate in a sealed tube, "in the only trial I have made, the tube burst." M. Faraday, however, used the same reaction and condensed the gas to a limpid colourless liquid. He said that much stronger tubes are needed for carbon dioxide than for other gases previously tried :

> Tubes which have held liquid carbon dioxide well for two or three weeks together, have, upon some increase in the warmth of the weather, spontaneously exploded with great violence ; and the precautions of glass masks, goggles, etc., which are at all times necessary in pursuing these experiments, are particularly so with carbon dioxide.

J. H. Niemann said that it is best to allow the acid to come in contact with the carbonate very slowly because of the development of heat in the reaction. G. Gore closed the tube with a rubber stopper. A. Loir and C. Drion cooled the gas by evaporating liquid ammonia over sulphuric acid under reduced press., and found it liquefied at ordinary press. In 1834, M. Thilorier liquefied the gas by compression in a pair of cast-iron vessels, one of which was used for generating and the other for liquefying the gas. He relied on press. alone to produce liquefaction. According to A. Pleischl, in 1835 one of the storing vessels used by M. Thilorier at the École de Pharmacie, Paris, exploded before the class, and, said J. von Liebig, "its fragments were scattered about with the most tremendous force ; it cut off both the legs of the unfortunate operator, M. Hervy, and the injury was followed by his death" (1. 13, 25). Wrought-iron was then employed ; J. Mareska and E. Donny used lead cylinders surrounded by copper jackets. W. N. Hill, L. P. Cailletet, A. Zimmermann, H. Gall, J. K. Mitchell, H. Debray, R. Addams, J. O. Natterer, have also indicated processes for the liquefaction of the gas. A. Thiel described the filling of glass tubes with liquid carbon dioxide. Numerous systems have been devised for liquefying carbon dioxide, particularly since liquid carbon dioxide is stored and sold in the liquid form. The modern compressors are usually of the multi-stage type in which the gas is compressed in a number of stages involving two, three, or four increases of press. Since the temp. of the gas is raised by compression, the gas is cooled by cold water between each stage. According to R. T. Stewart, and A. Lange, the cylinders in which the gas is stored are not completely filled, a space is left for the liquid to expand, otherwise there is a risk of explosion. The presence of air also increases the risk of explosion, for one per cent. of air in the cylinder increases the press. by three per cent. under the most favourable conditions.

J. Behrens, R. Mackenzie, F. Windhausen, H. Herberts, P. Winand, etc., have patents on the preparation of the liquid ; and O. M. C. Heyl, A. Knoop, W. Burstyn, A. Müller, P. Pagottet, etc., have discussed the holders for storing the liquid. There are a number of monographs on the subject : E. Luhmann, *Die Kohlensäure*, Wien, 1906 ; *Die Fabrikation der flüssigen Kohlensäure*, Berlin, 1904 ; J. C. Goosmann, *The Carbonic Acid Industry*, Chicago, 1907 ; O. Kausch, *Die Kohlensäure, ihre Herstellung und Verwendung*, Hannover, 1909 ; N. Wender, *Die Kohlensäure Industrie*, Berlin, 1901 ; A. M. Villon, *Les emplois industriels de l'acide carbonique*, Paris, 1892 ; T. Koller, *Die Imprägnirungstechnik*, Wien, 1896 ; C. A. Mitchell, *Mineral and Aerated Waters*, London, 1915.

M. Thilorier found that when liquid carbon dioxide is placed in a vessel provided with an opening in the form of a blowpipe jet he was able to produce local cooling effects, and he called the arrangement a *chalumeau de froid*—a cold-blast blowpipe. By releasing the gas from press. he obtained snow-like masses which he first thought to be actual snow formed by condensation from the moisture of the air. It was afterwards found that the chilling of the escaping carbon dioxide is so great that some of it becomes solid. J. K. Mitchell obtained the solid in a similar manner. L. Bleekrode recommended preparing the solid from bombs of the liquid gas by the method employed by H. Landolt, etc. A cloth bag is tied to the delivery valve of the bomb, and the solid collects in the bag when the delivery tube is opened. This method is as effective and more simple than the use of special ebonite or metal boxes—used by E. Ducretet, L. P. Cailletet, etc.—which are liable to have their parts frozen together and then cannot be quickly emptied. C. R. Darling recommended making a flannel bag by rolling coarse flannel round a stout tube or rod and tying up one end. The other end was fixed on to the nozzle of a cylinder of carbon dioxide. When the gas is turned on, a rod of solid carbon dioxide soon forms, and can be easily removed by undoing the bag or cutting it open. O. Hergt, A. Wultze, and N. Teclu have also described the preparation of the solid. A. Loir and C. Drion obtained the solid at about 2 atm. press. by cooling carbon dioxide with liquid ammonia.

H. V. Regnault [14] gave −77·75° to −78·16° for the **boiling point** of liquid carbon dioxide; M. Berthelot, and B. Schwalbe, −78·2°; C. S. M. Pouillet, and P. Villard, −79°; J. P. Kuenen and W. G. Robson, −78·32°; H. Erdmann, −78° at 760 mm. H. du Bois and A. P. Wills gave −79·2°; F. G. Keyes and co-workers, −78·53°; and J. Zeleny and R. H. Smith, 78·2°. K. Scheel represented the effect of press., $p$ mm., on the b.p. by: $B.p. = -78·5 + 0·01595(p-760) - 0·000011(p-760)^2$. For the **melting point**, J. K. Mitchell gave −65°; M. Faraday, −75°; P. Villard and R. Jarry, −56·7° at 5·1 atm. press.; B. Schwalbe, −57° at 5·3 atm. press., and −63·9° at 3·6 atm. press.; and H. Erdmann, −57°. J. P. Kuenen and W. G. Robson found the m.p. is displaced 1° by 47·9 atm. press. G. Tammann measured the effect of press. on the m.p.; and P. W. Bridgman found that the m.p. at one atm. press. is −56·6°, and for press. in kgrms. per sq. cm., the m.p. is

| Press. | 1000 | 2000 | 3000 | 4000 | 5000 | 6000 | 7000 | 12,000 |
|---|---|---|---|---|---|---|---|---|
| M.p. | −37·3° | −20·5° | −5·3° | 8·5° | 21·2° | 32·9° | 44·0° | 93·6° |
| $\delta v$ | — | — | 0·1071 | 0·0979 | 0·0896 | 0·0822 | 0·0755 | 0·0531 |

The change of volume on freezing is represented by $\delta v$. The results are plotted in Fig. 47.

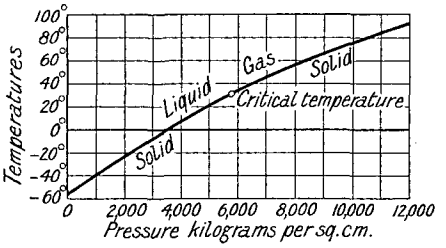



FIG. 47.—The Effect of Pressure on the Melting Point of Carbon Dioxide.

M. Faraday pointed out that owing to the high vap. press. of liquid carbon dioxide, it gives the paradoxical result that if the b.p. be defined as the temp. at which the vap. press. of the substance just balances that of the atmosphere, the b.p. of carbon dioxide is lower than its f.p. by about 22°. J. Johnston has drawn attention to the fact that at about 5800 atm. press., the melting temp. of the solid is the same as the critical temp. of the liquid; at press. higher than this, the solid sublimes or passes directly into the gas, and the curve represents the equilibrium between the solid and gaseous carbon dioxide. There is no break in the curve at the critical temp. of the liquid, above 31°, so that a mere change of press. will suffice to pass from the gas to crystalline solid. This suggests the questions: Can all gases at ordinary temp. be converted into solids by the mere application of a large enough press. without their assuming the liquid state? Can

water above its critical temp. be solidified by press. alone ? Can air be solidified at ordinary temp. by mere compression ?

The **triple point**, according to J. Zeleny and R. H. Smith, is —56·4° at 5·1 atm. press. ; J. P. Kuenen and W. G. Robson gave —56·2° at 5·1 atm. ; and P. Villard and R. Jarry, —56·7° at 5·1 atm. According to H. du Bois and A. P. Wills, the value of $dp/dT$ at the triple point is 5·5 atm. per degree. The triple point is represented in G. Tammann's equilibrium diagram, Fig. 48, by the point $O_1$ ; $O_1A$ is the vaporization curve of the liquid ; $O_1B$ is the sublimation curve of the solid ; and $O_1C$ represents the effect of press. on the m.p. being the boundary line of the solid and liquid phases. The portion $O_4C$ of the $O_1C$-curve is dotted to show that G. Tammann thought the solid to be in a metastable condition, with a transition point $O_4$. The solid stable under ordinary conditions was called *Solid I*, and the second form was called *Solid II*. Later G. Tammann showed that the alleged modification was due to a mal-observation. P. W. Bridgman found no evidence of a second solid phase at 25° and 67° for press. up to 12,000 kgrms. per sq. cm. The diagram is also discussed by H. W. B. Roozeboom.

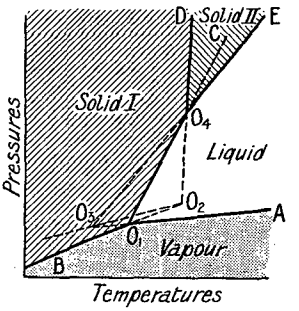



FIG. 48.—Equilibrium Diagram of Carbon Dioxide.

T. Andrews found the **critical temperature** of carbon dioxide to be 30·92° ; E. H. Amagat, 31·35° ; J. E. Verschaffelt, and L. P. Cailletet and co-workers, 31·1° ; E. Sarrau, 32·1° ; J. Chappius, 31·5° ; K. Wesendonck, 31·05° ; J. Dewar, 31·9° ; and E. Cardoso and R. Bell, 31° ± 0·10. Other observations have been made by J. B. Hannay, D. Berthelot, J. Jamin, W. Ramsay, G. Owen and A. L. Hughes, H. Happel, W. H. Keesom, H. K. Onnes and G. H. Fabius, E. Cardoso and R. Bell, etc. T. Andrews gave 73 to 77 atm. for the **critical pressure** ; W. H. Keesom, 72·93 atm. ; E. H. Amagat, 72·9 atm. ; E. Sarrau and J. Dewar, 77·0 atm. ; and E. Cardoso and R. Bell, 72·85 ± 0·10 atm. According to L. P. Cailletet, when a mixture of air and carbon dioxide is submitted to press., the liquefaction of the carbon dioxide is often greatly retarded. Thus, a mixture of equal vols. of air and carbon dioxide will support a press. of 400 atm. at 4° without visible change, When, however, 5 vols. of carbon dioxide are mixed with 1 vol. of air, the former is easily liquefied. If the press. be then raised to 150 or 200 atm., the meniscus of liquefied acid, before concave and well-defined, grows flat and indistinct, then it gradually becomes imperceptible, and the liquid at length disappears altogether. The tube then appears as if filled with homogeneous matter, which resists all further press. as a liquid would. When the press. is again slowly diminished, the liquid suddenly reappears, at a press. which is constant for given temp. A thick cloud appears in the tube, spreads, and vanishes as the liquid forms. The press. at which the liquid carbon dioxide reappears are at 5·5°, 130 atm. ; at 10°, 124 atm. ; at 13°, 120 atm. ; at 18°, 113 atm. ; at 19°, 110 atm. Carbon dioxide gas compressed beyond 250 atm. is not liquefied at 21°. It might be supposed that this disappearance of the liquid is apparent only, in consequence of the refractive index of compressed air increasing more rapidly than that of liquid carbon dioxide, so that at the point where the two indices become equal, the surface of the liquid would cease to be visible ; but, in that case, the surface of separation should again become visible when the press. is further increased. This, however, does not occur, and it is inferred that under high press. a gas and a liquid are capable of soln. in each other, so as to form a homogeneous whole. T. Andrews' value for the **critical volume** of carbon dioxide is 0·0066 and W. H. Keesom's 0·00443 ; and E. H. Amagat's value for the **critical density** is 0·464. T. Andrews gave 0·30 ; E. Sarrau, 0·4395 ; J. Dewar, 0·65 ; L. P. Cailletet and E. Mathias, 0·46 ; W. H. Keesom, 0·469 ; and H. K. Onnes and G. H. Fabius, 0·460. S. F. Pickering gave for the best representative values $\theta_c$=31·1 ; $p_c$=72·9 atm. ; and $D_c$=0·460. E. E. Walker estimated

the mol. association at the critical temp. to be 1·012; and $4RT_c/15p_cv_c=0·957$. G. Bakker calculated the thickness of the capillary film between homogeneous phases of the liquid and vapour of carbon dioxide.

| | −30° | −10° | 0° | 10° | 20° |
|---|---|---|---|---|---|
| Thickness . . . | 1·46 | 1·7 | 2·0 | 2·6 | 3·6 mol. layers |

G. Ansdell, J. D. van der Waals, and J. Dewar measured the effect of *hydrogen chloride* on the critical constants of carbon dioxide; J. Jamin, and J. E. Verschaffelt, of carbon dioxide and *hydrogen*; W. H. Keesom, *oxygen*; T. Andrews, and K. Tsuruta, *nitrogen*; J. Jamin, and U. Lala, *air*; A. Blümcke, R. Pictet, and F. Caubet, *sulphur dioxide* (*cf.* **1. 4, 8**); F. Caubet, *nitrous oxide*; J. P. Kuenen, and J. P. Kuenen and W. G. Robson, *ethane*; J. Dewar, and J. P. Kuenen, *acetylene*; L. P. Cailletet and P. Hautefeuille, *cyanogen*; J. P. Kuenen, and F. Caubet, *methyl chloride*; and J. Dewar, *chloroform*, *carbon disulphide*, *ether*, *benzene*, and *phosphorus trichloride*—*vide* chemical reactions of carbon dioxide. M. Centnerszwer and M. Zoppi, and E. H. Büchner have studied the effect with a number of *organic liquids*. P. Kohnstamm and J. C. Reeders studied the condensation phenomena with mixtures of carbon dioxide and *urethane*.

The **heat of vaporization**, according to J. Chappuis,[15] is 56·2 cals. per gram at 0° and one atm. press.; B. Schwalbe gave 50·75 cals. at 6·6°. E. Mathias gave 50·76 cals. at 6·5°; 31·80 cals. at 22·04°; and 14·40 cals. at 29·85°. L. P. Cailletet, and E. Mathias gave 11·60 cals. at 30°. The heat of vaporization, added E. Mathias, is zero at the critical temp. C. F. Jenkin and D. R. Pye gave for the heat of vaporization, $Q$ cals. per gram.

| | −50 | −40° | −30° | −20° | −10° | 0° | 10° | 20°. |
|---|---|---|---|---|---|---|---|---|
| $Q$ . . . | 79·9 | 75·7 | 71·3 | 66·5 | 60·9 | 54·1 | 46·2 | 36·5 |

J. P. Kuenen and W. G. Robson obtained 121 cals. at the b.p., 95·3 cals. at −65·7°, 56·0 cals. at 0°, and 86·1 cals. at the triple point. U. Behn obtained 142·4 cals. at the b.p.; P. A. Favre and J. T. Silbermann, 142·2 cals.; and J. Zeleny and R. H. Smith, 140 cals. R. Mollier, E. Ariès, and K. Langen calculated values for the latent heat of vaporization. L. P. Cailletet gave for the heat of vaporization, $Q$, of liquid carbon dioxide at $\theta°$ between −25° and 31°, $Q=118·485(31-\theta)-0·4707(31-\theta)^2$. E. Falck gave $Q=(4970+3·5T-0·03239T^2)(1-p/p_c)$, where $p_c$ denotes the critical press., and $p$ the vap. press. of the liquid at $T°$ K. C. F. Jenkin and D. R. Pye gave $\log_{10} Q=1·1164+0·4115 \log_{10}(31·5-\theta)$. F. G. Keyes and A. W. Kenney represented the observed data by $\log_{10} Q=1·2960+0·22215 \log_{10}(T_c-T)+0·054903\{\log_{10}(T_c-T)\}^2$; and $dQ/dT=-Q\{0·2222+0·11 \log_{10}(T_c-T)\}(T_c-T)^{-1}$. The heats of evaporation in cals. per gram; the external work of evaporation $p(v_1-v_2)$; and the internal energy of evaporation are given in Table XXV. C. Dieterici also studied the inner latent heat of evaporation. P. A. Favre gave 0·3128 cal. per gram for the **heat of**

TABLE XXV.—THERMODYNAMIC PROPERTIES OF CARBON DIOXIDE.

| Temp. | Press. atm. | Sp. vol. of liquid, $v_2$ c.c. per grm. | Sp. vol. of gas, $v_1$ c.c. per grm. | Heat of evaporation cals. per grm. | External work of evaporation. | Internal energy of evaporation. | $\frac{dp}{dT}$ |
|---|---|---|---|---|---|---|---|
| 31 | 72·9 | 2·175 | 2·175 | 0 | 0 | 0 | 1·624 |
| 30 | 71·25 | 1·712 | 3·37 | 19·77 | 2·85 | 16·92 | 1·353 |
| 20 | 57·03 | 1·299 | 5·32 | 38·61 | 5·51 | 33·10 | 1·104 |
| 10 | 44·31 | 1·158 | 7·56 | 48·50 | 6·88 | 41·62 | 0·906 |
| 0 | 34·28 | 1·079 | 10·44 | 56·15 | 7·78 | 48·37 | 0·739 |
| −10 | 26·07 | 1·020 | 14·32 | 62·67 | 8·40 | 54·27 | 0·595 |
| −20 | 19·40 | 0·971 | 19·72 | 68·48 | 8·81 | 59·64 | 0·4722 |
| −30 | 14·08 | 0·929 | 27·44 | 73·72 | 9·04 | 64·68 | 0·3660 |
| −40 | 9·90 | 0·895 | 38·92 | 78·59 | 9·11 | 69·48 | 0·2726 |
| −50 | 6·63 | 0·866 | 57·32 | 83·16 | 9·06 | 74·10 | 0·2271 |
| −56·2 | 5·15 | 0·850 | 72·81 | 85·85 | 8·99 | 76·86 | |

**fusion,** and 138·7 cals. for the latent **heat of sublimation.** P. W. Bridgman gave for the latent heat of fusion in kilogramcalories per gram with the press. in kgrms. per sq. cm. :

| Press. . . . . | 3000 | 4000 | 5000 | 6000 | 7000 | 12,000 |
|---|---|---|---|---|---|---|
| Latent ht. . . . | 19·92 | 20·17 | 21·39 | 21·77 | 21·90 | 22·54 |

E. Falck represented the heat of sublimation, $Q$, by $Q=-(6000+3{\cdot}5T-0{\cdot}009933T^2)(1-p/p_c)$, where $p_c$ denotes the critical press., and $p$ the sublimation press. at $T°$ K. U. Behn gave 142·4 cals. for the heat of sublimation. J. P. Kuenen and W. G. Robson gave 129·9 cals. for the heat of sublimation, 43·8 cals. for the heat of fusion. The heat of sublimation at the b.p. is 121 cals., and this increases with rise of temp. W. Nernst gave 3·2 for the **chemical constant ;** E. Falck gave 3·17 ; and F. G. Henglein, —0·41.

In 1835, M. Thilorier [16] showed that a mixture of liquid or solid carbon dioxide with ether evaporated rapidly and produced a temp. of —100°. By means of *Thilorier's freezing mixture,* M. Faraday obtained a temp. of —110°. L. P. Cailletet and E. Colardeau obtained —82° at ordinary press. with a mixture of carbon and nitrogen dioxides; and with methyl chloride, —82° at ordinary press., and —106° in vacuo; P. Villard and R. Jarry studied the mixture with methyl chloride. H. Moissan found that solid carbon dioxide with ethyl or methyl alcohol gives a temp. of —85° ; with methyl chloride or acetaldehyde, —90° ; with ethyl acetate, —95° ; and with acetone, —110°. A. Wohl and M. S. Losanitsch obtained —86° with acetone, and —87° with aldehyde ; and P. Villard and R. Jarry obtained no lowering of the temp. with mixtures of carbon dioxide and toluene. The theory of the phenomenon in the light of the phase rule has been discussed by H. W. B. Roozeboom. In Fig. 49, *I* (78°) represents the sublimation point of solid carbon dioxide at one atm. press. ; *F* represents the b.p. of the alcohol; *EDF*, the b.p. curve of the mixture ; *ECF*, the vap. curve ; and *E*, the b.p. of undercooled liquid carbon dioxide not experimentally realizable. The b.p., *C*, of the sat. soln. is always between the boiling and sublimation temp. of the carbon dioxide. If the b.p. *E* and *F* are very far apart, the vap. curve *ECF* is very steep, and it cuts the sublimation curve *IC* very close to the carbon dioxide axis. Hence, the b.p. of the three-phase system solid carbon dioxide, alcohol and vap., is at *A*, —80°, near to the sublimation temp. of solid carbon dioxide. The vap. curves of mixtures of carbon dioxide with other substances are not very well known, so that the hypothesis cannot be well tested.

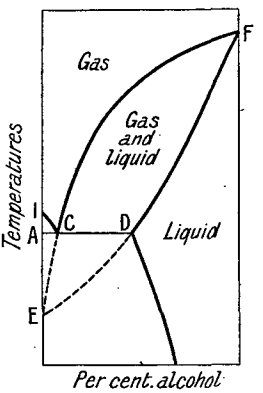


FIG. 49.—Freezing Mixtures of Solid Carbon Dioxide and Alcohol.

The ratio of the two **specific heats** of carbon dioxide was determined by H. Buff,[17] who found 1·277 ; A. Cazin obtained 1·291 ; A. Masson, 1·277 ; W. C. Röntgen, 1·3052 (19°) ; P. A. Müller, 1·2653 between 9·4° and 33·7° and 27·82–75·89 mm. ; O. Lummer and E. Pringsheim, 1·296 (4°–11°) ; J. W. Low, 1·291 (12°–20°) ; E. H. Amagat, 1·292 ; T. Martini, 1·345 at 0° ; J. Jamin and F. Richard, 1·29 ; G. de Lucchi, 1·292 (20°–25°) ; J. W. Capstick, 1·308 (20°) ; G. Maneuvrier and J. Fournier, 1·299 ; W. Makower gave 1·307 ; A. Kundt, 1·303 (16°) ; O. Buckendahl, 1·2990 at 0°, and 1·2899 at 1080° ; H. B. Dixon and co-workers, from 1·296 at 0° to 1·230 at 600° ; J. R. Partington, 1·3022 at 17° ; R. Thibaut gave 1·303 (15°) ; K. Schöler, 1·303 (20°) ; G. Schweikert, 1·301 (0°) ; J. R. Partington and H. J. Cant, 1·303 (20°) ; and B. Tornau, $1{\cdot}3165\pm0{\cdot}00032$ at 0°, and H. W. Moody, 1·3003 at 20° and 760 mm. The ratio of the sp. hts. decreases with rising temp., and increases with rising press., so that the two effects work one against the other. A. Wüllner gave 1·311 at 0°, and 1·282 at 100° ; A. Leduc, 1·319 at 0° and 1·283 at 100° ;

J. M. Crofts gave 1·254 between 15° and 532°, 1·253 (15°–545°), 1·252 (15°–557°), and 1·251 (15°–570°); R. Fürstenau gave 1·2506 at 484·5°, and 1·3008 at room temp. R. Thibaut gave 1·300 at 15° and 1 atm. press.; and 1·279 at 20° and one-third atm. press. E. H. Amagat obtained at 50°, 1·705 at 50 atm., 1·903 at 60 atm., and 2·327 at 70 atm. press. According to E. H. Amagat, the ratio of the two sp. hts. increases with rise of press. at constant temp., and decreases with rise of temp. at constant press. A. G. Worthing found at 7·78 atm. press. the ratio is 1·338 at 0·2°, 1·310 at 31°, 1·296 at 50°, and 1·256 at 98·5°; and at 28·52 atm. press., 1·702 at 0·2°, 1·499 at 31°, 1·448 at 50°, and 1·327 at 98·5°. B. Beckman found for the ratio, $\gamma$, of the two sp. hts. at press. $p$ mm., at 15°:

| $p$ | 760 | 392 | 244 | 149 | 100 | 76 |
|---|---|---|---|---|---|---|
| $\gamma$ | 1·3045 | 1·301 | 1·298 | 1·296 | 1·303 | 1·302 |

W. Küpper obtained $\gamma$=1·300, and when exposed to X-rays, $\gamma$=1·320, and to ultra-violet light, $\gamma$=1·322.

F. Clément and J. B. Désormes found for the sp. ht. of carbon dioxide at constant press., 0·24; F. de la Roche and J. E. Bérard, 0·2210; J. Apjohn, 0·2094; A. C. G. Suermann, 0·2124; H. N. Mercer, 0·2000; A. de la Rive and F. Marcet, 0·1751; and H. V. Regnault, 0·2164 when referred to equal weights, and 0·3308 when referred to equal vols. H. V. Regnault, H. B. Dixon, E. Wiedemann, W. D. Womersley, etc., observed that the sp. ht. increases with rise of temp. H. V. Regnault gave 0·1870 at 0° and 0·2145 at 100°; and E. Wiedemann gave 0·1952 at 0° and 0·2169 at 100°. H. V. Regnault's data, recalculated by H. F. Weber, referred to equal weights of water, gave 0·1383 between −28° and +7°; 0·1565, between 15° and 99°; and 0·1813 between 12° and 214°. E. Wiedemann found 0·1952 at 0°, 0·2169 at 100°, and 0·2387 at 200°. K. Scheel and W. Heuse gave 0·183 at −78°, and 0·202 at −20°; W. F. G. Swann, 0·202 at 20°, and 0·221 at 100°; L. Holborn and L. Austin, 0·2486 between 20° and 80°, 0·2306 between 20° and 440°, 0·2423 between 20° and 630°; L. Holborn and F. Henning found at 0°, 0·201, and the following values between 0° and $\theta$°, and at $\theta$°, $c_\theta$:

| $\theta$ | 200° | 400° | 600° | 800° | 1000° | 1200° | 1400° | 1600° |
|---|---|---|---|---|---|---|---|---|
| Sp. ht. | 0·215 | 0·228 | 0·239 | 0·249 | 0·257 | 0·264 | 0·270 | 0·274 |
| Sp. ht. $c_\theta$ | 0·229 | 0·252 | 0·271 | 0·285 | 0·295 | 0·301 | 0·303 | 0·300 |

and he represented the results between 0° and $\theta$° by $c_p$=0·2010+0·0000742$\theta$ −0·0$_7$18$\theta^2$; or, according to L. Holborn and L. Austin, the sp. ht. at $\theta$ is $c_p$=0·2028+0·001384$\theta$−0·0$_7$5$\theta^2$. T. Martini gave for the **molecular heat** $C_p$=7·89 at 0°. For the mean mol. heat between 0° and $\theta$°, H. V. Regnault gave $C_p$=8·28+0·00596$\theta$; E. Wiedemann, 8·56+0·005038$\theta$; L. Holborn and L. Austin, 8·92+0·00304$\theta$−0·0$_7$79$\theta^2$; and L. Holborn and F. Henning, 8·85+0·00327$\theta$ −0·0$_7$79$\theta^2$. For the true mol. heat at $\theta$°, H. V. Regnault's formula becomes 8·28+0·01192$\theta$; E. Wiedemann's, 8·56+0·010076$\theta$; L. Holborn and L. Austin, 8·92+0·00608$\theta$−0·0$_5$22$\theta^2$; and L. Holborn and F. Henning, 8·85+0·00653$\theta$ −0·0$_5$24$\theta^2$. R. Thibaut gave $C_p$=8·77 at 15°; K. Schöler, 8·76 at 20°; G. Schweikert, 8·85 at 0°; and J. R. Partington and H. J. Cant, 8·76 at 20°. G. N. Lewis and M. Randall gave for the mol. ht. of carbon dioxide between 0° and 2000°, $C_p$=7·0+0·0071$T$−0·00000186$T^2$. M. Trautz gave $C_p$=8·91+0·0065$T$; and S. W. Saunders, for the best representative value, $C_p$=7·34+0·003397$T$ −0·0$_6$610$T^2$. For the increase in the sp. ht. with rise of press., S. Lussana gave 0·201 at one atm., and 0·267 at 30 atm. C. de la Condamine, and V. Fischer calculated values for the sp. hts. at constant vol. and constant press.

H. V. Regnault found the sp. ht. of carbon dioxide at constant vol. to be 0·1843 between −28° and +17°, 0·2025 between 15° and 99°, and 0·2169 between 12° and 214°. L. Holborn and F. Henning gave for the mol. ht. at constant vol. 8·415; F. Keutel, $C_v$=6·59; K. Schöler, 6·72 (20°); R. Thibaut, 6·73 (15°); G. Schweikert, 6·80 (0°); J. R. Partington and H. J. Cant, 6·72 (20°); M. Trautz and O. Grosskinsky, 6·916 (15°), 6·925 (18°), and 6·932 (20°); R. Fürstenau, 7·0, and

J. Joly, 7·4. A. Winkelmann gave for the ratio $C_{100}/C_0=1·172$. H. F. Weber said that press. has very little influence on the sp. ht., but J. Joly found the sp. ht. rises with increasing press. more rapidly with carbon dioxide than with air. H. B. Dixon and F. W. Rixon found the sp. ht. of carbon dioxide at constant vol. to rise gradually with the temp., while variations of press. have but little influence. They obtained the following values for $c_v$ reduced to a press. of 100 atm. :

| | 16°–115° | 170°–118° | 17·5° | 21°–298° | 21°–398° |
|---|---|---|---|---|---|
| $c_v$ | 0·2000 | 0·2004 | 0·2092 | 0·2884 | 0·3565 |

J. M. Crofts obtained 7·815 between 15° and 532°, 7·847 between 15° and 545°, 7·878 between 15° and 557°, and 7·909 between 15° and 570°. E. Mallard and H. le Chatelier represented their results by $C_v=6·5+0·00387\ T$ ; H. le Chatelier, by $C_v=6·5+0·00387\theta$ ; and $C_v=6·3+0·006\theta-0·0_5118\theta^2$ K. Langen, by $C_v=6·7+0·0026T$ ; M. Pier, by $C_v=6·800+0·0033T-0·0595T^2+0·0_81T^3$, at temp. between 0° and $T$°. The relation deduced by J. M. Crofts from G. N. Lewis and M. Randall's values is $C_v=5·0+0·0071T-0·00000186T^2$. F. G. Keyes and A. W. Kenney gave $c_v=0·1547+0·0001595\theta-0·0_795\theta^2$ cals. per gram at 15°. Other values were given by F. Keutel, W. A. D. Rudge, A. Wüllner, R. Threlfall, *H. Valérius, R. Geipert, M. Trautz and B. Berneis, W. D. Womersley, R. T. Glazebrook*, C. F. Jenkin and D. R. Pye, I. B. Zoch, M. Trautz and K. Hebbel, H. N. Mercer, etc.

C. F. Jenkin and D. R. Pye found the sp. ht. of the liquid carbon dioxide to be 0·551 at 0°, 0·523 at −20°, and 0·480 at −40° ; C. Dieterici gave 0·50 at 0° ; and F. G. Keyes and A. W. Kenney calculated 0·543 at 0° and −20°, and 0·544 at −40°. B. Schwalbe found the sp. ht. of the liquid to be $c_p=0·2164$. A. Berndt showed that at constant vol. the sp. hts. of liquid and vap. between −5° and 25° are the same. A. Eucken found the sp. ht. of solid carbon dioxide to be 1·08 at −253·6°, and 13·38 at−73·5°. C. F. Jenkin and D. N. Shorthose measured the *total heat* in liquid carbon dioxide. J. Kapp measured the sp. ht. of binary mixtures of carbon dioxide with oxygen, and argon ; M. Berthelot and P. Vieille, of carbon dioxide with oxygen, and nitrogen ; and J. M. Crofts, of carbon dioxide with electrolytic gas.

The **heat of formation** of carbon dioxide has been discussed in connection with carbon. Determinations have been made by P. A. Favre and J. T. Silbermann,[18] M. Berthelot, J. Thomsen, H. W. Schröder van der Kolk, etc. M. Berthelot gave (C, 2O)=94 Cals. (CO, O)=66·81 to 68·28 Cals., and (CO, O, aq.)=72·69 Cals. ; while J. Thomsen gave with amorphous carbon (C, 2O)=96·96 Cals., (CO, O)=66·8 Cals., and (CO, O, aq.)=72·69 Cals., all at constant press. P. A. Favre and J. T. Silbermann gave for (C, 2O) at constant press. with wood charcoal 96·98 Cals. ; sugar charcoal, 96·53 Cals. ; graphite, 93·36 Cals. ; and the diamond, 93·24–94·55 Cals. M. Berthelot and P. Petit gave for diamond carbon (C, 2O)=94·3 Cals., for graphite carbon, 94·8 Cals., and for amorphous carbon, 97·65 Cals., all at constant vol. V. Njegovan, R. C. Tolman and R. M. Badger calculated the **entropy** of carbon dioxide ; and H. von Jüptner, the **free energy,** $F$, of the reaction $C+O_2=CO_2$ ; when $p_1$ and $p_2$ respectively denote the partial press. of oxygen and carbon dioxide, $F=98369·9-54·06T+6·31T\ \log\ T-0·00064T^2+4·56T\ \log\ (p_1/p_2)$. W. Schütt, A. Eucken and co-workers, and K. Langen have discussed the internal energy, and the entropy of carbon dioxide. K. Langen calculated a heat-entropy diagram down to −50°. J. Thomsen found the **heat of solution** of a mol of carbon dioxide in 1500 mols. of water to be 5·880 Cals., and for the **heat of neutralization** of a mol of aq. carbonic acid with $n$ mols of sodium hydroxide, $H_2CO_3$aq. $+n$NaOH :

| $n$ | 1 | 2 | 4 |
|---|---|---|---|
| Heat of neutralization | 110 | 202 | 204 Cals. |

P. A. Favre and C. A. Valson gave for the dil. soln. $Na_2O$aq.$+CO_2=Na_2CO_3$aq.$+25·88$ Cals. ; and N. N. Beketoff gave 75·28 Cals. for the same reaction. M. Berthelot

found for ($\frac{1}{2}CO_2$aq., $NH_3$aq.)=5·35 Cals. with a soln. of 1·25 grms. of carbon dioxide in a litre, or one eq. of the salt in 20 litres; and P. A. Favre and C. A. Valson gave 16·946 Cals. for the same reaction in dil. soln.

E. Mulder [19] found that a small proportion of carbon dioxide enhances the luminosity of the flame of coal gas; but P. F. Frankland found that large proportions act in the opposite direction, for 60 per cent. of carbon dioxide completely destroys the luminosity of the flame of ethylene. A. Bunte, G. Frère, F. Clowes and co-workers have studied this subject. E. Rosetti gave for the combustion temp. of mixtures of one vol. of coal gas with $n$ vols. of carbon dioxide:

| $n$ | 0·5 | 0·67 | 1·0 | 1·5 | 2·0 | 3·0 |
|---|---|---|---|---|---|---|
| Temp. of combustion | 1190° | 1170° | 1100° | 1020° | 880° | 780° |

The **index of refraction** of carbon dioxide, without spectral resolution, has been measured by many observers. J. B. Biot and F. J. Arago [20] gave $\mu$=1·0004497; P. L. Dulong, 1·0004495; J. Jamin, 1·0004500; W. Ramsay and M. W. Travers, 1·0004488. Other observations have been made by M. Croullebois, L. Boltzmann, C. and M. Cuthbertson, F. Mohr, J. A. Wasastjerna, L. Bleekrode, J. Klemencic, etc. G. W. Walker obtained for Na-light, 1·000451. For light $\lambda$=535·2$\mu\mu$, E. Ketteler found 1·0004507, and for $\lambda$=670·8$\mu\mu$, 1·0004477; E. Mascart, for $\lambda$=480·0$\mu\mu$, 1·0004587, and for $\lambda$=643·8$\mu\mu$, 1·0004532; E. Perreau, for $\lambda$=467·7$\mu\mu$, 1·0004550, and for $\lambda$=643·8$\mu\mu$, 1·0004487; H. C. Rentschler, for $\lambda$=334·2$\mu\mu$, 1·0004668, and for $\lambda$=577·1$\mu\mu$, 1·0004487; J. Koch, for $\lambda$=435·9$\mu\mu$, 1·0004563, and for $\lambda$=8678·4$\mu\mu$, 1·0004579; L. Stuckert, for $\lambda$=435·9$\mu\mu$, 1·0004589, and for $\lambda$=670·8$\mu\mu$, 1·0004466; and G. Gruschke, $\lambda$=447·2$\mu\mu$, 1·0004568, and for $\lambda$=667·8$\mu\mu$, 1·0004475. J. Koch found a marked anomaly in the ultra-red. M. Faraday, B. Schwalbe, and J. H. Niemann commented on the high refractivity of liquid carbon dioxide. L. Bleekrode found the index of refraction of liquid carbon dioxide is dependent on the temp., particularly in the vicinity of the critical temp., being 1·199 at 12·5°, 1·192 at 15·5°, 1·186 at 18·5°, and 1·173 at 24°. The crystals of the solid, said P. Villard and R. Jarry, have no action on polarized light. J. Chappius and C. Rivière gave for the effect of press. $p$ mm. up to 19 atm. at 21°, for the $D$-line, $\mu-1=0{\cdot}000540p(1+0{\cdot}0076p+0{\cdot}0000050p^2)$. V. Posejpal also studied the effect of reduced press. on the index of refraction. It was found that the laws $(\mu-1)/D$=constant, and $(\mu^2-1)/(\mu^2+2)D$=constant hold good for press. up to 19 atm. P. Phillips gave $(\mu^2+2)/(\mu^2-1)=6{\cdot}581+0{\cdot}1130D^2$. The **dispersion** has been measured by E. Mascart, M. Croullebois, etc. The last-named found $\mu_G-\mu_F$=0·000014; and $\mu_G-\mu_C$=0·000115; and for $(\mu_G-\mu_C)/(\mu_F-1)$=0·2214. L. H. Siertsema and M. de Haas found the dispersion constants are independent of press. between 20 and 47 atm. H. Becquerel found the magnetic rotatory power for Na-light to be 12·18; and the ratio of the value for carbon dioxide to that of carbon disulphide to be 0·000302. T. M. Lowry found the index of refraction and sp. inductive capacity agree with the assumption that the molecule is not internally ionized. P. Glan found the optical properties of reflecting surfaces are not affected by carbon dioxide. J. W. Brühl gave for the **molecular refraction**, at 15·5°, 6·38 for the liquid, and 6·47 for the gas. The **scattering of light** in carbon dioxide has been discussed by M. Raman, and C. V. Raman and K. S. Rao, A. S. Ganesan, K. R. Ramanathan, and by Lord Rayleigh. The **electromagnetic rotation**, or Verdet's constant, $\omega$, is, according to L. H. Siertsema, $\omega\times10^6=2{\cdot}682\lambda^{-1}+0{\cdot}8305\lambda^{-3}$ at 6·5° and at atm. press. when the wave-length, $\lambda$, is expressed in $\mu$. The electromagnetic birefringence was studied by R. de Mallemann, and N. Lyon.

The **spark spectrum** of carbon dioxide has been discussed in connection with carbon. Observations have been made by E. F. Barker,[21] A. Wüllner, K. Wesendonck, H. Deslandres and L. d'Azambuja, G. Gehlhoff, W. H. Bair, W. W. Coblentz, F. Paschen, K. J. Angström, A. Hagenbach, F. Himstedt and H. von Dechend, W. H. Bair, etc. Carbon dioxide is a colourless gas, and it shows no visible **absorption spectrum.** In the ultra-red, there is a band with maximum intensity

corresponding with wave-length 4·76$\mu$. The **ultra-red emission spectrum** of carbon dioxide at a press. of 0·6 mm., by W. W. Coblentz, is illustrated in Fig. 50, which can be compared with Fig. 35, for carbon monoxide. He added that the "greater intensity of the band with carbon monoxide would make it appear as though the 4·75$\mu$ band were due to this gas." The atm. shows the same absorption bands; so does the flame in which carbon dioxide is a product of the combustion. J. Okubo showed that the nearer ultra-red spectrum of carbon dioxide comprises intense bands at 2·71$\mu$ and 2·77$\mu$, and a somewhat weaker band at 2·61$\mu$. There are a number of feebler bands with various maxima between 3·02$\mu$ and 2·29$\mu$.

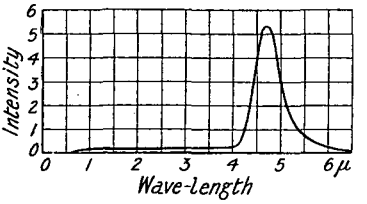



FIG. 50.—Ultra-red Emission Spectrum of Carbon Dioxide.

R. Schachenmeier made observations on the ultra-red spectrum of carbonates; and A. Balandin, and H. M. Randall, on the ultra-red spectrum of carbon dioxide. F. Paschen found that the effect of temp. on these bands is such that the maximum is displaced 4·270$\mu$ at 17°; at 600°, 4·344$\mu$; at 1000°, 4·388$\mu$; and at 1900°, 4·403$\mu$. There is also a band with a maximum 2·6$\mu$ in the ultra-red. H. Rubins and A. Aschkinass found a third absorption band with a maximum at 14·7$\mu$. According to H. N. Kreusler, and V. Schumann, there is a faint absorption for ultra-violet rays more refrangible than 200$\mu\mu$. W. H. Miller showed that the gas is transparent to the actinic rays. C. Schäfer studied the effect of press. on the ultra-violet spectrum of carbon dioxide.

The absorption of heat rays has been investigated by K. J. Angström, W. Barrett, H. Heine, J. E. Keeler, E. Lecher, E. von Bahr, W. C. Röntgen, J. Tyndall, etc. The selective absorption of the heat rays represents the power possessed by carbon dioxide of hindering terrestrial radiations, and, by blanketing the earth, helps to avert excessive changes of temp. This question has been discussed by S. Arrhenius. He tried to picture the effect of a change in the proportion of carbon dioxide in the atm. on the surface temp. of the earth. The temp. of the earth's surface was assumed to be in equilibrium with that of the atm.; if by any increase in the amount of carbon dioxide the atm. retained more heat than before, it would radiate more heat to the surface of the earth. The surface temp. would then rise until equilibrium between the two occurred. The rise was assumed to be governed by the radiation law, and hence it was estimated that if the carbon dioxide is increased 2·5 to 3·0 times its present value, the temp. in the Arctic regions would rise 8° to 9°, and produce a climate as mild as that of the Eocene Period; a decrease of 0·55 to 0·62 times its present value would cause a fall of 4° to 5° and produce a glacial period. F. Frech, and C. F. Tolman support S. Arrhenius' views. E. Kayser, and C. G. Abbot and F. E. Fowle hold that the carbon dioxide in the atm. cannot absorb more than 16 per cent. of the terrestrial radiations; that variations in its amount are of small effect; and that the proportion of aq. vap. in the atm. is so large as to make the climatic significance negligible. The principal absorbent of terrestrial radiation is aq. vap.

R. K. McClung,[22] and J. A. Crowther studied the ionization of carbon dioxide by hard and soft **X-rays**; P. Lenard, by **cathode rays**; T. H. Laby, R. A. Millikan and co-workers, and E. P. Metcalfe, by the $\alpha$-rays from uranium, etc.; R. D. Kleeman, and T. H. Laby and G. W. C. Kaye, by **$\gamma$-rays**; and R. D. Kleeman, and R. J. Strutt, by **Becquerel's rays.** P. L. Kapitza measured the loss of energy by an $\alpha$-particle passing through carbon dioxide; A. Lepape, the effect of carbon dioxide on the ionization current produced by $\alpha$-rays; F. Hauer, the ionization by $\alpha$-rays; and P. W. Burbidge, the absorption of X-rays. H. Baerwald, and A. Becker measured the absorption of cathode rays by carbon dioxide. H. Zickendraht studied the action of carbon dioxide on the fluorescence of sodium vap. The chemical effects of ultra-violet rays and radium radiations are indicated below. J. Elster and H. Geitel found that natural carbon dioxide from deep soils is radioactive.

G. Gehlhoff[23] found that the **cathode fall of potential** when an electric discharge passes through carbon dioxide is not the sum of the separate values for the component atoms. He eliminated the effects due to the decomposing action of the discharge on the gas—*vide infra*. F. Narr, C. Richter, A. Becker, and C. E. and H. Guye studied the effect of carbon dioxide on the discharge from an influence machine. According to A. Becker, mercury in contact with carbon dioxide takes on a positive charge. E. Ducretet, L. Bleekrode, L. P. Cailletet, and B. Schwalbe found that when solid carbon dioxide is made by passing the gas into a bag or ebonite vessel both the receiver and the solid carbon dioxide are charged negatively, while the escaping gas is charged positively. Similarly, J. Joly found that a jet of gas from a copper bomb gives off electric sparks. G. Hausknecht said that the best electrical effects are obtained if the gas is quite free from air. M. Faraday, and K. Wesendonck said that it is doubtful if the gas alone, quite free from dust and moisture, would develop an electric charge by friction against metal. J. Elster and H. Geitel showed that the so-called electricity of flames is but a special case of the more general positive electrification of gases in contact with incandescent bodies (**3**. 26, 1). A. L. Hughes and A. A. Dixon gave 10 volts for the **ionizing potential**; C. A. Mackay, 14·3 volts; and K. T. Compton, 6·47–8·2 volts. H. E. Hurst studied the **discharge potential** of carbon dioxide; and C. E. Guye and co-workers worked with the gas under press.; C. E. Guye and R. Rudy also investigated the electromagnetic rotation of the gas; and J. Kunz, the press. in the corona discharge.

E. Becquerel,[24] and E. Villari found the **electrical resistance** of carbon dioxide at a red heat to be 1·2 to 2·0 times that of air. G. Gore, L. P. Cailletet, and L. Bleekrode found liquid carbon dioxide to be a very poor conductor of electricity. The **electrical conductivity** of aq. soln. of carbon dioxide has been measured by E. Pfeiffer,[25] F. Kohlrausch, F. W. Knox, J. Walker and W. Cormack, etc. Aq. soln. of carbon dioxide have the properties of an acid—*vide infra*, action of water on carbon dioxide. It is therefore inferred that carbon dioxide is *carbonic anhydride*, and that the aq. soln. contains carbonic acid, $H_2CO_3$. This acid has not been isolated because it so readily decomposes into water and gaseous carbon dioxide. When the aq. soln., coloured red by litmus, is boiled, the gas escapes, and the soln. acquires the neutral tint. According to the ionic theory, the acidity of the soln. is due to the presence of $H'$-ions derived from the ionization of carbonic acid: $H_2CO_3 \rightleftharpoons H' + HCO_3'$. If $v$ denotes the vol. of the soln. in litres containing a mol. of carbonic acid, and $\alpha$ be the proportion of acid ionized, then,

$$\frac{1-\alpha}{v}K_1=\left(\frac{\alpha}{v}\right)^2; \text{ or } K_1=\frac{\alpha^2}{(1-\alpha)v}$$

where $K_1$ represents the ionization constant in $H_2CO_3 \rightleftharpoons H' + HCO_3'$. The subject has been discussed by A. Thiel, R. Strohecker, O. Haehnel, E. Wilke, and L. Pusch. J. Kendall measured the sp. conductivity of water in equilibrium with the carbon dioxide of the atm., and found the values $0·65\times10^{-6}$ at 0°; $0·75\times10^{-6}$ at 18°; and $0·80\times10^{-6}$ at 25°, and, in agreement with J. Walker and W. Cormack, who said that carbon dioxide is the only substance in the atm. which confers conductivity on water; the purest distilled water of the laboratory is a sat. soln. of carbon dioxide under existing atm. conditions. F. W. Knox gave for the eq. conductivity, $\lambda$ mhos, when a mol of the acid, $H_2CO_3$, is dissolved in $v$ litres of water:

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| $v$ . . . | 12·61 | 18·43 | 36·36 | 53·2 | 125 | 287 | 1099 |
| $\lambda$ . . . | 0·777 | 0·932 | 1·210 | 1·580 | 2·44 | 3·74 | 8·01 |
| $\alpha$ . . . | 0·00210 | 0·00261 | 0·00367 | 0·00443 | 0·00684 | 0·01048 | 0·02244 |
| $K_1\times10^7$ . | 3·76 | 3·70 | 3·72 | 3·70 | 3·77 | 3·86 | 4·69 |

J. Walker and W. Cormack gave for the conductivity at infinite dilution 3·565, and calculated for the transport number of the hydrocarbonate ion, $HCO_3'$, 40·5, and for the $H'$-ion, 316, from the conductivity of soln. of sodium hydrocarbonate; J. Kendall

gave 40·1 at 18°, 35 at 12·5°, and 25 at 0° for the $HCO_3'$-ion. Further observations give for the mean value of the **ionization constant,** $K_1=0·0_6304$, or $K_1=3·04\times10^{-7}$ at 18°, according to J. Walker and W. Cormack; $3·34\times10^{-7}$ at 12·5° and $3·75\times10^{-7}$ at 18°, according to F. W. Knox; and $2·24\times10^{-7}$ at 0°, $3·12\times10^{-7}$ at 18°, and $3·50\times10^{-7}$ at 25°, according to J. Kendall. The **heat of ionization,** $H_2CO_3aq \rightleftharpoons H' + HCO_3'$, given by J. Kendall was 0°–25°, −2·89 Cals.; 0°–18°, −2·91 Cals.; and 18°–25°, −2·83 Cals.; E. W. R. Pfeiffer gave −7·85 Cals. at 0°–12·5°; and F. W. Knox, −3·48 Cals. at 12·5°–18°. The ionization constant furnishes a ready means of comparing the strength of acids. Thus, at 18°,

| | Acetic acid. | Carbonic acid. | Hydrosulphuric acid. | Hydrocyanic acid. | Boric acid. |
|---|---|---|---|---|---|
| $K_1$ . . | $1·8\times10^{-5}$ | $3·0\times10^{-7}$ | $9·0\times10^{-8}$ | $1·3\times10^{-9}$ | $5·8\times10^{-10}$ |

The percentage degrees of ionization, or the percentage amount of the acid ionized, are:

| | $CH_3.COOH$ | $H_2CO_3$ | $H_2S$ | $H_2BO_3$ | HCy |
|---|---|---|---|---|---|
| $\frac{1}{100}N$-soln. . . . | 4·2 | 0·774 | 0·42 | 0·042 | 0·036 |
| $\frac{1}{10}N$-soln. . . . | 1·3 | 0·250 | 0·13 | 0·013 | 0·011 |

E. Pfeiffer, A. Lieben, J. Walker, etc., raised the question: *Is all the carbon dioxide in aq. soln. present as carbonic acid, or is part present as carbonic acid, and part present as free (or hydrated) carbon dioxide?* Let $a$ denote the number of mols of unchanged carbon dioxide; $b$, the number of mols of non-ionized carbonic acid; and $a$, the number of mols of ionized carbonic acid. Then $a+b+a=1$. From the mass law, assuming that there is equilibrium between the free carbon dioxide in soln. and the carbonic acid, $a/v=kb/v$, where $k$ is constant; hence, $b=a/k$. Substitute this value of $b$ in the first equation, and $a/k=(1-a)/(1+k)$; or $b=(1-a)/(1+k)$. The equilibrium condition between ionized and non-ionized carbonic acid gives $(a/v)^2=K_1(b/v)$, and on substituting for $b$ it follows that $a^2/(1-a)v=K_1/(1+k)$; but $k$ is constant, and hence $a^2/(1-a)v=K$. The constancy of $a^2/(1-a)v$ thus furnishes no evidence as to the proportion of the carbon dioxide in aq. soln. present as carbonic acid, for the same relation is obtained whatever be the proportion.

The complete ionization of carbonic acid $H_2CO_3\rightleftharpoons 2H' + CO_3''$ proceeds in two stages: $H_2CO_3\rightleftharpoons H' + HCO_3'$, for which the ionization constant has just been shown to be $K_1=3\times10^{-7}$. The second stage is represented by $HCO_3'=H' + CO_3''$, or $[H'][CO_3'']=K_2[HCO_3']$. From J. Shields' observations on the hydrolysis of aq. soln. of sodium carbonate, and F. Kohlrausch and A. Heydweiller's value for the ionization constant of water, G. Bodländer calculated for the ionization constant of the second hydrogen ion $K_2=1·295=10^{-11}$. Hence, $K_1$ is 23,000 times as great as $K_2$. H. Menzel gave $K_2=6·2\times10^{-11}$ at 18°. By combining $K_1$ and $K_2$, it follows that $H_2CO_3+CO_3''=2HCO_3'$; and $[HCO_3']^2/[H_2CO_3][CO_3'']=K_1/K_2$; and $K_1/K_2=K_3$. H. N. McCoy found $K_3$ at 25° to be 5300. More exact values for the second ionization constant were determined by F. Auerbach and H. Pick, and E. B. R. Prideaux, and they find $K_2=6\times10^{-11}$. This subject has been discussed in connection with the hydrolysis of the carbonates and hydrocarbonates of the alkalies and alkaline earth metals (*q.v.*). A. Thiel and R. Strohecker represent the degree of ionization in terms of the carbonic acid actually formed rather than in terms of the amount of carbon dioxide dissolved. They estimate that in a 0·00812 molar soln. of this gas at 4°, only 0·67 per cent. is present as carbonic acid. Making allowance for this, the ionization constant of the first hydrogen-ion is $5\times10^{-4}$. L. J. Henderson has discussed the function of carbonic acid in preserving a neutral reaction in natural waters, and thus maintaining the characteristic chemical inactivity of water. O. Hähnel found that at a press. of 52 atm., and at 15°, the strength of carbonic acid is of the same order as formic acid. R. Strohecker made observations on this subject and found that the ionization constant is $44\times10^{-5}$, making the acid behave like a hydroxyformic acid; D. H. Jackson and J. R. McDermet, on the effect of the de-aëration of natural waters on the carbonate equilibrium; and I. N. Kugelmass and A. T. Schohl, on the effect of the equilibrium on the physiology of bone calcification.

E. Wilke showed that the conductivity increases with time, possibly owing to disturbances produced by the current; the ionization constant thus appeared to increase from $3{\cdot}07\times10^{-7}$ to $4{\cdot}5\times10^{-7}$ in 3 hrs. Light acts similarly. The hydrogen ion conc. in the presence of alkali chlorides makes the carbonic acid appear like a strong acid, but the $H^{\cdot}$-ion conc. increases more rapidly than the conc. of the acid. This is explained by assuming that the aq. soln. of carbon dioxide contains some orthocarbonic acid, $H_4CO_4$, which, containing no ketonic oxygen, is a very weak acid; but in conc. salt soln. it is dehydrated, forming metacarbonic acid, $CO(OH)_2$, which behaves like a strong acid. E. P. Metcalfe studied the ionization of the gas.

According to E. Royer, and A. Coehn and S. Jahn, carbon dioxide is reduced electrolytically in aq. soln. of sodium hydrocarbonate, or better, potassium sulphate, but not in sodium carbonate or acid soln. With most cathodes, reduction takes place to a small extent; with a cathode of zinc, freshly coated with zinc from a potassium zinc cyanide bath, a 50 per cent. yield of formic acid is obtained. Repeated use of an amalgamated zinc cathode results at first in increased yields (up to 82 per cent.), but the cathode suddenly loses its activity. Amalgamated copper cathodes give constant yields (45 to 50 per cent.) on repeated use. After prolonged electrolysis of carbon dioxide in potassium sulphate soln., comparison of the acidity of the mixed cathode and anode soln. with the potassium permanganate titre shows the reduction to result in the formation of formic acid with little or no formaldehyde. Formic acid can also be obtained by electrolysis of an aq. soln. of carbon dioxide. R. Ehrenfeld electrolyzed, for 12 hrs. at ordinary temp., a soln. of commercial ammonium carbonate in one part of aq. ammonia, sp. gr. 0·910, and four parts of water contained in cells with the anode and cathode (platinum foil) separated by a porous partition. Ammonium formate was produced at the cathode when this consisted of amalgamated zinc and when a difference of potential of 5–10 volts and a current density of 0·01–0·08 amp. were employed. No formate could be detected (*a*) when iron, platinum, copper, lead, or nickel cathodes were used, (*b*) when the current density was less than 0·01 amp., nor (*c*) when the soln. was too dil., for example, one-fifth the above conc. Soln. of sodium carbonate or of carbonate and hydroxide do not yield formates under similar conditions. The formation is not due to the presence of carbamate in the commercial carbonate, but is attributed to the presence of $NH_4CO_3^{\cdot}$-anions in the conc. soln. A. Bach has given a series of equations representing the different stages of electrolysis, but these are quite imaginary, and, added W. Löb, lack any experimental foundation. The reduction of carbonic acid to carbon does not occur in any soln. of the carbonates, but F. Haber and S. Tolloczko found that if barium chloride be fused with 5–20 per cent. of barium carbonate, cooled, and electrolyzed at 550°–600° in a nickel crucible with a platinum cathode, carbon separates in a dendritic form. The anodic oxidation of carbonate soln. was found by E. J. Constam and A. von Hanssen, G. Hostelet, and F. Salzer to furnish percarbonic acid (*q.v.*). The electrolysis of carbonate soln. has been studied by P. Burckhard, H. Kolbe and R. Schmidt, C. Luckow, etc.

The **dielectric constant** of liquid carbon dioxide was found by F. Linde [26] to be 1·608 at −5°; 1·583 at 0°; 1·540 at 10°; and 1·526 at 15° for $\lambda=\infty$; and for the gas at 15° and 39 atm. press., 1·060; at 19·9 atm. press., 1·015; and at 9·4 atm. press., 1·009. Determinations were also made by L. Boltzmann, E. C. Fritts, J. Klemenic, and W. E. Ayrton and J. Perry. W. Herz found the dielectric constant at 10° to be 1·540; and at the critical temp. 1·27. H. Riegger gave 1·001392 at −73°. Carbon dioxide was first stated by M. Faraday,[27] F. Zantedeschi, and J. Plücker to be diamagnetic. R. Bernstein gave $+0{\cdot}0002\times10^{-6}$ for the **magnetic susceptibility** in vol. units at atm. press. and 15°; G. Quincke gave at 16°, and 1 atm. press. $+0{\cdot}017\times10^{-6}$ and at 10 atm. press., $+0{\cdot}12\times10^{-6}$. T. Soné gave $-0{\cdot}423\times10^{-6}$ for the sp. magnetic susceptibility, and $-0{\cdot}1781\times10^{-9}$ for the vol. susceptibility at 0° and 760 mm. A. Glaser investigated the diamagnetism of this gas. D. N. Mallik studied the magnetic rotation of the electric discharge in carbon dioxide. F. Weigt gave $(0{\cdot}1420\pm0{\cdot}0017)\times10^{-18}$ for the **electrical moment**

of carbon dioxide. W. M. Young measured the ionic mobility in the corona discharge; and H. A. Erikson, and G. C. Grindley and A. M. Tyndall, the mobility of ions in carbon dioxide.


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## § 35. The Solubility of Carbon Dioxide

J. Dalton,[1] and W. Henry noted that water dissolves approximately its own vol. of carbon dioxide. F. M. Buamert also observed that at 3·2° and 760 mm. press., one vol. of water dissolves 1·5184 vol. of the gas, and at 19·6°, 0·8545 vol. W. B. and R. E. Rogers, R. Bunsen, G. Geffcken, E. Bauer, E. Fernet, G. Just, F. Exner, J. H. Coste, K. Angström, E. Wiedemann, W. Kunerth, S. Gniewasz and A. Walfisz, N. de Khanikoff and V. Louguinine, W. Sander, C. Bohr and J. Bock, L. W. Winkler, P. Rischbieth, etc., have made observations on the solubility of carbon dioxide in water. C. Bohr and J. Bock gave for the solubility, $S$, expressed in grams of carbon dioxide in 100 grms. of water, and the absorption coeff., $\beta$ :

| | 0° | 5° | 10° | 15° | 20° | 25° | 30° | 40° | 50° | 60° |
|---|---|---|---|---|---|---|---|---|---|---|
| $\beta$ . . | 1·713 | 1·424 | 1·194 | 1·019 | 0·878 | 0·759 | 0·665 | 0·530 | 0·436 | 0·359 |
| $S$ . . | 0·335 | 0·277 | 0·231 | 0·197 | 0·169 | 0·145 | 0·126 | 0·097 | 0·076 | 0·058 |

thus showing that at a fixed press., the vol. of gas absorbed by a liquid decreases with rise of *temperature*. F. Henrich represented R. Bunsen's results at $\theta°$ by the formula: Absorption coeff., $\beta=1{\cdot}7326-0{\cdot}066724\theta+0{\cdot}00123946\theta^2$; and A. Naccari and J. Pagliani gave $\beta=1{\cdot}5062-0{\cdot}036511\theta+0{\cdot}00029176\theta^2$. A. Hantzsch and A. Vagt measured the distribution of carbon dioxide between air and water at different temp. J. Dalton, and W. Henry showed that the amount of gas dissolved at a given temp. is roughly proportional to the *pressure* as indicated by Henry's law (**1**. 10, 4). H. V. Regnault showed that the relation is not strictly followed; and N. de Khanikoff and V. Louguinine found that the amount of carbon dioxide dissolved is rather greater than corresponds with the proportional rule, and that the difference increased as the press. was augmented. S. von Wroblewsky observed that the coeff. of absorption increases less rapidly than the press. and tends towards a limiting value. Thus, if $S$ denotes the vol. of gas absorbed by one c.c. of water, he found that at the press. $p$ atm.:

| $p$. | | 1 | 5 | 10 | 15 | 20 | 25 | 30 |
|---|---|---|---|---|---|---|---|---|
| 0° | $S$ | 1·797 | 8·65 | 16·03 | 21·95 | 26·65 | 30·55 | 33·74 |
| | $S/p$ | 1·797 | 1·730 | 1·603 | 1·463 | 1·332 | 1·222 | 1·124 |
| 12·43° | $S$ | 1·086 | 5·15 | 9·65 | 13·63 | 17·11 | 20·31 | 23·25 |
| | $S/p$ | 1·086 | 1·030 | 1·965 | 0·909 | 0·855 | 0·812 | 0·775 |

W. Sander measured the solubility of carbon dioxide in water between 20° and 100°, and between 20 and 170 kgrms. per sq. cm. press. and found that at low temp. the results deviate from Henry's law, but the accord is closer when the vol. of gas absorbed is referred to the vol. of the soln. and not that of the solvent. The law is more nearly followed at higher temp., and at 100°, the solubility is proportional to the press. thus corresponding with Henry's law. This is shown by the following selection, where $C$ represents the vol. of gas (reduced to one kgrm. per sq. cm.) absorbed by one c.c. of the soln., and $p$, the press. in kgrms. per sq. cm.:

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| 20° | $p$ | 25 | 30 | 40 | 50 | 55 | |
| | $C$ | 17·77 | 19·77 | 21·52 | 28·09 | 29·75 | |
| 35° | $p$ | 30 | 40 | 50 | 60 | 70 | 80 |
| | $C$ | 13·57 | 20·00 | 24·64 | 22·50 | 27·62 | 32·85 |
| 60° | $p$ | 40 | 50 | 60 | 80 | 100 | 120 |
| | $C$ | 9·80 | 13·72 | 15·28 | 22·67 | 27·85 | 33·90 |
| 100° | $p$ | 70 | 90 | 110 | 130 | 150 | 170 |
| | $C$ | 6·40 | 10·85 | 16·31 | 16·89 | 17·49 | 22·78 |

The data are plotted in Fig. 51. W. P. Heath, C. G. Anthony, and W. A. Riley have calculated tables of the solubilities of carbon dioxide in water at different temp. and press. O. Haehnel also measured the effect of press. on the solubility of carbon dioxide. C. Zerbe tried unsuccessfully to remove 10 per cent. of carbon dioxide from a mixture containing carbon monoxide and hydrogen by scrubbing the gas with water at 150 atm. press. Excessive amounts of other gases were dissolved.

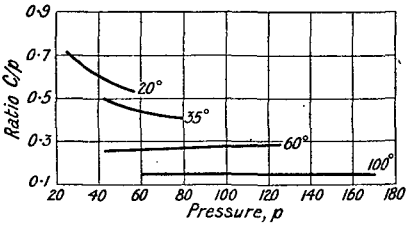



FIG. 51.—Effect of Temperature and Pressure on the Solubility of Carbon Dioxide in Water.

According to S. von Wroblewsky, there is a close relation between the solubility of carbon dioxide in water and the surface tension, $\sigma$, of the soln. at press. from 1 to 30 atm. The product of the surface tension and the press., $p$, is proportional to the coeff. of saturation, $S$, so that $\sigma p=KS$, where $K$ is a coeff. which increases with temp. The variation in the surface-tension is independent of the press., and depends only on the amount of gas dissolved in the superficial layer of the liquid. The solubility of carbon dioxide in water increases less rapidly than the press., and tends towards a limit which is apparently reached when the carbon dioxide liquefies, since the liquid does

not mix with water. The diminution of the surface-tension also decreases as the press. rises, and tends towards a limit which, at 0°, is reached when the press. is sufficient to liquefy the carbon dioxide. At this point the surface-tension of the water is reduced by one-half. W. A. Patrick represented the solubilities of a number of gases in water by the formula $S=K(\sigma p/p_0)^{n-1}$, where $S$ is the vol. of liquefied gas dissolved per gram of water (*i.e.* the weight of the gas dissolved per gram divided by the sp. gr. of the liquefied gas at that temp.); $p_0$ is the vapour press., and $\sigma$ the surface tension of the liquefied gas at that temp. of measurement; $p$ is the equilibrium gas press.; and $K$ and $n$ are specific constants. B. S. Neuhausen found the results satisfactory when $K=0{\cdot}006$, and $n-1=0{\cdot}33$. M. Thilorier, J. K. Mitchell, L. P. Cailletet, and B. Schwalbe found that liquid and solid carbon dioxide do not mix readily with water. A little liquid carbon dioxide dissolves when it is shaken with water, and the excess of the former floats on the surface of the water. According to H. Landolt, solid carbon dioxide sinks in water although a little may be floated by the rising of bubbles of gas without being wetted by the water.

K. Angström found the *specific gravity* of water after it has absorbed an equal vol. of carbon dioxide at 0° and 760 mm. is 1·00054, and unit vol. becomes 1·00125. E. L. Nichols and co-workers found that the temp. of *maximum density*, and the *freezing point* of water are lowered by dissolved carbon dioxide. They found the following expansions to attend the absorption of carbon dioxide:

| | 2° | 6° | 8° | 12° | 16° | 18° | 22° | 32° |
|---|---|---|---|---|---|---|---|---|
| Expansion . | 0·002144 | 0·001726 | 0·001670 | 0·001540 | 0·001378 | 0·001280 | 0·001210 | 0·001010 |

showing that the expansion is directly proportional to the amount of gas absorbed. G. A. Hagemann made an estimate of the energy which attends the association of carbon dioxide and water. A. Blümcke said that the compressed carbon dioxide in water behaves as if it were a liquid, not a gas.

The rate of evolution of a gas from a liquid, expressed in terms of the number of c.c. of gas at 0° and 760 mm., given off per minute per sq. cm. of surface, was called by C. Bohr, the *evasion coefficient*, and the converse process, the rate of absorption, was called the *invasion coefficient*. J. Hurtur measured the rate of absorption of carbon dioxide by calcium oxide. J. J. Hood studied the absorption of carbon dioxide by aq. soln. of potassium hydroxide; P. Riou, by soln. of potassium and sodium carbonates, and ammoniacal soln.; J. Meyer, and W. A. Roth, the rates of evolution and absorption of carbon dioxide by water. W. F. Knox found that the rate of evolution of carbon dioxide from its aq. soln. follows approximately a logarithmic rule, and E. P. Perman made some observations on this subject. T. Carlson found the rate of absorption of carbon dioxide by water at rest is dependent on the rate of diffusion of the gas into the bulk of the liquid from the sat. surface, so that if $C$ be the conc. of the gas dissolved at the time $t$, and $S$ the conc. of the sat. soln., the velocity of absorption, $dC/dt$, is

$$\frac{dC}{dt}=K(S-C)\,;\quad \text{or } \frac{1}{t}\log\frac{1}{S-C}=K$$

where $K$ is a constant dependent on the diffusion coeff., and the thickness $a$ of the saturation layer; if the liquid be stirred with a paddle making $n$ revolutions per minute, then $K=K'n^{\frac{2}{3}}Da$, where $K'$ is a constant dependent on the apparatus employed. A. Findlay and G. King found that the rate of evolution of carbon dioxide from soln. of that gas is fastest with soln. having the smallest surface tension; but A. Findlay and O. R. Howell found that in the presence of colloids the relationship is in the converse direction, and hence they inferred that "it is not the surface tension of the soln. which determines the rate of escape of a gas, but rather the internal press. of the liquid." A. Sieverts and A. Fritzsche, E. M. Baker, R. V. Williamson and J. H. Mathews, and P. G. Ledig and E. R. Weaver measured the rate of absorption of carbon dioxide by water and alkaline soln.

In general, *supersaturation* occurs more readily in gas soln. than in any other case. Supersaturation persists for a long time in rigorously clean glass vessels. L. Pratesi found that certain mineral waters—*e.g.* that from Contursi in Salerms—contain a larger amount of carbon dioxide in soln. than corresponds with the solubility of the gas. Ordinary seltzer water drawn from a siphon, and allowed to stand half an hour, contains 1·901 vols. of carbon dioxide under conditions where the solubility of the gas would be represented by 1·289 vols. Hence a sat. aq. soln. of carbon dioxide under press., left for some time under ordinary press., contains a larger quantity of gas than water simply sat. with the gas at ordinary press. Aq. soln. of carbon dioxide are very readily supersaturated. J. Metschl studied the supersaturation of alcohol and water by carbon dioxide.

Some observations on the subject were made at the beginning of the nineteenth century by J. J. Winterl, and H. C. Oersted; and there has been some discussion by D. Gernez, G. van der Mensbrugghe, C. F. Henrici, C. F. Schönbein, H. Schröder, C. Tomlinson, R. Fricke and C. Rohmann, F. B. Kenrick and co-workers, Lord Rayleigh, etc., on the formation of gas bubbles in supersaturated soln. of gas.

*W. Ostwald has shown that the supersaturation of a liquid by gas occurs if the pressure be reduced and gas nuclei are absent.* The study of surface-energy (1. 13, 22) shows that supersaturation must take place if gas nuclei are absent. Since the surface tension of a liquid tends to diminish the surface, there must be a greater press. in the interior of a spherical bubble than at a plane surface under the same circumstances, and the theory of capillarity gives for this the equation $p=2\gamma/r$, where $p$ is the press., $\gamma$ the surface tension, and $r$ the radius of the sphere. If, therefore, a bubble of gas is formed spontaneously, it will be under a far greater press. than corresponds to saturation under the given conditions. It appears from this that a bubble could not be formed spontaneously at all. For, as at the first instant the bubble must be infinitely small, the press., according to the equation, must be infinitely great. The spontaneous formation of bubbles shows that the assumption that the properties of a liquid remain the same up to infinitely small dimensions, is incorrect. If the limit for the ordinary properties of liquids is put at $10^{-8}$ cm., the press. in a bubble of this radius in water at room temp. is calculated to be 15,000 atm. Apparently nothing like this degree of supersaturation is necessary to cause spontaneous evolution of gas.

To remove the supersaturation, the soln. can be brought into an atm. of the gas at a reduced press. or of another gas in which the partial press. of the dissolved gas is zero. The addition of porous powders which enclose large surfaces with adsorbed air acts similarly; violent shaking acts by spreading numerous air-bubbles through the liquid; and boiling the solvent acts by introducing bubbles of vapour throughout the liquid. Each bubble of gas acts as a nucleus facilitating the formation of a new phase; the action of each bubble is local, and when it has risen to the surface and escaped from the liquid, no more bubbles are spontaneously evolved. Hence, a supersaturated soln. of a gas expels the nuclei which are necessary to relieve supersaturation. Many aërated beverages are charged with carbon dioxide at about 4 atm. press., and when the first effervescence which attends the pouring is over, small bubbles develop at the places where the glass has been scratched and some air has been imprisoned. This is illustrated by the fact that if a "sparkling" liquid be poured into a wetted glass vessel, it appears "flat"; and the introduction of powdered sugar or a roughened surface restarts the evolution of gas.

W. Hempel and J. Seidel[2] noticed that carbon dioxide unites with water when under 43 atm. press., forming a compound which melts at 8°, and decomposes at −2° under atm. press. A few **hydrates of carbon dioxide** have been reported. R. Bunsen computed that the water and carbon dioxide adsorbed by moist glass-wool are related as $CO_2 : H_2O = 2 : 1$, and he suggested that under the influence of the capillary press., it is possible that *hemihydrated carbon dioxide* is formed: $CO_2.\frac{1}{2}H_2O$. According to S. von Wroblewsky, when an excess of carbon dioxide at 0° and 45 atm. press. is allowed to stand in contact with water, some of the gas liquefies, and two liquids appear—the lower liquid is water with more or less carbon dioxide in soln., and the upper liquid is carbon dioxide. If the press. be slowly released, the liquid carbon dioxide slowly vaporizes, but if rapidly decreased to 12·3 atm.,

a solid collects on the walls of the containing vessel. He infers that this solid is a hydrate which decomposes at press. less than

| | | | | | | |
|---|---|---|---|---|---|---|
| Pressure . . . | 12·3 | 16·7 | 17·9 | 21·8 | 23·3 | 26·1 atm. |
| Temperature . . | 0° | 2·7° | 3·6° | 5·3° | 6·3° | 6·8° |

S. von Wroblewsky's, and W. Hempel and J. Seidel's analyses correspond with *octohydrated carbon dioxide*, $CO_2.8H_2O$; but P. Villard's analyses correspond with *hexahydrated carbon dioxide*, $CO_2.6H_2O$. P. Villard said that combination occurs under simple press., and the hydrate does not decompose below 0° under ordinary press. except in the presence of liquid water. M. Ballo made some observations on this subject. W. Hempel and J. Seidel also sealed a weighed quantity of water and solid carbon dioxide in a tube; at ordinary temp., the liquid formed two layers, the water underneath; on cooling the tube slowly, crystals formed; these began to melt at about 8°. The tube was then cooled to —79°, opened, furnished with a delivery tube dipping under mercury, and then allowed to rise in temperature; carbon dioxide was evolved furiously at first, but ceased to come off at —25°; at —2°, the evolution of gas again commenced, and the volume that came off between this temperature and 20° corresponded with the octohydrate or *enneahydrated carbon dioxide*, $CO_2.9H_2O$. P. Villard found that the crystals are hexagonal prisms, and when deposited from aq. soln., the crystals are acicular like those of ammonium chloride. S. von Wroblewsky said that the density of the hydrate is greater than that of water sat. with carbon dioxide. P. Villard gave 14·9 Cals. for the heat of formation of the hexahydrate, and he gave for the dissociation press., $p$,

| | −6° | 0° | 0·48° | 2·7° | 3·6° | 5·3° | 6·1° | 6·8° | 10·0° |
|---|---|---|---|---|---|---|---|---|---|
| $p$ . . . . . | 6·5 | 12·2 | 12·7 | 16·7 | 17·9 | 21·8 | 23·3 | 26·1 | 44·3 atm. |

The fact that the relative proportion of water and carbon dioxide has no influence on the dissociation press. is taken to indicate that only one hydrate is formed. The subject was discussed by H. W. B. Roozeboom. P. Villard's crystals had no action on polarized light.

When carbon dioxide dissolves in water it furnishes a soln. with the properties of a weak acid. How does the formation of carbonic acid affect the application of the law of partial press. (**1.** 10, 5)? The rule that at any given temp. the amount of, say, carbon dioxide absorbed from the atm. by water, is the product of the amount dissolved under 760 mm. press. of carbon dioxide alone, by the partial press. of that gas in air, holds good in spite of the chemical reaction $CO_2+H_2O=H_2CO_3$. Let the chemical symbols in brackets denote the conc. of the compound, then, from the law of mass action: $[CO_2][H_2O]=K_1[H_2CO_3]$, but the conc. of the water is so greatly in excess that its conc. can also be regarded as a constant, $K_2$, and if $K_1/K_2=K$, then $[CO_2]=K[H_2CO_3]$, meaning that the conc. of the carbonic acid, $H_2CO_3$, is proportional to the amount of carbon dioxide dissolved, and this in turn is proportional to the partial press. of the gas.

From the law of partial press., and C. Bohr and J. Bock's data,[3] it follows that a litre of water should dissolve from air containing 0·03 per cent. of carbon dioxide:

| | 0° | 5° | 10° | 15° | 20° | 25° | 30° |
|---|---|---|---|---|---|---|---|
| Carbon dioxide . . | 0·514 | 0·427 | 0·358 | 0·306 | 0·264 | 0·228 | 0·199 c.c. |

*Natural waters*, however, usually contain alkali or alkaline earth carbonates in soln. as hydrocarbonates, which give up their carbon dioxide on boiling. F. M. Baumert's and E. M. Péligot's analyses of the gases in rain-water show respectively 1·8 and 2·4 per cent. of carbon dioxide at ordinary temp. The data correspond with those required for air with 0·03 per cent. of carbon dioxide. R. Bunsen found in the gases of rain-water 2·92 per cent. carbon dioxide at 0°; 2·68 at 5°; 2·46 at 10°; 2·26 at 15°; and 2·14 at 20°. H. McLeod's and E. Frankland's analyses gave 6·2 per cent. of carbon dioxide, and corresponded with an atm. with 0·1 per cent. of that gas. E. Frankland's analyses of the gases from a Cumberland mountain stream gave

0·281 per cent. of carbon dioxide, and those from the water of the Thames gave 4·021 per cent., and E. Reicherts' analysis of the Jena water supply gave 2·47 per cent. of carbon dioxide. The variable proportions here correspond with the presence of variable amounts of hydrocarbonates in these natural waters. C. J. J. Fox found between 1 and 7 parts of carbon dioxide per 10,000 parts of *sea-water*; and that the total alkalinity varies, but for the open ocean it is eq. to about 40 *mgrms.* of OH per litre at 12°. The ratio of total carbon dioxide to total OH is linear, and there are no $CO_3''$-ions; all the combined carbon dioxide is in the form of $HCO_3'$-ions.

C. G. C. Bischof estimated that 60 per cent. of the total solids in waters of the principal rivers of Europe is dissolved as calcium hydrocarbonate and delivered into the sea. The ocean is not sat. with calcium hydrocarbonate; this, according to C. F. Tolman, is shown by the fact that (i) W. Dittmar found that except in one or two cases, lime was not deposited from the hundreds of samples of sea-water collected by the *Challenger*, after they had been kept for many years; (ii) B. Willis found that sea-shells from the bottom of the Pacific were much corroded; pteropod shells and foraminifera tests are slowly dissolved as they sink; and pteropod shells are not found below 1500 fathoms, and globigerina ooze, not below 2800 fathoms; (iii) J. Thoulet found that sea-water will dissolve calcium carbonate from shells, corals, etc.; and (iv) J. Usiglio observed no precipitation occurred in the evaporation of sea-water until the sp. gr. rose from 1·02 to 1·0503, and the deposit then consisted largely of calcium carbonate and ferric oxide. The analyses of O. Jacobsen, A. Hamberg, H. Tornöe, W. Dittmar, F. Natterer, and J. Y. Buchanan show that the amount of carbon dioxide in sea-water is not usually sufficient to transform all the normal calcium carbonate into hydrocarbonate; and that the largest part of the so-called free carbon dioxide is present as hydrocarbonate in equilibrium with the carbon dioxide in soln. and in the air. According to J. Johnston and E. D. Williamson, the warm surface layers of the ocean are practically sat. with carbonates, which are subject to precipitation not only by fluctuations of temp. but also by fluctuations in the proportion of carbon dioxide in the atm. above. W. Dittmar found that between 18° and 21°, the dissociation press. of the hydrocarbonates in sea-water is 0·0005 atm., and at temp. near 0° there is no dissociation at all. Since the partial press. of the carbon dioxide in the atm. is about 0·0003 atm., it follows that the warmer portions of the ocean are constantly supplying carbon dioxide to the atm., and the colder portions are constantly removing that gas. C. F. Tolman added:

> The increase in the ocean's capacity for carbon dioxide at low temp. and the invasion of polar waters towards the equator both tend to rob the atm. of carbon dioxide, and this is unaffected by any diminishing partial press. of that gas. In the temperate waters, the effects of increasing cold and decreasing partial press. seem to be fairly evenly balanced, with a possible advantage for the diminishing partial press., against which must be reckoned a decrease in the amount of these waters. In the equatorial waters, the effect of the decreasing press. exceeds that of falling temp., counterbalanced by a large decrease in the amount of these waters.

C. J. J. Fox concluded that for the open ocean it requires 17·6 times as much carbon dioxide to raise the partial press. of that gas as it does for the same vol. of air; or, if a quantity of carbon dioxide is poured into the air, as, for example, by volcanic action, two-thirds will eventually be absorbed by the sea. The final equilibrium will not be attained, however, until either the insoluble carbonates on the sea-bottom or the carbon dioxide in the air have completely gone into soln. in the form of $HCO_3'$. The conc. of the free ions, $HCO_3'$ and $H'$, for ocean-water are calculated to be respectively $2·24\times10^{-3}$ and $1·6\times10^{-6}$ to $2·6\times10^{-6}$ gram-eq. per litre; thus sea-water has a slightly higher conc. of $H'$-ions than distilled water. S. Palitzsch found great constancy in the conc. of the hydrogen ions in sea-water (excluding the Black Sea); the extreme variations were $0·0_711N$ to $0·0_845N$; and the conc. of the hydroxyl ions, $0·0_52N$ to $0·0_55N$. This is a sufficient excess to be

termed faint alkalinity. The ratio between hydrocarbonates and carbonic acid in sea-water is estimated by L. J. Henderson to be between 50 : 1 and 1000 : 1.

H. M. Noad [4] observed that no considerable amount of carbon dioxide is absorbed by conc. *sulphuric acid.* W. B. and R. E. Rogers found one vol. of conc. sulphuric acid absorbs 0·76 vol. of carbon dioxide at 16°; and one vol. of fuming sulphuric acid absorbs 1·25 vol. of the gas. They added that the carbon dioxide is not completely expelled by heating the acid soln. to 100°. The solubilities of carbon dioxide in aq. soln. of sulphuric acid at 15°–25° have been determined by A. Christoff, C. Bohr, J. Mai, and G. Geffcken; the last-named found for unit vol. of soln. with 24·52 grms. of $H_2SO_4$ per litre, 1·018 vol. of gas were dissolved at 15° and 0·794 vol. at 25°; and with 196·15 grms. of acid per litre, 0·828 vol. of gas at 15°, and 0·667 vol. at 25°. The first-named found that at 20° the solubility fell from 0·9674 for water to 0·6521 with 35·82 per cent. acid, and then rose to 0·7191 for 61·62 per cent. acid, and to 0·9924 for 95·6 per cent. acid. A. Hantzsch and A. Vagt measured the distribution of carbon dioxide between air and dil. sulphuric acid at different temp. G. Geffcken found for *hydrochloric acid* with 18·23 and 72·92 grms. of acid per litre, the respective solubilities 1·043 and 1·000 at 15°, and 0·806 and 0·795 at 25°; for *nitric acid* with 31·52 and 126·10 grms. of acid per litre, the respective solubilities 1·078 and 1·100 at 15°, and 0·840 and 0·877 at 25°. F. L. Usher found a $\frac{1}{2}N$-soln. of *acetic acid* had an absorption coeff. of 0·869. G. Just found that one c.c. of glacial acetic acid dissolved 5·614 c.c. of gas at 15°; 5·129 c.c. at 20°; and 4·679 c.c. at 25°; *acetic anhydride*, 6·128 (15°), 5·720 (20°), and 5·206 (25°); *propionic acid*, 4·787 (15°), 4·407 (20°), and 4·078 (25°); *butyric acid*, 4·084 (15°), 3·767 (20°), and 3·478 (25°). W. Kunerth measured the solubility in acetic acid. J. Setschenoff found for soln. with 12 and 595 grms. of *citric acid* per litre, the respective solubilities 1·007 and 0·719 c.c. of gas at 0° and 760 mm. per c.c. of soln.

J. Setschenoff found that the solubility of carbon dioxide in dil. salt soln. follows the same law as if the salt be absent provided there be no chemical reactions between the gas, the salt, and the solvent; but with increasing proportions of salt, the solubility of the gas decreases, presumably because the attractive power between the solvent and the gas is partially satisfied by the salt mol. He divides the salts into two groups with respect to their behaviour towards carbon dioxide. In the one group, the salts are not affected by the gas—*e.g.* sodium chloride; in the other group the salts react with the gas—*e.g.* sodium carbonate, phosphate, the borates, citrates, and oxalates. In the first group, the solubility of the gas decreases with increasing conc. of the soln., and in the other group the solubility of the gas increases with increasing conc. of the soln.

J. J. Mackenzie, A. Findlay and B. Shen, and J. Setschenoff measured the solubility of the gas in soln. of *ammonium chloride.* The last-named gave for soln. with 1 and 258 grms. of salt per litre solubilities respectively 1·005 and 0·770 c.c. at n.p.$\theta$. per c.c. of sat. soln. at 15·2°; for soln. with 16·72 and 501·5 grms of *lithium chloride* per litre he obtained the respective solubilities 1·035 and 0·120 c.c. of the gas calculated at n.p.$\theta$. per c.c. of sat. soln. at 15·2°—other determinations were made by A. Christoff. The effect of *sodium chloride* on the solubility of carbon dioxide has been investigated by H. Müller, E. Fernet, J. J. Mackenzie, A. Christoff, and J. Setschenoff. The last-named found that with a soln. containing 12·9 and 192 grms. of the salt per litre, the respective solubilities were 0·978 and 0·466 c.c. of gas at n.p.$\theta$. The effect of *potassium chloride* has been measured by J. J. Mackenzie, G. Geffcken, A. Findlay, and H. J. M. Creighton, and A. Findlay and B. Shen. The last-named found for soln. with 18·4 and 74·6 grms. of salt per litre, the respective solubilities 0·792 and 0·701 c.c. per c.c. of sat. soln. at 25°. The effect of *rubidium chloride* was measured by G. Geffcken, who found that with soln. containing 60·47 and 120·95 grms. of salt per litre the respective solubilities were 0·989 and 0·921 c.c. per c.c. of sat. soln. at 15°, and 0·769 and 0·788 at 25°; and with soln. containing 84·17 grms. of *cæsium chloride* per litre the respective solubilities were 1·006 and 0·781 c.c. per c.c. of sat. soln. at 15° and 25°. J. J. Mackenzie found for soln. with 4·365 and 15·793 per cent. of *calcium chloride* the respective absorption coeff. 0·942 and 0·632 at 8°; 0·759 and 0·520 at 16·5°; 0·673 and 0·471 at 22°; and 0·596 and 0·400 at 30°; similarly, for soln. with 9·511 and 31·194 per cent. of *strontium chloride*, the absorption coeff. 0·779 and 0·285 at 8°; 0·663 and 0·245 at 16·5°; 0·581 and 0·247 at 22°; and 0·508 and 0·223 at 30°; and for soln. with 7·316 and 25·215 per cent. of *barium chloride*, the respective absorption coeff. 0·969 and 0·495 at 8°; 0·744

and 0·618 at 16·5°; 0·680 and 0·383 at 22°; and 0·566 and 0·315 at 30°. J. Setschenoff found that soln. containing 115·1 and 690·4 grms. of *sodium bromide* per litre, dissolved respectively 0·775 and 0·221 c.c. of gas at n.p.$\theta$. per c.c. of soln. at 15·2°. The effect of *potassium bromide* was investigated by A. Christoff, G. Geffcken, and J. Setschenoff. The latter found for soln. with 83·9 and 503·1 grms. of the salt per litre the respective solubilities 0·908 and 0·579 c.c. of gas at n.p.$\theta$. per c.c. of soln. at 15·2°; and for soln. with 319·1 and 957·3 grms. of *potassium iodide* per litre, the respective solubilities 0·777 and 0·506 c.c. of gas at n.p.$\theta$. per c.c. of soln. at 15·2°. Measurements were also made by G. Geffcken, and A. Christoff. J. Setschenoff found for soln. with 233·3 and 699·8 grms. of *sodium chlorate* per litre the respective solubilities 0·625 and 0·527 c.c. of gas at n.p.$\theta$. per c.c. of soln. at 15·2°; and for soln. with 326 and 978 grms. of *potassium thiocyanate* per litre, the respective solubilities 0·691 and 0·387 c.c. of gas at n.p.$\theta$. per c.c. of soln. at 15·2°.

The effect of *ammonium sulphate* was measured by A. Christoff, and J. Setschenoff; the latter found that with soln. containing 72·2 and 144·4 grms. of the salt per litre, the respective solubilities were 0·712 and 0·575 c.c. of gas at n.p.$\theta$. per c.c. of soln. at 15·2°; and soln. with 14·2 and 284·4 grms. of *sodium sulphate* per litre dissolved respectively 0·950 and 0·234 c.c. of gas at n.p.$\theta$. per c.c. of soln. at 15·2°. A. Christoff found that 75 c.c. of 0·66*N*- and *N*-soln. of *potassium sulphate* dissolved respectively 0·1140 and 0·1002 grms. of carbon dioxide at 15·5° and 760 mm.; 75 c.c. of 0·66*N*- and 2*N*-soln. of *potassium hydrosulphate* dissolved respectively 0·1020 and 0·1000 grm. of gas at 15·5° and 760 mm.; and 75 c.c. of 2*N*-soln. of *cupric sulphate* dissolved 0·0751 grm. of gas. J. Y. Buchanan tested the action of carbon dioxide on soln. of *calcium sulphate*. J. Setschenoff, J. Y. Buchanan, and A. Christoff measured the effect of *magnesium sulphate* and of *zinc sulphate*. The former observed that soln. with 26·5 and 318 grms. of magnesium sulphate per litre dissolved respectively 0·901 and 0·188 c.c. of gas at n.p.$\theta$. per c.c. of soln. at 15·2°; and soln. with 38·3 and 460 grms. of *zinc sulphate* per litre dissolved respectively 0·903 and 0·209 c.c. of gas at n.p.$\theta$. per c.c. of soln. at 15·2°. A. Findlay and B. Shen found that at 25°, soln. with 95·1 and 224·7 grms. of hexahydrated *ammonium ferrous sulphate* per litre dissolved respectively 0·641 and 0·460 c.c. of gas per c.c. of soln. A. Christoff found that at 15·5°, 75 c.c. of a *N*-soln. of *ammonium ferric sulphate* dissolved at 0·0991 grm. of gas; and 75 c.c. of a *N*-soln. of *potassium aluminium sulphate* dissolved 0·1054 grm. of gas.

J. Setschenoff found that soln. with 2·8 and 810·4 grms. of *ammonium nitrate* per litre dissolved respectively 1·013 and 0·612 c.c. of gas at n.p.$\theta$. per c.c. of soln. at 15·2; and soln. with 89·3 and 625·2 grms. of *sodium nitrate* per litre dissolved respectively 0·835 and 0·244 c.c. of gas at n.p.$\theta$. per c.c. of soln. at 15·2°. A. Christoff, G. Geffcken, and J. Setschenoff measured the effect of *potassium nitrate*; the last-named found that soln. with 58·8 and 235·1 grms. of the salt per litre dissolved respectively 0·959 and 0·781 c.c. of gas at n.p.$\theta$. per c.c. of soln. at 15·2; he also found that a soln. with 41 grms. of *calcium nitrate* per litre, and one with 62·7 grms. of *barium nitrate* per litre dissolved respectively 0·923 and 0·922 c.c. of gas at n.p.$\theta$. per c.c. of soln. at 15·2°. A. Christoff found that at 15·5°, 75 c.c. of a *N*-soln. of normal dodecahydrated *sodium orthophosphate* dissolved 0·5828 grm. of gas. J. S. F. Pagenstecher, J. J. Berzelius, J. von Liebig, J. Setschenoff, R. L. Marchand, and R. Heidenhain and L. Meyer have studied the action of carbon dioxide on soln. of *sodium hydrophosphate*. A. Christoff found that at 15·5° the solubility of carbon dioxide, in c.c. of gas per c.c. of a soln. of normal decahydrated *sodium pyrophosphate*, is 0·8463 grm.; *sodium metaphosphate*, 0·0700 grm.; *N*-soln. of *potassium dihydrophosphate*, 0·0860; $\frac{1}{2}$*N*-soln. of *potassium hydrophosphate*, 0·4900 grm.; *N*-soln. of *potassium metaphosphate*, 0·1237; *N*-soln. of *potassium dihydroarsenate*, 0·0812 grm.; $\frac{1}{2}$*N*-soln. of *potassium hydroarsenate*, 0·1110; $\frac{1}{4}$*N*-soln. of *ammonium hydrometaborate*, $(NH_4)H(BO_2O)_2$, 0·7672 grm.; $\frac{1}{4}$*N*-soln. of *sodium metaborate*, 0·8122; and 0·025*N*- and a sat soln. of *borax* dissolved respectively 0·2205 and 1·8285 grms. of gas.

R. Bunsen [5] measured the solubility of carbon dioxide in *ethyl alcohol*, and found the solubility to be about twice as great as it is in water; F. Henrich represented these results by the expression $S=4{\cdot}3294-0{\cdot}094261\theta+0{\cdot}00123541\theta^2$, where $S$ denotes the vols. of carbon dioxide dissolved by one vol. of alcohol. C. Bohr found with 99 per cent. ethyl alcohol

| $\theta$ | −27° | −20° | −10° | 0° | 10° | 20° | 30° | 40° | 45° |
|---|---|---|---|---|---|---|---|---|---|
| $S$ | 38·41 | 7·51 | 5·75 | 4·44 | 3·57 | 2·98 | 2·57 | 2·20 | 2·01 |

where $S$ denotes the number of c.c. of gas at 0° and 760 mm. which 1 c.c. of the liquid dissolves at 760 mm. and $\theta$°. O. Müller found that if water is mixed with alcohol, the absorption coeff. decreases until the mixture contains about 28 per cent. of alcohol; the solubility then increases, attaining the same value with 45 per cent. alcohol as it has for water; the solubility thereafter increases rapidly until it attains the same value as it has for water. Thus, at 20°, the data are:

| Alcohol, per cent. | 1·07 | 22·76 | 28·46 | 31·17 | 42·15 | 71·1 | 99·7 |
|---|---|---|---|---|---|---|---|
| Absorption coeff. | 0·861 | 0·841 | 0·792 | 0·801 | 0·877 | 1·293 | 2·719 |

O. Lubarsch obtained similar results. W. Kunerth also measured the solubility in ethyl alcohol. B. Schwalbe said that liquid carbon dioxide dissolves in alcohol, and L. P. Cailletet and E. Colardeau noted that the temp. then falls to —72° under atm. press., and to —100° in vacuo. According to W. Hempel and J. Seidel, when aq. alcohol is sat. with solid carbon dioxide a complex $17CO_2.3C_2H_5OH.H_2O$ is formed, and when liquid carbon dioxide is distilled into methyl, ethyl, tertiary butyl, or amyl alcohol, and the excess of carbon dioxide is allowed to evaporate, the corresponding alkyl carbonates are formed; with propyl alcohol, the mixture separates into two liquid layers. E. H. Büchner also studied the action of liquid carbon dioxide on *n*-propyl alcohol. J. Zeleny and R. H. Smith found that the addition of alcohol made very little difference to the vap. press. of solid carbon dioxide. A. Findlay and B. Shen, O. Stern, and W. Sander measured the effect of temp. and press. on a number of organic liquids. The first-named found for the solubility, $S$ c.c. of carbon dioxide per c.c. of liquid at 25°, at $p$ mm. press., with aq. alcohol sp. gr. 0·9931 (2·95 grms. per 100 c.c.), and sp. gr. 0·9834 (8·83 grms. per 100 c.c.):

| | Sp. gr. 0·9931 | | | | Sp. gr. 0·9834 | | | |
|---|---|---|---|---|---|---|---|---|
| $p$ | 737 | 836 | 1073 | 1338 | 747 | 942 | 1090 | 1360 |
| $S$ | 0·812 | 0·813 | 0·811 | 0·811 | 0·786 | 0·784 | 0·785 | 0·788 |

A. Findlay and B. Shen found the solubility of carbon dioxide in *wort* containing 13 grms. of solids per 100 c.c. to be less than in water; and in *beer* to be less than in a mixture of alcohol and water containing the same proportion of alcohol as that of the beer. The solubility of carbon dioxide in beer has been investigated by T. Langer, and O. Mohr. G. Just found the solubilities of carbon dioxide in *methyl alcohol* to be 4·606 (15°), 4·205 (20°), and 3·837 (25°) c.c. of gas per c.c. of liquid; in 97 per cent. *ethyl alcohol*, 3·130 (15°), 2·923 (20°), and 2·706 (25°); in *propyl alcohol*, 2·498 (25°). F. L. Usher gave 0·868 c.c. for the solubility of carbon dioxide in a $\frac{1}{2}N$-soln. of *n-propyl* alcohol. W. Kunerth measured the solubilities in methyl, and amyl alcohols. G. Just found for *isobutyl alcohol*, 2·088 (15°), 1·964 (20°), and 1·849 (25°); in *amyl alcohol*, 2·058 (15°), 1·941 (20°), and 1·831 (25°); *methyl acetate*, 6·494 (25°); *isobutyl acetate*, 4·968 (20°), and 4·691 (25°); *amyl acetate*, 4·850 (15°), 4·411 (20°), and 4·119 (25°); and for *amyl formate*, 4·646 (15°), 4·329 (20°), and 4·026 (25°). O. Stern represented his results with methyl alcohol, ethyl alcohol, *acetone*, *methyl acetate*, and *ethyl acetate* at —59° and —78° in terms of $K$ c.c. of carbon dioxide reduced to 0° absorbed by a gram of liquid at the given press., $p$; hence the absorption coeff. is $KD$, where $D$ is the sp. gr. of the liquid at the given temp. The following values of $K$ were obtained at —59°:

| | | Methyl alcohol. | Ethyl alcohol. | Acetone. | Methyl acetate. | Ethyl acetate. |
|---|---|---|---|---|---|---|
| Sp. gr., $D$ | | 0·866 | 0·856 | 0·879 | 1·032 | 0·994 |
| $p$ | 100 mm. | 63·0 | 40·85 | 97·8 | 94·30 | 85·3 |
| | 200 mm. | 64·2 | 41·00 | 101·2 | 98·45 | 86·3 |
| | 400 mm. | 66·3 | 42·35 | 106·6 | 103·60 | 91·6 |
| | 700 mm. | 69·0 | 44·15 | 118·8 | 112·90 | 101·5 |

W. Kunerth measured the solubility in amyl acetate. W. Sander expressed his results for ethyl alcohol, propyl alcohol, *ethyl ether*, ethyl acetate, *benzene*, *chlorobenzene*, *nitrobenzene*, and *toluene* at 20°, 35°, 60°, and 100° in terms of the number of c.c. of carbon dioxide (reduced to one kgrm. per sq. cm.) dissolved by one c.c. of sat. soln. at the given temp. and press.

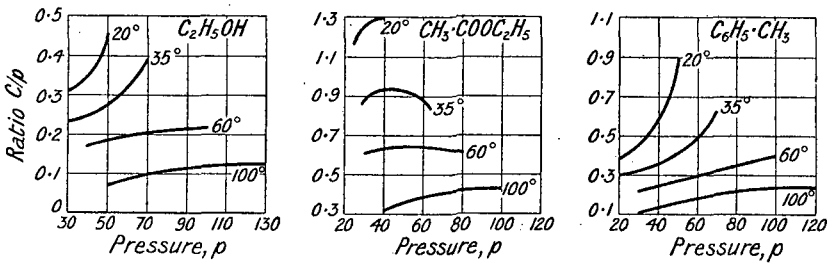
Temperature, 20°.

| $p$ | Ethyl alcohol. | Propyl alcohol. | Ethyl ether. | Ethyl acetate. | Benzene. | Chloro-benzene. | Bromo-benzene. | Nitro-benzene. | Toluene. |
|---|---|---|---|---|---|---|---|---|---|
| 20 | — | 56·16 | — | — | 71·16 | 62·61 | 50·83 | 57·12 | 57·91 |
| 30 | 104·8 | 86·62 | — | 188·2 | 125·3 | 95·22 | 82·29 | 92·50 | 103·3 |
| 40 | 149·7 | 122·10 | — | 227·9 | 192·4 | 137·3 | 121·1 | 115·9 | 155·9 |
| 50 | 188·8 | 174·60 | — | — | 264·3 | 187·5 | 160·0 | 155·9 | 235·8 |

Temperature, 100°.

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| 30 | — | — | — | — | — | 33·65 | 30·56 | 41·09 | 28·68 |
| 40 | — | 26·5 | — | 80·7 | 46·52 | 48·16 | 41·49 | 50·36 | 49·25 |
| 60 | 66·05 | 74·5 | 101·0 | 132·0 | 91·27 | 77·24 | 72·64 | 70·85 | 85·98 |
| 80 | 111·2 | 107·7 | 142·8 | 162·3 | 155·8 | 103·0 | 92·86 | 86·86 | 117·6 |
| 100 | 145·7 | 144·7 | 175·4 | 191·5 | 212·9 | 121·5 | 118·0 | — | 149·0 |
| 120 | 174·6 | 175·4 | — | — | 258·2 | 140·7 | 140·7 | — | 171·8 |
| 130 | 182·6 | — | — | — | — | 146·8 | — | — | 178·2 |

Henry's law is not generally applicable at low temp., but in most cases at 100°, the solubility is proportional to the press. for solvents related chemically, *e.g.* benzene, chlorobenzene, and bromobenzene, and the solubility decreases with increasing mol. wt. B. S. Neuhausen found the constants of W. A. Patrick's formula—*vide supra*—for methyl and ethyl alcohols are respectively $K=0{\cdot}0126$ and $0{\cdot}0103$; and $n^{-1}=0{\cdot}07$ and $0{\cdot}055$. The values for the conc. $C$, and press., $p$, of ethyl alcohol, ethyl acetate, and benzene are plotted in Figs. 52 to 54. A. Christoff found the solubility of carbon dioxide in one c.c. of ethy-




FIGS. 52 to 54.—Solubility of Carbon Dioxide in Ethyl Alcohol, Ethyl Acetate, Toluene.

ether to be 7·330 c.c. at 0°; 6·044 c.c. at 10°; and 5·465 c.c. at 15°; he also measured the solubility of carbon dioxide in mixtures of acetic acid and carbon tetrachloride, and of ethylene chloride and carbon disulphide. K. Ångström gave for the dilation coeff. of soln. of carbon dioxide in methyl alcohol, 0·00184; in ethyl alcohol, 0·00185; and in ether, 0·00200. L. P. Cailletet, B. Schwalbe, and E. H. Büchner said that liquid carbon dioxide dissolves in ether in all proportions. M. Faraday noted that with solid carbon dioxide and ether, the temp. falls to −77° under atm. press.; L. P. Cailletet and E. Colardeau, −77°; P. Villard and R. Jarry, −79°; H. V. Regnault, −78·26°; A. Loir and C. Drion, −81°; and B. Schwalbe, −77° to −97°; and in vacuo, M. Faraday obtained −103°; L. P. Cailletet and E. Colardeau, −103°; and B. Schwalbe, −110°. L. Bleekrode made some observations on this subject. G. Baumé and F. L. Perrot measured the f.p. of mixtures of *methyl ether* or methyl alcohol and carbon dioxide. According to W. Hempel and J. Seidel, a solid is formed when aq. ether is sat. with solid carbon dioxide; the composition of the solid varies with the temp. of formation; at a low temp. little else than carbon dioxide is present; the amount of ether, and still more that of water, increases with the temp. of formation; at −50°, the composition is $CO_2.(C_2H_5)_2O.4H_2O$. W. Sander determined the isotherms for sat. soln. of carbon dioxide in ether, and of ether vapour in carbon dioxide at 35°, 60°, and 100°. In the neighbourhood of the critical point, Henry's law is not even approximately valid. G. Just found the solubility in c.c. of gas per c.c. of liquid, of carbon dioxide in *acetone* to be 6·921 (20°) and 6·295 (25°); *ethylene chloride*, 4·061 (15°), 3·795 (20°), and 3·525 (25°); *ethylene bromide*, 2·424 (15°), 2·294 (20°), and 2·157 (25°); *chloroform*, 3·956 (15°), 3·681 (20°), and 3·430 (25°). W. Kunerth measured the solubility in chloroform, in ethylene bromide, and in acetone. M. Woukoloff found the solubility, $S$, of carbon dioxide in chloroform at 13° for different press., $p$ mm.:

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| $p$ | 36·57 | 109·62 | 255·48 | 367·64 | 479·29 | 589·2 | 694·98 | 762·0 |
| $S$ | 0·20376 | 0·92016 | 1·4675 | 2·1156 | 2·7850 | 3·39003 | 4·01633 | 4·43757 |

F. Dolezalek detected signs of a chemical action. K. Angström found the dilation coeff. to be 0·00188. G. Just found the solubility of carbon dioxide in *carbon tetrachloride*, 2·603 (15°), 2·502 (20°), and 2·294 (25°); *propylene bromide*, 2·586 (15°), 2·426 (20°), and 2·301 (25°); *isobutyl chloride*, 3·659 (15°), 3·388 (20°), and 3·105 (25°); *amyl chloride*, 3·363 (15°), 3·127 (20°), and 2·910 (25°); *amyl bromide*, 2·803 (15°), 2·638 (20°), and 2·455 (25°); *dichlorohydrine*, 2·034 (15°), 1·917 (20°), and 1·810 (25°); *carbon disulphide*, 0·9446 (15°), 0·8888 (20°), and 0·8699 (25°). M. Woukoloff found that the solubility of carbon dioxide in carbon disulphide increases approximately proportional with the press., but at low temp. is smaller than is required by Henry's law. G. Just gave for the solubility of carbon dioxide in *benzene*, 2·710 (15°), 2·540 (20°), and 2·425 (25°); *nitrobenzene*, 2·845 (15°), 2·655 (20°), and 2·456 (25°); K. Angström found the dilation coeff. of soln. of carbon dioxide in benzene to be 0·00200, and in nitrobenzene, 0·00168. G. Just gave for the solubility of carbon dioxide in *chlorobenzene*, 2·581 (15°), 2·420 (20°), and 2·265 (25°); *bromobenzene*, 2·092 (15°), 1·964 (20°), and 1·842 (25°); *iodobenzene*, 1·440 (15°), 1·371 (20°), and 1·301 (25°); *benzene trichloride*, 1·643 (25°); *benzyl chloride*, 2·180 (15°), 2·072 (20°), and 1·938 (25°); *toluene*, 2·557 (15°), 2·426 (20°), and 2·305 (25°); *benzaldehyde*, 3·304 (15°), 3·057 (20°), and 2·841 (25°); *aniline*, 1·531 (15°), 1·434 (20°), 1·324 (25°). M Loeb also measured the solubility in aniline; E. H. Büchner, in *diphenylamine*; and W. Kunerth, in aniline, and benzaldehyde. G. Just gave for the solubility of carbon dioxide in *o*-

*toluidine*, 1·539 (15°), 1·473 (20°), and 1·381 (25°); *m-toluidine*, 1·730 (15°), 1·581 (20°), and 1·436 (25°); *pyridine*, 4·291 (15°), 3·862 (20°), and 3·656 (25°); *carvol*, 2·914 (15°), 2·690 (20°), and 2·498 (25°); *cumol*, 1·978 (15°), 1·879 (20°), 1·782 (25°); *eugenol*, 1·762 (15°), 1·653 (20°), and 1·539 (25°); *carvene*, 2·030 (15°), 1·921 (20°), 1·802 (25°); *metaxylol*, 2·346 (15°), 2·216 (20°), and 2·090 (25°); and *glycerol*, 0·0302 (25°). W. Kunerth measured the solubility in pyridine. A. von Hammel gave for the absorption coeff. of carbon dioxide in mixtures containing *w* grms. of glycerol per 100 grms. of soln. at 15°:

| *w* | 0 | 26·11 | 43·72 | 62·14 | 77·75 | 90·74 | 99·26 |
|---|---|---|---|---|---|---|---|
| Absorption coeff. | 1·008 | 0·785 | 0·639 | 0·511 | 0·430 | 0·404 | 0·410 |

Similarly for *chloral hydrate* at 15°:

| *w* | 17·7 | 31·6 | 38·3 | 49·8 | 57·1 | 68·8 | 79·4 |
|---|---|---|---|---|---|---|---|
| Absorption coeff. | 0·885 | 0·803 | 0·781 | 0·760 | 0·765 | 0·797 | 0·903 |

I. F. Homfray found solid *p-azoxyphenctole* does not absorb carbon dioxide; absorption occurs when the solid is first melted, and an isotropic liquid is formed; then a second increase in absorption occurs; and thereafter the solubility decreases regularly with rise of temp. A. Findlay and B. Shen also obtained values for *chloral hydrate* and *sugar* soln. at 25°. F. L. Usher gave for soln. with 0·125, 0·25, 0·50, and 1·00 mol of *sucrose* per litre, the respective absorption coeff. at 20°, 0·846, 0·815, 0·756, and 0·649; for soln. with 0·5 mol of *dextrose*, 0·792; *mannitol*, 0·782; *glycine*, 0·843; *pyrogallol*, 0·853; *quinol*, 0·887; *resorcinol*, 0·901; *catechol*, 0·868; *urethane*, 0·869; *carbamide*, 0·864; *thiocarbamide*, 0·859; *antipyrine*, 0·859; and *acetamide*, 0·879. S. Gniewosz and A. Walfisz found the absorption coeff. of *petroleum* to be 1·31 at 10° and 1·17 at 20°.

The action of carbon dioxide on *blood* has been studied by S. Jolin,[6] L. Meyer, J. Setschenoff, etc. G. Geffcken [7] measured the solubility of carbon dioxide in *colloidal solutions* of arsenic sulphide, and of ferric hydroxide. A. Findlay and co-workers have also measured the effect of colloids and fine suspensions on the solubility of carbon dioxide in water at 25° and various press. The solubility increased slightly with increasing conc. of ferric hydroxide, gelatin, silicic acid, aniline, methyl orange, blood serum, peptone, protopeptone, and hæmoglobin; while the solubility diminishes slightly with increasing conc. of arsenious sulphide, dextrine, soluble starch, glycogen, egg-albumen, and serum-albumen. No perceptible effect was observed with silica or charcoal suspensions. When the solubility is increased by a given substance, the solubility curve is depressed with an increase of press., and conversely. In the case of starch, and other neutral colloids, the solubility passes through a minimum with an increase of press. A. Findlay and G. King made observations on the influence of suspensions and colloids on the evolution of carbon dioxide from supersaturated soln.

Special observations on the adsorption of carbon dioxide by *charcoal* were made by P. A. Favre and J. T. Silbermann,[8] J. Hunter, L. Joulin, H. Kayser, L. B. Richardson and J. C. Woodhouse, P. Chappius, A. Reychler, R. A. Smith, M. W. Travers, J. Dewar, J. L. Bärwald, E. W. R. Pfeiffer, etc. They showed the effect of press. and temp. on the adsorption by different kinds of charcoal. These results have been previously discussed in connection with carbon. Similarly also with the thermal effect studied by P. A. Favre and J. T. Silbermann, P. Chappius, J. Dewar, etc. With a mixture of 95 per cent. hydrogen and 5 per cent. carbon dioxide, R. Lorenz and E. Wiedbrauck found that there is a high proportion of hydrogen adsorbed at first, the amount then falls rapidly; while with carbon dioxide, the proportion adsorbed at first is small, but rises rapidly. J. Böhm discussed the adsorption of carbon dioxide by *coal*. C. Matignon and G. Marchal examined the corrosive action of carbon dioxide under 10 atm. press. during three years on *quartz*, *mica*, *dioptase*, *wollastonite*, *talc*, *asbestos*, and *glass*. J. B. Hannay found that glassy *silicates*, *borates*, and *phosphates* adsorb carbon dioxide under press. He also found that glass at about 200° and 200 atm. press. readily adsorbs carbon dioxide, and retains much gas when cooled under press.; if the glass be then rapidly heated to fusion, the sudden evolution of the gas makes the glass froth; whereas if slowly heated to 300°, the gas is given off without any appreciable effect. H. Kayser, J. T. Bottomley, L. Pfaundler, O. Schumann, H. Krause, also studied the adsorption of carbon dioxide by the walls of glass vessels, and by glass powder. R. Bunsen made observations extending over three years, and concluded: (1) The gas condensation does not reach a fixed point, even after several years; (2) during the continuation

of the experiment, notwithstanding instantaneous or continual changes of temp. and press., no giving up of the carbon dioxide was observable; (3) within temp. of $+23°$ to $-8°$ a rise of temp. produces an acceleration, a fall a corresponding retardation of the adsorption. In three years 5·135 c.c. of carbon dioxide under standard conditions were adsorbed by one metre of the glass wool. As the chemical affinity of the silica for the basic substances in the glass is greater than that of the carbon dioxide, the supposition of a combination of the latter with the glass is precluded; thus it appears that the carbon dioxide is condensed as such. The long continuation of the phenomenon can be explained by an imperfect interpenetration of the glass by the molecules of the liquid carbon dioxide. It was not proved whether after a sufficiently long interval of time this interpenetration becomes negligibly small so that the conditions remaining the same, neither condensation nor evaporation of the liquid carbon dioxide takes place, although either one or the other might be caused by a change of the conditions. For every series of temp. there may be a corresponding series of levels of the layer of the carbon dioxide. Atm. air behaves like carbon dioxide. F. Scheermesser found that *sand*, washed with hydrochloric acid and then calcined, slowly adsorbs traces of carbon dioxide, and mixtures of sand and *clay* adsorb more gas when moist than when dry; the gas is given off in sunlight and re-adsorbed in the shade. J. H. van den Broek, and J. Nicklès studied the adsorption of carbon dioxide by *soils*; G. Hüfner, the adsorption of carbon dioxide by *hydrophane* (opal); and L. A. Munro and F. M. G. Johnson, the adsorption of the gas by *alumina*.

S. von Wroblewsky, A. Reychler, and W. Hempel found that *caoutchouc* or *rubber* adsorbs carbon dioxide, and the first-named added that the phenomenon is purely physical, not chemical. J. D. Edwards and S. F. Pickering found the relative permeability of rubber to hydrogen and carbon dioxide is as 1 : 2·9; the rate of diffusion at 100° is about 17 times that at 0°. The permeability varies somewhat with the composition and age. According to G. Hüfner, grey caoutchouc absorbs nearly its own vol. of carbon dioxide at $-2°$, and the sp. absorption coeff. increases with a rise of temp. T. Graham found that *silver* adsorbs 0·486 to 0·545 vol. of carbon dioxide, and *gold*, 0·16 vol., and G. Neumann added that he found that 29 grms. of *copper* occluded 0·0055 to 0·0196 grm. of the gas. A. Sieverts and W. Krumbhaar found that carbon dioxide dissolves neither in molten nor in solid copper. H. S. Taylor and R. M. Burns studied the adsorption of carbon dioxide by *nickel*, *cobalt*, *iron*, *copper*, *palladium*, and *platinum*—*vide* the respective metals—and by *copper*, *manganese*, *cobalt*, and *silicon oxides*.

Liquid carbon dioxide is a poor **solvent.** G. Gore [9] found that it dissolves camphor and iodine sparingly; it dissolves fats less rapidly than carbon disulphide. It changes guttapercha into a brown coloured substance; and it makes rubber swell. L. P. Cailletet said that it does not dissolve sodium or calcium chloride, sodium sulphate, calcspar or chalk, stearin, paraffin, sulphur, or phosphorus. It changes potassium carbonate into the hydrocarbonate; it dissolves iodine, and fatty oils sparingly. P. Villard also made some observations on this subject. C. Doelter studied the action of liquid carbon dioxide and water on silicates. E. H. Büchner found that it does not dissolve sodium, calcium, and mercuric chlorides, potassium bromide, or potassium and mercuric iodides; cupric or ferrous sulphate; silver nitrate; sodium or calcium carbonate; mercuric cyanide, silica, arsenic trioxide, metaphosphoric acid, sodium or calcium phosphide, phosphorus sulphide; potassium fluosilicate; quaternary ammonium salts; carbon; silicon; aluminium; sulphur; potassium; or sodium. The following are sparingly soluble in this menstruum: phosphorus, iodine, bromine, boric acid, phosphorus pentachloride, and antimony and arsenic tribromides. The following are completely miscible with the liquid: acetylene, pentane, amylene, benzene, *p*-xylene, *p*-dichlorobenzene, acetic acid, camphor, and carbon disulphide; the following are partially miscible: anthracene, phenanthrene, tri-iodomethane, *p*-dibromobenzene, *p*-chloro- or bromo-nitrobenzene, 1.2.3- and 1.3.2-dichloronitrobenzene, borneol, phthalic anhydride, succinic anhydride, urea, and benzamide. The following have a limited solubility: tribromomethane, *o*-bromo-nitrobenzene, mono- and di-chloronitrobenzene, nitrobenzene, thymol, and urethane.

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## § 36. The Chemical Properties of Carbon Dioxide

The dissociation of carbon dioxide by **heat** has been described in connection with the action of oxygen on carbon. F. Haber and H. le Rossignol investigated the dissociation of carbon dioxide in the flame of burning carbon monoxide mixed with oxygen. According to S. Chadwick, J. E. Ramsbottom, and D. L. Chapman,[1] dry carbon dioxide gas exposed to **ultra-violet light** is partially resolved into carbon monoxide and oxygen. There is a 3 per cent. decomposition under atm. press., and a 46 per cent. decomposition under 36 mm. press. The moist gas was not decomposed under these conditions. Probably some ozone is also formed. H. Herchfinkel obtained similar results, and observed that the surface of the mercury confining the gas acquired a yellow film of mercuric oxide. According to A. Coehn and G. Sieper, with dry carbon dioxide there was an 18 per cent. decomposition, and when the merest trace of moisture was present, a 0·10 per cent. decomposition. Neither formic acid nor formaldehyde was formed. The water was not changed. The decomposition was inversely proportional to the press. and more than corresponded with the law of mass action. H. Tramm showed that the speed of combination of carbon monoxide and oxygen in ultra-violet light is the same for the moist or dry gas; the retarding effect of moisture on the photo-decomposition of carbon dioxide is not due to an acceleration in the formation of carbon dioxide but to a retardation in its decomposition. Sulphur dioxide acts like water as a retarder—*vide* the oxidation of carbon monoxide; and J. Peklo found that potassium cyanide inhibits the reaction.

The readiness with which carbon dioxide can be reduced to formaldehyde is considered to be most suggestive in revealing the mechanism of photosynthesis. This led R. Willstätter and A. Stoll to conclude that carbonic acid is rearranged by the absorption of light energy into a formaldehyde peroxide complex from which, by means of an enzyme—catalase—action, formaldehyde is liberated, oxygen evolved, and chlorophyll regenerated. E. Bauer and P. Büchi found no evidence of the formation of formaldehyde, oxalic acid, or formic acid in the photolysis of carbonic acid ; the production of formaldehyde—reported by E. C. C. Baly and co-workers—when carbonic acid, in the presence of a sensitive dye, is exposed to light was said to be due to the decomposition of the dye itself. O. Loew found that carbon dioxide in the presence of water is not reduced by exposure to **sunlight**. A. Lieben found no formic acid was produced after 50 hrs.' exposure to sunlight. According to A. Bach, a stream of purified carbon dioxide was passed through two flasks, each containing a 1·5 per cent. soln. of uranium acetate. One flask was exposed to direct sunlight ; the other was covered with black paper to exclude light. The contents of the flask containing the soln. treated with carbon dioxide and exposed to sunlight alone became turbid and of a more or less greenish colour in about 20 mins. ; after some time, there was a considerable deposit, which, when filtered and washed, had a violet colour. This precipitate, when exposed to air, became yellow, and was transformed into a mixture of uranous and uranic hydroxides, with a trace of a brownish-yellow substance, probably uranium peroxide. When the uranium peroxide was exposed to the action of hydrogen peroxide and formaldehyde, the yellowish

precipitate acquired a greenish colour, and was finally transformed into the violet-brown substance soluble in acetic acid. A. Bach explained the results by assuming that a soln. of carbonic acid in sunlight slowly forms percarbonic acid and formaldehyde, $3H_2CO_3=2H_2CO_4+H.CO.H$; and the percarbonic acid then decomposes into hydrogen peroxide, etc., $H_2CO_4=CO_2+H_2O_2$. R. Wolffenstein and E. Peltner could not prove the formation of the percarbonic acid. A. Bach showed that carbon dioxide and water in the presence of a dil. sulphuric acid soln. of dimethylaniline (A. Trillat's test), give the intense blue reaction characteristic of formaldehyde, after exposure to light—diffused daylight or even the light from a gas-flame is sufficient. H. Euler said that the reaction does not occur with freshly purified dimethylaniline; and he found that when a soln. of uranium acetate is exposed to sunlight, it gave in one hour the same precipitate of uranous and uranic hydroxides as was obtained in half an hour from the soln. exposed to the action of sunlight and carbon dioxide. The function of the carbon dioxide is to remove oxygen from the soln., and it may be replaced by another indifferent gas, such as hydrogen or nitrogen. H. A. Spoehr repeated the experiments of F. L. Usher and J. H. Priestley, D. Berthelot and H. Gaudechon, J. Stoklasa and W. Zdobnicky, and E. C. C. Baly and co-workers, and has failed to obtain evidence of the reduction of carbon dioxide to formaldehyde; but A K. Sanyal and N. R. Dhar found that the exposure of moist carbon dioxide for 72 hrs. to tropical sunlight produced appreciable quantities of formaldehyde. Carbon dioxide is reduced by hydrogen to formic acid in the presence of palladium black; the reaction is reversible, and there is no sign of the intermediate product, formaldehyde. E. Baur and co-workers could not confirm the photocatalysis of carbon dioxide by colloidal iron or uranium oxides, ferric chloride, or sodium uranate, as reported by B. Moore and T. A. Webster. The reaction was investigated by T. Thunberg, F. Weigert, H. H. Dixon and N. G. Ball. O. Warburg and E. Negelein investigated the effect of the wave-length of light on the assimilation of carbon dioxide. The yield is greatest in the red and least in the blue region. R. Wurmser also compared the effects of red, green, and blue light.

Carbon dioxide was found by W. Ramsay [2] and co-workers to be decomposed into carbon, carbon monoxide, and oxygen when exposed to **radium radiations.** E. Wourtzel found that the action is very slow. H. Herchfinkel said the reaction resembles that which occurs on exposing the gas to ultra-violet light, and that about one-hundredth of the carbon dioxide is reduced to monoxide. B. Walter also found that the radiations from radio-tellurium acted like ultra-violet light on carbon dioxide. According to P. Bergell, solid carbon dioxide absorbs radium emanation, and, on sublimation, the last fraction of the gas is radioactive.

In 1788, M. Landriani,[3] and, in 1785, M. van Marum observed that carbon dioxide is decomposed by frictional electricity, for the vol. of the gas is permanently increased, and it is no longer so readily absorbed by water. J. Dalton, W. Henry, and J. Plücker noticed that the passage of **electric sparks** through carbon dioxide decomposed the gas into carbon monoxide and oxygen. W. Henry said:

> When the electric shock has been repeatedly passed through a portion of this acid gas, its bulk is enlarged, and a permanent gas is produced which is evidently a mixture of oxygenous and hydrogenous gases; for, when an electric spark is passed through the gas that remains after the absorption of the carbonic acid by caustic alkali, it immediately explodes.

The decomposition, said H. St. C. Deville, is but slight because the spark also causes the products of the reactions to re-form carbon dioxide: $2CO_2=2CO+O_2$. Observations were also made by A. W. Hofmann, B. Lepsius, M. Berthelot, T. Andrews and P. G. Tait, H. B. Dixon and H. F. Lowe, etc. H. Buff and A. W. Hofmann showed that when the decomposition of the carbon dioxide has progressed for some time, the resulting carbon monoxide and oxygen recombine with explosive violence. A. W. Hofmann showed that the explosion occurs only

under special conditions, the spark should be 2·5 to 3·0 mm. long when the current is derived from two Bunsen's cells connected with a Ruhmkoff's coil and a small Leyden jar. A. Smithells suggested carbon dioxide at low press. in a vacuum tube may be fairly stable in the electric discharge, but J. N. Collie found that under these conditions decomposition to the extent of 65 per cent. may occur in 10 secs. There is evidence of recombination because, during the passage of the discharge, flickerings occurred in the tube when the negative electrode became hot, and the glow on the hot negative electrode changed from the livid blue exhibited by the mixture of decomposed gases to the purple colour, which was characteristic when the gas was first subjected to the electric discharge. The results are independent of the electrode, and from 50 to 62 per cent. is found to have decomposed when the gas at 5–6 mm. press. is confined in an electrodeless tube. No difference was observed whether the undried or specially dried gas was employed. A. W. Hofmann found that in the electric arc with iron electrodes the gas decomposed yielding its own vol. of carbon monoxide, while if the iron contained carbon, more carbon monoxide was formed. B. Lepsius found that with carbon electrodes one vol. of carbon dioxide yields two vols. of carbon monoxide. C. Montemartini found that the corona effect in circuits traversed by a continuous current decomposes carbon dioxide into oxygen and carbon monoxide.

T. Andrews and P. G. Tait found that carbon dioxide is slowly decomposed by the **silent discharge**—in, say, an ozone tube—and a bronze-green deposit appears on the anode. A. Thénard observed that carbon monoxide and oxygen are formed, and that the latter is partly converted into ozone. W. Löb said that the ozone which is formed re-oxidizes the carbon monoxide. Observations were made by B. C. Brodie, P. Hautefeuille and J. Chappius, E. Reitlinger and A. von Urbanitzky, A. W. Hofmann, etc. M. Berthelot noted the formation of solid carbon oxide—*vide* carbon suboxides. A. Holt found that the amount of decomposition is less the weaker the discharge, or the wider the annular space in the ozonizer; and with a discharge of constant intensity and at varying press., the amount of dried gas decomposed varies inversely as the press., while with moist gas, the amount decomposed varies directly as the press.:

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| Pressure . . | 30 | 165 | 300 | 652 | 50 | 220 | 448 | 628 | |
| Decomposition . | 48·4 | 31·0 | 19·9 | 2·6 | 3·8 | 5·5 | 10·3 | 14·0 | per cent. |
| | Dried gas | | | | Moist gas | | | | |

It is assumed that in the moist gas at low press. the discharge is almost entirely due to ultra-violet light, but, as the press. increases more and more, sparks are formed which decompose the gas. T. Noda and E. Warburg found that with a point discharge, the carbon dioxide is decomposed to the extent of 3 per cent., and that about 19 per cent. of the oxygen produced is ozonized. The number of coulombs required to decompose a gram-eq. of carbon dioxide is only 2610, which shows that the decomposition of this gas by the silent discharge is not an electrolytic process. It is shown also that of the electrical energy supplied only 1·1 per cent. is converted into chemical energy. For a negative point discharge, it appears that the amount of decomposition depends only on the total electricity, not on the current strength. Further, the number of coulombs per mol. of carbon dioxide decomposed increases as the density of the gas is diminished. It is also found that the number of coulombs falls off as the temp. rises.

In 1802, N. T. de Saussure[4] observed that when electric sparks are passed through a mixture of **hydrogen** and carbon dioxide, the vol. decreases. A similar observation was made by M. Traube, A. Naumann and C. Pistor, etc. J. N. Collie found that with the electric discharge at low press. the carbon monoxide formed *in statu nascendi* did not produce any detectable amount of formaldehyde, but the decomposition of the carbon dioxide appeared to be retarded by the hydrogen. C. Zenghelis said that the gases in a nascent state owe their activity to their being in an extremely finely-divided condition because carbon dioxide in a sat. aq. soln. is

reduced by hydrogen passed into the soln. through filter-paper, or parchment. The action is accelerated by sunlight or ultra-violet light. Formaldehyde is the first product of the action. Carbon dioxide is slowly reduced by hydrogen when both gases are present in the same aq. soln.

S. M. Losanitsch and M. Z. Jovitschitsch found on exposing a mixture of carbon dioxide and hydrogen to the silent discharge, some formic acid is produced. M. Berthelot said that some carbohydrates are formed when the hydrogen is in excess: $nCO_2+2nH_2=C_nH_{2n}O_n+nH_2O$; if less hydrogen is present, the product is richer in oxygen; and if nitrogen be present a nitrogenous product, $(COH_3N)_n$, or $(COH_3N)_n+nH_2O$, is formed, while in the presence of water, ammonium nitrate appears. W. Löb also noted that some formic acid is produced by the action of the silent discharge on a moist mixture of carbon dioxide and hydrogen; no hydrogen peroxide was detected, but some ozone was formed, and this appears to hinder or prevent the formation of hydrogen peroxide. He represents the reactions: $2CO_2=2CO+O_2$; $2H_2+O_2=2H_2O$; $H_2+CO=H.COH$; $CO+H_2O=H.CO.OH$; and possibly also $CO_2+H_2=H.CO.OH$. No glycolaldehyde was detected. E. Royer found formic acid is produced when carbon dioxide is passed into water contained in the porous pot of Bunsen's or Grove's cell; and that more is formed with un-amalgamated than with amalgamated zinc. H. Thiele observed no result when a mixture of hydrogen and carbon dioxide in a quartz bulb is exposed to ultra-violet light; but A. Coehn and G. Sieper observed that formaldehyde is produced with a mixture of equal vols. of carbon dioxide and hydrogen.

A. Schrötter found that at a dull red heat carbon dioxide is reduced by hydrogen to carbon monoxide; G. Gore added that the reduction does not proceed so far as to give carbon. A. Naumann and C. Pistor observed no reduction at 900°, and C. Hoitsema said that the mixture: $CO_2+H_2=CO+H_2O$ can be kept a long time at 600° without attaining a state of equilibrium. According to M. Berthelot, when a mixture consisting of carbon dioxide and hydrogen is raised to a high temp., the state of equilibrium is established, not between the binary systems $(CO_2+H_2)$ and $(CO+H_2O)$, but between the more complicated system $\{(n-a)CO_2+a(CO+O)\}$, resulting from the partial dissociation of carbon dioxide and the partial dissociation of steam, $\{(m-\beta)H_2O+\beta(H_2+O)\}$, while a further complication results from the dissociation of carbon monoxide which reacts in the following sense, $\{pCO=(p-2)CO+CO_2+C\}$. O. Boudouard found that different mixtures of hydrogen and carbon dioxide at 850° and at 1100° attained a state of equilibrium in a few hours, and the distribution of the products $CO_2+H_2\rightleftharpoons CO+H_2O$ were in accord with H. le Chatelier's theorem. Press. had no influence on the equilibrium conditions since the number of reacting mols. is the same as the number produced by the reaction. The conditions of equilibrium have been discussed in connection with the reverse reaction between carbon monoxide and steam.

Reduced iron was found, by P. Sabatier and J. B. Senderens, and A. Gautier and P. Clausmann, to act catalytically on the reduction of carbon dioxide by hydrogen at 420°, forming methane. P. Sabatier and J. B. Senderens found that reduced cobalt at 300° begins to form methane, and at 360°–400°, the reaction is rapid; reduced nickel begins to act at 230°, and at 300° the reaction $CO_2+4H_2=CH_4+2H_2O+41{\cdot}2$ Cals. occurs. S. Medsforth studied the action of nickel, and the effect of the oxides of Ce, Th, Be, Cr, Al, Si, Zr, Mo, V, Sn, Mg, Cu, and Ag on the nickel catalyst. H. S. Elworthy and E. H. Williamson patented the application for manufacturing methane. M. Mayer and co-workers also studied the reaction. P. Sabatier and J. B. Senderens found reduced copper acts catalytically, $CO_2+H_2=CO+H_2O$; and that there is no appreciable formation of methane with finely divided platinum or palladium at 420°. E. Orloff found that carbon dioxide is not reduced to formaldehyde by nickel or palladium at 95°–100°, but at higher temp. methane and ethane are formed. According to A. Bach, when carbon dioxide is reduced by hydrogenized palladium, formaldehyde is produced. H. B. Dixon observed the reduction of carbon monoxide by hydrogen when a

platinum spiral is electrically heated to redness in the mixed gases. E. Müller and H. Barck found that the reduction of carbon dioxide by hydrogen is greatly accelerated in the presence of chromium and iron; with manganese, some carbide is formed. A. P. Dubrunfaut found that when hydrogen is passed over calcium carbonate at a red heat, carbon and water are formed; similarly also when a mixture of carbon dioxide and hydrogen is passed over red-hot pumice, he said that the reduction occurs in two stages: $CO_2+H_2=H_2O+CO$, and $CO+H_2=C+H_2O$.

According to R. Bunsen, if a mixture of hydrogen, **oxygen,** and carbon dioxide be inflamed, the ratio of the reduced to the non-reduced carbon dioxide changes *per saltum* when different proportions of the combustible gases are employed. On the contrary, A. Horstmann showed that the results are quite in agreement with the law of mass action, in which the equilibrium concerned is: $CO_2+H_2=H_2O+CO$. M. Berthelot said that if the mixture burns explosively, the carbon dioxide is not changed, and only when the combustion proceeds slowly is carbon monoxide formed. He also found that when a mixture of equal vols. of carbon dioxide and oxygen in sealed tubes was exposed to the action of a silent discharge, 16 per cent. of the gas was decomposed with the formation of a gas acting as a strong oxidizing agent. If this gas be regarded as ozone then it is produced in the proportion of from 30 to 40 per cent. of the amount of oxygen set free, which is larger than the quantity of ozone formed from pure oxygen. All attempts to isolate the gas have failed, owing to its strong oxidizing properties, and it is suggested that possibly percarbonic acid is formed.

According to A. Lieben,[5] at ordinary temp. hydrogen *in statu nascendi* does not reduce carbon dioxide dissolved in water, nor did W. Löb detect the formation of perceptible amounts of formaldehyde or formic acid under these conditions. A. Lieben, however, observed that carbonates of the alkalies or alkaline earths (not magnesium hydrocarbonate) are reduced to formates by hydrogen *in statu nascendi* derived from the action of magnesium or platinized magnesium. Light has no effect on the reaction. H. Moissan found that the **alkali hydrides**—sodium, potassium, rubidium, cæsium—do not react with thoroughly dried carbon dioxide at ordinary temp.; but, in the presence of the merest trace of water, between −85° and +54°, **potassium hydride** and carbon dioxide form potassium formate. M. Mayer and V. Altmayer found that **calcium hydride** reacts with carbon dioxide: $4CaH_2+2CO_2=CH_4+4CaO+C+2H_2$.

S. M. Losanitsch and M. Z. Jovitschitsch[6] found that carbon dioxide and water vapour react under the influence of the silent discharge, producing formic acid, ozone, and hydrogen dioxide. W. Löb made similar observations—*vide supra*. For the action of **hydrogen peroxide**, *vide* percarbonates. The solubility of carbon dioxide in **water** has been previously discussed. An aq. soln. of carbon dioxide has the properties of a weak acid—*vide* the conductivity of the aq. soln. At atm. press., the aq. soln. gives a claret-red with blue litmus; and, according to F. J. Malaguti, at a press. of two atm., the red colour is more marked. R. Kersting said that water containing 0·000004 part of carbon dioxide will colour neutral litmus violet. According to J. B. A. Dumas and J. S. Stas, and H. St. C. Deville, a soln. coloured claret-red by litmus has its original colour restored by exposure to air, owing to the escape of carbon dioxide. The colour is quickly discharged by boiling the soln. According to F. A. Flückiger, and H. Rebenstorff, a soln. of phenolphthalein reddened by sodium hydroxide is decolorized by carbon dioxide. The colour with methyl orange is scarcely affected by carbonic acid, but B. von Szyszkowsky found a sat. soln. of sodium chloride coloured with methyl orange is more sensitive to carbonic acid than is an aq. soln. The feeble acidity of carbonic acid explains why only the more electropositive metals are affected by this acid—*vide* the action of the metals on carbonic acid. Carbonic acid is stronger than tartaric acid (D. A. Goldammer), nitrous acid (C. Marie and R. Marquis, J. Meunier, and R. B. Moore), and boric acid (L. Grünhut). R. Höber studied the effect of carbonic acid on the alkalinity of **blood.**

H. Moissan[7] found that at ordinary temp. **fluorine** does not react with carbon dioxide. J. Schiel found that carbonyl chloride is formed when a mixture of carbon dioxide and **chlorine** is passed over red-hot carbon. According to R. Lucion, dry chlorine at 300° and at a bright red heat is without action on carbon dioxide. With chlorine and moist carbon dioxide, however, hydrogen chloride is formed in the usual way; 55 per cent. of the chlorine disappeared in this way when the carbon dioxide was mixed with 8 per cent. of chlorine; when, however, the chlorine formed only one per cent. of the mixture, then only 11 per cent. of it was converted into hydrogen chloride. With air as diluent, just the reverse took place, and the percentages of chlorine attacked were 14 in the first instance and 80 with the one per cent. mixture. According to J. Dewar, carbon dioxide mixed with many substances and at high press. behaves as if it formed unstable compounds which are decomposed and reproduced according to the conditions of the experiment; with **bromine** at 40° and 60 atm. press., two distinct layers are formed one of which is liquid carbon dioxide with a little bromine in soln.; at 90 atm. press. the two liquids are miscible; with carbon dioxide and **hydrogen chloride** liquefaction occurs at

| | 0° | 5·0° | 8·0° | 10·1° | 18·5° | 34·0° | 35·0° |
|---|---|---|---|---|---|---|---|
| Pressure . . . | 36·0 | 39·0 | 43·8 | 48·2 | 59·0 | 83·0 | 90·0 atm. |

H. Müller stated that an aq. soln. of **sodium chloride** is decomposed by carbon dioxide with the evolution of hydrogen chloride, and H. Schulz said that if a 5 per cent. soln. be tinted with 0·001 per cent. of methyl violet, the colour is destroyed by passing carbon dioxide through the soln. J. Röhmann and E. Malachowsky added that the decoloration is really due to the precipitation of the methyl violet by the salts in soln. N. N. Beketoff observed no change when a dil. soln. of **barium chloride** or **calcium chloride** is treated with carbon dioxide under 40–45 atm. press. H. Müller, however, observed that **lead chloride** gives a precipitate of lead chlorocarbonate. W. Spring found that when carbon dioxide is passed over lead chloride at 400°–500°, chlorine is given off. H. Struve, and G. Pellagri found that **potassium iodide,** in the presence of water, is decomposed by carbon dioxide; and, added G. Papasogli, if the potassium iodide is quite pure, no decomposition occurs at ordinary temp., but at a higher temp., hydrogen iodide is set free.

A. J. Balard found that **hypochlorites** are decomposed by carbon dioxide, and chlorine monoxide is set free. J. L. Gay Lussac found that the reaction is incomplete when the hypochlorites are in soln. A. W. Williamson studied the action of carbon dioxide on **barium hypochlorite;** and J. Kolb, H. G. de Claubry, A. Morin, and C. Göpner the action on **calcium hypochlorite** (*q.v.*). N. A. E. Millon stated that the **chlorites** are decomposed by carbon dioxide. According to G. Papasogli, and C. F. Cross, **potassium iodate** alone is not decomposed by carbon dioxide, but if some potassium iodide is also present, iodine is set free. M. Gröger found that the reaction is incomplete.

G. Chevrier[8] found that carbonyl sulphide (*q.v.*) is formed when a mixture of **sulphur** vapour and carbon dioxide is exposed to the silent discharge; and A. Cossa found that the same product is obtained when carbon dioxide acts on boiling sulphur. M. Berthelot, however, said that dry carbon dioxide has no action on boiling sulphur, and that the small quantity of carbonyl sulphide which is formed when a mixture of sulphur vapour and carbon dioxide is passed through a red-hot porcelain tube is derived from the carbon monoxide produced by the dissociation of the carbon dioxide. S. Petuchoff could detect no carbon as a result of this operation. A. Smith and W. B. Holmes showed that when molten sulphur is treated with carbon dioxide it does not give the insoluble form when cold. S. Petuchoff found that at 1200°, sulphur, and carbon dioxide derived from the decomposition of carbonates, produces carbon monoxide, sulphur dioxide, and carbon. H. Köhler passed a mixture of carbon dioxide and **hydrogen sulphide** through a red-hot tube and found sulphur, carbon monoxide, and water are formed: $CO_2+H_2S=CO+H_2O+S$.

The reaction is possibly : $CO_2+H_2S=COS+H_2O$, but the carbonyl sulphide is decomposed at the temp. of the experiment. A. Gautier represented the reaction : $8CO_2+9H_2S=3COS+5CO+H_2+8H_2O+6S$ ; no hydrocarbons were found. M. Berthelot found that when a mixture of carbon dioxide and hydrogen sulphide is exposed to the silent discharge, each gas is decomposed separately and the products react, forming sulphur dioxide, and trioxide. B. Holmberg noted that when carbon dioxide is passed into an alcoholic soln. of **potassium hydrosulphide,** potassium ethylcarbonate, potassium hydrocarbonate, etc., are formed : $KSH+CO_2+C_2H_5OH=KO.CO.OC_2H_5+H_2S$ ; and $KSH+CO_2+H_2O=H_2S+KHCO_3$. E. Berl and A. Rittener represent the action of carbon dioxide on **sodium sulphide** at 14° and 80° by : $Na_2S+CO_2+H_2O=NaSH+NaHCO_3$, and $NaSH+CO_2+H_2O\rightleftharpoons NaHCO_3+H_2S$ respectively. E. Berl and A. Rittener, and L. A. Buchner studied the action of carbon dioxide on calcium hydrosulphide, $Ca(SH)_2$ ; and M. Berthelot, the action on potassium polysulphide. The physical properties of mixed carbon dioxide and **sulphur dioxide** have been previously discussed—*vide supra*, and **1**. 4, 8. M. Berthelot found that when **potassium sulphite** or hydrosulphite is heated to redness in a stream of carbon dioxide, the alkali sulphate, polysulphide, and a little carbonate are formed ; while under similar conditions carbon dioxide does not act on **potassium sulphate.** J. Davy said that water sat. with carbon dioxide under press. has no more action on dihydrated **calcium sulphate** than has water alone.

N. T. de Saussure [9] observed that carbon dioxide is reduced to carbon monoxide when heated in the presence of **carbon.** V. A. Jacquelain studied the slow combustion of carbon in an atm. of carbon dioxide when heated by the oxyhydrogen flame, or by the carbon monoxide-oxygen flame. A. P. Dubrunfaut stated that if hydrogen or moisture be excluded, carbon does not reduce carbon dioxide. J. B. A. Dumas said that at a red heat the reduction of dried carbon dioxide is effected by dried carbon. This subject has been discussed in connection with the action of oxygen on carbon. B. Rathke gave for the heat of reduction $CO_2+C=2CO-36{\cdot}7$ Cals., and stated that the reaction is incomplete at a red heat. According to B. Unger, the reduction does not occur at 960° ; this statement, however, is not correct. P. Sabatier and J. B. Senderens could detect no action between 230° and 400° ; A. Naumann and C. Pistor said that the reaction sets in about 550° ; O. Boudouard said that no reduction is appreciable below 450°, and at 950° the reaction is complete. The reversibility of the reaction was established by H. St. C. Deville about 1864, and the equilibrium conditions have been discussed in connection with the action of oxygen on carbon. H. von Jüptner studied the equilibria of the gases in gas producers. C. A. Parsons showed that when carbon is electrically heated in an atm. of carbon dioxide under press., carbon monoxide is almost wholly formed. M. Foix found that the diamond has practically no action on carbon dioxide, so that the reaction $CO_2+C_{diamond}=2CO$ is not reversible. G. Gore observed no reduction of carbon dioxide to carbon when it is heated with **hydrocarbons**. J. Lang found that the reduction of carbon dioxide by **methane** begins between 700° and 800° ; the reaction is very slow between 703° and 814° ; above this, carbon monoxide is formed in proportions increasing with the rise of temp., and some carbon is formed above 1000°. P. and A. Thénard observed that a mixture of carbon monoxide and methane in the silent electric discharge gives a liquid product ; and W. Löb showed that carbon monoxide and hydrogen are formed. A. Frank observed that when a mixture of **acetylene** and carbon dioxide is heated, or exposed under press. to the silent discharge, amorphous carbon is formed : $2C_2H_2+CO_2=2H_2O+5C$. J. Dewar found that when equal vols. of acetylene and carbon dioxide are liquefied, the incompletely miscible liquids mix completely at 13° and 25·23 atm., 26·8° and 34·1 atm., 41° and 75·52 atm. Similar phenomena were observed with carbon dioxide and **benzene,** and S. Miyamoto found that a silent discharge through the vapour of benzene and carbon dioxide forms a phenol, $C_{30}H_{30}O_9$. W. Löb observed that the action of the silent discharge on a mixture of **ethyl alcohol,** carbon dioxide, and water vapour gave much carbon monoxide, some formal-

dehyde, and formic acid, and traces of acetaldehyde. J. Dewar found that with mixtures of carbon dioxide and **ether,** at 20° and 20 atm. the gases condense to a liquid in which the two constituents are miscible in all proportions; a separation occurs at 42° and 55 atm., and at 68° and 110 atm. J. Dewar, and J. P. Kuenen studied the condensation phenomena with mixtures of carbon dioxide and **chloroform.** According to P. Schützenberger, carbonyl chloride is formed when a mixture of carbon dioxide and **carbon tetrachloride** is passed through a red-hot tube packed with pumice-stone: $CO_2+CCl_4=2COCl_2$. J. Dewar studied the condensation phenomena with mixtures of carbon dioxide and carbon tetrachloride, and with **methyl chloride.** As previously indicated, a mixture of carbon dioxide and **carbon disulphide** when passed through a hot tube furnishes carbonyl sulphide. The conditions were studied by W. Hempel. The reaction was also studied by A. Deninger. When the mixed gases are passed over heated copper, A. Eiolart observed a reaction represented by: $CO_2+CS_2+4Cu=2CO+2Cu_2S$. M. Thilorier said that liquid carbon dioxide and disulphide are miscible in all proportions. L. P. Cailletet said the miscibility extends only over a limited range. J. Dewar found at 19°, carbon dioxide liquefies in the presence of carbon disulphide at 49 atm. press.; at 35°, at 78 atm.; at 40°, at 85 atm.; and at 58°, at 110 atm. press. The liquid carbon dioxide then floats on the surface of the disulphide; at 47° and 80 atm., the layers of liquid are not so well marked; at 110 atm., the upper liquid almost wholly disappeared, and on reducing the press. to 80 atm. the liquids were completely mixed. A reduction of 5 atm. in the press. caused the liquid again to separate into layers. J. A. Wanklyn found that acetic acid is formed when carbon dioxide reacts with **sodium methyl,** and propionic acid, with **sodium ethyl.** Numerous other reactions of carbon dioxide with organic compounds have been reported by K. Brunner, etc. For the action of carbon dioxides on the **carbonates,** *vide* the metal hydrocarbonates. G. Gore observed no separation of carbon when the vapour of **ammonium carbonate** and carbon dioxide are passed through a red-hot tube. L. Naudin and F. de Montholon said that dry carbon dioxide has no action on dried **potassium cyanide;** but in the presence of water, hydrocyanic acid and potassium carbonate are slowly formed. When carbon dioxide is passed over heated **potassium thiocyanate,** J. Milbauer found that sulphur, carbonyl sulphide, carbon monoxide, and potassium cyanate are formed: $KCNS=KCN+S$; $KCN+CO_2=CO+KCNO$; or $KCNS+CO_2=KCNO+COS$; and $COS\rightleftharpoons CO+S$. G. Gigli found that a soln. of **potassium ferrocyanide,** sat. with carbon dioxide gave some hydrocyanic acid when distilled, and a greenish product, probably potassium ferrous ferrocyanide, $K_2Fe(FeCy_6)$, was formed. The reaction is not essentially different from that between sulphuric acid and potassium ferrocyanide. J. Matuschek represented the reaction by: $2K_4FeCy_6+4CO_2+9H_2O+O=2Fe(OH)_3+4K_2CO_3+12HCy$; and with **potassium ferricyanide,** $2K_3FeCy_6+3CO_2+9H_2O=2Fe(OH)_3+3K_2CO_3+12HCy$. In both cases the potassium carbonate and hydrocyanic acid react giving ammonia and formic acid. C. L. Carey studied the absorption of carbon dioxide by gels of **agar-agar, gelatine,** and **starch.**

G. Gore[10] found that **silicon** does not decompose carbon dioxide in the presence of water, and that a mixture of **silicon tetrafluoride** and carbon dioxide is not changed when passed through a red-hot tube. L. Dovéri, C. Struckmann, A. Johnstone, C. Doelter, W. P. Headdon, C. G. C. Bischof, W. R. and R. E. Rogers, H. St. C. Deville, T. Dietrich, A. Cossa, A. Pavesi and E. Rotondi, R. J. Müller, etc., have studied the action of carbon dioxide or aq. soln. of carbon dioxide on **silica** or **silicate rocks**—*vide* the silicates. H. Herbst found the gas is not adsorbed by silicic acid. R. Bunsen studied the action on **glass** of water charged with carbon dioxide under press. L. Pfaundler believed that a chemical action occurs, for, when a strong light is projected upon a glass tube filled with compressed carbon dioxide near its critical point, the surface of the glass above the level of the liquefied gas is found to be corroded as though with hydrofluoric acid. It is thus not improbable that a chemical action, effected within a few minutes under the influence

of a strong press. and intense light, can proceed slowly, under a slight press. and ordinary daylight. H. Weil, and B. von Szyszkowsky found that **ultramarine** in contact with soln. of sodium chloride charged with carbon dioxide gives off hydrogen sulphide; and P. N. Raikow found that ultramarine is not changed after it has been in contact with carbon dioxide for many hours. D. Gerasimoff studied the action of carbon dioxide on **alkali titanates.** H. Herbst found carbon dioxide is not adsorbed by wad, dried wood, paraffin, or sugar.

F. Briegleb and A. Geuther [11] observed that carbon dioxide reacts with heated **magnesium nitride**, producing cyanogen, carbon, and carbon monoxide. F. Wöhler found that when a mixture of dried **ammonia** and carbon dioxide is moderately heated, ammonium carbamate, $NH_2.COONH_4$, and at a higher temp., carbamide, $CO(NH_2)_2$, and ammonium carbamate are formed; but, added R. E. Hughes and F. Soddy, if the two gases are thoroughly dried no reaction occurs. E. C. C. Baly and co-workers studied the photosynthesis of naturally occurring nitrogen compounds from carbon dioxide and ammonia. E. Rengade found with **sodioammonium**, $NaNH_3$, below −50°, sodium carbamate, $NH_2.COONa$, is produced. Similarly also with **potassioammonium,** $KNH_3$. At a rather higher temp., −10° to −5° with potassioammonium, and −35° to −25° with sodioammonium, hydrogen is liberated and the alkali formates are produced. F. Beilstein and A. Geuther observed that with **sodium amide,** $NaNH_2$, dried carbon dioxide forms cyanamide. The reaction has been studied by W. P. Winter, and E. Drechsel; according to the latter, the reaction progresses in stages: $NaNH_2+CO_2=NH_2COONa$; $NH_2COONa=H_2O+NaCNO$; and $NaCNO+NaNH_2=H_2O+Na_2CN_2$. J. Dewar found that carbon dioxide and **nitrous oxide**, when liquefied, mix together in all proportions; and on reducing the press., one liquid evaporates before the other, and gives a distinct line of separation. R. B. Moore liberated nitrogen oxide from soln. of **potassium nitrite, sodium nitrite,** and **silver nitrite** by carbon dioxide. E. R. Marle obtained a similar result with a soln. of potassium nitrite. D. Huizinga stated that carbon dioxide liberates nitrous acid from **ammonium nitrite,** but, added E. von Gorup-Besanez, only if a trace of hydrochloric acid is present. L. Meunier said that carbon dioxide does not liberate nitrous acid from sodium nitrite, but C. Marie and R. Marquis claim that this is wrong because (i) Purified carbon dioxide was passed into a soln. of sodium nitrite containing potassium iodide and starch paste; the development of a blue colour indicated the liberation of iodine by nitrous acid; (ii) A soln. of potassium iodide and sodium nitrite produced no coloration in chloroform, whilst a similar soln. sat. with carbon dioxide caused the chloroform to become violet; (iii) A soln. of potassium iodide and starch was coloured blue by carbon dioxide which had previously passed through a soln. of sodium nitrite; and (iv) an aq. soln. of $\beta$-naphthylamine and sulphanilic acid, which gives an orange-red colour with even traces of nitrous acid, gives the same reaction when carbon dioxide is passed into a soln. of sodium nitrite.

According to A. R. Leeds,[12] moist **phosphorus** does not reduce carbon dioxide to the monoxide, but it forms phosphine. J. H. Niemann found that liquid carbon dioxide is not affected by phosphorus. According to L. P. Cailletet and M. Bordet, when a mixture of equal vols. of phosphine and carbon dioxide is compressed in the presence of water a white crystalline body is formed without any gaseous residue; the solid is a mixture of phosphonium hydroxide, and hydrated carbon dioxide; and it is not formed above 22°. M. Berthelot said that when a mixture of **phosphine** and carbon dioxide is passed through a tube at dull redness, there is no evidence of the formation of hydrocarbons, and at a bright red heat, carbon monoxide and hydrogen are formed; while G. Gore said that no carbon is produced under these conditions. T. E. Thorpe and A. E. Tutton found that carbon dioxide does not act on **phosphorus trioxide** either at ordinary temp. or when heated. According to J. Dewar, when a mixture of carbon dioxide and **phosphorus trichloride** is compressed at 16·2° and 42·95 atm. or at 23° and 46·91 atm., the gases liquefy—the carbon dioxide condenses first, and the liquids mix together in a few minutes. At

30° and 49·94 atm. the carbon dioxide is less soluble in the liquid phosphorus trichloride than at lower temp. According to A. Barillé, dry carbon dioxide does not act on dry **calcium phosphate**. He found that the metal phosphates in contact with water under press. behave like calcium phosphate and form carbonatophosphates (*vide* **3.** 24, 30)—*e.g.* the phosphates of the alkalies and alkaline earths, ammonium, and magnesium. These all form hydrocarbonates. The other phosphates simply dissolve in the carbonic acid without decomposition. F. K. Cameron and A. Seidell said that the presence of carbon dioxide does not affect the action of water on calcium hydrophosphate, but it raises the quantity of dissolved phosphoric acid in the case of calcium dihydrophosphate, and normal calcium phosphate. J. Davy said that water sat. with carbon dioxide under press. dissolves normal calcium phosphate rather more than does water alone—*vide* calcium phosphates. E. Shepherd observed no reduction of carbon dioxide to the monoxide when in the presence of **ferrous phosphate** and exposed to light. E. N. Horsford, however, said that a mixture of carbon dioxide, in the presence of water, sodium phosphate, and ferrous sulphate, is reduced to carbon monoxide in light or in darkness. H. Struve has also studied the reaction. L. J. Henderson and O. F. Black studied the equilibrium conditions between carbon dioxide, sodium hydrocarbonate, hydrophosphate, and dihydrophosphate. D. Gerasimoff investigated the action of carbon dioxide on the alkali **vanadates, tantalates,** and **columbates.**

According to R. Lorenz,[13] **boron** at a red heat reduces carbon dioxide to boron trioxide and carbon. L. C. Jones found that an excess of carbon dioxide in contact with the **borates** can slowly displace the boric acid. J. Davy observed no difference in the action of water sat. with carbon dioxide under press. and of water alone on **alumina.** D. Gerasimoff studied the action of carbon dioxide on the alkali **aluminates,** and **tungstates.** E. Schweizer showed that carbon dioxide converts **potassium chromate** in aq. soln. into potassium dichromate and carbonate. The reaction was studied by P. Sabatier, F. Mohr, etc. A. Bach's observations on the action of carbon dioxide on soln. of **uranium salts** have been discussed in connection with the action of light on carbon dioxide and water. The reaction has also been investigated by H. Euler, F. L. Usher and J. H. Priestley, E. Mameli and G. Pollacci, A. J. Ewart, etc.

H. Davy,[14] and J. L. Gay Lussac and L. J. Thénard found that when heated with **potassium** or **sodium,** carbon dioxide is reduced to carbon, and some alkali carbonate is formed. E. Drechsel said that sodium, mixed with some calcined quartz sand, absorbs dried carbon dioxide at 260° and forms some sodium oxalate; similar results were obtained with a 2 per cent. sodium amalgam. H. Kolbe and R. Schmidt found that if kept in a warm moist atm. of carbon dioxide for 24 hrs., potassium is converted into a mixture of potassium hydrocarbonate and formate: $2K+2CO_2+H_2O=KHCO_3+H.COOK$; M. Ballo gives $2H_2CO_3+2K=KHCO_3+H.COOK+H_2O$. H. Kolbe and R. Schmidt added that the yield of formate with sodium is less than with potassium. A. Lieben found that 0·5 to 3·0 per cent. potassium and sodium amalgams, or **barium** amalgam with aq. soln. of carbon dioxide, furnish a mixed soln. of hydrocarbonate and formate. Light had no influence on the result. Alcoholic soln. behave similarly. Small quantities are also formed if phosphoric or sulphuric acid be present, but the amount of formic acid produced decreases with increasing proportions of the mineral acid. C. Kippenberger, and A. Bach also obtained formic acid by the action of the alkali amalgams on carbonic acid. H. Moissan found that **calcium** at a dull red heat reduces carbon dioxide, forming calcium oxide and carbon. G. Gore said that potassium and sodium are not affected by liquid carbon dioxide. M. Thilorier stated that liquid carbon dioxide is decomposed by potassium, and L. P. Cailletet added that liquid carbon dioxide is not reduced by sodium or sodium amalgam, but that some sodium hydrocarbonate is formed owing to the presence of a trace of moisture in the liquid. H. Limpricht stated that at a dark red heat **copper** reduces carbon dioxide to the monoxide; but A. Perrot observed no reduction either at a bright red heat or at a

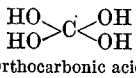
dull red heat when purified copper was used; reduction occurred if the copper contained a trace of iron or zinc; while, according to A. Schrötter, copper decomposes carbon dioxide at a bright red heat only when hydrogen is present. E. Lautemann, O. L. Erdmann, and G. Neumann have made observations on this subject. According to M. Thilorier, copper is not affected by liquid carbon dioxide.

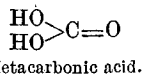
J. Parkinson found that **magnesium** at a red heat burns with incandescence in carbon dioxide and carbon is formed. F. Kessler isolated the carbon by washing the product of the reaction with dil. nitric acid. C. Winkler said that much of the carbon reacts with the carbon dioxide forming carbon monoxide, which is therefore a secondary product of the reaction. H. R. Ellis found that the amorphous carbon contains much graphite. The reaction has also been discussed by V. Wartha, H. Cretier, and T. L. Phipson. According to K. Brunner, magnesium powder burns on solid carbon dioxide producing a grey cake which, when treated with dil. hydrochloric acid, leaves black flecks of carbon. According to M. Ballo, S. Kappel, and G. Giorgis, magnesium dissolves in a soln. of carbonic acid with the evolution of hydrogen and the formation of magnesium carbonate which dissolves as hydrocarbonate in the excess of the soln. A. Lieben found that a little formic acid is produced by the action of an aq. soln. of carbonic acid on magnesium with or without the addition of traces of acid; H. J. H. Fenton obtained formaldehyde as a result of this reaction, and the yield was considerably increased in the presence of feeble bases—like ammonia, aluminium hydroxide, aniline, etc. A. Lieben obtained formic acid as a result of treating an aq. soln. of carbonic acid with magnesium in the presence of sodium phosphate, ammonium carbonate, or potassium sulphate, and baryta-water; he also found that **zinc** reacts with carbonic acid like magnesium, and that platinized zinc does not reduce carbon dioxide either in alkaline or ammoniacal soln. According to M. Thilorier, zinc is not affected by liquid carbon dioxide. H. Jahn found that moist carbon dioxide is reduced to the dioxide when heated with zinc-dust. N. T. de Saussure said that in the presence of **mercury** the passage of electric sparks through carbon dioxide produces mercuric oxide with the separation of carbon. W. von Bolton found that mercury vapour in the presence of moisture separates some carbon from carbon dioxide. J. D. van der Plaats studied the vaporization and surface tension of mercury in an atm. of carbon dioxide. N. Wender found that moist carbon dioxide at a high press. has but a very slight action on aluminium. A. Guntz and A. Masson found that, as a rule, finely powdered **aluminium** is only slightly affected when heated in carbon dioxide, but the commercial powder often becomes incandescent under these conditions, and some aluminium carbide is formed. If a trace of aluminium chloride or iodide is present, the conversion to carbide is more or less complete. A. Lieben found that aluminium behaves like magnesium towards carbonic acid, and with aluminium amalgam in the presence of alkali salts, small quantities of formates are produced. K. Brunner found that aluminium powder burns on solid carbon dioxide and gives a dense graphitic carbon. A. Guntz found that finely divided **manganese** burns in carbon dioxide, forming manganese oxide; E. Müller and H. Barck showed that some manganese carbide is also formed at 800°. The solubility of **lead** in water is decreased by carbonic acid. The subject has been investigated by G. Flögel, M. Müller, F. Clowes, E. Reichardt, C. Guldensteeden-Egeling, G. A. Barbaglia and P. Gucci, S. Buzicka, G. von Knorre, etc.—*vide* lead. According to M. Thilorier, lead is not affected by liquid carbon dioxide. N. T. de Saussure observed that when **iron** is heated in carbon dioxide, ferrous and ferric oxides are formed and carbon is produced. G. Tissandier also noted the formation of carbon monoxide. J. B. A. Dumas, and J. Braithwaite made some observations on this subject; and P. Sabatier and J. B. Senderens said that carbon dioxide is not perceptibly reduced by iron between 330° and 450°. M. Thilorier said iron is not affected by liquid carbon dioxide. According to G. Besseyre, hydrogen is given off in the action of carbon dioxide and water on iron, if air be excluded, and ferrous carbonate passes into soln. If the excess of carbon dioxide be removed and air has access, ferric hydroxide separates

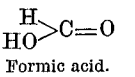
from the soln. C. von Hauer, O. Kröhnke, P. Petit, and J. Rothe and F. W. Hinrichsen have studied this subject—*vide* iron. I. L. Bell noted that carbon dioxide is soon reduced by finely divided **nickel** at a dull red heat; and, added P. Sabatier and J. B. Senderens, no appreciable reduction occurs between 230° and 400°. I. Langmuir observed no spluttering of **platinum,** or **platinum-rhodium,** wires in carbon dioxide at 1300°, but with the latter it began at 1400°. F. Emich found that the spluttering of **iridium** in carbon dioxide increases with the rise of temp., and this more rapidly than in a mixture of oxygen and nitrogen; and he suggested that the action involves the oxidation and deoxidation of iridium, $4CO_2+Ir \rightleftharpoons IrO_4+4CO$.

Carbon dioxide reacts with many of the **metal oxides** and **hydroxides,** forming carbonates—*e.g.* the oxides or hydroxides of the alkalies and alkaline earths. F. K. Cameron and W. O. Robinson[15] studied the action on metal hydroxides of carbon dioxide under press. at 0°. Red-hot **stannous oxide** was found by A. Wagner to reduce carbon dioxide to the monoxide; and when a mixture of ferrous chloride and sodium carbonate is heated to redness in a stream of carbon dioxide, some carbon monoxide is formed. L. Gruner found that **ferrous oxide** is transformed into ferrosoferric oxide when heated in a stream of carbon dioxide, but there is no separation of carbon. F. Förster studied the action of carbon dioxide on **lead oxide.** According to W. F. Channing, enough heat is developed by solid **potassium and sodium hydroxides** in contact with solid carbon dioxide, to inflame gun-cotton; there is no rise of temp. with **barium, strontium, and calcium oxides,** but there is with the corresponding hydroxides. No perceptible heating occurs with **lead, zinc, and copper oxides,** but there is a slight heating effect with the hydroxides. E. Gilchrist investigated the use of solid sodium hydroxide as an absorbent for carbon dioxide in mine rescue apparatus. R. Dubrisay studied the neutralization of carbonic acid by sodium hydroxide. According to L. P. Cailletet, liquid carbon dioxide reacts with **potassium carbonate,** forming a complex which remains in soln. possibly as **potassium pyrocarbonate,** $K_2CO_5CO_2$.

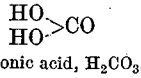
With our present knowledge two carbonic acids appear possible. **Orthocarbonic** acid corresponding with $C(OH)_4$, or $H_4CO_4$, is not known, although some **orthocarbonates** are known—*e.g.* ethyl orthocarbonate, $C(OC_2H_5)_4$, was prepared by H. Bassett.[16] E. Wilke considers it probable that aq. soln. of carbon dioxide contain orthocarbonic acid. The ordinary carbonates are really **metacarbonates** derived from **metacarbonic acid,** $CO(OH)_2$, so that metacarbonic acid is the first dehydration product of orthocarbonic acid. The so-called **formic acid** may be regarded as a derivative of metacarbonic acid made by replacing one hydroxyl group by hydrogen;

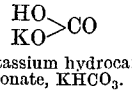

Orthocarbonic acid.

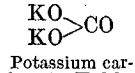

Metacarbonic acid.


Formic acid.

Metacarbonic acid is a weak dibasic acid, and it furnishes a series of **hydrocarbonates** in which the group $HCO_3$ acts as a monad radicle, and a series of normal **carbonates** in which the group $CO_3$ acts as a dyad radicle. The constitutions of carbonic acid and each of these types of salts are usually represented:


Carbonic acid, $H_2CO_3$.


Potassium hydrocarbonate, $KHCO_3$.


Potassium carbonate, $K_2CO_3$.

The metacarbonates also furnish some complex salts. The individual carbonates are discussed in connection with the metals. J. F. Armand discussed the general problem as early as 1804. The carbonates are all decomposed by treatment with the mineral acids, although the native carbonates of magnesium—magnesite, and dolomite—and of iron—siderite—do not effervesce with the cold mineral acids;

but if the carbonate be powdered or the acid be warmed, dissolution readily occurs, and carbon dioxide is evolved. The carbonates of the alkaline earths are sparingly soluble in water, and when an aq. soln. of a hydroxide of one of these earths is exposed to the action of carbon dioxide, the soln. becomes turbid and a voluminous precipitate of the carbonate is formed in the cold. The precipitate soon becomes compact and crystalline when the liquid is warmed. Lime-water or baryta-water is therefore used in the detection of carbon dioxide. If a small quantity of a carbonate is being tested, the mixture is warmed to drive the carbon dioxide into the reagent; and a non-volatile acid—sulphuric or phosphoric acid—is used for the decomposition of the carbonate so as to avoid a volatile acid being carried along with the carbon dioxide, and preventing the formation of a precipitate. According to J. L. Lassaigne, baryta-water is rendered turbid by a soln. of sodium carbonate containing one part of carbon dioxide in between 40,000 and 80,000 parts of water; and a sensible precipitation occurs with lime-water when the proportion of water does not exceed 20,000 parts of water to one of carbon dioxide. According to J. J. Welter, and C. L. Berthollet, lime-water actually dissolves a little carbonate, so that the lime-water employed for the qualitative test should be digested for some time with calcium carbonate. If an excess of carbon dioxide be passed through the soln. of lime-water, the precipitate redissolves, and the liquid becomes clear. This is due to the formation of soluble calcium hydrocarbonate: $CaCO_3+CO_2+H_2O=Ca(HCO_3)_2$. If this soln. be boiled, the hydrocarbonate is decomposed, the carbon dioxide escapes, and the calcium carbonate is reprecipitated. Similarly, if lime-water be added to the soln. of the hydrocarbonate calcium carbonate is precipitated, $Ca(HCO_3)_2+Ca(OH)_2=2CaCO_3+2H_2O$.

Unlike sodium carbonate, sodium hydrocarbonate does not give a precipitate with magnesium sulphate, and hence G. Patein recommended this reaction as a distinguishing test for hydrocarbonate and carbonate. M. von Pettenkofer detected free carbonic acid in the presence of hydrocarbonates by means of a soln. of one part of rosolic acid in 500 parts of 85 per cent. alcohol, and adding baryta-water until it begins to acquire a red tinge. 0·5 c.c. of this soln. will remain red if no free carbonic acid be present, and it will become colourless or faintly yellow if free carbonic acid is present. According to F. M. Perkin, carbon dioxide and hydrocarbonates liberate hypochlorous acid from soln. of hypochlorites. On adding a soln. of the substance to be tested to a mixed soln. of potassium bromide and bleaching powder, bromine is at once liberated should the substance be a hydrocarbonate, and may be dissolved by shaking with 2 c.c. of chloroform. Normal carbonates have no action. T. Salzer recommended using Nessler's reagent (**4.** 31, 26) as a test for free carbonic acid or hydrocarbonates, because if these substances are present, the ammonia reaction does not occur. According to L. Dobbin, the reagent can also be used to detect fixed alkali hydroxides in the presence of the fixed alkali carbonates, for the former alone give a brown precipitate. The test is not reliable in the presence of sulphides. The great avidity of sodium hydroxide for carbon dioxide may be illustrated by several ingenious experiments. One of the simplest is to collect a cylinder of carbon dioxide over mercury and then pipette some sodium hydroxide soln. under the edge of the cylinder. The sodium hydroxide rises to the top of the mercury, absorbs the gas, and the mercury rises in the cylinder accordingly. Potassium hydroxide is better suited as an absorbent for carbon dioxide than sodium hydroxide, because when a gas charged with carbon dioxide is bubbled through a wash-bottle the exit may become choked with solid sodium hydrocarbonate; the sodium hydrocarbonate is less soluble in water than potassium hydrocarbonate. Soln. of sodium hydroxide are largely employed in analytical work as absorbents for carbon dioxide. If air charged with carbon dioxide be drawn through a soln. of sodium hydroxide in a weighed wash-bottle, the increase in weight represents the weight of carbon dioxide absorbed by the hydroxide. If the vol. of the air be known, the amount of carbon dioxide in that vol. of air follows at once. Similarly in gas analysis, the amount of carbon dioxide is

determined from the contraction in vol. which a given vol. of the gas suffers after the gas has been in contact with sodium hydroxide.

The carbon dioxide in carbonates can be determined gravimetrically by the loss in weight consequent on the evolution of the gas displaced by an acid. Something approaching three hundred portable instruments have been described for this purpose. The gas is absorbed by alkali-lye as indicated above and weighed, or the gas can be absorbed by a standard soln. of baryta-water, the remaining baryta-water can then be titrated with a standard soln. of an acid using phenolphthalein as indicator. This enables the amount of baryta carbonated to be computed, and hence the quantity of carbon dioxide absorbed. This process was devised by M. von Pettenkofer in 1857. O. Warburg showed that warm soln. of barium hydroxide absorb carbon dioxide far more rapidly than cold soln.

**Physiological action of carbon dioxide.**—Atmospheric air contains 0·03 per cent. of carbon dioxide, and the air of crowded halls may have as much as 0·5 per cent. without causing any appreciable effect. According to L. Hill,[17] when the proportion rises to 3 per cent., the breathing becomes deeper and faster, and the pulse becomes fuller and faster; 4 per cent. produces unpleasant panting, and diminishes the power to work; 6 to 7 per cent. causes distressful panting; 10 per cent. produces violent panting, throbbing of the arteries, and flushing of the face; and 25 per cent. may cause death in animals after exposure for several hours. The respiration of dangerous mixtures of carbon dioxide and air are attended by a feeling of heaviness, giddiness, noises in the ear, tightness across the chest, and an inclination to sleep. The muscles then lose their power, and the individual if standing falls to the ground. There then follow asphyxia, coma, stertorous breathing, cyanosis—possibly convulsions and delirium—and death may ensue if the victim be not rescued.

According to J. S. Haldane and co-workers, the air *within the lungs* normally contains about 5·6 per cent. of carbon dioxide; when this reaches about 8 per cent. dizziness and loss of memory occur, with higher percentages there may be loss of consciousness, but no immediate danger until the proportion exceeds 20 to 30 per cent. Recovery is rapid and complete. L. Hill found that diving under water, or holding the breath as long as possible, may raise the carbon dioxide in the air in the lungs to 7 to 10 per cent. A temporary rise of 3 per cent. is thus quite a natural phenomenon. The organism may acquire a certain tolerance for the gas and breathe air contaminated with an amount of carbon dioxide which would be noxious to the untrained organism. J. S. Haldane and co-workers showed that the oxygenation of the blood helps to drive off the carbon dioxide, while the deoxygenation of the blood helps the absorption of carbon dioxide so that the exhalation of carbon dioxide by the lungs is to a large extent dependent on the taking up of oxygen.

Poisoning by carbon dioxide is probably a misnomer in that the lethal effects are due to a deficiency of oxygen rather than to an excess of carbon dioxide. Carbon dioxide asphyxia may occur in coal mines from the presence of choke damp generated by explosions and gob fires; in deep wells, cellars, excavations, and underground passages; in brewer's vats; and in the neighbourhood of lime-kilns and brick-kilns in operation.

The equilibrium between carbonic acid and bicarbonates in the regulation of the reactions of blood has been discussed by H. Friedenthal, and L. J. Henderson, K. A. Hasselbalch and C. Lundsgaard found that the $H^{\cdot}$-ion conc. of blood is about $0{\cdot}0_7 44N$, and is subject to slight variations, decreasing as the blood passes through the lungs and increasing during the greater circulation. K. Spiro and L. J. Henderson have discussed the change of distribution of the red blood corpuscles and plasma as the tension of the carbonic acid changes:

As the blood passes through the tissues it receives carbonic acid, and the vol. of the red corpuscles increases owing to the entry of water from the plasma; chlorine simultaneously passes in the same direction; and other changes occur. In the lungs with the escape of carbon dioxide, the process is reversed. In each complete cycle of the circulation, there

occurs a complete cycle of changes between the constituents of the corpuscles and the plasma.

The effect of carbon dioxide on micro-organisms has been discussed by C. Nourry and C. Michel,[18] etc.; on fermentation by L. Lindet,[19] G. Foth, etc.; and on plant seeds by P. Becquerel, S. Jentys, etc.

**The uses of carbon dioxide.**—Carbon dioxide [20] is largely used in the preparation of the so-called artificial mineral waters; and for impregnating beers, wines, etc. Carbon dioxide is used [21] in the manufacture of carbonetted beverages, where it improves the appearance, and imparts to them sparkle and "life." It is said to have a marked stimulating effect on the olfactory and gustatory nerves, accentuating flavours, and making the senses more delicately perceptive. It also has a bactericidal action in keeping down the bacterial counts of carbonetted beverages. The gas is used in packing certain food products where flavours and odours are liable to be spoiled—presumably owing to the oxidation of certain constituents, if packed in air. It has also been recommended in the storage of fruits. Carbon dioxide is substituted for air in the atm. of the freezer in some systems of making ice-cream. It is used in manufacturing various carbonates—*e.g.* white lead, barium carbonate, sodium hydrocarbonate, etc.; in the ammonia-soda and the cryolite processes for alkali carbonates; and in the precipitation of aluminium hydroxide in one process for the purification of bauxite. Liquid carbon dioxide is used as a refrigerating agent, and it has several advantages over ammonia and sulphur dioxide. There are many other applications—liquid carbon dioxide has been used for hardening steel, extinguishing fires, raising sunken ships, etc. Carbon dioxide is used in sugar works for removing lime from the limed sugar-cane juice. Liquefied carbon dioxide in cylinders is used as a decentralized source of press. over 500 lbs. per sq. in. Carbon dioxide is used as a fire extinguisher in closed spaces where it acts by excluding oxygen from burning bodies; or by diluting the air. It is used as a mild irritant and stimulant on the respiratory centres; for local refrigeration; and as a cauterant. It is used in the rubber industry for filling the air-bags which support tyres in the process of vulcanizing. It has been recommended for removing extremely hard and adherent boiler scale.

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## § 37. Hard and Soft Water

Water comes very near to the "universal solvent" of the alchemists' dreams. Natural water holds carbon dioxide in soln., and when such water comes in contact with magnesium and limestone rocks, some may be dissolved.[1] Water holding magnesium and calcium salts in soln. is said to be **hard.** The term is applied on account of the difficulty of obtaining a soap-lather with such water. Soap is a compound of sodium with a fatty acid. The soap is decomposed by magnesium

or calcium salts. The fatty acid unites with the latter to form an insoluble curdy precipitate. This action continues until all the lime and magnesian salts have been precipitated. Any further addition of soap at once produces a lather, and the soap can then be used as a cleansing agent. If a soln. of soap of definite strength and a definite vol. of water be employed, the hardness of a given sample of water can be represented in terms of the amount of soap required to produce a lather. The hardness of water thus refers to the " soap-destroying power " of the water, and it is expressed in degrees. *Each degree of hardness corresponds with one grain of calcium carbonate, or its equivalent in other calcium or magnesium salts, per gallon of water.* Hardness is also expressed in parts of calcium carbonate, or its eq., per 100,000 parts of water. Waters containing but small quantities of lime and magnesian salts lather freely with soap, and they are accordingly called **soft waters.** A water less than 5° hardness may be called " soft," and a water between 18° and 20° hardness is " moderately hard," and if over 30° hardness, " very hard." Very soft waters are liable to attack metals like lead, zinc, and iron.

The process of removing salts from hard water is called **softening the water.** In **T. Clark's lime process for softening water** the necessary amount of milk of lime or lime-water is added to convert all the acid carbonates of calcium and magnesium into the normal carbonates. We have here the curious paradox—" add lime to remove lime." The theory of the action is summarized in the equation : $Ca(HCO_3)_2+Ca(OH)_2=2CaCO_3+2H_2O$. M. R. Herrle and F. M. Gleeson showed that in the progressive addition of lime-water to hard water, the hardness decreases uniformly so long as the chemical action between the lime and the salts in the water takes place. When this action is complete, the water is at its minimum hardness (7°, Fig. 55), and any further addition of lime-water increases the hardness and the alkalinity of the water. Expressing the amount of lime added to the water in lbs. of lime per 1000 galls. of hard water; the hardness in c.c. of standard soap soln.; and the alkalinity in c.c. of 0·04*N*-acid with phenolphthalein as indicator, the results with a natural water of 20° hardness were :

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Lime . | 0·0 | 0·52 | 1·57 | 2·62 | 2·91 | 3·14 | 4·20 | 5·25 |
| Hardness . | 20·0° | 17·5° | 12·5° | 7·5° | 7·0° | 7·5° | 13·5° | 19·5° |
| Alkalinity . | 0 | 0 | 0·8 | 0·30 | 0·36 | 0·43 | 0·75 | 1·13 |

Hard water may be wholly or partially softened by boiling. That part of the hardness so removed is termed temporary hardness; the degree of hardness which remains after prolonged boiling is called **permanent hardness.** Temporary hardness is due to calcium and magnesium hydrocarbonates; permanent hardness is due to the presence of calcium and magnesium chlorides or sulphates. There is also a kind of " pseudo-hardness " due to the insolubility of soap in water containing sodium chloride. The so-called *marine soaps* are used for such waters. After removing the temporary hardness, if present, by boiling or by T. Clark's lime-process, the permanent hardness may be removed by the addition of sodium carbonate—**the soda process.** The sodium carbonate precipitates the calcium and magnesium as insoluble carbonates : $CaSO_4+Na_2CO_3=CaCO_3+Na_2SO_4$. The water still contains sodium sulphate and sodium chloride, but the presence of a small quantity of these salts is not usually objectionable. M. R. Herrle and F. M. Gleeson showed that with the progressive addition of soda-ash the hardness of water rapidly diminishes to a minimum (11°, Fig. 56), and the chemical action between the soda-ash and the salts of the hard water is complete. Further additions of soda-ash produce no change on the hardness, but merely increase the alkalinity. Expressing the hardness and alkalinity as before, but expressing the amount of soda-ash added as lbs. of soda-ash per 1000 galls. of hard water, the results with a natural water were :

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| Soda-ash . | 0·0 | 0·52 | 1·05 | 1·57 | 2·10 | 2·62 | 3·14 | 3·66 | 4·20 |
| Hardness . | — | 16° | 15·5° | 13° | 11·5° | 11° | 11° | 11° | 11° |
| Alkalinity . | 1·45 | 1·55 | 1·65 | 1·70 | 1·75 | 1·85 | 2·00 | 2·25 | 2·43 |

It follows, therefore, that the addition of lime to hard water produced a minimum hardness of 7° by precipitating some of the soluble salts producing hardness due to calcium and magnesium; the other salts of these elements still in soln. are removed by soda-ash but not by lime; similarly, the addition of soda-ash produced a minimum hardness of 11° by precipitating some of the salts producing hardness due to calcium and magnesium; the other salts of these elements still in soln. are removed by the addition of lime, but not by soda-ash. By adding both reagents in proper proportions—the so-called **soda-lime process**—nearly all the salts producing hardness are removed. This is illustrated by Fig. 56.

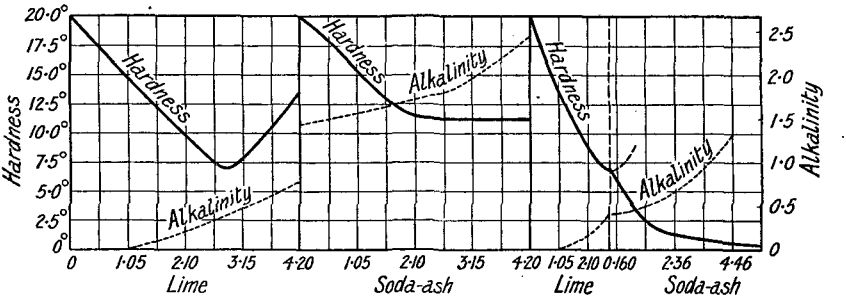



FIG. 55. FIG. 56. FIG. 57.

FIGS. 55–57.—Change of Hardness and Alkalinity of Natural Water with Additions of Lime, and Soda-ash—Separately and Consecutively.

The processes used for softening potable hard water may thus be summarized: (1) Distillation; (2) Boiling; (3) The addition of lime with or without soda-ash or other chemicals; and (4) The permutite process—*vide* alkali aluminosilicates. The Report of the Rivers Pollution Commission classified unpolluted water as is shown in Table XXVI, which represents the average of a number of analyses of each type.

TABLE XXVI.—AVERAGE COMPOSITION OF UNPOLLUTED NATURAL WATERS

| Class of water. | Total solids. | Organic carbon. | Organic nitrogen. | Ammonia. | Nitrogen (nitrates and nitrites). | Total combined nitrogen. | Chlorine. | Hardness. | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | Temporary. | Permanent. | Total. |
| Rain . . . | 2·95 | 0·070 | 0·015 | 0·029 | 0·003 | 0·042 | 0·822 | 0·4 | 0·5 | 0·9 |
| Upland surface | 9·67 | 0·322 | 0·032 | 0·002 | 0·009 | 0·042 | 1·130 | 1·5 | 4·3 | 5·8 |
| Deep well . . | 43·78 | 0·061 | 0·018 | 0·012 | 0·495 | 0·522 | 5·11 | 15·8 | 9·2 | 25·0 |
| Spring . . . | 28·20 | 0·056 | 0·013 | 0·001 | 0·383 | 0·396 | 2·49 | 11·0 | 7·5 | 18·5 |

**Boiler scale.**—The furring of kettles, and the formation of boiler scale, is due to the precipitation of calcium and magnesium salts. Boiler scale is a poor conductor of heat, and hence the efficiency of a boiler which has scaled is seriously impaired. The boiler scale and the metal have different rates of contraction and expansion by heat. If the water in the boiler gets low, and the metal overheated, the scale may separate from the metal. If cold water now runs into the boiler, the scale quickly cools, contracts, and cracks. Water pours through the cracks on to the hot metal; a large volume of steam is generated, and the sudden pressure may be great enough to burst the boiler. Hard water in steam boilers not only produces boiler scale, but it may corrode the boiler shell, and cause foaming and bumping. The corrosion

and pitting of boilers is usually produced by soft waters from swampy districts which contain organic acids in soln. ; by water from mining districts containing mineral acids in soln. (*e.g.* sulphuric acid from the oxidation of pyrites) ; and by water containing magnesium or calcium chlorides and nitrates. A great many nostrums for preventing boiler scale and corrosion have been proposed. In some, the water is treated before it enters the boiler ; in others, the water is softened in the boiler itself. Whatever agents be used, they must be cheap ; easily applied ; yield no acid when used ; and precipitate the salts which make the water hard in a flocculent powdery condition easily blown from the boiler. Among the commoner agents are : sodium or calcium hydroxide, and sodium carbonate discussed above ; sodium aluminate, $NaAlO_2$, which acts as represented by the equation : $2NaAlO_2+Ca(HCO_3)_2+2H_2O=Na_2CO_3+2Al(OH)_3+CaCO_3$ ; sodium fluoride which acts : $2NaF+Ca(HCO_3)_2=2NaHCO_3+CaF_2$ ; normal sodium phosphate which acts : $2Na_3PO_4+3CaSO_4=3Na_2SO_4+Ca_3(PO_4)_2$ ; etc.

There are numerous works specially dealing with the purification of water for boiler and domestic purposes ; *e.g.* S. and E. Rideal, *Water Supplies, Their Purification, Filtration, and Sterilization*, London, 1914 ; J. Don and J. Chisholm, *Modern Methods of Water Purification*, London, 1913 ; W. W. Christie, *Water : Its Purification and Use in the Industries*, London, 1912 ; W. P. Booth, *Water Softening and Treatment*, London, 1920 ; F. Fischer, *Das Wasser*, Leipzig, 1914.

**Hard water in nature.**—Water highly charged with dissolved calcium bicarbonate may be dripping through the roof of a cave or subterranean cavern. Some carbon dioxide escapes from the soln , and a certain amount of calcium carbonate is deposited. Each drop adds its own little share of calcium carbonate. The deposit grows—maybe on the roof, when it is called a stalactite ; maybe on the floor, when it is called a stalagmite. All depends upon the time occupied by each drop in gathering and dropping. The stalagmite grows upwards from the ground, and the stalactite grows downwards, like an icicle, from the roof. In time, the two may meet and form a pillar. Fig. 58 conveys but little idea of the beauty of some limestone



FIG. 58.—Stalactites and Stalagmites in the Yarrangobilly Caves, N.S.W.

caverns in which stalactites and stalagmites have been growing. The photograph shows stalactites, stalagmites, and pillars which have no doubt been formed in this manner. The San Filippo spring (Tuscany) is said to deposit lime at the rate of 12 inches a month, and the spring has formed a bed of limestone rock 250 feet thick, $1\frac{1}{4}$ miles long, and $\frac{1}{3}$ mile wide. The building stone called *travertine* (Tiberstone) is probably a limestone deposited from a mineral spring. The Colosseum and much of ancient and modern Rome were built with this stone.

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## § 38. Percarbonic Acid and the Percarbonates

Die Natur einiger Percarbonate ist heute noch nicht einwandfrei geklärt.—C. F. VON GIRSEWALD.

Guided by analogy with the persulphates, E. J. Constam and A. von Hansen [1] sought to prepare a series of percarbonates. They assumed that the ionization of the normal carbonates takes place in stages, and that when conc. soln. are electrolyzed, the ions $MCO_3'$ formed in the first stage of the ionization will accumulate in the anode compartment, and there unite to form a percarbonate, $2MCO_3'+2\oplus=M_2C_2O_6$, as in the analogous case of the persulphates, $2MSO_4'+2\oplus=M_2S_2O_8$. It was necessary to work at low temp., but under that condition sodium and ammonium carbonates have too small a solubility, and the soln. are too dil. to give the desired result. The experiment, however, was successful with potassium and rubidium carbonates. When a sat. aq. soln. of potassium carbonate is electrolyzed and the temp. continuously diminished, the anodic evolution of oxygen becomes less and less, and at −10° has practically ceased; simultaneously a bluish solid, potassium percarbonate, is formed. There is generally a marked odour of ozone at the beginning of the electrolysis, but this disappears in a short time.

W. D. Brown thus applied E. J. Constam and A. von Hansen's process: A porous cell of 200 c.c. capacity was placed in a cylindrical vessel of such size that the outer or anode space had a capacity of 150 c.c. In the porous cell was the cathode of nickel gauze and the cathode soln. of 20–40 per cent. potassium carbonate. Around the porous cell, in the conc. soln. of potassium carbonate, a platinum wire was wound as a spiral. The whole was immersed in a mixture of ice and common salt, which brought the temp. down to −15°. A conc. soln. of potassium carbonate, at 15°, has a sp. gr. of 1·556. On lowering the temp. of this soln., no crystallization takes place; but if the salt be impure, or if crystallization takes place on lowering the temp., then, on passing a current, no crystals of potassium percarbonate are formed. It is necessary to have a high anode density and a low cathode density. This was attained by having the nickel gauze cathode and platinum wire anode. The wire was 0·0345 cm. thick and 48 cms. long, making an anode surface of 0·05 sq. dm. With a current of 3 amps. at about 10 volts, and a current density of about 60 amps. per sq. dm., the soln. was heated too much and potassium hydrocarbonate was formed. On shortening the anode wire to 24 cms., and passing a current of 1½ amps., the current density remained the same, and a mass of blue crystals of the percarbonate, floating on the anode soln., was obtained. E. J. Constam and A. von Hansen found that if the electrolysis is commenced at −15°, with a conc. soln., the yield is not much affected by small variations of temp.—indeed, the temp. may rise to 0° without seriously impairing the yield. If the conc. of the electrolyte falls below sp. gr. 1·52, a rise in temp. diminishes the yield. It is preferable gradually to lower the temp. as the electrolysis proceeds, owing to the decrease in the conc. of the soln. The percarbonate is very soluble in water, and to get a deposition of solid percarbonate it is necessary to keep the anode liquor sat. with respect to potassium carbonate. This is done by continuously running through a funnel a conc. soln. of potassium carbonate to the bottom of the anode compartment, and allowing the lighter electrolyzed liquor to overflow. This liquor carries the suspended solid percarbonate which is then collected on a vacuum filter. At −10° with a soln. of sp. gr. 1·56, a yield of 25–55 per cent. of percarbonate was obtained with a current density of 0·5–2·0 amps. per sq. dm.; but when the current density rose to 60 amps. per sq. dm., the yield rose to 85–95 per cent. F. Salzer found that the yield was considerably diminished by platinizing the anode, for this increases the surface and decreases the current density; the potential of a smooth anode is greater than that of a platinized one. Iron, nickel, copper, and silver anodes were found by A. von Hansen to be unsatisfactory. F. Salzer found that the presence of hydroxyl ions or of hydro-

carbonates diminished the yield. The sky-blue, hygroscopic potassium percarbonate so prepared is dried by spreading it on a porous plate and exposing it to a current of air; the temp. may be raised to 40° towards the end of the drying. The product contains 87–93 per cent. of percarbonate. A. von Hansen said that the product cannot be purified by recrystallization from water, but it may be purified by digestion with an excess of a conc. soln of potassium hydroxide at −5° to −10° for some time; the percarbonate is then washed with alcohol to remove the hydroxide, and the dried product has 95 to 99 per cent. of per carbonate. E. H. Riesenfeld and B. Reinhold claim to have made a 100 per cent. product by the electrolysis of a conc. soln. of potassium carbonate containing 82·5 grms. of $K_2CO_3.2H_2O$ per 100 grms. of water at −30° to −40°. P. Lami has also described the electrolytic preparation of this salt.

According to E. J. Constam and A. von Hansen, potassium percarbonate is a hygroscopic sky-blue powder, which, when dried, loses almost all its colour and appears white. Analyses correspond with the composition $K_2C_2O_4$. The dry salt is fairly stable; there is a slow decomposition: $4K_2C_2O_6=4K_2CO_3+4CO_2+2O_2$, but if moist it soon decomposes: $2K_2C_2O_6+2H_2O=4KHCO_3+O_2$. When gently warmed the salt decomposes: $2K_2C_2O_6=2K_2CO_3+2CO_2+O_2$, but the reaction is completed only above 200°. The salt dissolves in ice-cold water almost without decomposition, but at ordinary temp.—particularly between 45° and 50°—it decomposes with the evolution of oxygen. It is assumed that the first action is the resolution of the percarbonate into hydrogen dioxide and hydrocarbonate: $K_2C_2O_6+2H_2O=2KHCO_3+H_2O_2$, so that the oxygen is derived from the decomposition of the hydrogen dioxide in alkaline soln. The rate of decomposition of the ammonium salt furnished W. Biltz and W. Gahl constants in agreement with a unimolecular reaction, although other methods of calculation corresponded with a bimolecular reaction. The value of the constant changes with the conc. of the soln. The mechanism of the reaction, like that with ammonium nitrite, has not been established. The salt is but sparingly soluble in alcohol. With dil. sulphuric acid there is a quantitative yield of hydrogen dioxide: $K_2C_2O_6+H_2SO_4=K_2SO_4+2CO_2+H_2O_2$. The acid soln. bleaches potassium permanganate: $5K_2C_2O_6+8H_2SO_4+2KMnO_4=2MnSO_4+6K_2SO_4+8H_2O+10CO_2+5O_2$. The strength of potassium percarbonate as an oxidizing agent can thus be determined by titration with a standard sulphuric acid soln. of permanganate. A dil. aq. soln. of potassium hydroxide, even at −2°, forms potassium carbonate and hydrogen dioxide: $K_2C_2O_6+2KOH=2K_2CO_3+H_2O_2$. The hydrogen dioxide rapidly decomposes in the alkaline soln. For a conc. aq. soln. of potassium hydroxide, *vide supra*. The oxidizing properties of potassium percarbonate are illustrated by its converting lead sulphide to the sulphate, ferrous to ferric salts, and stannous to stannic salts; decolorizing indigo-blue, and bleaching cotton, silk, wool. The reducing properties of the salt are illustrated by its action on silver oxide, manganese dioxide, and lead dioxide, when the carbonates of the respective metals are formed, and oxygen is evolved—*e.g.* $K_2C_2O_6+PbO_2=PbCO_3+K_2CO_3+O_2$. It can be regarded as **potassium perdicarbonate**, and is probably constituted:

$$\begin{matrix}\text{KO.CO.O}\\ \text{KO.CO.O}\end{matrix} \quad \textit{i.e.} \quad O=C<\begin{matrix}O-O\\ OK\ KO\end{matrix}>C=O$$

In general, said F. P. Treadwell, potassium percarbonate in aq. soln. behaves like hydrogen dioxide. Sodium dioxide acts more quickly than potassium percarbonate on chromium sulphate; the former with manganese sulphate gives a brown precipitate of manganese dioxide, while the latter gives a small quantity of the brown precipitate, but much manganese carbonate which is immediately converted to the brown dioxide when sodium hydroxide is added. The percarbonate liberates iodine from hydriodic acid. According to E. H. Riesenfeld and B. Reinhold, when a solid percarbonate is added to a conc. neutral soln. of potassium iodide, iodine is immediately set free. This is taken to show that hydrogen dioxide has not been formed because that compound liberates iodine very slowly from potassium iodide; if, however, a soln. of the percarbonate be used instead of the solid salt, the amount of iodine set free decreases with the length of time the soln. of percarbonate has

been kept before it was added to the potassium iodide. This is because the salt in soln. is gradually decomposed into potassium hydrocarbonate and hydrogen dioxide. There has been a controversy between E. H. Riesenfeld and B. Reinhold, S. M. Tanatar, and R. Wolffenstein as to the validity of potassium iodide as a test for distinguishing the percarbonates from carbonates containing hydrogen dioxide of crystallization. R. Willastätter, and E. H. Riesenfeld and W. Mau so distinguished the persulphates from sulphates with hydrogen dioxide of crystallization, and it is inferred that the analogous reaction is valid with the carbonates. A. Monnier found that percarbonates give a reddish precipitate with a dil. soln. of titanous chloride; no precipitation or coloration with a 0·5 per cent. alcoholic soln. of benzidine; and a blue coloration with a soln. of potassium dichromate acidified with sulphuric acid—*vide* perborates.

E. J. Constam and A. von Hansen prepared **rubidium percarbonate,** $Rb_2C_2O_6$, in a manner analogous to the potassium salt; the properties of the two salts were similar. They did not succeed in obtaining the solid **sodium percarbonate** and **ammonium percarbonate,** although these salts were probably present in soln. Similar remarks apply to E. H. Riesenfeld and B. Reinhold's attempt to isolate the corresponding **lithium percarbonate,** sodium percarbonate, rubidium perdicarbonate, and **cæsium perdicarbonate.** L. Schwedes prepared sodium percarbonate by passing carbon dioxide into a paste made of sodium dioxide and alcohol. The residue appears as a white flocculent mass with 50 per cent. of the percarbonate. H. Wade treated sodium carbonate with hydrogen dioxide in presence of a limited quantity of water and of sodium chloride for salting out the product. The use of calcined sodium carbonate is advantageous, and so is the presence of negative catalysts—sodium silicate or magnesium chloride—as shown by F. Noll. P. Kasanezky dissolved 5 grms. of freshly prepared ammonium carbonate in 40 c.c. of 20 per cent. hydrogen peroxide, and the soln., after cooling in ice, was mixed with 5 c.c. of aq. ammonia sat. at 0°. The addition to the liquid of 2–3 vols. of alcohol then gave a white, crystalline precipitate of a salt having the constitution $NH_4.O.O.CO.O.NH_4$, $2H_2O$. The salt is readily soluble in water, by which it is almost completely decomposed into hydrogen peroxide and ammonium carbonate. W. Biltz and W. Gahl found that the decomposition of ammonium percarbonate may be represented as a unimolecular reaction.

In 1899, S. M. Tanatar found that when a soln. of sodium carbonate is dissolved in cold 3 per cent. hydrogen peroxide, and the soln. treated with alcohol, a white crystalline precipitate is obtained. After washing with alcohol and ether, and drying over sulphuric acid, the product has the composition $Na_2CO_4.1\frac{1}{2}H_2O$, or the alternative $Na_2CO_3.H_2O_2.\frac{1}{2}H_2O$. Against the latter formula, S. M. Tanatar urged (i) that the heat of decomposition of a $\frac{1}{10}N$-soln. by $\frac{1}{10}N$-nitric acid is 7·21 to 7·26 Cals., whereas that of an aq. soln. of sodium carbonate is 5·33 Cals.; and (ii) that the partition coeff. of hydrogen dioxide between ether and aq. soln. of sodium carbonate shows that the carbonate unites with 30 per cent. of the hydrogen dioxide. The argument, however, is inconclusive in distinguishing between a percarbonate and a compound of sodium carbonate and hydrogen dioxide. E. H. Riesenfeld and W. Mau showed that (i) ether will not extract hydrogen dioxide from E. J. Constam and A. von Hansen's salt, but it will do so from S. M. Tanatar's salt; and (ii) there is no liberation of iodine when the latter salt is added to a neutral soln. of potassium iodide. It is therefore inferred that S. M. Tanatar's salt is not a true percarbonate, but is rather hemihydrated **sodium perhydroxycarbonate** $Na_2CO_3.H_2O_2.\frac{1}{2}H_2O$. When the salt is heated over 100° it gives off oxygen and water, but no carbon dioxide. It dissolves in water with the absorption of 3·9 Cals., and the aq. soln. forms hydrogen dioxide and sodium carbonate. With acids, it yields carbon dioxide and hydrogen dioxide; but with hydrochloric and hydriodic acids the halogens are set free. Salts of the alkaline earths and the metals give unstable precipitates which develop oxygen and form carbonates. S. M. Tanatar made **sodium sesquiperhydroxycarbonate,** $Na_2CO_3.1\frac{1}{2}H_2O_2$, using twice as much hydrogen dioxide as he employed

in making the salt $Na_2CO_3.H_2O_2.\frac{1}{2}H_2O$. He symbolized it $Na_2CO_4.\frac{1}{2}H_2O_2.H_2O$. The two salts are alike in appearance and properties. S. M. Tanatar made the potassium salt $K_2CO_4.3H_2O$ in a similar way. The product was contaminated with a little potassium carbonate, and is probably dihydrated **potassium perhydroxycarbonate**, $K_2CO_3.H_2O_2.2H_2O$. P. Kasanezky obtained hemihydrated **potassium diperhydroxycarbonate**, $K_2CO_3.2H_2O_2.\frac{1}{2}H_2O$, by mixing one molar proportion of potassium carbonate with five molar proportions of 25 per cent. hydrogen dioxide, or by mixing potassium hydrocarbonate with a tenfold excess of 30 per cent. hydrogen dioxide and precipitating the salt with alcohol. The product consists of rhombic prisms mixed with monoclinic prisms. It is resolved into potassium carbonate and hydrogen dioxide when dissolved in water. P. Kasanezky also made **potassium triperhydroxycarbonate**, $K_2CO_3.3H_2O_2$, by adding 7·5 c.c. of 25 per cent. hydrogen dioxide to a gram of the preceding salt, and treating the product with alcohol. The salt dissolves in water with the evolution of oxygen. E. Peltner prepared **rubidium triperhydroxycarbonate**, $Rb_2CO_3.3H_2O_2$, or $Rb_2CO_4.2H_2O_2.H_2O$; hydrated **rubidium diperhydroxycarbonate**, $Rb_2CO_3.2H_2O_2.H_2O$, or $Rb_2CO_4.H_2O_2.2H_2O$; and sesquihydrated **rubidium perhydroxycarbonate**, $Rb_2CO_3.H_2O_2.1\frac{1}{2}H_2O$, or $Rb_2CO_4.2\frac{1}{2}H_2O$, by dissolving one molar proportion of rubidium carbonate in one, two, or three molar proportions of 30 per cent. hydrogen dioxide soln., and sufficient water to obtain a clear soln. on adding alcohol to the cooled soln., these substances are precipitated in the form of white, crystalline solids; they are all very hygroscopic, and evolve oxygen on being dried in a vacuum, but if kept dry they do not turn yellow. The dried substances evolve more oxygen on moistening with water. P. Kasanezky dissolved 5 grms. of freshly-prepared ammonium carbonate in 40 c.c. of 20 per cent. hydrogen dioxide, and, after cooling in ice, mixed the soln. with 5 c.c. of aq. ammonia sat. at 0°. The addition to the liquid of 2–3 vols. of alcohol then gave a white, crystalline precipitate of hydrated **ammonium perhydroxycarbonate**, $(NH_4)_2CO_3.H_2O_2.H_2O$, which he regarded as having the constitution $(NH_4)_2CO_4.2H_2O$, or $(NH_4O.O)_2CO.2H_2O$. The salt is readily soluble in water, by which it is decomposed into ammonium carbonate and hydrogen dioxide.

R. Wolffenstein and E. Peltner prepared a number of percarbonates by the action of carbon dioxide on sodium dioxide or on sodium hydroperoxide obtained by the action of a mol of sodium ethoxide on $\frac{1}{2}$ mol of hydrogen dioxide, and washing the precipitate with alcohol. It is claimed that the products are true percarbonates, and not merely carbonates with hydrogen dioxide of crystallization. The first product sesquihydrated **sodium permonocarbonate**, $Na_2CO_4.1\frac{1}{2}H_2O$, is obtained by triturating in a dish cooled by a freezing mixture, 38 grms. of sodium dioxide with 50 grms. of ice, and then passing a slow current of carbon dioxide through the mixture while it is being stirred. The mass becomes mushy as water is split off, and 38 grms. more sodium dioxide are added in small portions at a time. The current of gas is stopped when the increase in weight is 44 grms., or, according to E. H. Riesenfeld and W. Mau, when a sample of the liquor requires twice as much hydrochloric acid for neutralization with methyl orange as indicator as it does with phenolphthalein as indicator. The unstable salt is washed with alcohol and ether, and dried in vacuo. The salt slowly loses oxygen in the desiccator, and decomposition is complete in a couple of months. If 18·75 grms. of freshly prepared sodium hydroperoxide are mixed with 5·2 grms. of water and the mixture cooled by a freezing mixture while it is treated with carbon dioxide until the increase in weight is 6·8 grms., a salt is obtained whose composition corresponds with $Na_2CO_5.H_2O$. According to E. H. Riesenfeld and W. Mau, it is doubtful, however, if this formulation is correct. Its behaviour towards a neutral soln. of potassium iodide is related with that of $Na_2CO_4$ as that of $Na_2C_2O_6.H_2O_2$ is related with that of $Na_2C_2O_6$. Hence, the salt is regarded as **sodium perhydroxypermonocarbonate**, $Na_2CO_4.H_2O_2$. By analogy with the formula of permonosulphuric acid, $HO.SO_2.O.OH$, the constitutional formula of the permonocarbonate is given as NaO.O.CO.O.Na. H. Bauer,

and E. Merck have described analogous processes for making the percarbonates. F. Noll emphasized the importance of removing metal compounds present as impurities which act catalytically in decomposing the per-salt. E. Merck prepared **barium permonocarbonate**, $BaCO_4.nH_2O$, by the action of carbon dioxide on hydrated barium dioxide. R. Wolffenstein and E. Peltner prepared the salt in a similar way. Neither alcohol nor ether extracts hydrogen dioxide, and it is therefore not considered to be constituted $BaCO_3.H_2O_2$.

According to R. Wolffenstein and E. Peltner, **sodium perdicarbonate,** $Na_2C_2O_6$, is obtained by mixing 2 to 3 grms. of sodium dioxide with 100 c.c. of ice-cold absolute alcohol, and passing carbon dioxide into the well-stirred mixture, at 0° to 5°, for 5 or 6 hrs. or until the soln. no longer reacts alkaline towards phenolphthalein. The mass of glistening crystals is washed with alcohol and ether, and dried in air for a short time on a porous plate. The analyses corresponded with $Na_2C_2O_6.\frac{1}{2}C_2H_5OH$; and, if moist sodium dioxide is used to absorb the carbon dioxide, the crystals obtained have the composition $Na_2C_2O_6.\frac{1}{2}H_2O$. Again, if 5 c.c. of 30 per cent. hydrogen dioxide are added to the mixture before the treatment with carbon dioxide, or stirred with the mixture after the absorption of carbon dioxide is complete, crystals are obtained corresponding with $NaHCO_4$. E. H. Riesenfeld and W. Mau showed that the behaviour of the salt towards a neutral soln. of potassium iodide corresponds with the assumption that the product is **sodium perhydroxyperdicarbonate**, $Na_2C_2O_6.H_2O_2$. They also prepared **potassium perdicarbonate,** $K_2C_2O_6$, by the above process using potassium dioxide, absolute alcohol, and carbon dioxide. This salt has the same empirical composition as the salt obtained by E. J. Constam and A. von Hansen. The two compounds in soln. or in the solid state react differently towards a neutral soln. of potassium iodide, and they are therefore isomers. The supposed constitutional difference is illustrated by the formulæ:

| KO–CO–O<br>KO–CO–O | KO.O–CO<br>KO–CO>O |
|---|---|
| E. J. Constam and A. von Hansen's salt, $K_2C_2O_6$ | R. Wolffenstein and E. Peltner's salt, $K_2C_2O_6$ |

The following percarbonic acids are oxidized carbonic acids:

| $CO<^{O.OH}_{OH}$ | $CO<^{O.OH}_{O.OH}$ | O.CO.OH<br>O.CO.OH | O.CO.O.OH<br>O.CO.OH | O.CO.O.OH<br>O.CO.O.OH |
|---|---|---|---|---|
| $H_2CO_4$ | $H_2CO_5$ | $H_2C_2O_6$ | $H_2C_2O_7$ | $H_2C_2O_8$ |

as well as the derivatives HO.CO.O.CO.O.OH, etc. The alkali salts of $H_2CO_4$ and of $H_2C_2O_6$ in its two isomeric forms have been prepared. The alleged derivatives of $H_2CO_5$—namely, $Na_2CO_5.H_2O$—and of $H_2C_2O_7$—namely, $Na_2C_2O_7.H_2O$—are probably salts of the lower oxidized percarbonic acids with hydrogen dioxide of crystallization. The simpler problems connected with the percarbonates are not definitely settled. Even the evidence on which the distinction between percarbonates and addition compounds of hydrogen dioxide and the normal carbonates is based, is inconclusive. Free **percarbonic acid** has not been isolated. A. Bach claimed that it can exist in ethereal soln. at a low temp., for if a soln. of 0·5 grm. of solid phosphoric acid, ether, and a few drops of water are added to 2 grms. of potassium percarbonate, there is a violent reaction. When the ethereal soln. is poured off, and treated with an alcoholic soln. of potassium hydroxide, a bluish-white precipitate of potassium percarbonate is formed. This is taken to show that the ether held percarbonic acid in soln. R. Wolffenstein and E. Peltner, however, deny the alleged facts.

The above terminology is based on that usually employed for the persulphates; E. H. Riesenfeld and W. Mau suggested calling the derivatives of $H_2CO_4$, *monoperoxycarbonates*, and those of $H_2C_2O_6$, *monoperoxydicarbonates*. R. Wolffenstein and E. Peltner called $Na_2C_2O_6$, *sodium dioxide dicarbonate*; $Na_2C_2O_7$, *sodium trioxide dicarbonate*, etc.

Potassium percarbonate is used in photography under the name *antihypo* for removing the last traces of sodium thiosulphate; it has been recommended for bleaching purposes; and for oxidations in some analytical processes. Sodium permonocarbonate has been used for medical purposes, as a disinfectant, and in the preparation of hydrogen dioxide.

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## § 39. The Sulphides of Carbon

A number of carbon sulphides has been reported: (i) *Carbon disulphide*, $CS_2$, is the best defined sulphide; (ii) The existence of a gaseous *carbon monosulphide*, CS, and of its polymerized forms, $C_nS_n$, appears highly probable. The evidence of the existence of (iii) *carbon ditritasulphide*, $C_3S_2$, and of its polymerized forms is not so satisfactory; and there is some doubt about the existence of (iv) *carbon sesquisulphide*, or *carbon trihemisulphide*, $C_2S_3$; (v) *carbon tetritasulphide*, $C_4S$; and of (vi) *carbon dipentitasulphide*, $C_5S_2$, as chemical individuals.

O. Loew [1] claimed to have made *carbon tetritasulphide*, or *carbon quadrantosulphide*, $C_4S$, by distilling phosphorous sulphide with acetic acid, and extracting the soluble matters with carbon disulphide. It is said to decompose when heated; to be soluble in conc. sulphuric acid; and to be attacked vigorously by warm nitric acid. A similar sulphide was mentioned by F. Clément and J. B. Désormes, and J. J. Berzelius. L. Raab claimed to have made *carbon dipentitasulphide*, $C_5S_2$, by the action of sodium on carbon disulphide. The brownish-red product is soluble in alkali-lye and ammonia, but not in carbon disulphide, alcohol, or ether. It is said to be fusible at 135°, and decomposable at 150°. O. Loew reported the formation of *carbon sesquisulphide* or *carbon trihemisulphide*, $C_2S_3$, by digesting the product of the action of phosphorous sulphide on acetic acid, or of sodium or sodium amalgam on carbon disulphide, with conc. aq. ammonia, and passing chlorine into the soln.—keeping the ammonia in excess. The product was purified by digesting it with sodium sulphite, washing with hot water, and with alcohol, and finally drying. The brown powder has no smell; it is decomposed into its constituents first over 210°. It is slightly soluble in carbon disulphide; and is scarcely attacked by ammonia. A boiling soln. of baryta water or potash-lye forms the metal sulphide and oxalate. Nitric acid oxidizes it to an acid which forms an easily soluble barium salt, and sparingly soluble lead and silver salts. C. Löwig gave the acid the formula $(CS)_2O.H_2O$, or $(COSH)_2$—possibly thio-oxalic acid. The individuality of these three carbon sulphides has not been definitely established, and they may be impure polymerides of carbon monosulphide. J. P. Wibaut and A. Stoffel attribute the sulphur in coke and coal to the presence of carbon sulphides which do not decompose at 1000°. They say that in coking, the sulphur of the pyrites is liberated and unites with the carbon, forming compounds stable at this temp. J. P. Wibaut made such sulphides with 2·03 and 3·5 per cent. of sulphur by heating sugar-charcoal and sulphur at 400°–1000° under reduced press.

B. von Lengyel prepared **carbon ditritasulphide,** $C_3S_2$, by boiling purified and dried carbon disulphide in a reflux apparatus while the vapour is exposed to an electric arc maintained between two carbon poles for two or three hours, the interior of the apparatus becomes blackened, and a black substance is found suspended in the liquid. If this is filtered off, a cherry-red liquid is obtained, which has a remarkably strong odour, and produces great irritation of the eyes. This liquid is allowed to stand for 6–8 days over metallic copper to remove free sulphur, and is then evaporated by means of a current of dry air. A deep red liquid is thus left which has the composition $C_3S_2$. A. Stock and P. Prätorius prepared the compound by passing carbon disulphide through a heated quartz tube, the most favourable temp. being 1000°–1100°; carbon is deposited in the tube at the same time, and diminishes the yield of ditritasulphide. If the quartz tube is filled with a spiral of iron wire, the formation of ditritasulphide takes place below 800°, but it soon ceases owing to the formation of iron sulphide. They also found that the compound is formed, along with many by-products, when an arc is struck between carbon or metal electrodes; under liquid carbon disulphide the disintegration of the anode exposes fresh, hot surfaces continually to the carbon disulphide. Iron, copper, and aluminium electrodes gave no ditritasulphide, whilst electrodes of arsenic, bismuth, lead, tin, antimony, cadmium, or zinc yielded the required compound, large quantities of the metallic sulphides being formed at the same time. The best results were obtained with a carbon cathode and an anode consisting of antimony mixed with 7 per cent. of carbon. The brownish-red soln. obtained is filtered, and then shaken with mercury and phosphoric oxide to remove sulphur and polysulphides and water. A soln. of carbon ditritasulphide in carbon disulphide is thus obtained, from which by distillation, finally under a high vacuum, the pure substance is obtained in a receiver cooled to −40° as a yellowish-red solid.

Carbon ditritasulphide at ordinary temp. forms a bright red strongly refracting liquid; B. von Lengyel found that it evaporates in the air very slowly, and its vapour has a most vigorous action on the mucous membrane, a very small trace causing violent catarrh. Placed on the skin, it merely produces a black spot. The sp. gr. of the liquid is 1·27389. According to A. Stock and P. Prätorius, the m.p. is −0·5°. The vap. density corresponds with the formula $C_3S_2$; so also does the mol. wt. in carbon disulphide; and, according to B. von Lengyel, the mol. wt. by the f.p. method in benzene soln. A. Stock and P. Prätorius consider carbon ditritasulphide to be the anhydride of thiomalonic acid, since, when treated with aniline, it readily forms thiomalonanilide. Hence its constitution is represented S : C : C : C : S. This sulphide is therefore analogous with carbon ditritoxide (*q.v.*). When heated, the ditritasulphide is converted into a hard, black mass with the same percentage composition, and which is probably a polymeride. When the liquid is rapidly heated to 100°–120°, this change takes place with explosive violence, but occurs gradually when it is gently warmed. A. Stock and P. Prätorius found that the polymerization at 90° is a reaction of the second order, and has been observed by measuring the diminution of press. The reaction occurs on the surface of the containing vessel. B. von Lengyel observed that the polymeride is formed when the liquid is preserved for a few weeks, and its formation is in all cases accompanied by the production of a little carbon disulphide. The liquid can be distilled under diminished press. at 60°–70°, but a portion of it is always converted into the solid modification. The liquid substance is insoluble in water, in which it sinks, but is readily soluble in alcohol, ether, chloroform, benzene, and carbon disulphide. From a conc. soln. in the solvent last mentioned, the solid modification is deposited, but a dil. soln. is more stable. According to A. Stock and P. Prätorius, the alcoholic soln. decomposes after a short time. Dil. soln. in carbon disulphide are salmon-coloured, more conc. soln., yellowish-brown; above 1 per cent. conc. the soln. gradually deposit black, polymerization products, even in the dark; soln. below 1 per cent. conc. are stable in the dark, but not in the sunlight. Carbon disulphide soln. have no action on copper or mercury, but are decomposed by the sulphides

of these metals, owing, probably, to the formation of additive products. B. von Lengyel found that the ditritasulphide burns with a luminous, smoky flame, carbon and sulphur dioxides being formed. Aq. potassium and sodium hydroxides give almost black soln., in which acids produce black precipitates, whilst alcoholic potash acts vigorously and yields a deep brown soln. A drop of conc. sulphuric acid causes violent hissing, and the whole mass is converted into the solid modification. Conc. nitric acid causes ignition, whilst a more dil. acid dissolves the liquid, neither carbon dioxide nor sulphuric acid being formed. The solid modification is hard, has a fine, granular fracture, and is insoluble in water and all ordinary solvents. Aq. potassium hydroxide dissolves it completely, and it appears to be precipitated unaltered on the addition of an acid. When heated, it decomposes, with the formation of sulphur, which sublimes, and a gas which contains sulphur, but is not carbon disulphide. A. Stock and P. Prätorius found that the black polymerization product is not affected by water, sodium hydroxide, hydrochloric acid, or chlorine water. Heated in a vacuum it gives carbon disulphide and a black residue which still contains 39 per cent. of sulphur. When bromine is added to a soln. of the liquid tricarbon disulphide in chloroform, heat is evolved, and a yellow precipitate produced; this is **carbon disulphohexabromide**, $C_3S_2Br_6$, which has an aromatic odour, and is insoluble, or only very slightly soluble, in all solvents. Under similar conditions, a yellow precipitate is produced with chlorine, but not with iodine.

There has been a number of reports of the preparation of the sulphur analogue of carbon monoxide, CO, namely, **carbon monosulphide,** CS. In 1857, for example, A. Baudrimont claimed to have made this compound as a colourless gas smelling like ether, (i) by passing the vap. of carbon disulphide over red-hot pumice-stone, or platinum sponge; (ii) by decomposing the same compound by heating it to redness with carbon or hydrogen; (iii) by heating antimony sulphide with an excess of carbon; (iv) by the action of carbon monoxide on hydrogen sulphide at a high temp.; (v) by the action of sulphur dioxide or chloride on methane at a high temp.; and (vi) by the action of heat on sulphur cyanide. J. F. Persoz claimed that he had prepared this compound twenty years earlier than A. Baudrimont. M. Berthelot, L. Playfair, and A. Husemann showed that A. Baudrimont's observations are probably wrong; H. Buff and A. W. Hofmann did not obtain the alleged compound by the action of an electrically heated spiral, nor did A. W. Hofmann obtain it by the action of induction sparks on the vap. of carbon disulphide; and B. Rathke did not obtain the monosulphide by passing the vapour of thiocarbonyl chloride, $CSCl_2$, over heated copper.

O. Loew stated that the gradual decomposition of carbon disulphide, exposed to direct sunlight, is attended by the separation of solid *carbon hemitrisulphide*, $C_2S_3$, and the excess sulphur remains dissolved in the carbon disulphide. T. Sidot found that carbon monosulphide is formed when carbon disulphide is exposed to sunlight. The deposit on the walls of the vessel was washed with carbon disulphide. It is a red powder of sp. gr. 1·65; without taste or smell; and is insoluble in water, alcohol, turpentine, or benzene. It colours dil. nitric acid red and is inflamed by the conc. acid. A boiling conc. soln. of potassium hydroxide dissolves it, forming a dark brown soln. from which the monosulphide is precipitated by adding an excess of acid. The monosulphide decomposes at 200° into carbon and sulphur, and when heated with sulphur, it forms carbon disulphide and colourless crystals which were not investigated. According to J. Dewar and H. O. Jones, the product obtained by T. Sidot was a polymerized form of carbon monosulphide. S. Kern claimed to have made carbon monosulphide by allowing the disulphide to stand for a long time in contact with iron wire; iron disulphide is simultaneously formed. S. M. Losanitsch and M. Z. Jovitschitsch found that when carbon disulphide is decomposed by the silent electric discharge in the presence of hydrogen or carbon monoxide, what is supposed to be carbon monosulphide is formed: $CS_2+H_2=H_2S+CS$, and $CS_2+CO=COS+CS$. J. Thomsen said that when nitrogen sat. with the vap. of

carbon disulphide is passed repeatedly over heated copper, the copper removes some sulphur from the carbon disulphide, leaving carbon monosulphide.

J. Dewar and H. O. Jones found that thiocarbonyl chloride reacts rapidly at ordinary temp. with nickel carbonyl (*q.v.*): $n\mathrm{CSCl_2}+n\mathrm{Ni(CO)_4}=n\mathrm{NiCl_2}+4n\mathrm{CO}+(\mathrm{CS})_n$. The nickel chloride can be extracted by water, and a brown solid remains. The analyses agree with $(\mathrm{CS})_n$. The reaction takes place, although less rapidly, at −20°, and the same result is obtained when the reacting substances are dissolved in dry ether, light petroleum, carbon tetrachloride, or chloroform. Even when the reacting liquids are carefully dried over phosphoric oxide, the carbon monosulphide is still obtained. The purification of the substance is rendered difficult by the fact that it retains water and thiocarbonyl chloride with great persistence. To remove these as far as possible, the product obtained after extracting with water was dried at 100°, and then at 150° or 200°, under reduced press. The finely divided substance had a sp. gr. of about 1·6; after compression into a solid block, the value 1·83 was obtained. The mol. vol. is therefore 24, which is about 10 per cent. greater than the sum of the at. vol. of its constituents. Carbon monosulphide is not altered by dil. sulphuric acid, but with the conc. acid it gives a purplish-brown soln., the colour of which is slowly destroyed at the b.p. when carbon dioxide and sulphur dioxide are evolved. When the purplish-brown soln. is poured into water, unchanged carbon monosulphide is precipitated. It is dissolved by conc. nitric acid at the ordinary temp., giving a red soln. the colour of which is only slowly destroyed on heating. It dissolves in aq. or alcoholic soln. of ammonia, ammonium sulphide, and potassium hydroxide, sulphide and hydrosulphide, giving deep brown soln., from which acids precipitate the carbon monosulphide unchanged. When heated in a good vacuum, no change takes place below 360°, except the liberation of a small quantity of hydrogen sulphide; at a low, red heat, carbon disulphide is formed according to $2(\mathrm{CS})_x=x\mathrm{C}+x\mathrm{CS_2}$. When heated in a current of dry hydrogen, hydrogen sulphide is evolved; when heated in dry chlorine, sulphur is evolved. Owing to its non-volatility, it seems probable that the red substance obtained by long exposure of carbon disulphide to sunlight is also a polymeric form of carbon monosulphide.

According to A. Deninger, gaseous carbon monosulphide is formed when sodium sulphide is heated with chloroform at 180°, and when silver sulphide is heated with iodoform. It is best obtained, mixed with hydrogen, by bringing 15 grms. of sodium into 125 c.c. of dry aniline, and adding 150 c.c. of carbon disulphide. A gas is given off which is passed through aq. soda, over india-rubber, and, finally, through triethylphosphine. It has the composition of carbon monosulphide; it readily burns with a blue flame, forming sulphurous anhydride. The gas is very readily absorbed by alcohol and aniline, has a pleasant smell of purified carbon disulphide, and condenses in a freezing mixture to a very volatile liquid, the constants of which have not been determined. When mixed with oxygen and ignited, it explodes violently. J. Dewar and H. O. Jones also found that when carbon disulphide vap. at low press. is subjected to the action of the silent discharge, in an ozonizer, it appears to be decomposed with formation of sulphur and gaseous carbon monosulphide. When the gas resulting from the discharge tube is passed through a tube cooled by liquid air, the monosulphide is condensed along with the unchanged disulphide. If the condensing tube is removed from the liquid air and its temp. allowed to rise, the monosulphide polymerizes with explosive violence to form the brown, solid substance, $(\mathrm{CS})_n$. The explosive properties of the product from the ozone tube are not due to the presence of impurities in the carbon disulphide, and it is formed at temp. between −80° and 220°, but the yield is less at the higher temp. In presence of excess of carbon disulphide vap., the gaseous monosulphide appears to be fairly stable under certain conditions. Some of it is still present after passing the product from the ozonizer through a tube immersed in boiling sulphur, or even through a short length of red-hot tube. A beam of light reveals no solid particles in the gas. If the gas is cooled in one tube at −120° followed by another at −185°, it is separated

into two parts—a white crystalline solid which melts only when the temp. has risen to nearly 0°, collects in the first tube; the substance which gives rise to the brown solid does not condense at —120°, but is collected at —185°. The product from the ozonizer is completely destroyed by passing through 10 cms. of a red-hot tube loosely packed with asbestos; it is also absorbed, destroyed, or caused to polymerize by cocoanut charcoal, either at —78°, or at 250°, or at the ordinary temp. When passed over finely shredded rubber some of the carbon disulphide is removed from the gas. The ozonizer product is destroyed by finely-divided platinum, nickel, or silver; ferric oxide (not ignited), yellow mercuric oxide, silver oxide, and barium peroxide react with it, giving sulphides. Solid potassium hydroxide, silver nitrate, lead acetate, and sodium peroxide have little or no action. Nitric acid and conc. sulphuric acid bring about decomposition. Mixtures of carbon disulphide vapour with hydrogen, nitrogen, ether, methyl iodide, or chloroform have no effect on the phenomena observed. The vap. of thiocarbonyl chloride, ethyl thiocarbonate, ethyl dithiocarbonate, ethyl trithiocarbonate, and thiophene do not give rise to carbon monosulphide. The stability at high temp. is consistent with the behaviour of an endothermic substance. At the ordinary temp. the gaseous monosulphide polymerizes rapidly, even at low press. and in presence of a large excess of carbon disulphide. Comparisons of the brown carbon monosulphide produced in different ways show that they have probably different degrees of polymerization. The sp. ht. between 15° and —185° of the polymeric form of carbon monosulphide obtained from thiocarbonyl chloride is 0·127, the mol. ht. being 5·59, as compared with the calculated value 5·556. The heat of combustion is 178,050 cals., and the heat of formation 10,000 cals.

H. Kolbe [2] prepared **thiocarbonyl chloride,** $CSCl_2$, the sulphur analogue of carbonyl chloride, $COCl_2$, by the action of dry chlorine on carbon disulphide. From H. Müller's observations it follows that if iodine is dissolved in the carbon disulphide, the action is accelerated; with a boiling soln. sulphur chloride, carbon tetrachloride, and thiocarbonyl chloride are produced. H. Kolbe also made thiocarbonyl chloride by passing a mixture of hydrogen sulphide and the vap. of carbon tetrachloride through a red-hot tube: $CCl_4+H_2S=2HCl+CSCl_2$. G. Gustavson made it by heating carbon tetrachloride and sulphur in a sealed tube at 180°–200°. R. de Fazzi said that the yield is small. B. Rathke observed that it is formed when thiocarbonyl tetrachloride, $CSCl_4$, is reduced with powdered silver; or, according to P. Klason, when reduced with tin and hydrochloric acid. M. Kern and M. Sandoz warmed 30 parts of thiocarbonyl tetrachloride with 37 parts of dihydrated stannous chloride, 10 parts of conc. hydrochloric acid, and 7 parts of water in a closed vessel for 12 hrs. at 30°–35°. J. W. James obtained it by the action of chlorine on methyl thiocyanate. P. F. Frankland and co-workers made it by reducing thiocarbonyl tetrachloride with tin and hydrochloric acid, using 550 grms. of thiocarbonyl tetrachloride, 175 grms. of tin, and 500 c.c. of a mixture of equal vols. of commercial hydrochloric acid and water. The thiocarbonyl tetrachloride is added as rapidly as is consistent with the efficient condensation of the distillate. The yield is 55–60 per cent. R. de Fazi found that the action of iron on thiocarbonyl tetrachloride may give ferrous chloride and carbon tetrachloride, yet, with certain catalysts, the reaction may proceed: $CCl_3.SCl+Fe\rightarrow FeCl_2+CSCl_2$, with an 80 per cent. yield. He also found that sulphur does not react with carbon tetrachloride, even at the b.p., but in a sealed tube at 200° there is a slight reaction: $CCl_4+3S\rightarrow CSCl_2+S_2Cl_2$, the yield is slightly increased if a little iodine be present; and if a mixture of a little iodine with sulphur and carbon tetrachloride be boiled for a long time a little thiocarbonyl chloride is formed. Powdered iron can replace iodine as catalyst; red phosphorus and phosphorus pentasulphide do not act as catalysts. Ferrous sulphide and carbon tetrachloride do not act below 100°, but if iodine be present, a little thiocarbonyl chloride is formed; and ferrous sulphide and carbon tetrachloride, without iodine, in a sealed tube gave a larger yield than any other substances tried: $CCl_4+FeS=FeCl_2+CSCl_2$.

Thiocarbonyl chloride, also called *thiophosgene*, is a red mobile liquid with a suffocating odour, and decomposes in moist air giving off fumes. O. S. Billeter and A. Strohl gave 1·5085 for the sp. gr. at 15°; and 72·8° for the b.p. at 730 mm. P. Klason gave 73·5° for the b.p. at 760 mm. P. Klason, and H. Bergreen said that it decomposes a little when heated to 200°, forming carbon disulphide and tetrachloride. G. Carrara found the index of refraction for the *D*-line to be 1·54424. B. Rathke said that the compound decomposes into *trichloromethyl-dithioformic chloride*, $CCl_3.CSSCl$, when exposed to sunlight, but if thoroughly purified, no change was observed. According to B. Rathke and co-workers, O. S. Billeter and co-workers, and P. Klasen, if exposed for some months to sunlight, polymerization occurs, and a colourless crystalline solid is formed; it has a slight smell, is unchanged in air; and melts at 112·5°. It absorbs water vapour, and at 180° is transformed into the liquid. H. Kolbe, and H. Bergreen observed that water slowly decomposes thiocarbonyl chloride in the cold, and more rapidly when heated, forming carbon dioxide, hydrogen chloride and sulphide. B. Rathke found that with an aq. soln. of potassium hydroxide it is immediately decomposed. P. Klason, and O. S. Billeter and A. Strohl said that when treated with alcohol, carbonyl sulphide, ethyl chloride, and *carbon hydrosulphotrisulphonate*, $HS.C(HSO_3)_3$, are formed. P. Klason found that when thiocarbonyl chloride is treated with chlorine, it forms thiocarbonyl tetrachloride; and when treated with sulphur in a sealed tube at 130°–150°, it forms chlorodithioformic chloride, $Cl.CSSCl$. According to B. Rathke, aq. ammonia quickly decomposes thiocarbonyl chloride, forming ammonium thiocyanate, etc. H. Bergreen found that when dried ammonia is passed into an ethereal soln. of thiocarbonyl chloride, ammonium chloride, and thiocyanate are formed, and when treated with ammonium chloride at 200°, or, according to B. Rathke, with aluminium chloride, carbon disulphide and tetrachloride are formed. Reactions with organic compounds have been studied by B. Rathke, H. Bergreen, P. Klason, G. M. Dyson and H. J. George, and O. S. Billeter and co-workers.

According to B. Rathke,[3] when chlorine is passed into a soln. of one part of iodine in 500 parts of carbon disulphide, sulphur chloride and **thiocarbonyl tetrachloride**, $CSCl_4$, are formed. The products of the reaction can be separated by fractional distillation under reduced press. This compound can be regarded as *trichloromethylsulphur chloride*, $CCl_3.SCl$, or *perchloro-methylmercaptan*. P. Klason made it by the action of chlorine on thiocarbonyl chloride in the cold; and J. W. James, by the action of chlorine on methyl thiocyanate. P. F. Frankland and fellow-workers made it by the action of chlorine on carbon disulphide in the presence of iodine:

Add 4 grms. of iodine to 2 kgrms. of carbon disulphide dried over calcium chloride; pass chlorine from a cylinder and dried by calcium chloride, so that the temp. does not rise above 20°–25°, and almost all the gas is absorbed. When the increase in weight is approximately that required by $2CS_2+5Cl_2=2CSCl_4+S_2Cl_2$, the passage of chlorine is stopped, and the mixture is run in a thin stream into hot water contained in a large vessel through which a current of steam is blown so as to decompose the sulphur chloride, and to distil off the tetrachloride. Much sulphur dioxide is evolved, and a train of four condensers is used to collect the required product. The first condenser is air-cooled; the second is cooled by ice; and the last two are cooled by a mixture of ice and salt. The tetrachloride is again distilled in steam; dried over calcium chloride; and distilled with a fractionating column until the temp. rises to 140°.

Thiocarbonyl tetrachloride is a golden-yellow liquid, with an intense disagreeable odour, and it strongly attacks the eyes and respiratory organs. B. Rathke found the sp. gr. to be 1·712 at 12·8°/0°; G. Carrara gave 1·71785 at 11°/4°; and P. Klason, 1·712 at 0°, 1·7049 at 11°, and 1·6953 at 17·5°. B. Rathke gave 146° to 148° for the b.p.; and P. Klason, 149°. The boiling liquid suffers a slight decomposition. When heated in a sealed tube at 200°, B. Rathke found that carbon tetrachloride and sulphur chloride are formed. G. Carrara found 1·54835 for the index of refraction with the *D*-line. According to B. Rathke, when heated with water at 160°, carbon dioxide, hydrogen chloride, and sulphur are formed; the

decomposition is rapid in soln. of potassium hydroxide. P. Klason, and J. W. James found that chlorine alone, or better in the presence of a trace of iodine, transforms it into carbon tetrachloride and sulphur chloride. P. Klason found that with sulphur at 150°–160°, carbon tetrachloride, thiocarbonyl chloride, hexachlorodimethyl di- and tri-sulphide are formed. Aq. ammonia was found by B. Rathke to give ammonium thiocyanate; and cold nitric acid, sp. gr. 1·2, forms *trichloromethyl-sulphuryl chloride*, $CCl_3.SO_2Cl$. P. Klason found that tin and hydrochloric acid reduce the tetrachloride to thiocarbonyl chloride, and with silver-dust, hexachlorodimethyl disulphide is formed. M. Albrecht obtained carbon hydrosulphopotassium trisulphonate, $HS.C(KSO_3)_3$, by the action of potassium sulphite. B. Rathke investigated a number of reactions with organic compounds.

P. Klason [4] made **thiocarbonyl thiochloride,** $CS_2Cl_2$, by heating a mixture of sulphur and thiocarbonyl chloride in a sealed tube between 130° and 150°, and fractionally distilling the product in vacuo. It is a yellow oil, which boils in vacuo at about 140°; it is decomposed by chlorine into thiocarbonyl tetrachloride, and by sulphur at 160° into sulphur chloride and carbon disulphide. P. Klason, and B. Rathke made **hexachlorodimethyl disulphide,** $CCl_3.S.S.CCl_3$, by the action of powdered silver on an excess of thiocarbonyl tetrachloride. According to P. Klason, the viscid yellow oil boils undecomposed in vacuo at 135°; and is but slightly volatilized in steam. It decomposes when heated under ordinary press., forming thiocarbonyl chloride and tetrachloride. When heated with sulphur at 170° it forms **hexachlorodimethyl trisulphide,** $CCl_3.S.S.S.CCl_3$. The same compound is produced when thiocarbonyl tetrachloride is heated above its b.p., or treated with sulphur at 150°–160°. B. Rathke made it by allowing a mixture of thiocarbonyl chloride and sulphur chloride to stand for a long time; and it is present in the products of the action of dried chlorine on iodiferous carbon disulphide. This compound can be crystallized from alcohol when it furnishes colourless prisms, which are easily soluble in ether, carbon disulphide, and warm alcohol. It fuses at 57·4°, and it distils undecomposed in vacuo at 190°; but under ordinary press. it furnishes thiocarbonyl chloride, carbon tetrachloride, sulphur chloride, and thiocarbonyl tetrachloride as decomposition products. The corresponding compound, **hexabromodimethyl trisulphide,** $CBr_3.S.S.S.CBr_3$, was made by C. Hell and F. Urech by the action of bromine on carbon disulphide; by A. von Bartal by the action of sulphur on carbon tetrabromide; and by W. Plotnikoff by treating $CS_2Br_4.AlBr_3$, successively with water, alcohol, and ether, and crystallizing from petroleum-ether, when clear prisms were obtained. If crystallized from ether the crystals are tabular. A. von Bartal gave 123°–124° for the m.p., and C. Hell and F. Urech, 125°, and they added that the compound becomes red on melting. It is insoluble in water; sparingly soluble in cold ether, alcohol, and glacial acetic acid; soluble in benzene, petroleum ether, and chloroform; and very soluble in carbon disulphide and bromine. It decomposes slowly when boiled with alcohol; at ordinary temp., 100 parts of boiling alcohol, said C. Hell and F. Urech, dissolve 5·5 parts of the compound; 100 parts of ether dissolve 2·35 parts at 0°, and 4·95 parts at the b.p. They also found it to dissolve without decomposition in boiling conc. sulphuric acid. When heated with an excess of bromine and water, in a sealed tube, carbon dioxide, carbonyl sulphide, hydrogen bromide, and sulphuric acid are formed. Dil. aq. soln. of the alkali hydroxides have no action in the cold; but if heated with conc. soda-lye or baryta-water, when air is excluded, polysulphide, carbonate, and bromide are formed but no sulphate is produced; but if boiled with an excess of lead oxide and water, a sulphate is formed. According to A. von Bayer, hexabromodimethyl trisulphide forms addition products with methyl iodide and with iodoform.

According to C. Hell and F. Urech, when hexabromodimethyl trisulphide is heated above its m.p., small quantities of a compound of unknown constitution: $C_9Br_4S_4$, are produced, and A. von Bartal obtained the same compound by the action of carbon tetrabromide on sulphur. C. Hell and F. Urech said the indigo-blue powder retains 2 to 3 mols of water, and if heated for a long time at 150°, A. von Bartal found the water was expelled. The

blue colour is attributed to the presence of the –S.S– group. The anhydrous compound is scarcely volatile. A. von Bartal, and C. Hell and F. Urech said that the compound is insoluble in ordinary solvents, easily soluble in phenol, and in hot conc. sulphuric acid forming a blue soln.; it is sparingly soluble in hot aniline; and easily soluble in conc. nitric or hydrochloric acid, forming a violet soln. which later becomes red.


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## § 40. The History, Occurrence, and Preparation of Carbon Disulphide

In 1796, W. A. Lampadius [1] attempted to determine the amount of sulphur in a sample of iron pyrites; he heated a mixture of that mineral with carbon, and obtained an oily, sulphurous, volatile liquid. He tried heating the mineral with wood, anthracite, etc., and still obtained the oily liquid accompanied by hydrogen sulphide, volatile hydrocarbons, and empyreumatic matters. He called the product *le soufre liquid*, and *le alcool de soufre*, and regarded it as a compound of sulphur and hydrogen. In 1802, F. Clément and J. B. Désormes tried to find if charcoal which had been calcined still contained hydrogen, and, on heating the charcoal with sulphur, obtained a liquid which they regarded as *le bisulfure d'hydrogène*. They found that it did not behave towards a soln. of lead acetate like hydrogen sulphide, and finally concluded that it contained no hydrogen, and they named it *le soufre carburé*. They tried without success to find the exact proportions of sulphur and carbon in *le soufre carburé*. Some unsatisfactory observations were made by A. B. Berthollet, J. B. Trommsdorff, H. Davy, L. N. Vauquelin and P. J. Robiquet, and M. Cluzel, from which it was not made clear whether or not the liquid contained hydrogen, and even nitrogen. In a report by A. B. Berthollet, some experiments by L. N. Vauquelin are described in which the vapour was passed over heated

copper, whereupon carbon and copper sulphides were formed, and it was concluded that the former contained 14–15 parts of carbon and 85–86 parts of sulphur. The compound was also analyzed by J. J. Berzelius and A. Marcet. These analyses show that the liquid is **carbon disulphide,** $CS_2$. J. J. Berzelius made a special study of the properties of the compound in 1822; and W. C. Zeise investigated its action on a number of oxides, alcohol, etc. J. P. Wibaut showed that sulphur is retained by carbon which has been heated in the vap. of sulphur, and he assumes that the product is a mixture of carbon and a sulphide of carbon which is non-volatile at 1000°.

Carbon disulphide has been found in the petroleums and benzenes of commerce by H. Hager,[2] C. Vincent and B. Delachanal, and K. Helbing; in the gases from cess-pools, by M. Scanlan and A. Anderson; in coal gas, by A. W. Hofmann, and R. Witzeck; and in oil of mustard (allyl thiocyanate), by A. W. Hofmann, and E. Mylius.

F. Clément and J. B. Désormes,[3] G. J. Mulder, etc., prepared carbon disulphide by heating carbon in the vap. of sulphur. The volatile compound of carbon and sulphur is condensed in vessels surrounded with cold water. The product is contaminated with free sulphur, which volatilizes with the carbon disulphide; some hydrogen sulphide is formed at the same time by the action of sulphur on the hydrogen in the charcoal. T. Sidot showed that at a mean red heat a greater yield is obtained than at a dull red or a bright red-heat. M. Berthelot, and W. Stein showed that the reaction is reversible, for, when carbon disulphide is heated to redness, it decomposes into its elements: $CS_2 \rightleftharpoons C+S_2$. Accordingly, F. Koref found that the equilibrium constant $K=[S_2]/[CS_2]$ is 0·078 at 823°; 0·115 at 906°; 0·179 at 1009°; and 0·258 at 1383°. He found the observed results at $T°$ K. can be represented by $\log K=-2740T^{-1}+1·38$. In the decomposition experiments, the value of the constant fell with time owing to the formation of silicon sulphide, $SiS_2$, which acts as a carrier of sulphur, reconverting the carbon set free into carbon disulphide. In the manufacturing process, the charcoal is contained in vertical cast iron or earthenware retorts, 10–12 ft. high and 1–2 ft. diam., set in a suitable furnace. The heat of the furnace melts the sulphur placed in a hopper near the base of the retort, the sulphur vap. rises through the red-hot charcoal and forms carbon disulphide which escapes at the top; the end of the exit pipe dips under water where much of the carbon disulphide is condensed. The condensation is completed in long condensing coils—30 ft. long—and the escaping hydrogen sulphide can be absorbed by slaked lime (E. Diess), or ferric hydrate (A. Payen). Various modifications have been suggested by J. Farbaky, P. Schuberg, E. Diess, A. Galy-Cazalat and A. Huillard, I. Singer, Chemische Fabrik Griesheim-Electron, etc. A. E. Delph found that the deposit which forms on iron or steel in contact with carbon disulphide vap. at 400°, can be prevented by a thin coating of aluminium. In E. R. Taylor's electric process a cylindrical furnace 40 ft. high and 16 ft. in diameter is packed with coke from the top, Fig. 59; the coke is renewed through the side hopper *C*. An alternating current is sent through the electrodes *E* set at right angles to one another at the base of

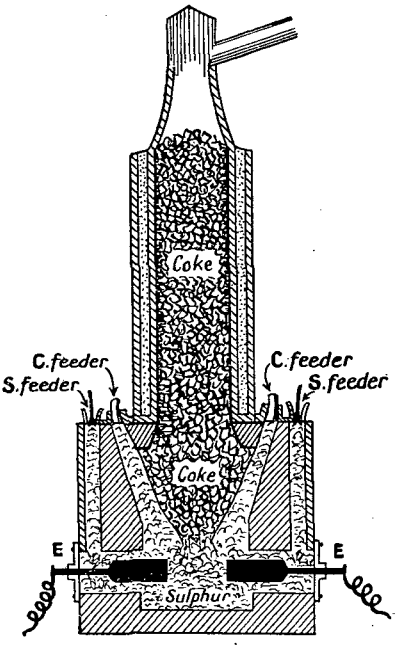



FIG. 59.—Taylor's Carbon Disulphide Furnace.

the furnace. The heat melts the sulphur on the floor of the furnace; the vap. of sulphur rises through the coke, forming carbon disulphide. Fresh sulphur is introduced through the hopper shown in the diagram. The carbon disulphide passes off at the top of the furnace, and is condensed in the condensing coils. The electrical process is practically continuous and is free from the troublesome leakages and heat-losses incidental to the retort process. The subject has been discussed by G. A. Richter, and B. Waeser.

B. Rassow and K. Hoffmann have investigated the conditions under which carbon disulphide is formed from sulphur dioxide and heated wood charcoal. At 700°, only traces of carbon disulphide are formed. Above 750°, the yield gradually increases, carbon oxysulphide, carbon dioxide, sulphur vap., and small quantities of carbon monoxide also being formed. At 850°–900°, the yield of carbon disulphide reaches a maximum and accounts for 35 per cent. of the sulphur dioxide, 55 per cent. being found as oxysulphide and 10 per cent. as free sulphur. At temp. above 900°, the free sulphur increases at the expense of the carbon disulphide and oxysulphide, and above 1100° the sole products of the reaction are free sulphur and carbon monoxide. The low yield obtainable and the danger, and the trouble attending the handling of the oxysulphide, render this method of preparing carbon disulphide impracticable for industrial purposes. W. A. Lampadius, and E. and L. Labois obtained carbon disulphide by heating a mixture of carbon with iron or copper pyrites, or antimony sulphide. M. Berthelot, C Brunner, W. Stein, G. J. Mulder, A. Schrötter, T. Sidot, P. A. Favre and J. T. Silbermann obtained it by heating various carbonaceous substances—horn, wax, sugar, etc.—with sulphur; and A. Mittasch and E. Willfroth, by heating a mixture of carbon monoxide and sulphur vap. along with a suitable catalyst. B. Rathke found that it is formed by heating carbon tetrachloride and phosphorous sulphide in a sealed tube at 200°; J. Gadamer, by heating allyl thiocyanate with water in a sealed tube at 100°–105°; A. W. Hofmann, by distilling natural oil of mustard; F. A. Went, by distilling cultivations of schizophyllum lobatum—a fungus which occurs in Java on old fallen branches of pectocarpus, bamboo stems, etc.—if in hydrogen, the fungus produces no carbon disulphide, or only traces; G. Capelle, by passing acetylene into molten sulphur; and R. Willstätter and T. Wirth, by heating thioformamide hydrochloride out of contact with air.

**The purification of carbon disulphide.**—When the carbon disulphide is required of a high degree of purity, B. Delachanal and A. Mermet[4] recommended preparing it by the decomposition of a metal thiocarbonate. The crude carbon disulphide obtained by the action of sulphur vap. on carbon has a fœtid odour due to the presence of organic sulphur compounds, hydrogen sulphide, etc. The crude liquid also has sulphur in soln., and this can be largely removed by distillation. E. Deiss, for instance, fractionally distilled the crude liquid and found that the constituents with a repulsive odour collected in the first fractions, and sulphur in the last fractions. The middle fractions were purest. M. Bonière purified the crude liquid by distillation from a conc. soln. of sodium hydroxide, and passing the vapours through alkaline liquids and soln. of salts of iron, lead, or copper. S. Cloëz purified carbon disulphide by agitation with finely powdered mercuric chloride, followed by distillation over an inodorous fat. N. A. E. Millon, and A. Commaille distilled the liquid from milk of lime, and allowed it to stand in contact with litharge or with copper, zinc, or iron turnings; G. C. Wittstein expressed doubts as to the efficacy of this procedure. I. Singer washed the liquid with milk of lime and distilled the product mixed with a soln. of lead acetate. T. Sidot, and S. Cloëz agitated the impure liquid with mercury; and S. Kern, with a mixture of lead and lead nitrate. L. H. Friedburg distilled the liquid over palm oil, digested the product with fuming nitric acid, washed with water, and rectified. P. C. Marquart stated that the violet colour observed when carbon disulphide is treated with fuming nitric acid is due to iodine nearly always present as an impurity in the acid. E. Allary treated the crude liquor with potassium perman-

ganate ; and E. Obach distilled the liquid over quicklime ; agitated the product with potassium permanganate, mercury, and mercuric sulphate ; and finally rectified it. P. Palmieri agitated 100 parts of the crude liquid with 2–3 parts of dried copper sulphate ; and subsequently rectified over dry copper sulphate. The result was good. A. Chenevier treated a litre of crude carbon disulphide with 0·5 c.c. of bromine for 3–4 hrs., removed the excess of bromine by potash-lye, or copper turnings, and distilled the product. M. von Unruh agitated the crude liquid with mercury, and porous calcium chloride, and distilled it in the dark. O. Ruff and H. Golla digested the carbon disulphide with a sat. soln. of sodium sulphide for 24 hrs. The sodium thiocarbonate was separated, treated with copper sulphate, and the resulting copper thiocarbonate decomposed by passing steam into the soln. The pure carbon disulphide so obtained was distilled in steam, and finally dried with phosphorus pentoxide.


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## § 41. The Physical Properties of Carbon Disulphide

Impure carbon disulphide is a liquid which has *l'odeur des œufs pourris*, but the smell of the purified liquid is not unpleasant, and it recalls that of chloroform. W. A. Wahl [1] obtained spherulitic **crystals** by cooling the liquid, and, when these were melted and recrystallized, long needle-like crystals, very strongly doubly refracting, were formed which belonged to the monoclinic or triclinic system—probably the latter. V. and C. Meyer found the **vapour density** to be 2·68 when the theoretical value for $CS_2$ is 2·62. A. Schulze found that the vap. density of carbon disulphide indicates a 2 per cent. association. The vap. density (air unity) and **specific volume** (c.c. per gram) of the vap. of carbon disulphide between 48·38° and 85·03° were determined by A. Wüllner and O. Grotrian; and between −29·34° and the critical temp. by A. Battelli. R. Lorenz and W. Herz, and G. M. Schwab measured the mol. vol. A. Batelli gave:

| | −29·34° | 8·26° | 78·82° | 130·48° | 171·52° | 209·32° | 273·0° |
|---|---|---|---|---|---|---|---|
| Sp. vol. | 20482·3 | 1251·3 | 137·21 | 46·162 | 23·892 | 10·094 | 2·718 |
| Vap. density | 2·6205 | 2·6539 | 2·76205 | 2·9206 | 3·1218 | 3·8057 | 7·8280 |

A. O. Rankine estimates the collision area of the mol. of carbon disulphide vap. to be between $1{\cdot}37\times10^{-5}$ and $1{\cdot}23\times10^{-15}$ sq. cm. J. L. Gay Lussac gave 1·293 for the **specific gravity** of the liquid at 0°, and 1·271 at 15°; H. L. Buff gave 1·29858 at 0°, 1·27904 at 10°, 1·26652 at 17°, and 1·227431 at 46°. J. H. Gladstone gave 1·2909 at 23°, and 1·2594 at 30°; R. Nasini, 1·2634 at 20°/4°; C. E. Linebarger, 1·25958 at 25°; A. Haagen, 1·2661 at 20°; R. Schiff, 1·2233 at 46·5°/4°; T. E. Thorpe, 1·29215 at 0°/4°, and 1·22242 at 46·04°/4°; H. V. Regnault, 1·2823 at 5°–10°, 1·275 at 10°–15°, and 1·2676 at 15°–20°; J. I. Pierre, 1·29312 at 0°; A. Winkelmann, 1·2665 at 16·06°; J. Timmermans, 1·29270 at 0°–4°; W. Ramsay, 1·2176 at 43°; L. H. Friedburg, 1·266 at 15·2°; and J. Drecker, 1·26569 at 17·86°, 1·26446 at 18·58°, 1·25031 at 28·21°, and 1·23863 at 35·96°. E. Beckmann found the sp. gr. at the b.p. to be 1·2223, and M. von Unruh, 1·2209. Values were also obtained by W. A. Lampadius, F. Clément and J. B. Désormes, M. L. Frankenheim, A. de la Rive, H. F. Weber, F. D. Brown, J. J. Berzelius and A. Marcet, M. Cluzel, J. P. Couerbe, A. Ritzel, J. W. Brühl, etc. A. Wüllner represented the sp. gr., $S$, at $\theta°$ between 7° and 24° by the equation $S=1{\cdot}29366-0{\cdot}001506\theta$; J. I. Pierre gave $1{\cdot}292=S(1+0{\cdot}0011140\theta+0{\cdot}0_5137\theta^2+0{\cdot}0_71912\theta^3)$; and J. Timmermans for the sp. gr. at $T°$ K., upwards from absolute zero, $S=1{\cdot}67367-0{\cdot}00130856T-0{\cdot}0_63180T^2$. The sp. gr. of binary mixtures of carbon disulphide with ethyl and propyl alcohols were determined by J. Holmes; with acetic ether, toluene, and chloroform, by C. E. Linebarger; and with carbon tetrachloride, and benzene, by F. D. Brown. The changes which occur on mixing carbon disulphide with alcohol, chloroform, or benzene were measured by F. Guthrie. C. Drucker found that the molecular elevation of the **critical solution temperature** for carbon disulphide and methyl alcohol is specific for each substance added to the binary system. N. Schoorl and A. Regenbogen studied the ternary system—water, alcohol, and carbon disulphide.

The coeff. of **compressibility**, $\beta$, of carbon disulphide was found by M. Amaury and C. Descamps [2] at 14° to be $63{\cdot}5\times10^{-6}$ per atm.; L. P. Cailletet, $98\times10^{-6}$ per atm. at 8° and 607 atm.; W. C. Röntgen, $89\times10^{-6}$ at 18°; E. H. Amagat, $87\times10^{-6}$ per atm. between 9 and 38 atm. at 15·6°, and $174\times10^{-6}$ at 99·3°; or, $0{\cdot}0_490$ at 20°, $0{\cdot}0_3107$ at 40°, $0{\cdot}0_3128$ at 60°, and $0{\cdot}0_3149$ at 80°; and P. W. Bridgman gave $0{\cdot}0_492$ at 20°, $0{\cdot}0_3107$ at 40°, $0{\cdot}0_3133$ at 60°, and $0{\cdot}0_3150$ at 80°. The last-named also found the effects of press. (kgrms. per sq. cm.) and temp. on the vol. of carbon disulphide indicated in Table XXVII. W. Seitz made observations on this subject. According to A. Ritzel, at a press. $p$ atm., the compressibility coeff. is:

| | | | | |
|---|---|---|---|---|
| 20° | $p$ | 107 | 262·5 | 441·5 | 679·5 |
| | $\beta\times10^6$ | 77·2 | 69·6 | 60·1 | 51·0 |
| 25° | $p$ | 115·5 | 236·0 | 342·0 | 495·5 |
| | $\beta\times10^6$ | 83·2 | 71·9 | 69·3 | 61·7 |

A. Schulze found the *pv*-curves of carbon disulphide at 78·82°, and 130·48° show that the mol. association decreases with increasing temp.; and at constant temp., increases with increasing press. Compressibility measurements show at 80°, 0·5 per cent. more association at 2 atm. than at 1 atm. press.

TABLE XXVII.—THE EFFECTS OF PRESSURE AND TEMPERATURE ON THE VOLUME OF CARBON DISULPHIDE.

| Press. | 20° | 30° | 40° | 50° | 60° | 70° | 80° |
|---|---|---|---|---|---|---|---|
| 1 | 1·0235 | 1·0357 | 1·0490 | 1·0630 | 1·0775 | 1·0928 | 1·0992 |
| 1000 | 0·9586 | 0·9671 | 0·9752 | 0·9829 | 0·9907 | 0·9991 | 1·0083 |
| 2000 | 0·9173 | 0·9240 | 0·9302 | 0·9362 | 0·9423 | 0·9485 | 0·9552 |
| 4000 | 0·8647 | 0·8688 | 0·8732 | 0·8770 | 0·8823 | 0·8855 | 0·8902 |
| 6000 | 0·8295 | 0·8329 | 0·8367 | 0·8406 | 0·8442 | 0·8472 | 0·8501 |
| 8000 | 0·8022 | 0·8061 | 0·8100 | 0·8131 | 0·8162 | 0·8191 | 0·8220 |
| 10000 | 0·7805 | 0·7844 | 0·7879 | 0·7910 | 0·7940 | 0·7969 | 0·7997 |
| 12000 | 0·7638 | 0·7658 | 0·7682 | 0·7710 | 0·7743 | 0·7772 | 0·7795 |

A. Ritzel measured the compressibility of mixtures of carbon disulphide and acetone. T. M. Gardner studied the adiabatic expansion of carbon disulphide vap.; and A. Horstmann, H. Herwig, T. E. Thorpe, and E. H. Amagat, the expansion and compression of the vap. R. Gans discussed the symmetry of the mol. of carbon disulphide. W. Ramsay and J. Shields found the **surface tension** of the liquid in contact with the sat. vap. to be $\sigma=33·58$ dynes per cm. at 19·4° and at 46·1°, $\sigma=29·41$ dynes per cm.; the **specific cohesion** $a^2=5·40$ sq. mm. at 19·4°, and 4·90 sq. mm. at 46·1°. S. von Wroblewsky examined the effect of dissolved carbon dioxide on the surface tension of the disulphide. The mean **molecular surface energy** was 2·022, the characteristic of a non-associated liquid. M. L. Krankenheim gave for $\sigma$ dynes per cm., and $a^2$ sq. mm., 32·2 and 5·10 at 0°, and 29·8 and 4·48 at 25°; W. F. Magie gave 31·74 and 5·071 at 20°; and A. M. Worthington, 29·33 and 4·71 at 25°. A. Ritzel gave $\sigma=31·64$ dynes per cm. at 25°. R. Lorenz and W. Herz gave $\sigma=27·3$ at the b.p., and 48·9 at the m.p. The surface tensions of mixtures of carbon disulphide and chloroform were determined by W. Ramsay and E. Aston. A. Wijkander gave for the **viscosity** of the liquid (water unity) at 20°, 0·205; at 25°, 0·191; and at 30°, 0·190. T. E. Thorpe and J. W. Rodger gave for the viscosity coeff., $\eta$:

| | 0·40° | 9·45° | 19·94° | 30·30° | 40·62° | 45·96° |
|---|---|---|---|---|---|---|
| $\eta$ . . | 0·00428 | 0·00397 | 0·00367 | 0·00342 | 0·00317 | 0·00306 |

and they represented the viscosity coeff. at $\theta°$ by $\eta=24·379(199·17+\theta)^{-1·6328}$. Observations were also made by M. Brillouin. The viscosity of the vap. at 0° was found by J. Puluj to be 0·0000924. V. Henri discussed the electronic structure of the mol. The viscosity of binary mixtures of carbon disulphide with ethyl alcohol was determined by A. E. Dunstan; with ether, acetic ether, benzene, and toluene, by C. E. Linebarger. P. Walden gave 2170 atm. for the **internal pressure** of carbon disulphide; and I. Traube gave 1980 atm. F. S. Mortimer calculated the internal press. from solubility data. D. L. Hammick used for the constant $a$ in J. D. van der Waals' equation, 0·02412 atm. J. E. Mills studied the **molecular attraction**. J. Stefan found the **diffusion** coeff. of air in carbon disulphide to be 0·0995. J. Duclaux and J. Errera studied the filtration of carbon disulphide through colloidal membranes. A. Masson found the **velocity of sound** in carbon disulphide at 0° to be 189·00 metres per sec.; A. Lechner, 204·7 metres per sec. at 48°; and E. H. Stevens, in the vap. at 99·7°, 223·2 metres per sec.

The coeff. of **thermal expansion** of carbon disulphide has been determined by G. W. Muncke,[3] who gave for the vol., $v$, at $\theta°$, $v=v_0(1+0·0011256\theta$

$+0{\cdot}0_5 1715049\theta^2+0{\cdot}0_8 121166\theta^3$), where $v_0$ is the vol. at 0°; J. 1. Pierre gave $v=v_0(1+0{\cdot}0011398\theta+0{\cdot}0_5 13707\theta^2+0{\cdot}0_7 19123\theta^3)$; G. A. Hirn. $v=v_0(1+0{\cdot}00116806\theta+0{\cdot}0_5 16490\theta^2-0{\cdot}0_9 81112\theta^3+0{\cdot}0_{10}6095\theta^4)$, between 30° and 160°; and T. E. Thorpe, $v = v_0(1 + 0{\cdot}001150056\theta + 0{\cdot}0_5 111621\theta^2 + 0{\cdot}0_7 17475\theta^3)$. P. Walden gave $v=v_0(1+0{\cdot}00117\theta)$ between 0° and 30°. E. H. Amagat found that under normal press., ether is more expansible than carbon disulphide, under 2500 atm. press., the expansibility of the two liquids is the same; and under 3000 atm., the expansibility of carbon disulphide is the greater. W. Seitz made observations on the thermal expansion of carbon disulphide at low temp.; and J. J. Saslawsky studied the relation between the thermal expansion and the critical temp. The **thermal conductivity** of carbon disulphide was found by R. Goldschmidt to be 0·0003879 cal. per cm. per sec. per degree at 0°; by H. F. Weber, 0·000417 at 5·4°; and 0·000343 between 9° and 15°; by L. Graetz, 0·000267 at 13°; by C. Chree, 0·000537 at 15·5°; and by A. Winkelmann, 0·00200 at 10° to 18°. E. Pauli found the ratio of the thermal conductivity of the vapour at 100° and at 10° to be $k_{100}/k_0=1{\cdot}516$. P. W. Bridgman gave 0·000382 at 30° and 0·000362 at 75°; and if the value at 0 kgrm. per sq. cm. press. be unity at 30°, the value at 1000 kgrms. per sq. cm. is 1·174, and at 12,000 kgrms. per sq. cm., 1·962.

The **specific heat** of carbon disulphide was found by A. Battelli [4] to be 0·195 at −96°; and 0·238 at 0°; H. V. Regnault gave 0·2303 at −30°, 0·2352 at 0°; and 0·2401 at 30°, and he represented the sp. ht. at $\theta$° by $0{\cdot}2352+0{\cdot}0001620\theta$; G. A. Hirn gave 0·2388 for the sp. ht. at 30°; W. Sutherland, 0·260 at 120° and 0·2882 at 160°; and C. Forch gave 0·242 at 18°. H. V. Regnault found 0·160 for the sp. ht. of carbon disulphide vap. at constant press. between 86° and 190°; and M. Pier gave 0·137 for the sp. ht. at constant vol. between 0° and 2000.° K. Zakrzewsky found for the sp. ht. at constant vol. to be:

| | −90° | −70° | −50° | −20° | 0° |
|---|---|---|---|---|---|
| Sp. ht. . . | 0·110 | 0·114 | 0·121 | 0·139 | 0·160 |

For the ratio of the two sp. hts., P. A. Müller gave 1·189 between 21° and 40°; K. Bindel, 1·205 between 3° and 67°; E. H. Stevens, 1·234 at 99·7°; and R. Thibaut, 1·199 at 17° and 202 mm. The sp. hts. of binary mixtures of carbon disulphide and ethyl alcohol, chloroform, and benzene have been determined by J. H. Schüller. A table of the **vapour pressures** of carbon disulphide between −30° and the critical temp., at intervals of 10°, has been determined by A. Battelli. He found at −30°, 7·97 mm.; at −20°, 42·41 mm., and at −10°, 128·39 mm. At the critical temp. 273·05°, the critical press. was 55,380 mm. The other results are indicated in Table XXVIII. H. V. Regnault represented his observations at $\theta$° between −20°

TABLE XXVIII.—VAPOUR PRESSURE OF CARBON DISULPHIDE (mm. mercury).

| Temp. | 0° | 10° | 20° | 30° | 40° | 50° | 60° | 70° | 80° | 90° |
|---|---|---|---|---|---|---|---|---|---|---|
| | 128·39 | 198·01 | 296·48 | 432·76 | 616 75 | 859·49 | 1172·9 | 1569·6 | 2062·1 | 2662·8 |
| 1 | 3383·4 | 4234·4 | 5225·0 | 6362·0 | 7651·6 | 9094·9 | 10963·2 | 12448·8 | 17095·1 | 20317·8 |
| 2 | 23813·3 | 27555·4 | 31518·9 | 35675·0 | 39993·7 | 44444·6 | 48997 2 | 53622·0 | — | — |

and 150°, by $\log p=a+ba^{\theta+20}+C\beta^{\theta+20}$, where $a$ $\log p=5{\cdot}401162-3{\cdot}4405663a^{\theta+20}-0{\cdot}28573686\beta^{\theta+20}$, where $\log a=1{\cdot}9977628$, and $\log \beta=1{\cdot}9911997$. C. Antoine represented his results by $\log p=1{\cdot}2020\{5{\cdot}8181-1000(\theta+246)^{-1}\}$. A. Jarolimek gave $\theta=120p^{0{\cdot}25}-73{\cdot}5$. W. Sajontschewsky and M. Avenarius measured the vap. press. between 140° and 271·8°; and A. Wüllner and O. Grotian between 20·44° and 85·01°. A. Juliusberger studied the subject. A. Stock and co-workers represented their measurements on the vap. press. of carbon disulphide between 11° and −181° by $\log p=-1682{\cdot}38T^{-1}+1{\cdot}75 \log T-0{\cdot}0052980T+5{\cdot}44895$. C. E. Carbonelli, and R. Lorenz made a study of the variation of the vap. press.

of carbon disulphide with temp. F. Guthrie studied the vap. press. of binary mixtures of carbon disulphide with ether or chloroform; J. von Zawidzky, of carbon disulphide with methylal, or acetone; and W. K. Lewis and E. V. Murphree, of carbon disulphide and water. M. A. Rosanoff and C. W. Easley studied the distillation of binary mixtures of carbon disulphide with carbon tetrachloride, or benzene; and C. Drucker, and E. C. McKelvy and D. H. Simpson, mixtures of carbon disulphide with ethyl or methyl alcohol.

S. von Wroblewsky and K. Olzschewsky [5] found that at about —116°, carbon disulphide freezes to a crystalline solid with a **melting point** of —110°. G. Carrara and A. Coppadoro gave —108·6° for the m.p.; J. Timmermans, —111·6°; F. G. Keyes and co-workers, —112·97°; L. Holborn and W. Wien, —112·8°; and G. Tammann, —112·8°. The last-named also represented the effect on the m.p. of press. $p$ kgrms. per sq. cm., $dT=0{\cdot}0160p$. Observations on the **boiling point** of carbon disulphide were made by W. A. Lampadius, J. I. Pierre, J. L. Gay Lussac, H. Kopp, A. Haagen, W. Ramsay, L. H. Friedburg, J. M. Crafts, F. A. Henglein, W. Sajontschewsky, and M. Avenarius. For the b.p. R. Schiff gave 47·0° at 768·5 mm.; T. Andrews, 46·2° at 769 mm.; M. von Unruh, 46·25° at 760 mm.; T. E. Thorpe, 46·04° at 760 mm.; H. V. Regnault, 46·20 at° 760 mm.; H. Arctowsky, 46·27 at 757 mm.; R. Nasini, 47·5° at 764 mm.; and J. Timmermans, 46·25° at 760 mm. H. B. Baker found the b.p. is raised a number of degrees if the carbon disulphide be very thoroughly dried. E. Hendrick discussed H. B. Baker's observations and enquiries if the presence of a trace of water separates or loosens molecular aggregates. According to M. von Unruh, the b.p. changes between 740° and 765 mm., 0·4144° for 10 mm. change of press.; this is eq. to 1° for 24·13 mm. change of press. He also found the **molecular raising of the boiling point** to be 2370 per 100 grms., or 1940 per 100 c.c. E. Beckmann gave for the b.p. constant 23·7 per grm. H. V. Regnault gave for the latent **heat of vaporization,** 90 cals. per grm. at 0°; 100·48 cals. at 100°, and 102·36 cals. at 140°; A. Winkelmann, 89·5 cals. at 0°; F. Koref, 86·9 cals. at 14·1°; K. Wirtz, 83·1 cals. at 46·1°; D. L. Hammick, 85 cals. per gram; T. Andrews, 86·87 cals. at 46·2°; and C. C. Person, 105·7 cals. at 46·6°. H. V. Regnault gave for the heat of vaporization at $\theta$°, $90{\cdot}00-0{\cdot}089220\theta-0{\cdot}0004938\theta^2$; and A. Winkelmann, $89{\cdot}50-0{\cdot}065300\theta-0{\cdot}0010976\theta^2-0{\cdot}00000342450\theta^3$. The rapid evaporation of carbon disulphide produces a low temp., and experiments on this subject were made by J. Murray in 1812.

M. Avenarius gave 276·0° for the **critical temperature** of carbon disulphide, and B. Galitzine, 279·6°. C. Cagniard de la Tour gave 275·0° for the critical temp., 77·8 atm. for the **critical pressure,** and 0·0096 for the **critical volume.** For the critical temp. and press., respectively, W. Sajontschewsky gave 271·8° and 74·7 atm.; J. B. Hannay and J. Hogarth, 272·96° and 77·9 atm.; J. Dewar, 277·7° and 78·1 atm.; J. B. Hannay, 277·68° and 78·14 atm.; and A. Battelli, 275·05° and 72·868 atm., and for the critical vol., 0·009011. The data of C. Cagniard de la Tour gave for **J. D. van der Waals' constants** $a=0{\cdot}02185$, and $b=0{\cdot}003225$; W. Sajontschewsky, $a=0{\cdot}02166$, and $b=0{\cdot}003339$; J. B. Hannay and J. Hogarth, $a=0{\cdot}02166$, and $b=0{\cdot}003209$; J. B. Hannay, $a=0{\cdot}02197$, and $b=0{\cdot}003227$; and A. Battelli, $a=0{\cdot}02316$, and $b=0{\cdot}003134$. W. Herz gave 3·17 for the **chemical constant,** and W. Nernst, 3·1.

Carbon disulphide is an endothermal compound. J. Thomsen [6] gave for the **heat of formation** from amorphous carbon and rhombic sulphur, $(C, 2S)=CS_{2gas}-26{\cdot}01$ Cals.; or $CS_{2liquid}-19{\cdot}61$ Cals.; and from the diamond M. Berthelot and C. Matignon gave for the gaseous carbon disulphide —25·4 Cals., and for the liquid —19 Cals. M. Berthelot gave for the **heat of combustion,** 252·8–253·3 Cals.; and J. Thomsen, 265·1 Cals. J. J. Berzelius and A. Marcet said that the temp. of combustion of carbon disulphide in oxygen is sufficient to melt platinum wire. The thermal values of binary mixtures of carbon disulphide with ethyl alcohol, and with benzene were determined by A. Winkelmann. A. Marcet discussed the production of cold by the evaporation of carbon disulphide.

Carbon disulphide has a high **refractive index** and a high **dispersion.** In this it is exceeded by very few liquids; those of methylene iodide, bromonaphthalene, and phenyl-mustard oil are greater. Hence, the use of carbon disulphide for filling hollow glass prisms for spectroscopic work. A large number of measurements of the refractive index has been made by E. E. Hall and A. R. Payne, etc.[7] E. Flatoff's results, Table XXIX. show the effect of variations of temp. and of wave-length, $\lambda$, on the refractive index. H. Rubens found for the ultra-red, at 20°:

| $\lambda$ | 589 | 777 | 873 | 999 | 1164 | 1396 | 1745 | 1998$\mu\mu$ |
|---|---|---|---|---|---|---|---|---|
| $\mu$ | 1·6275 | 1·6072 | 1·6017 | 1·5968 | 1·5928 | 1·5891 | 1·5856 | 1·5840 |

while F. F. Martens gave for the ultra-violet 2·159 when $\lambda$=260$\mu$, and W. Fricke gave:

| $\lambda$ | 266 | 274 | 288 | 298 | 304 | 317 | 326 | 335$\mu\mu$ |
|---|---|---|---|---|---|---|---|---|
| $\mu$ | 2·123 | 2·009 | 1·912 | 1·875 | 1·852 | 1·807 | 1·782 | 1·79 |

TABLE XXIX.—THE EFFECT OF TEMPERATURE AND WAVE-LENGTH OF LIGHT ON THE REFRACTIVE INDEX OF CARBON DISULPHIDE.

| $\lambda$ | −10° | 0° | 20° | 40°. |
|---|---|---|---|---|
| 367·61 | — | 2·12324 | 2·08823 | — |
| 274·87 | 2·04983 | 2·03484 | 2·00474 | 1·97489 |
| 361·19 | 1·76695 | 1·75719 | 1·73806 | 1·71811 |
| 394·41 | 1·72888 | 1·71989 | 1·70180 | 1·68278 |
| 441·59 | 1·69684 | 1·68850 | 1·67135 | 1·65323 |
| 467 83 | 1·68420 | 1·67606 | 1·65923 | 1·64181 |
| 480·01 | 1·67931 | 1·67131 | 1·65466 | 1·63733 |
| 508·60 | 1·66974 | 1·66187 | 1·64541 | 1·62842 |
| 533·85 | 1·66286 | 1·65506 | 1·63877 | 1·62192 |
| 589·31 | 1·65139 | 1·64362 | 1·62761 | 1·61115 |

C. Bergholm gave 1·668 at −20°; 1·651 at 0°; 1·635 at 20°; and 1·616 at 41·5°. L. Lorenz found for the vap. of carbon disulphide 1·1478 for $\lambda$=0·589$\mu$; and 1·1457 for $\lambda$=0·671$\mu$; E. Mascart gave 1·1485 for $\lambda$=0·589$\mu$. Observations were also made by P. L. Dulong, M. Croullebois, J. Kanonnikoff, etc., on the refractive index of carbon disulphide vap. Measurements on the refractive index of binary mixtures of carbon disulphide with ether were made by C. Forch; with methylal by J. von Zawidzky; with acetone and chloroform by A. Beythein and R. Hennicke, J. von Zawidzky, and E. E. Sundwik. S. Procopiu studied the effect of suspended crystalline particles on the birefringence of carbon disulphide. The dispersion of carbon disulphide has been studied by H. Rubens, F. F. Martens, and E. Flatoff. There is anomalous dispersion with $\lambda$=326–335$\mu\mu$. A. G. Ganesan, and C. V. Raman and K. S. Rao studied the scattering and extinction of light in liquid carbon disulphide. W. W. Coblentz[8] studied the transmission spectrum and refraction in the ultra-red; and V. Henri, the absorption spectrum; N. K. Sethi, the interference bands of liquid carbon disulphide; W. H. Keesom and J. de Smedt, the diffraction rings produced in carbon disulphide by X-rays; and S. Procopiu, the depolarization of light by carbon disulphide containing particles in suspension; and R. Gans, the Tyndall effect. T. M. Lowry considers that the sp. inductive capacity and the index of refraction give no evidence of internal ionization in the molecule. A. S. Ganesan studied the **scattering of light** by carbon disulphide.

The **electromagnetic rotation** of the plane of polarized light, has been measured by E. Verdet, who found when the value for the *E*-line is unity at 25°, 17·07 for the *G*-line; for the *F*-line, 1·234; for the *D*-line, 0·768; and for the *C*-line, 0·592. The subject has been investigated by A. de la Rive, A. Haagen, E. O. Hulbert, A. Kündt and W. C. Röntgen, and E. Bichat. J. E. H. Gordon obtained 0·05238 for the Tl-line at 13°. For the Na-line, Lord Rayleigh gave 0·04200 at 18°;

G. Quincke, 0·04409 (21·06°); A. Köpsel, 0·04199 (18°); E. Becquerel, 0·04341 (0°); and J. W. Rodger and W. Watson, at $\theta°$, $0·04347(1-0·001696\theta)$. Carbon disulphide, unlike other liquids hitherto examined, was found by A. Cotton and H. Mouton to have a negative **magnetic double refraction.** The **electric double refraction** was studied by C. F. Hagenow, C. Bergholm, G. W. Elmén, and W. König. N. Lyon and F. Wolfram measured the effect of temp. between 18° and —78·5° on the electrical double refraction. Kerr's constant was measured by G. Quincke, and O. D. Tauern; the latter gave $30·42\times10^{-8}$ for Na-light. C. Bergholm, and M. Pauthenier investigated the temp. coeff. of the electro-optical Kerr's effect; and L. Ebert, the dielectric polarization. The **absorption spectrum** of the liquid in the visible and ultra-violet regions was examined by F. F. Martens,[9] J. Pauer, and W. Spring; and in the ultra-red, by H. Rubens; the absorption spectrum of the vap. in the visible and ultra-violet was examined by J. Pauer, G. Bruhat and M. Pauthenier, and J. Dewar and G. D. Liveing; and in the ultra-red by E. von Bahr. J. Pauer, F. F. Martens, and E. Flatoff examined the absorption spectrum of soln. of carbon disulphide. R. D. Kleeman investigated the ionization of the vap. by secondary **$\gamma$-rays.** M. Ishino and B. Arakatsu found that negatively charged sulphur atoms are produced by the action of **$\alpha$-rays** in the positive-ray tube. W. H. Keesom and J. de Smedt studied the diffraction of **X-rays** in the liquid. K. T. Compton calculated the **ionizing potential** at 3·57 volts. J. Müller and C. H. L. von Babo studied the fluorescence of the flame of burning carbon disulphide.

According to T. Sidot,[10] metals like silver, aluminium, and iron are electrified by friction with carbon disulphide. L. Bleekrode found the liquid to have a very low **electrical conductivity**; and M. Saïd-Effendi gave 0·055 for the conductivity when that of water is unity. G. di Ciommox gave for the **specific resistance** of carbon disulphide $1·2\times10^{12}$ rec. ohms. Many others have made observations on this subject. Carbon disulphide was found by M. Lapschin and M. Tichanowitsch not to be decomposed by the current from 950 Bunsen's cells. A. C. Becquerel found that when an aq. soln. of carbon disulphide is electrolyzed, sulphuric acid and carbon dioxide appear at the positive pole, and hydrogen sulphide and hydrocarbons at the negative pole. J. Hopkinson [11] found the **dielectric constant** of liquid carbon disulphide to be 2·61 for $\lambda=\infty$; L. Kahlenberg and R. B. Anthony gave 2·63 at 23·5; and A. Francke, 2·63. P. Drude obtained 2·64 at 17° for $\lambda=73$ cms. K. Tangl gave 2·626 at 20°; and C. Bergholm, 2·74 at —20°; 2·676 at 0°; 2·626 at 20°; and 2·573 at 41·5°. K. Bädeker gave 1·00239 for the dielectric constant of the vap. at 100°, and I. Klemencic, 1·00905 at 0° and atm. press. P. Walden and co-workers, and W. H. Martin studied this subject; H. Isnardi measured the effect of temp., and F. Waibel, the effect of press. on the dielectric constant of carbon disulphide. M. Grützmacher measured the dielectric constant of mixtures of carbon disulphide with carbon tetrachloride, and with benzene, and also that of the components of the binary mixtures. For the **magnetic susceptibility**, G. Meslin [12] gave $-0·59\times10^{-6}$ mass units; S. Henrichsen, $-0·74\times10^{-6}$ vol. units at 20°; H. du Bois, $-0·82\times10^{-6}$ vol. units at 15°; and G. Quincke, $-0·76\times10^{-6}$ vol. units at 19°.

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## § 42. The Chemical Properties of Carbon Disulphide

The decomposition of carbon disulphide by **heat** has been previously discussed. H. Buff and A. W. Hofmann said that carbon disulphide vap. is slowly decomposed by a red-hot, electrically-heated platinum wire. L. Playfair [1] said that carbon disulphide is not decomposed when passed over red-hot pumice or charcoal. H. B. Baker said that the vap. decomposes between 200°–218°. H. B. Dixon and E. J. Russell observed that a prolonged heating is necessary at 230° before the slightest evidence of any decomposition of the disulphide can be detected, and no change is perceptible when carbon disulphide is passed through a tube at 400°; at a red heat, however, carbon disulphide was found by M. Berthelot to be resolved into its elements. In the presence of carbon, said W. Stein, the amount decomposed at a red heat is very small, and consequently, an excess of carbon is used when carbon disulphide is being prepared. J. H. van't Hoff showed that carbon disulphide, being an endothermal compound, fits in with his rule that a rise of temp. favours those substances formed with an absorption of heat. For an endothermal compound, $C+2S=CS_2-26$ Cals., carbon disulphide is fairly stable. T. E. Thorpe showed that when a small quantity of mercuric fulminate is detonated in the vap. of carbon disulphide, sulphur and carbon are formed, but not by the **mechanical shock** which attends the explosion of gunpowder, etc. In accord with M. Berthelot's theory:

> The shock of the explosion communicates to the layer of the gaseous mols. in immediate proximity to the fulminate an enormous active force, whereby the mol. edifice is shaken to pieces, and the initial active force is augmented to a degree corresponding to the heat evolved by the decomposition of the gas. A new shock is thereby produced in the next layer, and the action is repeated and so propagated until the molecular system is completely destroyed.

According to O. Loew,[2] when carbon disulphide is exposed for many months to **sunlight**, while protected from air, it decomposes, forming sulphur and a brown sulphide, $C_nS_n$. T. Sidot, and S. Kern made observations on the decomposition

of carbon disulphide when exposed to light. H. B. Dixon and E. J. Russell, B. von Lengyl, and J. Jamin and G. Maneuvrier, likewise observed the decomposition of the liquid in the light from an electric arc. G. Bruhat and M. Pauthenier observed that carbon disulphide in a quartz cell deposits sulphur when exposed to the light from a mercury arc-lamp. The long-wave limit of decomposition was $\lambda=366\mu\mu$. A. W. Hofmann found that carbon disulphide vap. is not decomposed by **electric sparks.** S. M. Losanitsch found that under the influence of the silent discharge, carbon disulphide vap. is converted into a polymeride, $(CS_2)_n$, and an almost black substance, which decomposes into its components when heated. A mixture of carbon disulphide and **hydrogen** under the influence of the silent discharge furnishes a brown substance, $C_3H_2S_6$, which M. Berthelot described as a compound, $C_2H_2S_4$. The action of heat on a mixture of carbon disulphide and hydrogen was studied by M. Berthelot, A. Cossa, and A. V. Harcourt; R. Witzeck investigated the heating of the mixture in a sealed tube at 250°–370°. If treated with zinc and hydrochloric acid, A. Girard, and A. Gawalowsky reduced carbon disulphide to trimolecular thioformaldehyde, $(CH_2S)_3$. A. Mittasch found that if the mixed vapours are passed over heated nickel, mercaptan products are obtained. According to E. V. Evans and H. Stanier, carbon disulphide vapour mixed with coal-gas and passed over heated nickel is reduced, and the main reaction is symbolized: $CS_2+2H_2=C+2H_2S$. The nickel is converted into subsulphide which acts as a cyclic catalyst. The presence of thoria, alumina, or chromic oxide acts as a promotor. The reaction is utilized in C. Carpenter and E. V. Evans' system of purifying coal-gas from carbon disulphide. G. Just studied the solubility of hydrogen in carbon disulphide.

Carbon disulphide very readily inflames in **air,** and burns with a blue flame, according to W. A. Lampadius;[3] or a white and purple-red flame, according to L. N. Vauquelin and P. J. Robiquet. J. J. Berzelius and A. Marcet exploded a mixture of carbon disulphide and **oxygen** by an electric spark, and obtained sulphur dioxide and carbon dioxide as products of the combustion when the supply of oxygen is great enough, but if the supply of oxygen be small, carbon monoxide is produced as well. According to G. R. Stewart and J. S. Burd, in the combustion of mixtures of 2·5–4·0 per cent. of carbon disulphide and air, from 40–60 per cent. of the carbon disulphide is oxidized according to the equations, $CS_2+3O_2=CO_2+2SO_2$; from 25–35 per cent. follows the reaction, $2CS_2+5O_2=2CO+4SO_2$; the remainder is unchanged. Sulphur trioxide does not seem to be formed. With a mixture containing 2·5 per cent. of carbon disulphide, the resulting gases contain about 15 per cent. of oxygen, 1 per cent. of carbon dioxide, usually less than 1 per cent. of carbon disulphide and carbon monoxide, and about 4 per cent. of sulphur dioxide. H. B. Baker showed that thoroughly dried vap. of carbon disulphide mixed with dried oxygen explodes just as readily as when moisture is present. A. Pedler found the heat developed during the explosion of a mixture of air and oxygen is so great that some nitrogen is oxidized, and the nitrogen oxide combines with the sulphur dioxide so that the gaseous product of the explosion occupies a less vol. than corresponds with $CS_2+3O_2=CO_2+2SO_2$. G. S. Turpin observed that carbon disulphide undergoes a slow combustion when heated with air or oxygen, forming a reddish-brown solid, which N. Smith found to have the composition $C_{16}H_6O_4S_8$. H. B. Baker concluded that combustion must be preceded by decomposition into carbon and sulphur, and suggests as a possible explanation of the combustion of pure carbon disulphide that, in this nascent state, carbon and sulphur may combine with oxygen, whether dry or not. H. B. Dixon and E. J. Russell found that if a stream of air and oxygen be passed over carbon disulphide, and the mixture flows through a tube at 200°, there is a gentle phosphorescent combustion resulting in the formation of sulphur dioxide and the condensation of a reddish-brown volatile substance. They found no signs of the resolution of carbon disulphide into its elements prior to combustion either when the gases are passed through a steady flame, as in A. Smithells' separator, or at the

high temp. of the explosion wave. When the gases are exploded over mercury, a black deposit may be formed, but this is finely divided mercury sulphide. A. Laffite showed that the spectrum of an exploding mixture of carbon disulphide and oxygen is continuous. The **rate of explosion,** in metres per second, with mixtures containing one molar proportion of carbon dioxide and $n$ molar proportions of oxygen, is :

| $n$ . . . | 1 | 1·5 | 2 | 3 | 4 | 5 | 6 |
|---|---|---|---|---|---|---|---|
| Rate explosion | 1592 | 1702 | 1751 | 1802 | 1753 | 1732 | 2640 |

The maximum velocity is thus obtained when sufficient oxygen is present to burn the carbon and sulphur respectively to their dioxides. The explosion wave is not propagated in the mixture $CS_2+\frac{1}{2}O_2$. According to H. le Chatelier and O. Boudouard, the lower limit of inflammability is with mixtures containing 0·063 grm. of carbon disulphide per litre of air. H. B. Dixon and E. J. Russell said that the mixture richest in carbon disulphide which can be made to detonate or give the explosion wave contains one vol. of oxygen to 1·5 vols. of carbon disulphide vap. ; and in the other direction the limit is not so quickly reached, for mixtures containing 6–7 vols. of oxygen and one vol. of carbon disulphide vap. still detonate. They found that the reaction which takes place when carbon disulphide is exploded with oxygen could not be expressed by any simple equation : (*a*) When excess of oxygen is used, the products are carbon dioxide, sulphur trioxide, sometimes free sulphur ; and in the explosion wave, carbon monoxide, carbonyl sulphide, and unchanged carbon disulphide. (*b*) With an insufficient quantity of oxygen, the products are carbon dioxide, sulphur dioxide, carbon monoxide, carbonyl sulphide, and carbon disulphide. When the amount of oxygen is successively diminished, the quantity of sulphur dioxide falls off, and that of the carbon monoxide, carbonyl sulphide, and unchanged carbon disulphide increases. (*c*) Even with small amounts of oxygen, there is always a division of the oxygen between the carbon and sulphur. Using a mixture, $CS_2+\frac{1}{2}O_2$, only a portion of the carbon disulphide takes part in the reaction. P. Laffite studied the formation of the explosion wave in mixtures of oxygen and carbon disulphide. H. T. Tizard and D. R. Pye noted the formation of hydrogen sulphide when a mixture of carbon disulphide vap. and moist air is exploded : $CS_2+2H_2O=2H_2S+CO_2$. When burnt in the Smithells' separator, the phenomena are altogether different from those observed in the explosions. The interconal gases consist of nearly equal vols. of sulphur dioxide and carbon monoxide, together with sulphur vap. and some unchanged carbon disulphide, and small quantities of carbonyl sulphide and carbon dioxide. W. A. Lampadius said that carbon disulphide takes fire in air below 100°, and it is said by M. Berthelot to be more inflammable than ether. J. J. Berzelius and A. Marcet estimated the **ignition temperature** to be "just above the b.p. of mercury"—*i.e.* 357°–358°. E. Frankland gave 149° ; R. Böttger, 228° ; H. B. Baker gives the ignition point of carbon disulphide mixed with oxygen as 258°–260°. G. S. Turpin states that when carbon disulphide is mixed with ten times its vol. of oxygen, the slow combustion develops into ignition at 160° ; and when mixed with ten times its vol. of air it ignites at 290°. H. B. Dixon and E. J. Russell stated that the change from the slow phosphorescent combustion to actual ignition is not sharp, and that carbon disulphide cannot be said to have any definite ignition point. In some cases they ignited a mixture of oxygen and carbon disulphide below 180°, at other times no ignition occurred at 230°. E. Berl and H. Fischer gave for the explosion limits of mixtures of air and carbon disulphide vap. in a glass globe 27 mm. diameter, 2·22 and 31·20 per cent. carbon disulphide, and in a glass globe 18 mm. diameter, 2·69 and 30·20 per cent. In an iron vessel at ordinary temp. 3·38–29·20, and at 100°, 1·35–33·10 per cent. According to T. Wulf, E. Sell, B. Delachanal and A. Mermet, and M. Tiffereau a mixture of carbon disulphide vap. with oxygen burns with a very bright blue flame which is particularly rich in actinic rays, and is applicable to photographic work. H. C. C. Dibbits studied the spectrum of the carbon disulphide flame. According to E. Pringsheim :

The temp. of the flame of carbon disulphide can be made very low; the light is not brilliant but is distinctly blue and can readily be seen in a darkened room. The temp. is so low and the amount of heat generated is so small that one can hold one's finger in the flame indefinitely without feeling more than a moderate sensation of heat. . . . The carbon disulphide flame was regulated so that it just burned; the flame was very long and pointed in shape. Repeated measurements with a thermocouple, at the hottest portion of the flame just below the point, gave temp. between 114° and 146°. We can therefore say definitely that this flame continues burning at temp. below 150°, below the ignition temp. of the inflammable mixture which gives rise to the flame. The light emitted by this flame has a very considerable photographic action. . . . The flame gives a continuous spectrum which is much weaker in the red part than in the blue and violet; it is very like the spectrum obtained when sulphur or hydrogen sulphide burns in the air. There can be no doubt but that we are dealing with gases which luminesce in consequence of chemical reactions and not in consequence of high temp.

According to M. Berthelot, a mixture of air and carbon disulphide vap. may be exposed to diffused daylight for a year without any change taking place, but if exposed to bright sunlight, some reaction takes place in an hour or two, and a yellowish-white substance is deposited which contains sulphur, carbon, and oxygen, whilst carbon monoxide and carbon dioxide are also formed, and remain mixed with the residual oxygen and the nitrogen. No nitrogen enters into combination, and in this respect the action of light differs from that of the silent electric discharge. The most important point about the reaction is that the light has no effect until it reaches a certain and somewhat high intensity; it is, therefore, analogous to the many reactions that do not take place below a particular temp. J. J. Berzelius and A. Marcet said that when carbon disulphide is kept under water for a long time in vessels containing air, it acquires a yellow colour, and is partially oxidized to sulphur and carbon dioxides. According to O. Loew, the slow action of **water** on carbon disulphide in sunlight produces a little formic acid; and when carbon disulphide is heated with water and iron filings in a sealed tube at 100°, ferrous formate, iron sulphide, carbon dioxide, and two sulphur compounds are formed. N. Smith found that the slow combustion of carbon disulphide in the presence of water vap., at 175°–180°, furnishes a product with the composition $C_{16}H_6O_4S_8$. This compound has acidic properties, and an *ammonium salt* and a *silver salt*, $Ag_5C_{16}HO_4S_8$, were prepared. L. Gurwitsch observed that the reaction $CS_2+2H_2O=2H_2S+CO_2$ is catalyzed by partially dehydrated alumina hydrate. G. Chancel and F. Parmentier measured the **solubility**, $S$ grms. per 100 c.c. of soln., of carbon disulphide in water, and found

| | 0° | 10° | 15° | 20° | 25° | 30° | 40° | 45° | 49° |
|---|---|---|---|---|---|---|---|---|---|
| $S$ . . | 0·204 | 0·194 | 0·187 | 0·179 | 0·169 | 0·155 | 0·111 | 0·070 | 0·014 |

A. Rex gave at 0°, 10°, 20°, and 30° respectively 0·258, 0·239, 0·217, and 0·195 grm. of carbon disulphide per 100 grms. of water. According to W. Herz, at 22°, 100 c.c. of water dissolve 0·174 c.c. of carbon disulphide, and the vol. of the soln. is 100·208 c.c., and the sp. gr. 0·9981; reciprocally, 100 c.c. of carbon disulphide dissolve 0·961 c.c. of water and the vol. of the soln. is 100·961, and the sp. gr. 1·253. The solubility of carbon disulphide in water was also measured by E. M. Péligot, W. T. Page, F. Sestini, M. Ckiandi-Bey, and J. B. A. Dumas. P. Villard said that no **hydrated carbon disulphide** can be formed at ordinary press., but at 75 atm. press. crystals of a hydrate are formed between 0° and 1°. M. Berthelot reported $2CS_2.3H_2O$; M. Ballo, $CS_2.H_2O$; and E. Duclaux, $2CS_2.H_2O$. A. Marcet, V. Wartha, and F. P. Venable have made observations on possible hydrates. According to C. Caigniard de la Tour, when the temp. of a mixture of water and carbon disulphide in a sealed glass tube is gradually raised, the mixture becomes turbid, then clear. The colour at first is greenish but gradually darkens, becoming at last nearly black. The carbon disulphide rises to the top of the water and then passes into the state of vap. On cooling, the green colour of the water changes to yellow, and the undecomposed carbon disulphide again sinks to the bottom. F. Schlagdenhauffen obtained a mixture of carbon dioxide and hydrogen sulphide by heating

the mixture of water and carbon disulphide in a sealed tube at 150°. M. Berthelot found that a mixture of the vap. of carbon disulphide and water give methane and ethylene when passed over iron or copper at a dull red-heat. At lower temp., said R. Witzeck, some carbonyl sulphide is formed. By heating the mixture of water and carbon disulphide under press., P. Schützenberger obtained crystalline *carbon hydrosulphide*, $CS_2.H_2S$.

According to H. Moissan,[4] the vap. of the carbon disulphide inflames when in contact with cold **fluorine**; and if a current of fluorine is passed into the liquid disulphide each bubble of gas becomes luminous. A mixture of carbon and sulphur fluorides is produced, but no free carbon. J. J. Berzelius and A. Marcet observed that carbon disulphide is decomposed by **chlorine.** According to B. Rathke, dry chlorine at ordinary temp. reacts very slowly with carbon disulphide, forming sulphur chloride, carbon tetrachloride, and some thiocarbonyl chloride. A. Mouneyrat found that aluminium chloride acts as a catalyst on the reaction; B. Aronheim, molybdenum pentachloride; and A. W. Hofmann, antimony pentachloride. In the presence of iodine, P. Klason, and B. Rathke found that chlorine reacts with carbon disulphide producing sulphur chloride, carbon tetrachloride, and perchloromethyl mercaptan, $CCl_3.SCl$. R. Weber also obtained red crystals of sulphur chloroiodide, $ICl_3.SCl_4$. P. Klason investigated the different stages in the reaction between chlorine and carbon disulphide. H. Müller investigated the action of chlorine on boiling iodiferous carbon disulphide. Moist chlorine was found by H. Kolbe to act more rapidly than the dry gas, and he obtained *trichloromethyl sulphuryl chloride*, $CCl_3.SO_2Cl$, as a product of the reaction, and B. Rathke, and M. Albrecht obtained *perchloromethylmercaptan*, or **thiocarbonyl tetrachloride,** $CCl_3.SCl$. According to H. Kolbe and A. W. Hofmann, when a mixture of dry chlorine, and the vapour of carbon disulphide is passed through a red-hot tube, sulphur chloride and carbon tetrachloride are formed. C. Hell and F. Urech obtained an oil, **carbon disulphotetrabromide,** $CS_2Br_4$, when dry **bromine** is allowed to stand in contact with carbon disulphide for several days, or when a mixture of carbon disulphide and bromine water is allowed to stand for some time. M. I. Konowaloff and W. Plotnikoff obtained a number of compounds of carbon disulphide with bromine, aluminium bromide, ethyl bromide, bromoform, etc. —*e.g.* $CS_2Br_4.AlBr_3$; $CS_2Br_4.2AlBr_3$; $CS_2Br_4.AlBr_3.CHBr_3$; $CS_2.2AlBr_3.2C_2H_5Br$; $CS_2Br_2.AlBr_3.C_2H_5Br$; $CS_2AlBr_3(CH_2Br.CH_2Br)$; and $CS_2.AlBr_3(CH_3.CHBr_2)$. F. Urech, and J. Habermann obtained carbon tetrabromide by the action of bromine on carbon disulphide in the presence of water or alkali-lye, and exposed to sunlight. T. Bolas and C. E. Groves found that when a mixture of carbon disulphide and bromine is heated for a long time in a sealed tube at 180°–200°, carbon tetrabromide is formed. R. Höland, and T. Bolas and C. E. Groves found that the reaction is accelerated by the presence of iodine, or by the bromides of antimony, arsenic, bismuth, gold, etc.; and A. Mouneyrat, by aluminium chloride. R. Weber showed that **iodine trichloride** acts like chlorine in the presence of iodine. J. B. Hannay represented the reaction: $4CS_2+6ICl_3=2CCl_4+2CSCl_2+3S_2Cl_2+3I_2$; it was also studied by R. Weber. The solubility of bromine in carbon disulphide has been investigated by H. Arctowsky—*vide* bromine. The solubility of **iodine** in carbon disulphide, and the partition of bromine and of iodine between water and carbon disulphide was measured by M. Berthelot and E. Jungfleisch, E. Angelescu and D. Dumitrescu, and A. A. Jakowkin—*vide* iodine. The sp. ht. of soln. of iodine and of bromine in carbon disulphide were measured by J. C. G. de Marignac. E. Drechsel found that carbon disulphide is not attacked by **hydriodic acid** in a sealed tube at 150°; M. Berthelot studied the action of carbon disulphide and **hydrogen iodide** at a red heat and noted that methane is produced. A. J. Balard found that the vap. of carbon disulphide explodes when in contact with **chlorine monoxide,** forming carbon dioxide, sulphuric acid, sulphur chloride, and chlorine; P. Schützenberger found that with chlorine monoxide, carbonyl and thionyl chlorides are produced. A. J. Balard found that with a soln. of **hypochlorous**

**acid,** chlorine, carbon dioxide, and sulphuric and hydrochloric acids are produced. I. C. Ritsema represented the action of alkali **hypochlorite** by $8KOCl+CS_2+6KOH=2K_2SO_4+K_2CO_3+8KCl+3H_2O$. W. M. Dehn said that when carbon disulphide was treated with sodium **hypobromite,** the oil disappeared rapidly, and enough heat was developed to boil the unchanged carbon disulphide. When treated with different quantities of sodium hypobromite, soln. were obtained containing sulphide, sulphite, sulphate, formate, and carbonate. An excess of sodium hypobromite yielded quantitatively the sulphur as sulphate. According to C. Cagniard de la Tour, if a mixed aq. soln. of **potassium chlorate** and carbon disulphide is heated in a sealed tube, the liquid effervesces and some sulphur is formed. On opening the cooled tube, a gas escapes and the water has an acid reaction. A. Ditte represented the reaction between **iodic acid,** water, and carbon disulphide by the equations: $2HIO_3+CS_2=I_2+CO_2+H_2SO_4+S$; and $2HIO_3+2CS_2+2H_2O=2CO_2+2HI+H_2SO_4+H_2S+2S$. F. Schlagdenhauffen found that iodic acid, **bromic acid,** and the **iodates, bromates,** and **chlorates,** and hypochlorites oxidize carbon disulphide when heated in a sealed tube, forming hydrogen halide, a metal halide, etc. The solubility of **sulphur** in carbon disulphide has been studied by G. Gore,[5] A. Cossa, H. Arctowsky, etc.—*vide* sulphur. J. J. Berzelius studied the properties of the soln. The sp. gr. of the soln. has been measured by G. J. Pfeiffer; the sp. ht. by J. C. G. de Marignac; and the refractive index by V. Berghoff, and C. Forch. The solubility of **selenium** in carbon disulphide was measured by E. Mitscherlich and G. Gore,—*vide* selenium. G. Gore investigated the solubility of the **sulphur and selenium chlorides, bromides** and **iodides** (*q.v.*) in carbon disulphide. According to P. Schützenberger, if a mixture of **hydrogen sulphide** and the vap. of carbon disulphide be passed through a tube cooled to −25°, an unstable crystalline compound, *carbon hydrosulphide*, $CS_2.H_2S$, is formed; and, according to M. Berthelot, if the mixture be passed over copper or iron at a dark red heat, methane and ethylene are produced. According to J. J. Berzelius, soln. of the **alkali sulphides,** and, according to B. Holmberg, soln. of the **alkali hydrosulphides,** absorb carbon disulphide and form alkali thiocarbonate, in the latter case with the development of hydrogen sulphide. According to A. Gélis, carbon disulphide unites with **sodium disulphide,** $Na_2S_2$, to form *sodium perthiocarbonate*, $Na_2CS_4$, with the development of heat. F. Sestini studied the solubility of carbon disulphide in liquid **sulphur dioxide;** he found that mixtures of sulphur dioxide and carbon disulphide, dry or moist, do not give carbon monoxide when heated. M. Albrecht found that when carbon disulphide is boiled with **potassium sulphite** in the presence of some alcohol potassium methyl mercaptan trisulphonate, $HS.C(KSO_3)_3$, is formed. According to A. Geuther, carbon disulphide is miscible with **sulphuric acid** free from water. M. Brault and A. B. Poggiale found that carbon disulphide is decomposed by cold sulphuric acid, forming sulphur and carbon; and when a mixture of the vap. of these two substances is passed through a red-hot tube, carbon monoxide, sulphur dioxide, hydrogen sulphide, and sulphur are formed. H. E. Armstrong represented the reaction at 100° between **sulphur trioxide** and carbon disulphide by the equation $SO_3+CS_2=S+SO_2+COS$. J. Dewar and G. Cranston found that **chlorosulphonic acid** reacts in an analogous manner.

M. Berthelot [6] noted that under the action of the silent discharge a mixture of carbon disulphide vap. and **argon,** in the presence of the liquid at 20°, showed the argon to be absorbed, and he believed that combination occurred. He also studied the absorption of **helium** and **nitrogen** by carbon disulphide. G. Just measured the solubility of nitrogen in the liquid. According to J. J. Berzelius and A. Marcet, dry **ammonia** is slowly absorbed by carbon disulphide producing a substance whose composition depends on the conditions of the experiment. W. C. Zeise said that no ammonium carbonate is formed, but the dark brown liquid which is produced contains ammonium thiocarbonate and thiocyanate. N. A. E. Millon found that if evaporated in moist ammoniacal air, the vap. is oxidized, forming a dense cloud. A. Laurent, J. Tcherniac and H. Gunzburg, H. Debus, M. Freund and G. Bachrach,

G. J. Mulder, and C. H. van Zouteveen also studied the reaction in aq. or alcoholic soln. Carbon disulphide dissolves abundantly in alcohol sat. with ammonia gas, and, added W. C. Zeise :

> The soln. remains alkaline, even with a large excess of carbon disulphide. Even when protected from the air it soon turns yellow, then brown, and smells of hydrogen sulphide. After the lapse of from 10 to 30 mins., it deposits yellow feathery crystals of ammonium thiocarbonate ; then more shining crystals of ammonium thiocyanate are formed, while those of the carbonatohydrosulphide diminish in quantity. The alcoholic liquid still retains very large quantities of ammonium thiocyanate and hydrosulphide, which, on distillation or exposure to the air, are resolved into ammonium hydrosulphide which escapes, sulphur which crystallizes out, ammonium thiocyanate which remains in soln. In the first stage of the reaction three mols. each of ammonia and carbon disulphide react to form a mol. each of ammonium thiocarbonate and thiocyanate ; the decrease in the proportion of the former, the increase in the proportion of the latter, and the formation of ammonium sulphide are probably due to a reaction between two mols. of thiocarbonate and one mol. of ammonia, to form three mols. of hydrogen sulphide, and one of thiocyanic acid.

According to A. Goldberg, if carbon disulphide and alcoholic ammonia are heated at 60° under press., one-half the sulphur is converted into ammonium sulphide, and he attempted to apply the reaction in quantitative analysis. At a red-heat, ammonia and carbon disulphide vap. were stated by F. Schlagdenhauffen to react. According to G. Inghilleri, when carbon disulphide and **ammonium carbonate** are heated in a sealed tube at 100°–110°, ammonium dithiocarbonate is produced ; at 120°–130°, ammonium thiocyanate ; and at 160°, an almost quantitative yield of thiocarbamide is obtained ; if the mixture in alcoholic soln. is heated on a water-bath, an almost quantitative yield of ammonium thiocyanate is obtained. F. Beilstein and A. Geuther found that when the vap. of carbon disulphide is passed over heated **sodium amide,** sodium thiocyanate is formed. C. A. L. de Bruyn studied the reaction between **hydroxylamine** and carbon disulphide, which is attended by the separation of sulphur. A. Goldberg attempted to separate the sulphur from a mixture of carbon disulphide and benzene by the hydroxylamine reaction. T. Curtius and K. Heidenriech found that carbon disulphide and **hydrazine hydrate,** in the cold, form dithiocarbazinic acid, $H_2N.NH.CS.SH$ ; and M. Busch boiled a mixture of carbon disulphide with hydrazine and alcoholic soln. of potassium hydroxide and obtained thiodiazoldithiol. A. W. Browne and A. B. Hoel showed that the vap. of carbon disulphide is irreversibly and quantitatively absorbed by aq. soln. of **potassium or sodium azide** at room temp., and the use of the reagent as an absorbent in gas analysis was discussed by A. J. Currier and A. W. Browne.

The character of the flame furnished by a burning mixture of carbon disulphide vap. and nitric oxide has been indicated in connection with the oxygen and carbon disulphide flame. According to L. H. Friedburg, **nitric acid** at ordinary temp. has no action on carbon disulphide ; and, according to S. Cloez and E. Guignet, there is no reaction with the boiling acid ; but, according to M. Tiffereau, the carbon disulphide is oxidized at ordinary temp. if the mixture be exposed to sunlight. F. Schlagdenhauffen found that the mixed vap. of carbon disulphide and nitric acid passed through a red-hot tube form sulphuric acid and nitrous fumes. The vap. of carbon disulphide also reduces the **nitrites**. According to F. Schlagdenhauffen and M. Bloch, when an excess of **aqua regia** is distilled with carbon disulphide—either immediately after mixing or after contact for some hours—red nitrous fumes and unattacked carbon disulphide first pass over, followed by a very volatile substance, which can be condensed by using a freezing mixture of ice and salt ; it proved to be *trichloromethylsulphurous chloride*, $SO(OCCl_3)Cl$.

The solubility of **phosphorus** in carbon disulphide has been measured by A. Vogel,[7] H. Giran, etc.—*vide* phosphorus. J. C. G. de Marignac measured the sp. ht. of the soln., and V. Berghoff, the indices of refraction. M. Berthelot found the vap. of carbon disulphide and **phosphine** produce methane and ethylene when passed over copper or iron at dull redness. According to L. P. Cailletet and M. Bordet, when a mixture of dry phosphine and carbon disulphide is compressed,

no compound is formed, but in the presence of a little water, a white crystalline solid is deposited which dissociates when the temp. is raised, or the press. relieved. According to E. Drechsel, carbon disulphide and **phosphonium iodide** react in an iron tube at 150°, forming trimethyl phosphine hydriodide; and if an excess of carbon disulphide is used, H. Jahn found that methane is produced. A. W. Hofmann found that **triethylphosphine** unites with carbon disulphide, forming red prismatic crystals, $P(C_2H_5)_3.CS_2$. The solubilities of the **chlorides, bromides, and iodides of phosphorus, arsenic, and antimony** in carbon disulphide have been measured by G. Gore. L. Carius, and B. Rathke studied the action of **phosphorus pentachloride** and obtained thiocarbonyl chloride, etc. F. Schlagdenhauffen found that when carbon disulphide and **arsenious acid** or **arsenic acid** and the salts of these acids are heated in a sealed tube, arsenic sulphide is formed. According to A. W. Hofmann, carbon disulphide reacts vigorously with **antimony pentachloride,** forming carbon tetrachloride, antimony trichloride, sulphur, and sulphur chloride. B. Aronheim, A. Husemann, A. Bertrand and E. Finot also studied the reaction. H. Moissan found that the vap. of carbon disulphide attacks **boron** at a bright red heat, forming boron sulphide; he also found **boron triiodide** to be soluble in carbon disulphide. According to E. Frémy, **boron trioxide** is converted into the sulphide when heated in the vap. of carbon disulphide.

The adsorption of the vap. of carbon disulphide by **carbon** has been studied by J. Hunter,[8] A. Eiloart, J. N. Bronsted and V. K. la Mer, and J. Driver and J. B. Firth. According to S. M. Losanitsch, when the vap. of carbon disulphide and **ethylene** are exposed to the silent electric discharge, brownish-yellow *carbon ethylene disulphide*, $5CS_2.2C_2H_4$, is formed; with **acetylene,** black *carbon acetylene disulphide*, $3CS_2.2C_2H_2$, is produced; and with **carbon monoxide,** brown *carbon carbonyl disulphide*, $3CS_2.2CO$, is obtained. G. Just measured the solubility of **carbon dioxide** in carbon disulphide. E. Schöne said that carbon dioxide and disulphide form carbon monoxide and sulphur when passed through a red-hot tube; and C. Winkler said that some carbonyl sulphide is formed, particularly if the mixed gases are passed over heated platinized asbestos. The main reactions with carbon dioxide are represented: $CO_2+CS_2=2CO+2S$, and $CO+S+H_2O \rightleftharpoons CO_2+H_2S$; the secondary reactions: $CO+S \rightleftharpoons COS$; and $H_2S \rightleftharpoons H_2+S$. T. Carnelley found that when a mixture of vap. of carbon disulphide and **ethyl alcohol** is passed over copper at a dull red-heat, carbonyl sulphide, etc., are formed. C. Tuchschmidt and O. Follenius studied the solubility of carbon disulphide in c.c. per 100 c.c. of aq. soln. of ethyl alcohol at 17°, and found

| | | | | | | |
|---|---|---|---|---|---|---|
| Alcohol . . | 100 | 98·15 | 93·54 | 84·12 | 48·40 | 47·90 per cent. |
| $CS_2$ . . . | 90 | 132 | 70 | 30 | 2 | 0 c.c. |

F. Guthrie found a soln. of ethyl alcohol with 94·94 per cent. of carbon disulphide remains clear down to −18·4°; with 89·54 per cent. $CS_2$, it becomes turbid at −14·4°; with 79·96 per cent. $CS_2$, it becomes turbid at −16·1°; with 65·11 per cent. $CS_2$, it becomes turbid at −17·7°; and soln. with 59·58 to 29·92 per cent. $CS_2$, remain clear down to −20°. E. C. McKelvy and D. H. Simpson studied the solubility in ethyl alcohol and in **methyl alcohol.** V. Rothmund found that with methyl alcohol two layers are formed and that the percentage amounts of carbon disulphide in the two layers are:

| | 10° | 20° | 25° | 30° | 35° | 40·5° |
|---|---|---|---|---|---|---|
| $CH_3OH$ layer . . | 45·1 | 50·8 | 54·1 | 58·4 | 64·0 | 80·5 |
| $CS_2$ layer . . . | 98·3 | 97·2 | 96·4 | 95·5 | 93·5 | 80·5 |

The critical soln. temp. is 40·5°. J. H. Schüller, J. C. G. de Marignac, A. Winkelmann, L. Frank, F. Guthrie, and F. D. Brown have studied the properties of mixtures of carbon disulphide with **ether, chloroform, benzene,** and **carbon tetrachloride**—*vide supra*. For the action of alcohols in the presence of alkalies—*vide infra*, the xanthogenates. Numerous reactions of carbon disulphide with organic compounds have been studied. According to C. Liebermann, **paraffin** can

absorb three times its weight of carbon disulphide, and has accordingly been recommended as an absorbent for the disulphide in desiccators. E. Frémy and A. Colson found that at a high temp. carbon disulphide reacts with **silicon,** forming silicon sulphide.

It will be observed that carbon disulphide has marked **solvent qualities;** it dissolves nitrogen chloride, hydrogen sulphide and persulphide, bromine, iodine, sulphur, selenium, arsenic, antimony, the chlorides of phosphorus, sulphur, selenium, arsenic, antimony, tin, titanium, sulphur dioxide, nitrogen oxides, carbonyl sulphide, etc. It also dissolves fats, oils, ethereal oils, resins, colouring agents, camphor, caoutchouc, gutta-percha, wax, paraffin, etc.—F. Schlagdenhauffen, G. Gore, etc.

According to J. J. Berzelius,[9] heated **potassium** takes fire in the vap. of carbon disulphide, and burns with a reddish flame, and becomes covered with a black crust, which dissolves in water with the separation of carbon. According to O. Loew, when **sodium** and carbon disulphide are heated in a sealed tube at 140°–150°, sodium sulphide and *sodium thiosesquicarbonate*, $Na_2C_2S_3$, are formed. The latter, with water, gives *thiosesquicarbonic acid*, $H_2C_2S_3$. L. Raab obtained a product, $C_5S_2$. By treating a liquid alloy of potassium and sodium with rectified carbon disulphide, T. E. Thorpe obtained a yellowish-brown powder which he said was more explosive than nitrogen iodide. Observations on the action of carbon disulphide on the alkali metals or their amalgams have been made by C. Löwig, H. Feigel, R. Hermann, C. Reichl and E. Guignet. When carbon disulphide vap. is passed over red-hot **copper** or **iron,** not sufficient to decompose it completely, it is converted into a rose-red liquid which contains carbon monosulphide and undecomposed disulphide; at the same time, the copper is converted into sulphide, and, added M. Cluzel, the sulphide is covered with a layer of carbonaceous matter, but L. J. Thénard and L. N. Vauquelin obtained no evidence supporting the latter statement. S. Kern also said that iron at ordinary temp. transforms carbon disulphide into the monosulphide; and, according to V. Merz and W. Weith, there is formed at 250°–270°, iron sulphide and a dark brown substance which is probably an iron sulphocarbide. The last-named also obtained with copper at 200°–250°, copper sulphide and a black carbon sulphide. A. Cavazzi passed the vap. of carbon disulphide over heated copper, iron, **silver, magnesium, zinc,** and **aluminium,** and obtained the metal sulphides and graphitoidal carbon; no compound of carbon with sulphur was observed to be formed. According to E. Lionnet, if a strip of **tin** foil be wrapped spirally about a gold or platinum wire, and dipped in carbon disulphide, tin sulphide and colourless crystals are formed. He thought the crystals were veritable diamonds (*q.v.*). P. Schützenberger passed the vap. of carbon disulphide over **platinum** sponge at 400°–450°, and obtained a *platinum sulphocarbide,* $Pt_2CS_2$.

J. J. Berzelius and A. Marcet found that the **alkaline earth oxides** are converted into sulphides and carbonates; and the former also found that **iron oxide, manganese oxide,** and **tin oxide** are converted into the corresponding sulphides and sulphur and carbon dioxides. Carbon disulphide is a powerful sulphurizing agent; according to E. Frémy,[10] *le plus energetique qu'on connaisse,* for it readily converts the metal oxides into their sulphides. F. Schlagdenhauffen obtained the corresponding sulphides by heating **lead oxide, zinc oxide, cobalt oxide, antimony oxide,** iron oxide, and manganese oxide, with carbon disulphide in a sealed tube at 250°. According to E. Frémy, and F. G. Reichel, carbon disulphide vap. converts red-hot **magnesia** and **alumina** into the corresponding sulphides. A. Gautier found that when carbon disulphide is passed over red-hot **china clay** (kaolin), carbonyl sulphide, silicon sulphide, and aluminium thiosilicate are formed; while with alumina, aluminium sulphide and carbonyl sulphide are formed. H. Rose found **tantalic oxide** is likewise converted into the sulphide.

Aq. soln. of **alkali hydroxides** slowly dissolve carbon disulphide, forming alkali carbonate and thiocarbonate: $6KOH+3CS_2=K_2CO_3+2K_2CS_3+3H_2O$. F. Sestini

also found that by digesting carbon disulphide and an aq. soln. of an **alkali carbonate** at 60°, carbon dioxide is evolved, and alkali thiocarbonate is formed. D. Walker, and F. Sestini found that an aq. soln. of **calcium hydroxide** at ordinary temp. or at 50°, furnishes orange-yellow needles of *calcium hydroxythiocarbonate*, $CaCS_3.Ca(OH)_2.6(\text{or } 7)H_2O$; **barium hydroxide,** and **magnesium hydroxide,** under similar conditions, form respectively *barium and magnesium hydroxythiocarbonates*; but carbon disulphide does not act on **zinc hydroxide.** G. Chancel and F. Parmentier found that when baryta-water is mixed with an aq. soln. of carbon disulphide, or with a mixture of carbon disulphide and water, very little action takes place at the ordinary temp., but if the mixture is heated an abundant precipitate of barium carbonate is formed, and the supernatant liquid becomes yellow. If the mixture is heated in sealed tubes at 100° for some time, the liquid gradually becomes colourless, and the amount of barium carbonate formed is greater than that calculated from the equation given by J. J. Berzelius, $3CS_2+6MOH=M_2CO_3+2M_2CS_3+3H_2O$. When carbon disulphide is heated with an excess of a somewhat dil. soln. of barium hydroxide at 100°, in sealed tubes previously filled with nitrogen, the reaction is represented by the equation: $CS_2+2Ba(HO)_2=BaCO_3+Ba(SH)_2+H_2O$. If the mixture is heated in contact with air, the same proportion of barium carbonate is formed, but it is mixed with a certain quantity of barium sulphate formed by the oxidation of the hydrosulphide. F. Schlagdenhauffen investigated the action of carbon disulphide on many salts. Molten **potassium nitrate** oxidizes the vap. to carbon dioxide, nitrous fumes, potassium thiocyanate, and sulphate; **potassium nitrite** behaves similarly; and when potassium or **lead nitrite** and carbon disulphide are heated in a sealed tube, carbon dioxide, the metal thiocyanate, etc., are formed. E. Obach found that carbon disulphide is scarcely affected by a cold soln. of **potassium permanganate,** but, according to S. Cloez and E. Guignet, a boiling soln. is quantitatively reduced, forming sulphuric acid, and carbon dioxide. F. Schlagdenhauffen found that carbon disulphide reduces **chromic acid** and the **chromates,** the lower oxide of chromium being formed when the mixture is heated in a sealed tube; similar results were obtained with **molybdic, tungstic, vanadic,** and **titanic acids.** He also found that many **metal salts** when heated with carbon disulphide in a sealed tube to 200°–250°, in the presence or absence of water, furnish sulphides, and carbon dioxide and the acids of the salts are set free—**cuprous chloride** is but little attacked at 250°, and **cuprous iodide** is not affected at 300°. H. Müller studied the behaviour of some metal salts towards carbon disulphide.

A. C. Becquerel, and F. Wöhler studied the action of a copper plate dipping in superposed layers of carbon disulphide and an aq. soln. of **cupric nitrate.** The former said copper suboxide, the latter said cupric sulphide, is deposited in the lower part. According to G. Gore, carbon disulphide dissolves **stannic chloride** and **titanic chloride.** H. Arctowsky measured the solubility of stannic chloride in carbon disulphide at low temp.; and he also found that at 20°, 100 grms. of a sat. soln. contained 0·042 grm. of **mercuric chloride,** or 0·187 grm. of **mercuric bromide,** or 0·320 grm. of **mercuric iodide.** C. E. Linebarger also measured the solubility of the three mercuric halides in carbon disulphide. H. Arctowsky also found **mercuric nitrate** is very soluble in boiling carbon disulphide; **ferric chloride,** and **lead nitrate** are also soluble in carbon disulphide, but most other salts of the metals are insoluble. B. Aronheim studied the effect of **molybdenum chloride** on carbon disulphide.

**Reactions of analytical interest.**—According to A. W. Hofmann,[11] carbon disulphide can be quantitatively determined by passing the vap. through an ethereal soln. of triethylphosphine; and the red crystalline compound $P(C_2H_5)_3.CS_2$ dried in vacuo and weighed; according to E. Fischer, M. Busch, and C. Liebermann and A. Seyewitz, the white compound it forms with phenylhydrazine, namely, $C_6H.NH.NH.CS.S.NH.NH.C_6H_5$, can be used in a similar manner. According to G. Chancel and F. Parmentier, carbon disulphide can be estimated by heating in a sealed tube at 100° a mixture of carbon disulphide and baryta-water; barium

sulphide is formed. This is converted into barium sulphate and weighed. According to G. Denigès, when a mercuric salt is warmed with carbon disulphide, a disulphohalide, $HgX_2.2HgS$, is formed as a characteristic crystalline precipitate. A. Goldberg treated carbon disulphide with aq. ammonia whereby a mixture of hydrosulphide and thiocyanate is formed: $CS_2+3NH_3 \rightarrow NH_4HS+NH_4CNS$. The sulphide is then titrated with ammoniacal soln. of a zinc salt. When carbon disulphide is treated with an alcoholic soln. of potassium hydroxide, potassium xanthate, $KS.CS.OC_2H_5$, is formed. This can be estimated by titration with standard cupric sulphate as recommended by H. Macagno, E. A. Grete, O. Hehner and W. L. Carpenter, or E. P. Harding and J. Doran: $2CuSO_4+4(KS.CS.OC_2H_5) = Cu(S.CS.OC_2H_5)_2+C_2H_5O.CS.S.S.CS.OC_2H_5+2K_2SO_4$. The copper xanthate can be converted to the oxide and weighed as recommended by H. Macagno, E. S. Johnson, or M. Ragg. The xanthate can be oxidized to sulphate by titration with standard permanganate as recommended by W. Schmitz-Dumont; with standard hydrogen dioxide as recommended by J. Petersen, or D. Stravorinus; or with potassium iodide after the soln. has been neutralized with sodium carbonate as recommended by L. G. Radcliffe, M. Gastine, or E. Rupp and L. Krauss.

**The physiological action of carbon disulphide.**—Carbon disulphide is a blood poison and is fatal to all forms of animal life.[12] Observations on animals show that it forms with the hæmoglobin of the blood, and this is attended by disintegration of the red corpuscles. There is anæsthesia of the whole body, and death occurs through paralysis of the respiratory centre. Artificial respiration does not restore life. It is a convenient agent for the destruction of noxious insects, moths, bugs, etc. It has also been recommended for exterminating rats and mice. Frogs and cats are said to be less affected by carbon disulphide than are birds, rabbits, and guinea-pigs. In factories, where carbon disulphide is used daily for dissolving caoutchouc, etc., it acts as a chronic poison, producing peripheral neuritis, and disorders of the digestive tract. T. Bokorny studied the action of carbon disulphide on plants; B. Heinze, and K. Störmer, on soils; and P. Zöller, H. Schiff, and M. Ckiandi-Bey, its action on bacteria.

**The uses of carbon disulphide.**—Carbon disulphide is employed in the vulcanization of rubber; in the extraction of essential oils; and as a solvent for oils, fats, and waxes; it is used in the preparation of carbon tetrachloride, ammonium thiocyanate, viscose or artificial silk, and many organic compounds; as an insecticide in the preservation of grain and foods; in the preparation of antidotes to phylloxera; as a parasiticide; as a local anæsthetic; etc. In industrial work, special precautions have to be taken against the inflammability and poisonous nature of the fumes.


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## § 43. The Thiocarbonic Acids and the Thiocarbonates

The thiocarbonates were discovered by J. J. Berzelius [1] in 1826, and described in his paper: *Om svafnelsalter.* He noticed that carbon disulphide dissolves in a soln. of sodium sulphide, and when alcohol is added, sodium thiocarbonate is precipitated as a yellowish-brown oil; further, if dil. hydrochloric acid is added to sodium thiocarbonate, the free thiocarbonic acid, which he called *Kohlenschwefelwasserstoffsäure*, separates as a yellowish-red oil. W. C. Zeise called the acid *Rothsäure*, or *Hydrothiocarbonsäure.* The thiocarbonates are analogous to the carbonates with sulphur in place of oxygen; and carbon disulphide, by this view, is thiocarbonic anhydride, $CS_2$, and thiocarbonic acid is constituted $H_2CS_3$. The thiocarbonates are salts of the type $M_2'CS_3$. They are in general unstable, although thiocarbonic acid itself is much more stable than carbonic acid; a fact possibly associated with the gaseous character of the carbonic anhydride, and the liquid character of thiocarbonic anhydride at ordinary temp. Just as ordinary carbonic acid, $CO(OH)_2$, is metacarbonic acid, derived from orthocarbonic acid, $C(OH)_4$, by the loss of a mol. of water, so can ordinary thiocarbonic acid be regarded as **metathiocarbonic acid,** $CS(SH)_2$, derived from **orthothiocarbonic acid,** $C(SH)_4$, by the loss of a mol. of hydrogen sulphide. The ortho-acid is not known, but P. Cläsown prepared an oily liquid *ethyl orthothiocarbonate,* $C(SC_2H_5)_4$, by the action of carbon tetrachloride on sodium ethyl sulphide, $Na.S.C_2H_5$. There are six possible sulphur derivatives of metathiocarbonic acid, and they can be designated in many ways. A. Henninger applied the affix *sulpho-* when the oxygen atom of the carbonyl group is displaced by sulphur, and *thio-* when the oxygen atoms of the hydroxyl groups are displaced; or the affix *thiol-* or *thio-* can be used when sulphur displaces the oxygen of the hydroxyl groups, and *thion-* for a similar displacement in the carbonyl group. The sulphur atoms of the SH-groups can be designated $\alpha$-, and the sulphur atom of the CS-group, $\beta$-; and the acids with one, two, and three sulphur atoms respectively called mono-, di-, and tri-thiocarbonic acids with $\alpha$- or $\beta$-prefixed to represent the disposition of the sulphur atoms present. In the case of trithiocarbonic acid, of course no prefix is needed. Thus,

| $HO>CO$ | $HO>CS$ | $HS>CO$ | $HS>CS$ | $HS>CO$ | $HS>CS$ |
|---|---|---|---|---|---|
| Carbonic acid. | Sulphocarbonic acid; or thioncarbonic acid; $\beta$-thiocarbonic acid. | Thiocarbonic acid; or thiolcarbonic acid; $\alpha$-thiocarbonic acid. | Sulphothiocarbonic acid; or thiolthioncarbonic acid. $\alpha\beta$-dithiocarbonic acid. | Dithiocarbonic acid; or dithiolcarbonic acid; $\alpha\alpha$-dithiocarbonic acid. | Dithiolthioncarbonic acid; trithiocarbonic acid; usually thiocarbonic acid. |

It will be observed that thioncarbonic and thiolcarbonic acids are isomeric monothiocarbonic acids; and thiolthioncarbonic and dithiolcarbonic acids are isomeric dithiocarbonic acids. W. C. Zeise found that carbon disulphide dissolves in an alcoholic soln. of potassium hydroxide, forming *potassium ethylxanthate,* $C_2H_5O.CS.SK$. This is the potassium salt of what W. C. Zeise called *rotwerdended Salz* or *Xanthogensäure*, and is now called **xanthic acid** or **xanthogenic acid,** $C_2H_5O.CS.SH$—$\xi\alpha\nu\theta\acute{o}\varsigma$, yellow; $\gamma\epsilon\nu\nu\acute{a}\omega$, I generate—in allusion to the colour of the copper salt. When the potassium salt is treated with dil. sulphuric acid at 0°, the free acid is produced as an oily liquid. When heated to 24°, the acid decomposes into ethyl alcohol and carbon disulphide, and hence, unless xanthic acid undergoes some peculiar intra-molecular change before decomposition it is inferred that it cannot be constituted: $C_2H_5S.CS.OH$, or $C_2H_5S.CO.SH$. Xanthic acid is therefore the ethyl derivative of thiolthioncarbonic acid. Xanthic acid usually decomposes violently a few minutes after it has been prepared owing to the catalytic action of the alcohol formed as a product of its decomposition. If intimately mixed with phosphoric oxide, the acid is far more stable and it can be kept for weeks. The rate of decomposition of the acid is greatly influenced by the solvent. Thus, the velocity constant for ethyl alcohol is 1,000,000, and for carbon disulphide, unity.

There is no relation between the dielectric constant of the solvent and the speed of the reaction. H. von Halban and co-workers have studied the kinetics of the decomposition. The influence of different solvents on the speed of a reaction is well illustrated by the following experiment due to H. von Halban and A. Kirsch.

A soln. of 0·8 grm. of potassium xanthate in water at 0° is treated with 40 c.c. xylene and the calculated amount of ice-cold dil. sulphuric acid. The mixture is shaken vigorously in a separating funnel and the xylene soln. is removed, dried with calcium chloride, followed by phosphoric oxide; filtered and diluted to 50 c.c. If one c.c. of this soln. with 10 c.c. of the given solvent is treated with 10 c.c. of a soln. of 0·29 grm. of hydrated cobalt nitrate in 100 c.c. of alcohol, a dark green soluble cobaltic xanthate is formed, and some xanthic acid remains undecomposed. With ethyl alcohol and acetone as solvents, decomposition is complete in a few minutes; with nitromethane, the xanthic acid is not quite all decomposed after half an hour's action, and with glacial acetic acid after an hour's action; boiling for half an hour with chloroform, ether, benzene, carbon disulphide does not decompose all the xanthic acid.

Other alcohols give products analogous to xanthic acid, thus, J. B. A. Dumas and E. Péligot, P. Desains, and H. S. Fry made **methylxanthic acid,** $CH_3O.CS.SH$, by the action of magnesium on a soln. of carbon disulphide in methyl alcohol. *Potassium ethyl α-thiocarbonate,* $C_2H_5O.CO.SH$, prepared by H. Debus,[2] G. Chancel, and C. Bender is a derivative of thiolcarbonic acid; *diethyl β-thiocarbonate,* $C_2H_5O.CS.OC_2H_5$, prepared by R. Nasini; *ethyl chloro-β-thiocarbonate,* $C_2H_5O.CS.Cl$, prepared by P. Klason; and *xanthogenamide,* $C_2H_5O.CS.NH_2$, prepared by F. Salomon, H. Debus, and G. Chancel, are representatives of thioncarbonic acid; *potassium ethyl αβ-dithiocarbonate,* or xanthic or xanthogenic acid, $C_2H_5O.CS.SH$, prepared as indicated above, is a derivative of thiolthioncarbonic acid; *diethyl-αα-dithiocarbonate,* $C_2H_5S.CO.SC_2H_5$, prepared by R. Schmitt and L. Glutz, F. Salomon, and R. Seitfert, is a representative of dithiolcarbonic acid; and *monoethyl trithiocarbonate,* $C_2H_5S.CS.SH$, prepared by G. Chancel, and *diethyl trithiocarbonate,* $C_2H_5S.CS.SC_2H_5$, prepared by P. Klason, P. Schweitzer, H. Debus, A. Husemann, R. Nasini and A. Scala, and C. Löwig, are derivatives of trithiocarbonic acid.

As indicated above, *dithiolthioncarbonic acid,* or *trithiocarbonic acid,* or simply **thiocarbonic acid,** $H_2CS_3$, was prepared by J. J. Berzelius[3] by adding cold dil. hydrochloric acid to a soln. of a thiocarbonate. The acid separates as a dark yellow or reddish-brown oil. W. C. Zeise added that if too much acid is added in the preparation, the oil dissolves, and if the acid be too conc. hydrogen sulphide is evolved. J. G. O'Donoghue and Z. Kahan prepared it by slowly dropping a soln. of calcium thiocarbonate into conc. hydrochloric acid. Both soln. were previously cooled in a freezing mixture, and the vessel containing the mixture was allowed to stand for some time after all the calcium thiocarbonate soln. had been added. After an hour or two, the liquid was decanted, the last drops being separated with a separating funnel. The oil was sometimes washed rapidly with ice-cold water. It was then placed in a small flask surrounded by a freezing mixture, calcium chloride added, and the flask attached to a good pump until bubbles no longer appeared to arise from the oil. In this way hydrochloric acid and water were removed, and the oil was finally dried over phosphorus pentoxide. E. W. Yeoman found that if purified thiocarbonates are employed, and oxygen be excluded, no oil is produced at 0°; but if air has access, then an oily liquid slowly separates. Impure thiocarbonates, and purified perthiocarbonates give an oily liquid at ordinary temp. The red oil is therefore assumed to be **perthiocarbonic acid,** $H_2CS_4$, and it separates from the soln. owing to its insolubility; it is further assumed that thiocarbonic acid, $H_2CS_3$, is soluble in water. If this be correct, the following description refers to perthiocarbonic acid and not to thiocarbonic acid.

Thiocarbonic acid is an oily liquid with a disagreeable, pungent odour. J. G. O'Donoghue and Z. Kahan state that their analyses of the oil always showed an excess of sulphur beyond that required for $H_2CS_3$, so that it was inferred that the acid always holds some sulphur in soln. The oil can be distilled at 50° with decom-

position. Abortive attempts were made to distil the acid under diminished press. from a flask connected with two receivers surrounded by liquid air. J. J. Berzelius stated that the oil decomposed into carbon disulphide and hydrogen sulphide. According to J. G. O'Donoghue and Z. Kahan, thiocarbonic acid is soluble in alcohol, giving a yellow soln. which decomposes rapidly with deposition of sulphur and formation of carbon disulphide and hydrogen sulphide. It is also soluble in liquid ammonia, turpentine, toluene, ether, or chloroform, in all of which solvents it very soon decomposes, but is most stable in the two latter. H. von Halban and co-workers measured the rate at which the thiocarbonates decompose when dissolved in different solvents; they also measured the absorption spectra of soln. of trithiocarbonic acid and of its ethyl salt in chloroform, alcohol, light petroleum, ether, and toluene; and of the barium salt in water. Marked differences were obtained in the spectra of the acids and the salts. The existence of the free acid in the soln. was indicated by the similarity between the spectrum of a soln. of the sodium salt and that for a soln. of the acid in an organic solvent. In liquid air or solid carbon dioxide, this carbonic acid forms a pink solid which melts again to a red liquid on removing the refrigerator. The acid is insoluble in water, but is at once decomposed by it, with evolution of hydrogen sulphide and formation of carbon disulphide and sulphur. This also occurs in a soln. of common salt. It is much more stable towards strong acids, especially hydrochloric acid, under which it can be kept for several days if cool. The colour, however, gradually fades, and finally only carbon disulphide is left. In air, it gradually evaporates, often leaving a brownish-black residue consisting largely of sulphur. Sometimes it has been kept for a few days in a loosely-stoppered flask without any considerable loss. The oil dissolves flowers of sulphur readily with a slight darkening in colour, and it is possible, therefore, that the colour of the oil is due to dissolved sulphur. It does not burn on water like carbon disulphide. Sodium and potassium act on the dry oil or on its ethereal soln. Potassium decomposes it very violently, giving an immediate yellow, crystalline precipitate of potassium thiocarbonate, whilst, in the former case, sodium thiocarbonate gradually separates. Hydrogen sulphide and probably hydrogen are evolved in both cases. Magnesium powder has apparently little action on the oil, and on trituration with mercury a red solid is obtained. It is soluble in an excess of hydrochloric or sulphuric acid, and reacts with the alkali carbonates liberating carbon dioxide, and forming thiocarbonates.

J. J. Berzelius and A. Marcet found that carbon disulphide slowly absorbs ammonia to form a slightly yellow amorphous powder which can be sublimed; it absorbs water with avidity, forming first an orange-yellow soln., presumably of ammonium thiocarbonate, and then a lemon-yellow liquid, which is converted into ammonia, sulphuric acid, and carbonic acid. W. C. Zeise made **ammonium thiocarbonate,** $(NH_4)_2CS_3$, by mixing a sat. alcoholic soln. of ammonia with one-tenth of its vol. of carbon disulphide; cooling the mixture after it has become brown, pouring off the mother-liquor, washing the crystals several times with alcohol, then with ether, and finally drying the crystals by press. between filter paper. E. Mulder said that if the right proportions are used, the thiocarbonate alone crystallizes out. The mother-liquor was found by W. C. Zeise to contain much ammonium thiocarbonate and sulphide; and H. Debus said that when alcoholic ammonia and carbon disulphide react, ammonium thiocyanate and thiocarbamate are formed as well as ammonium thiocarbonate. Indeed, said J. G. O'Donoghue and Z. Kahan, the pale yellow, crystalline precipitate obtained by shaking dried carbon disulphide with a sat. soln. of ammonia in alcohol, behaves quite differently from ammonium thiocarbonate. E. W. Yeoman saturated with hydrogen sulphide a 20 per cent. soln. of dry ammonia in alcohol, and after warming to 35°–40° and simultaneously passing in hydrogen to exclude air, added a slight excess of carbon disulphide, and dry ether until a permanent turbidity was produced. On cooling the soln. slowly, red crystals separated. These were collected in hydrogen, washed with dry ether, and dried in a current of hydrogen at ordinary temp. A. Gélis

made ammonium thiocarbonate by the action of carbon disulphide on ammonium sulphide. J. G. O'Donoghue and Z. Kahan made it by the action of liquid ammonia on an alcoholic soln. of thiocarbonic acid; the yellowish-pink soln., on evaporation, gave a yellow solid which soon decomposed: $(NH_4)_2CS_3=(NH_4)_2S+CS_2$; and $(NH_4)_2S=2NH_3+H_2S$. J. Volhard, and C. Delitsch made ammonium thiocarbonate by *heating ammonium thiocyanate to 170° for 100–120 hrs., or to 180°–190° for* 20 hrs.

Ammonium thiocarbonate, said W. C. Zeise, forms pale yellow crystals, which, when exposed to air, volatilize completely in a few days. If protected from moisture, the salt may be sublimed almost unchanged, but a small quantity of ammonium sulphide appears to be formed during the process. E. W. Yeoman found that the salt dissociates completely at 100°, and leaves no residue. The salt dissolves rapidly and copiously in water; a soln. with one part of the salt in eight parts of water is red; with a greater proportion of water, the soln. is brown; and with a still greater proportion of water, yellow; if the aq. soln. be kept in a closed vessel, it turns reddish-brown; the soln. is decolorized on exposure to air, and a grey carbonaceous precipitate settles. E. W. Yeoman said that aq. soln. of the salt are very unstable, easily losing carbon disulphide, hydrogen sulphide, and ammonia, and some oxidation occurs. This change occurs rapidly when the aq. soln. is boiled in an open vessel, very little thiocyanate or carbamide being formed. J. H. Gladstone gave 1·065 for the sp. gr. of a soln. of an eq. of the salt with 35·47 eq. of water, and for the refractive indices 1·3918 with the *A*-line, and the *D*-line. A. Gélis said that the soln. decomposes at 90°–100°, forming ammonium thiocyanate and hydrogen sulphide. According to W. C. Zeise, when the salt is moistened with alcohol, and exposed to the air, it immediately assumes a deeper yellow tint, and in a few seconds it becomes red; if the salt has been very well washed with ether and pressed thoroughly dry, it will retain its colour for 5 min. in air, and in closed vessels for a longer time. The salt dissolves sparingly in alcohol, and is still less soluble in ether. When left with alcohol in a closed vessel, the salt decomposes: $(NH_4)_2CS_3=(NH_4)CS_2(NH_2)+H_2S$. When mixed with an aq. soln. of potassium hydroxide and evaporated, the residue is potassium thiocyanate; with lime-water, it furnishes a yellow powder, and the soln. still contains thiocarbonates. E. W. Yeoman found that the aq. soln. dissolves a gram-atom of sulphur per mol of salt. Hydrochloric and sulphuric acids decolorize the red aq. soln. and render it turbid owing to the separation of thiocarbonic acid, and, with an excess of more conc. acids, the precipitate is dissolved. When a conc. aq. soln. is treated with conc. acids, hydrogen sulphide is given off; but with moderately dil. sulphuric acid, thiocarbonic acid is formed without the evolution of hydrogen sulphide. H. Hager, J. A. Palmer, and H. Siemssen have discussed the use of ammonium thiocarbonate in place of ammonium sulphide in analytical chemistry. O. Loew treated a soln. of thiocarbonic acid in ammonium sulphide, with hydrochloric acid, and digested the precipitate with aq. ammonia. The red soln. was supposed to contain *ammonium sesquithiocarbonate*, $(NH_4)_2C_2S_3$, and decomposed on evaporation or on standing (see p. 134).

J. J. Berzelius, and C. W. Zeise prepared **potassium thiocarbonate**, $K_2CS_3$, by dissolving carbon disulphide in a soln. of potassium monosulphide, or hydroxide —in the latter case some carbonate, as well as thiocarbonate, is formed: $3CS_2+6KOH=K_2CO_3+2K_2CS_3+3H_2O$. He recommended adding carbon disulphide to an alcoholic soln. of potassium sulphide so long as it dissolves; the lowest stratum which separates on standing is separated from the two upper ones—the middle stratum is mainly carbon disulphide, and the top one mainly alcohol—and evaporated at 30° for crystallization; or saturating at 30° an aq. soln. of potassium sulphide with carbon disulphide in a closed vessel quite full of the mixture, and evaporating as before at 30°. H. Hager made the salt by digesting potassium hydroxide with a soln. of sulphur in carbon disulphide; and B. Holmberg, and E. Bijlmann treated an alcoholic soln. of potassium hydrosulphide with carbon disulphide. E. W. Yeoman dissolved 2 grms. of potassium in absolute alcohol, converted the soln. into hydro-

sulphide, at 45°–50°, and then added carbon disulphide. As the soln. cooled yellow crystals were formed. These were washed with dry ether, and dried in a current of dry hydrogen at 45°. J. G. O'Donoghue and Z. Kahan precipitated the salt by adding an alcoholic soln. of potassium hydroxide to thiocarbonic acid. The salt was purified by evaporating the soln. in liquid ammonia. According to J. J. Berzelius, the yellow crystalline salt is very deliquescent; and it loses water of crystallization between 60° and 80°. When heated out of contact with air, it forms potassium sulphide and carbon. It is readily soluble in water, and sparingly soluble in alcohol. According to N. Tarugi and A. Magri, when an aq. soln. of potassium thiocarbonate is boiled out of contact with air and in an atm. of nitrogen, the first phase of the decomposition occurring is represented by the equation $K_2CS_3=K_2S+CS_2$. The potassium sulphide thus formed subsequently undergoes hydrolysis, giving potassium hydroxide and hydrogen sulphide: $K_2S+2H_2O=2KOH+H_2S$. In presence of air or oxygen, the decomposition of the thiocarbonate effected by boiling its soln. is represented by the equation: $2K_2CS_3+2H_2O+2O_2=K_2S_2O_3+K_2CO_3+CS_2+2H_2S$. Finally, in an atm. of carbon dioxide, decomposition occurs according to the equation: $K_2CS_3+CO_2+H_2O=K_2CO_3+CS_2+H_2S$. J. J. Berzelius' equation: $K_2CS_3+3H_2O=K_2CO_3+3H_2S$, does not represent the reaction. Under the action of sunlight and in presence of air, soln. of thiocarbonates undergo, at the ordinary temp. and with an increased velocity, the same transformation as takes place on boiling in absence of sunlight. In vessels evacuated and then exposed to sunlight, thiocarbonates remain unaltered for a long time, the equilibrium $K_2CS_3 \rightleftharpoons K_2S+CS_2$ not being disturbed by the removal of one of the products of the decomposition. Towards organic compounds, thiocarbonates behave in such a way as to confirm the fact that they decompose into a sulphide and carbon disulphide. Thus, with aniline, potassium thiocarbonate yields the condensation product of thioformanilide. Under other conditions, thiocarbonates behave like simple sulphides; thus benzoyl chloride and a thiocarbonate in equimol. proportions yield benzoyl disulphide, which is also formed by the interaction of benzoyl chloride and potassium hydrogen sulphide. According to J. G. O'Donoghue and Z. Kahan, it is readily soluble in liquid ammonia. E. W. Yeoman found a soln. containing a mol of the salt in water dissolves a gram-atom of sulphur.

H. Hager, and T. Rosenblatt discussed the use of the salt in place of ammonium sulphide in analytical work. The detection and determination of thiocarbonates have been discussed by A. and T. Gélis, C. Vincent, E. L. de Bouquet, E. Fallières, G. Dannecy, O. Hehner and H. S. Carpenter, etc. The thiocarbonate is converted into the lead or zinc salt, and decomposed by acetic acid (B. Delachanal and A. Mermet), by arsenious acid (M. David and A. Rommier), or by heat (L. Finot and A. Bertrand). The resulting carbon disulphide is received in olive oil, or alcoholic potash (B. Delachanal and A. Mermet), or measured in a graduated cylinder (M. David and A. Rommier), or estimated by the loss of weight (L. Finot and A. Bertrand), or the alcoholic potash and xanthate is titrated with iodine (B. Delachanal and A. Mermet). P. Thénard, J. Maistre, M. de Georges, A. Mares, F. Sestini, and A. Mermet have discussed the use of thiocarbonates for the destruction of the *phylloxera vestatrix*, and other cryptogamous diseases of plants.

According to J. J. Berzelius, **lithium thiocarbonate**, $Li_2CS_3$, is obtained by a process similar to that which he employed for the potassium salt. The salt is more deliquescent than the sodium or potassium salt; and it is readily soluble in both water and alcohol. J. J. Berzelius made **sodium thiocarbonate**, $Na_2CS_3$, by digesting an aq. soln. of sodium monosulphide with carbon disulphide in a closed vessel at 30°, and evaporating the liquid. A. Husemann half sat. sodium hydroxide with hydrogen sulphide, and mixed the product with carbon disulphide. He then added alcohol or a mixture of ether and alcohol and obtained sodium thiocarbonate as a red oil which was freed from carbon disulphide by heat. I. Taylor made the salt by the action of sodium amalgam—preferably in the presence of a strip of platinum—on water in the presence of carbon disulphide—carbon dioxide and hydrogen

are evolved. J. G. O'Donoghue and Z. Kahan found that when dry, freshly-prepared sodium ethoxide is added to thiocarbonic acid, a yellow crystalline precipitate is gradually formed which can be washed with cold alcohol. E. W. Yeoman made it by a process analogous to that used for the potassium salt. According to J. J. Berzelius, the yellow salt can be crystallized from its aq. soln. The yellow needle-like crystals of the salt are very deliquescent, and readily soluble in water and alcohol. It is insoluble in ether or benzene, both of which precipitate the salt from its alcoholic soln. According to E. W. Yeoman, sodium thiocarbonate is stable in dry air free from carbon dioxide. If moisture be present, the salt decomposes with the loss of carbon disulphide, and is oxidized: $Na_2CS_3=Na_2S+CS_2$; $Na_2S+H_2O=NaHS+NaOH$; $2NaSH+O=Na_2S_2+H_2O$; and $Na_2S_2+3O=Na_2S_2O_3$. The salt decomposes, when strongly heated, into sodium disulphide and carbon disulphide. According to J. J. Berzelius, when dried and heated to redness in closed vessels, it decomposes into a mixture of carbon and sodium sulphide. E. W. Yeoman found that if water be excluded, the salt is stable in a current of hydrogen at 60°; but at 75°, carbon disulphide escapes, but the loss is not great even at 100°. A current of dry air free from carbon dioxide does not cause any more decomposition than occurs with hydrogen. An aq. soln. is stable in the absence of oxygen and carbon dioxide, but in the presence of oxygen, carbon disulphide separates, and thiosulphates, polysulphides, and sulphur are formed, while the unchanged thiocarbonate dissolves sulphur, forming perthiocarbonate, which also decomposes by the loss of carbon disulphide and the subsequent oxidation of the alkali sulphide. J. J. Berzelius represented the reaction with water: $Na_2CS_3+3H_2O=Na_2CO_3+3H_2S$, which E. W. Yeoman found to be true when an air-free soln. is heated in a sealed tube at 100°, the reactions being $Na_2CS_3=Na_2S+CS_2$; $Na_2S+2H_2O=2NaOH+H_2S$; and $6NaOH+3CS_2=Na_2CO_3+2Na_2CS_3+3H_2O$. The re-formed thio-carbonate again decomposes, and after prolonged heating, the reaction reduces to that given by J. J. Berzelius. The reaction is never quite complete. If air be present, thiosulphate and polysulphide are formed. When sodium thiocarbonate is distilled with air-free water, in the absence of air and carbon dioxide, hydrogen sulphide and carbon disulphide are formed; the residue contains sodium sulphide and its hydrolytic products, but no carbonate and only a trace of thiosulphate due to leakage of air. This agrees with N. Tarugi and A. Magri's observations. If a stream of air be drawn through a boiling soln., E. W. Yeoman obtained results in partial agreement with those of N. Tarugi and A. Magri, who represented the reaction: $2Na_2CS_3+2H_2O+2O_2=Na_2S_2O_3+CS_2+Na_2CO_3+2H_2S$. The salt and its aq. soln. are decomposed by carbon dioxide, forming carbonate and carbon disulphide; sulphur dioxide forms sulphite and carbon disulphide. A soln of a mol of the salt in water dissolves a gram-atom of sulphur, as observed by A. Gélis. In alcoholic soln., it was found that $Na_2S+CS_2=Na_2CS_3+5{\cdot}7$ Cals.; and $Na_2S_2+CS_2=Na_2CS_4+8{\cdot}55$ Cals.; $Na_2CS_3+S=Na_2CS_4+4{\cdot}29$ Cals.

M. Cluzel stated that when carbon disulphide is passed over red-hot copper, carbon is separated and deposited on the surface of the metal, but J. J. Berzelius, and L. J. Thénard and L. N. Vauquelin said that the carbon disulphide combines as a whole with the metal, forming a shining black substance which, when treated with nitric acid, leaves a residue of carbon. A. Cavazzi observed the formation of no compound of carbon and sulphur with copper under these conditions—*vide supra*, action of carbon disulphide on copper. J. J. Berzelius found that cupric salts give a dark brown precipitate when added to a soln. of calcium thiocarbonate; the precipitate was considered to be **cupric thiocarbonate**; it is soluble in an excess of calcium sulphide; and when heated, it gives off carbon disulphide, and sulphur, and cuprous sulphide remains. M. Ragg said that when a soln. of a cupric salt is treated with an alkali xanthate, not only is cupric thiocarbonate, $CuCS_3$, but also **cupric oxydithiocarbonate**, $CuCOS_2$, and **cupric dioxythiocarbonate**, $CuCO_2S$, are formed. K. A. Hofmann and F. Höchtlen obtained a complex of *cuprous thiocarbonate*, $Cu_2CS_3$, and potassium cyanide, namely, **potassium cuprous dicyanothio-**

**carbonate,** $Cu_2CS_3.2KCy.2H_2O$, by the action of ammonium cuprous thiocarbonate on a soln. of potassium thiocarbonate. According to K. A. Hofmann, and K. A. Hofmann and F. Höchtlen, **ammonium cuprous thiocarbonate,** $NH_4CuCS_3$, is obtained by treating a mixture of cuprous chloride, dissolved in conc. hydrochloric acid and excess of ammonia (10 per cent.), with carbon disulphide at 0°; after remaining three days, a separation of hair-like crystals takes place, and after another two days these are converted into the new salt. This crystallizes in thick, green tablets having a metallic lustre, and is only very sparingly soluble in conc. ammonia, and gives a brown soln. and a precipitate of brownish-black flocks with dil. sodium hydroxide. It is also obtained by the action of ammonia and carbon disulphide on copper sulphate at 10°. K. A. Hofmann and F. Höchtlen also prepared **potassium cuprous thiocarbonate,** $KCuCS_3$, by adding a conc. soln. of cupric chloride to carbon disulphide dissolved in aq. potassium hydroxide at 0°; it crystallizes in thick plates having a greenish lustre. Both salts are converted by acetic acid or, better, by sodium hydrogen sulphite, into **cuprosic sulphotrithiocarbonate,** $Cu_2S.2CuCS_3$, or $C_2S_7Cu_4$, which forms six-sided plates with a bronze-like lustre and is insoluble in water.

K. A. Hofmann also reported a *copper amminoxythiocarbonate,* $Cu_3C_2S_5(NH_3)_6O_6$, to be obtained by allowing a mixture of copper sulphate, 6 per cent. ammonia, and carbon disulphide to remain at 0° for 4–5 weeks. It crystallizes in black, monoclinic tablets, dissolves easily in ammonia with a blue coloration, is insoluble in water, and is not decomposed when allowed to remain over sulphuric acid. Dil. sodium hydroxide has only a surface action on the compound; but it is completely decomposed by conc. sodium hydroxide with the formation of cupric hydroxide, etc.

According to J. J. Berzelius, aq. soln. of calcium thiocarbonate and silver nitrate furnish a dark brown precipitate, presumably **silver thiocarbonate.** It dissolves in an excess of the calcium salt, giving a dark brown soln. The dried precipitate is black, shining, and difficult to pulverize; and when heated in a closed vessel, gives off sulphur, a little carbon disulphide, and leaves a mixture of silver sulphide and carbon. W. C. Zeise also made analogous observations with silver salts and the alkali thiocarbonates. J. J. Berzelius found that an aq. soln. of auric chloride and calcium thiocarbonate gives a turbid mixture which becomes clear, depositing a greyish-brown precipitate—possibly **gold thiocarbonate.** This, when heated, gives off sulphur and leaves gold blackened by charcoal.

J. J. Berzelius digested calcium sulphide, water, and an excess of carbon disulphide in a closed vessel at 30°, and obtained a dark red liquid, which, when evaporated in vacuo, gave a yellowish-brown crystalline mass, this, when thoroughly dried, was citron-yellow. It was regarded as normal *calcium thiocarbonate,* $CaCS_3$. On exposure to air, water is absorbed, and the colour becomes brownish-red. The product is readily dissolved by alcohol and water, but in the latter case, a basic salt remains as a residue. The aq. soln. is decomposed by boiling, and calcium carbonate is deposited. It is, however, doubtful if the normal thiocarbonate has been made; all E. W. Yeoman's attempts gave complexes of the normal salt with calcium hydroxide. Quite a number of these basic salts has been reported, but there is little to show which are chemical individuals. F. Sestini reported the formation of orange-red, prismatic crystals of **calcium hexahydroxythiocarbonate,** $3Ca(OH)_2.CaCS_3.7H_2O$, by exposing a mixture of water, calcium hydroxide, and carbon disulphide to the action of solar light in summer; in 6–8 hrs. the liquid acquires a yellowish-red colour, and then deposits the crystals. The same compound is made by heating milk of lime with carbon disulphide for 2 hrs. at 50°; and adding a soln. of calcium hydroxide to the cooled filtrate. F. Sestini utilized the reaction for the detection of carbon disulphide in soln. D. Walker obtained bright orange-red needles of **calcium tetrahydroxythiocarbonate,** $2Ca(OH)_2.CaCS_3.6H_2O$, by agitating milk of lime with carbon disulphide. The salt is sparingly soluble in cold water, and is decomposed by boiling water; it is insoluble in carbon disulphide, and in alcohol. E. W. Yeoman obtained reddish-yellow needles of a similar salt, $3Ca(OH)_2.CaCS_3.9H_2O$, from aq. soln., and similar needles, but with the composi-

tion **dihydrated calcium dihydroxythiocarbonate,** $Ca(OH)_2.CaCS_3.2H_2O$, from alcoholic soln. S. Dyson discussed the occurrence of thiocarbonates in gas liquor from gas-works. The foul-lime of gas-works is lime which has been used for removing hydrogen sulphide from coal gas; this when moist, and mixed with an equal weight of slaked lime, is an absorbent for carbon disulphide in gases. The absorption stops at a stage when about one-third of the sulphide has been converted into thiocarbonate, on the assumption that the reaction is $CaS+CS_2=CaCS_3$. V. H. Veley has studied the reactions. He showed that dry calcium sulphide does not absorb the vap. of carbon disulphide, but the moist sulphide does absorb the vap.; nor does the absorption occur with calcium hydrosulphide. Calcium sulphide, nearly anhydrous, was placed under a small quantity of water, and hydrogen, sat. with carbon disulphide vap., passed into the mixture; the superincumbent water turned gradually to a red tint, and the soln. was separated from the sulphide by the method indicated above. The liquid was then placed under the air-pump; after a few days, red, prismatic needles appeared, from which the adherent water was drained as far as possible, and they were again dried under the air-pump. Analyses corresponded with **heptahydrated calcium tetrahydroxythiocarbonate,** $2Ca(OH)_2.CaCS_3.7H_2O$. The red prismatic crystals were very deliquescent, and on contact with air, lost their red colour, and became yellow and less soluble in water. An aq. soln. gave a red oil, thiocarbonic acid, when treated with hydrochloric acid. Further, when hydrogen, charged with the vap. of carbon disulphide, is passed into a soln. of calcium hydrosulphide, $Ca(SH)_2$, white crystals of calcium hydroxyhydrosulphide, $Ca(OH)(SH)$, are formed, and there is a copious evolution of hydrogen sulphide; on continuing the passage of the gas, the crystals become yellow, and the liquid becomes nearly solid owing to the formation of a yellow crystalline mass. The crystals were drained from the mother-liquor, washed twice with distilled water, and dried in vacuo. The analysis of the yellow crystals corresponded with **decahydrated calcium tetrahydroxythiocarbonate,** $2Ca(OH)_2.CaCS_3.10H_2O$. This salt dissolves in water, forming a red soln. which, on evaporation, yields red crystals resembling the heptahydrate. There is a slight decomposition during the evaporation. Hence, V. H. Veley inferred that in removing carbon disulphide from coal gas, calcium sulphide or hydrosulphide is first converted into the hydroxyhydrosulphide; and this compound suspended in water is the active absorbent—hydrogen sulphide and a basic calcium thiocarbonate being simultaneously formed: $3Ca(SH)(OH)+CS_2+H_2O=2H_2S+2Ca(OH)_2.CaCS_3$. Calcium thiocarbonate exposed to air is slowly converted into the carbonate, a change which is immediately effected by heating to 60°–80°; in conc. soln., carbon disulphide is evolved, and calcium sulphide remains. The product is again effective as an absorbent for carbon disulphide. Basic calcium thiocarbonate is decomposed by hydrogen sulphide.

J. J. Berzelius reported the formation of a brownish-red liquid by the action of carbon disulphide on strontium sulphide and water in a closed vessel at 30°. On evaporation in vacuo, a lemon-yellow mass of **strontium thiocarbonate,** possibly $SrCS_3$, is formed. E. W. Yeoman obtained the tetrahydrate, $SrCS_3.4H_2O$, by suspending 10 grms. of strontium hydroxide in 60 c.c. of 95 per cent. alcohol, and converting it into the hydrosulphide by means of hydrogen sulphide at 70° with the exclusion of air. The carbonate was removed by filtration in hydrogen. A slight excess of carbon disulphide was added to the soln., and the mixture was kept for half an hour at 40°. Dark red needles were obtained on adding ether to the soln., and when dried in vacuo, the crystals were yellow. The mass becomes reddish-brown when moistened with water; and it is more soluble in water than the barium salt. F. Sestini obtained a non-crystalline mass of what he considered to be *strontium hexahydroxythiocarbonate*, resembling the corresponding calcium salt.

G. Chancel and F. Parmentier showed that baryta-water and carbon disulphide have very little action on one another in the cold, but at higher temp., a yellow liquid is formed, and barium carbonate precipitated. In a sealed tube at 100°, the reaction $CS_2+2Ba(OH)_2=BaCO_3+Ba(SH)_2+H_2O$ is quantitative. J. J. Berzelius

found that hydrated barium sulphide rapidly unites with carbon disulphide, forming a lemon-yellow, non-crystalline **barium thiocarbonate**, possibly $BaCS_3$, which dissolves sparingly in water, forming a brownish-yellow soln., which, with more water, becomes red. On evaporation of the aq. soln. in vacuo, yellow crystals are obtained; and these, when moistened with water, become red, but on drying the yellow colour is restored. V. H. Veley added that the salt is readily soluble in hot water and is, at the same time, decomposed. He did not succeed in preparing the salt in a fit state for analysis, using water, alcohol—dil. and absolute—ether, and carbon disulphide as solvents. E. W. Yeoman made the barium salt by a process analogous to that used for strontium thiocarbonate. Unlike V. H. Veley, E. W. Yeoman found the barium salt even more stable than the other thiocarbonates. The chemical reactions resemble those of the sodium salt.

V. H. Veley found that carbon disulphide was not absorbed by solid barium hydroxide, or anhydrous barium sulphide; nor by a soln. of the hydrosulphide, or the crystalline hydroxyhydrosulphide mixed with a large excess of water—in which case, the hydroxyhydrosulphide is probably decomposed into the hydroxide and hydrosulphide. Carbon disulphide is copiously absorbed by the crystalline hydroxyhydrosulphide and a basic salt, possibly resembling the corresponding calcium salt, is obtained. D. Walker also made a **barium tetrahydroxythiocarbonate**, $2Ba(OH)_2.CaCS_3.6H_2O$, analogous to the calcium salt, and by a similar process. P. Thénard obtained the salt by shaking an aq. soln. of barium sulphide with carbon disulphide, washing the product with alcohol, and drying in vacuo. He said that 100 parts of water dissolve 1·5 parts of the salt. O. Loew claimed to have made *barium sesquithiocarbonate*, $BaC_2S_3$, by warming sesquithiocarbonic acid, $H_2C_2S_3$, with barium hydrosulphide, and passing carbon dioxide through the filtrate so long as hydrogen sulphide is evolved. On evaporation, a non-crystalline mass is obtained which decomposes on exposure to air.

According to J. J. Berzelius, when magnesium sulphate is added to a soln. of barium thiocarbonate, and the filtrate evaporated in vacuo, a little carbon disulphide escapes, and the non-crystalline lemon-yellow residue is considered to be **magnesium thiocarbonate**. E. W. Yeoman also made this salt. Cold water in contact with this compound dissolves a part, forming a yellow soln., and leaving undissolved a basic salt, which is decomposed by boiling water leaving magnesium carbonate undissolved. F. Sestini claimed to have made a non-crystalline basic salt analogous to that which he obtained with calcium salts; D. Walker likewise claimed to have made a basic salt by a process analogous to that which he used for the calcium salt. According to I. Taylor, when a strip of magnesium, in contact with platinum as a catalyst, is immersed in a mixture of water and carbon disulphide, the liquid, in the course of a couple of days, acquires a yellow colour owing to the formation of magnesium thiocarbonate: $3CS_2+2Mg+H_2O=2MgCS_3+CO+H_2$. J. J. Berzelius found that when soln. of a zinc salt and calcium thiocarbonate are mixed, a yellowish-white precipitate is formed which, on drying, becomes reddish-yellow and translucent—it was supposed to be **zinc thiocarbonate**. According to A. Cavazzi, zinc and carbon disulphide vap. at a high temp. furnish zinc sulphide. D. Walker said that zinc hydroxide is not affected by agitation with carbon disulphide. J. G. O'Donoghue and Z. Kahan made zinc thiocarbonate, $ZnCS_3$, as a pale yellow crystalline powder by the action of thiocarbonic acid alone, or in alcoholic or ethereal soln. on a zinc salt with a weak acid, at the temp. of solid carbon dioxide. The thiocarbonate is very unstable, and rapidly decomposes, forming zinc sulphide. K. A. Hofmann treated a zinc salt with carbon disulphide, and a 10 per cent. soln. of ammonia, and obtained a salmon-yellow crystalline powder of **zinc diamminothiocarbonate**, $ZnCS_3.2NH_3$. J. J. Berzelius obtained a lemon-yellow precipitate, supposed to have been **cadmium thiocarbonate**, by a process similar to that employed for the zinc salt. J. G. O'Donoghue and Z. Kahan obtained the thiocarbonate, $CdCS_3$, by a process like that they employed for the zinc salt. The deep yellow precipitate soon changed to a reddish-yellow colour, and then to reddish-brown cadmium sulphide.

K. A. Hofmann obtained **cadmium diamminothiocarbonate**, $CdCS_3.2NH_3$, in lustrous plates, by the same process as that employed for the corresponding zinc salt; it decomposed when dried, forming cadmium sulphide. J. J. Berzelius found that mercuric salts react with soln. of calcium thiocarbonate, yielding a black precipitate, which dissolved in an excess of the thiocarbonate, and in drying gave off carbon disulphide, and left behind black mercuric sulphide. W. C. Zeise obtained a yellow precipitate—possibly **mercuric thiocarbonate**—by mixing soln. of ammonium thiocarbonate and a mercuric salt. The precipitate changes in the course of a few hours, with the separation of some carbon disulphide.

According to J. J. Berzelius, an aq. soln. of calcium thiocarbonate gives a dark brown precipitate with stannous salts—possibly **stannous thiocarbonate**—and a brownish-yellow precipitate with stannic salts—possibly **stannic thiocarbonate**, J. J. Berzelius also found that lead salts give a dark brown precipitate with calcium thiocarbonate, and W. C. Zeise, a red precipitate with ammonium thiocarbonate. The precipitate was considered to be **lead thiocarbonate**, $PbCS_3$. J. G. O'Donoghue and Z. Kahan made it by the process they employed for the zinc salt. It appeared as a red salt with the composition $PbCS_3$, and when pure, the salt darkened only slowly in air—usually the salt turns black in about half an hour. This change corresponds with $PbCS_3=CS_2+PbS$, and occurs rapidly in vacuo, and is quantitative when the salt is heated in a current of hydrogen. J. J. Berzelius found that the salt under water decomposes in a few hours, but under alcohol, the decomposition is slower. The salt is instantly blackened by the action of a soln. of ammonium sulphide or of potassium hydroxide; at ordinary temp., sulphuric acid, nitric acid, or iodine has no appreciable effect on lead thiocarbonate. The salt was further examined by B. Delachanal and A. Mermet. A Gautier and L. Hallopeau also obtained crystals of undetermined composition by the action of the vapour of carbon disulphide on white-hot lead. J. J. Berzelius found that calcium thiocarbonate added to a soln. of a bismuth salt, gives a dark brown precipitate—possibly **bismuth thiocarbonate**—soluble in an excess of the precipitant, forming a reddish-brown soln.; he also obtained with chromic salts a greyish-green precipitate—possibly **chromium thiocarbonate**—which when heated in a closed vessel gave carbon disulphide and brown chromium sesquisulphide; with manganous salts, a dark brown liquid which turns yellow and then deposits a reddish-brown powder—possibly **manganese thiocarbonate**—which is sparingly soluble in water, forming a yellow soln., and decomposes when heated, forming carbon dioxide, sulphur, and manganese sulphide; with ferrous salts, a deep wine-red liquid is formed which becomes darker and ultimately appears ink-black by reflected light—if the ferrous salt be in excess, a black powder is deposited—possibly **ferrous thiocarbonate**; with ferric salts, a deep red precipitate is formed which retains its colour when dried, and is possibly **ferric thiocarbonate**, for, when heated, it gives off carbon disulphide and sulphur, and leaves a residue of iron sulphide; with cobalt salts, a deep olive-green soln. is formed which appears black by reflected light, and in 24 hrs. deposits black flakes—**cobalt thiocarbonate**—leaving the mother-liquor dark brown; and with nickel salts, a dark brownish-red soln. is obtained which, in 24 hrs., deposits black flakes—**nickel thiocarbonate**—and becomes brownish-yellow. C. D. Braun, and A. Mermet noted that aq. soln. of the alkali thiocarbonates give an intense red coloration with ammoniacal soln. of nickel salts. O. F. Wiede and K. A. Hofmann made **nickel triammino-thiocarbonate**, $NiCS_3 3NH_3$, by gently warming a mixture of nickelous hydroxide, ammonia, and carbon disulphide. It crystallizes in transparent, ruby-red needles, is sparingly soluble in water, but easily in sodium hydroxide with an intense, yellowish-red coloration, and, when heated, gives off carbon disulphide. On exposure to the air, it gives off part of the ammonia and carbon disulphide. They also made **cobalt hexammino-thiocarbonate**, $Co_2C_2S_6.6NH_3$, by passing nitric oxide through a mixture of freshly prepared cobaltous hydroxide, aq. ammonia, and carbon disulphide. The salt, which is mixed with an amorphous by-product, is purified by washing with alcohol. It crystallizes in black, lustrous

rhombohedra, dissolves sparingly in water, yielding a yellowish-green soln. and dissolves in sodium hydroxide with a dark green coloration, at first without evolution of ammonia. It is decomposed by strong acids with precipitation of sulphur, and, when heated, gives off carbon disulphide. By prolonged heating with sodium hydroxide, all the nitrogen is given off as ammonia. It can also be prepared by warming a mixture of cobalt hydroxide, ammonia, and carbon disulphide. K. A. Hofmann and co-workers made an analogous **iron hexammino-thiocarbonate**, $Fe_2C_2S_7.6NH_3.2H_2O$.

K. A. Hofmann obtained the complex $Co_2C_2S_8(NH_3)_6O_3$ and cobalt pentammmosulphite by allowing the above hexammino-thiocarbonate to remain some months in contact with 10 per cent. aq. ammonia. The pentammine crystallizes in thin plates which can be removed by washing the mixture with conc. ammonia. The complex $Co_2C_2S_7(NH_3)_6$ is made by boiling the ammonium cobaltous salt of cobaltisulphurous acid with ammonia. With fuming hydrochloric acid, $Co_2C_2S_7(NH_3)_6$ forms $Co_2C_2S_{14}ClO_{10}H_{26}$; with acetic acid, $(CS_3)_3Co_2S(NH_3)_2.C_2H_4O_2.4H_2O$; and with acetic anhydride, $Co_2C_2S_85NH_3$ is formed. When the hexammino-thiocarbonate is treated with diazobenzene nitrate at 0° for 24 hrs., black prismatic crystals of $Co_2C_2S_8(NH_3)_6.H_2O$ are formed, and with nitrous oxide, cobalt triamminotrinitrite is formed. This is taken to prove that no ammonia is combined between the cobalt and sulphur, for, if this were the case, groups of the constitution $CoNH_3.S.NH_3Co$ or $Co.NH_3.S.C$ would be formed, and the compound $C_2S_7Co_2(NH_3)_6$ should give the reactions of hydrogen sulphide or thiocarbonic acid. Brownish-red crystals of $Co_2C_2S_7(NH_3)_5.2H_2O$ are produced when cobaltic hydroxide is treated at 10° with 10 per cent. aq. ammonia and carbon disulphide; if this mixture is allowed to stand 4–5 days, black prisms of $CoCS_4H.3NH_3$ are formed.

According to J. J. Berzelius, an aq. soln. of calcium thiocarbonate gives a dark brown precipitate with a soln. of a platinic salt; the precipitate is soluble in an excess of the thiocarbonate, forming a brownish-yellow soln.; when dried, the precipitate is nearly black, and is presumably **platinic thiocarbonate**. When heated it gives off carbon disulphide, and sulphur, and leaves platinum sulphide behind. According to K. A. Hofmann, **iridium thiocarbonate** and **rhodium thiocarbonate** are formed in a similar way. These three **thiocarbonates** readily combine with ammonia. Hydrated **platinum diamminothiocarbonate**, $PtCS_3(NH_3)_2.12H_2O$, is obtained from potassium platinous chloride, conc. ammonia, and carbon disulphide. It crystallizes in long, red needles, is insoluble in cold water, ammonia, or sodium hydroxide, and gives up its water of crystallization when allowed to remain in vacuo over sulphuric acid. It gives no coloration with sodium nitroferrocyanide, nor a mercaptan nor methyl sulphide when boiled with methyl iodide. Under certain conditions, which have not yet been determined, **platinum tetramminothiocarbonate**, $Pt_2Cl_2(NH_3)_4CS_3$, is formed, and crystallizes in slender, red needles; and **platinum amminothiocarbonate**, $C_2S_5PtNH_3$, is obtained from ammonium platinum chloride, ammonia, and carbon disulphide; it crystallizes in lustrous, black crystals, and is easily soluble in dil. sodium hydroxide.


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## § 44. Perthiocarbonates

Perthiocarbonates analogous to the percarbonates prepared by electrolysis have not been obtained, but salts corresponding with the percarbonates produced by acting on the carbonates with hydrogen dioxide have been made. Thus, A. Gélis [1] found that when carbon disulphide is treated with sodium disulphide, $Na_2S_2$, **sodium perthiocarbonate**, $Na_2CS_4$, is obtained; and a similar compound was made by the direct action of sulphur on the thiocarbonates. There is no analogous mode of preparation with the percarbonates, and this fact brings out the greater tendency of sulphur atoms to form chains than is evinced by oxygen atoms. E. W. Yeoman prepared sodium perthiocarbonate in the following manner:

[1] Sodium (2·3 grms.) was dissolved in 40 c.c. of absolute alcohol and mixed with a soln. of 2·3 grms. of sulphur in 40 c.c. of alcohol so as to form an alcoholic soln. of sodium sulphide, which was converted into the disulphide by the addition of 3·2 grms. of sulphur. A slight excess of carbon disulphide was added, the colour of the soln. changing from yellow to red. On addition of ether to this perthiocarbonate soln. a reddish-yellow oil was precipitated, which slowly solidified to a microcrystalline mass of brownish-yellow needles. On keeping, the filtrate deposited a further amount in nodular aggregates of prismatic, doubly refracting needles. The crystalline mass was collected, washed with ether in an atm. of hydrogen, and finally dried at 60° in a stream of the same gas.

Alternatively, the sodium disulphide required may be prepared by the direct addition of sulphur to the sodium hydrosulphide without addition of a second mol. of sodium ethoxide, the disulphide being then formed with the evolution of hydrogen sulphide. The salt is very deliquescent, and readily dissolves in water, forming a yellow soln.; it also dissolves in alcohol, from which it is precipitated by ether or benzene. The salt is stable in dry air free from carbon dioxide, but it is quickly decomposed in moist air owing to the loss of carbon disulphide and the oxidation of

the residue mainly to thiosulphate : $Na_2CS_4=Na_2S_2+CS_2$ ; and $Na_2S_2+5H_2O+3O=Na_2S_2O_3.5H_2O$. When heated, the perthiocarbonate behaves like the thiocarbonate excepting that sodium disulphide takes the place of the monosulphide. The aq. soln. can be kept unchanged for a long time in the absence of air ; but if air has access, carbon disulphide and sodium thiosulphate are formed. When the air-free soln. is heated in a sealed tube, sodium thiosulphate is formed ; some sulphur separates when the tube is cooled, and much hydrogen sulphide escapes on opening the tube. The reactions, in the main, resemble those with sodium thiocarbonate. If an aq. soln. of the salt be distilled in the absence of air, it loses its carbon disulphide ; if a current of air be passed through the boiling soln. some carbonate is formed—there was never a 50 per cent. conversion to the carbonate. The salt is quickly decomposed by carbon dioxide, forming carbon disulphide, a carbonate, sulphur, and hydrogen sulphide. With sulphur dioxide, thiosulphate, sulphur, and carbon disulphide are formed : $2Na_2CS_4+3SO_2=2Na_2S_2O_3+3S+2CS_2$. A soln. of the salt does not dissolve sulphur. The additional sulphur atom in the perthiocarbonates is readily removable by reagents which have a direct action on sulphur, such as hydrocyanic acid or sodium cyanide. When excess of the latter reagent is added to the pure yellow soln. of the perthiocarbonate the colour soon changes from yellow to the characteristic red of the thiocarbonates, the additional atom of sulphur being removed and converted by the cyanide into thiocyanate. E. W. Yeoman prepared **potassium perthiocarbonate**, $K_2CS_4.\frac{1}{2}H_2O$, by the method employed for the sodium salt. Attempts to remove the water resulted in the decomposition of the salt. The reactions resemble those with sodium perthiocarbonate. H. von Halban and co-workers examined the spectra of soln. of **perthiocarbonic acid**, $H_2CS_4$, in chloroform, toluene, and light petroleum, and of the sodium salt in aqueous soln. They also measured the rate of decomposition of the acid in several organic solvents.

E. W. Yeoman prepared **ammonium perthiocarbonate**, $(NH_4)_2CS_4.H_2O$, by converting a 20 per cent. alcoholic soln. of ammonia into the hydrosulphide and adding the exact amount of sulphur to convert it into the disulphide, $(NH_4)_2S_2$, all the operations being made in the absence of air. On addition of carbon disulphide, the perthiocarbonate was immediately precipitated as a yellow, crystalline solid. The crystals were collected, washed with dry ether with the usual precautions, and the ether was removed as completely as possible in a current of hydrogen at the ordinary temp. The anhydrous salt was obtained in monoclinic or triclinic crystals by allowing an alcoholic soln. of the monohydrate to evaporate spontaneously at ordinary temp. The salt decomposes completely when heated to 100° in a current of hydrogen and leaves a residue of sulphur. The general behaviour of the perthiocarbonate resembles that of the thiocarbonate. At the ordinary temp., aq. soln. are only very slowly converted into the thiocyanate, excess of ammonia hastening the reaction. As with the trithiocarbonate, the conversion to thiocyanate is complete if the salt is heated in a sealed tube with alcoholic ammonia at 100°. The soln. of both ammonium trithiocarbonate and perthiocarbonate are very unstable, partly because of the well-known change which ammonium trithiocarbonate undergoes, whereby it loses hydrogen sulphide in two stages, passing successively into ammonium dithiocarbonate and ammonium thiocyanate, and partly on account of the ready manner in which it undergoes complete dissociation into ammonia, hydrogen sulphide, and carbon disulphide.

E. W. Yeoman prepared a basic salt, **calcium tetrahydroxyperthiocarbonate**, $CaCS_4.2Ca(OH)_2.8H_2O$, by converting calcium oxide into an aq. soln. of the polysulphide, and passing a current of hydrogen sulphide sat. with carbon disulphide vap. On evaporating the soln. in vacuo, dark red needles of the basic salt were formed. With alcoholic soln., an impure perthiocarbonate was formed. E. W. Yeoman succeeded in preparing soln. of **strontium, barium, and magnesium perthiocarbonates** by allowing aq. soln. of the thiocarbonates to dissolve in sulphur. Attempts to make the solids were not successful.

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## § 45. The Thiocarbamic Acids and the Thiocarbamates

The analogy between carbonic acid and thiocarbonic acid, and between the carbonates and the thiocarbonates, extends also to carbamic acid (**2**. 20, 34) and the thiocarbamic acids:



Carbamic acid



Thiocarbamic acid



Ammonium dithiocarbamate

In harmony with the observations on the thiocarbonic acids, there are three possible thiocarbamic acids, namely:



Thioncarbamic acid; or *β-thiocarbamic acid*



Thiolcarbamic acid; or *α-thiocarbamic acid*



Thiolthioncarbamic acid; or *dithiocarbamic acid*

F. Salomon[1] made **methyl thioncarbamate,** $NH_2CS.OCH_3$; and H. Debus, G. Chancel, and F. Salomon made **ethyl thioncarbamate.** These esters are derivatives of thioncarbamic acid. E. Blankenhorn made **methyl thiolcarbamate;** and A. Pinner, F. Salomon, and A. Fleischer, **ethyl thiolcarbamate,** which are derivatives of thiolcarbamic acid. M. Berthelot made **ammonium thiolcarbamate,** $NH_2.CO.SNH_4$, by passing gaseous carbonyl sulphide into alcoholic ammonia; E. Schmidt and A. Kretzschmar, by passing the same gas into aq. ammonia at 0°. The salt forms colourless crystals, very soluble in water, moderately soluble in alcohol, and insoluble in ether. The dry salt becomes yellow on exposure to air, forming ammonium thiocyanate. According to E. Mulder, water at 100° converts ammonium thiocarbamate into ammonium hydrosulphide and hydrocarbonate. The dry salt forms thiourea when heated in a sealed tube at 135°, or when its cold aq. soln. is treated with lead hydroxide. Ferric chloride forms a red liquid which ultimately yields a precipitate. A. Fleischer found that mercuric oxide, in the cold, converts ammonium thiolcarbamate into ammonium cyanate. When the ammonium salt is treated with acids, **thiolcarbamic acid,** $NH_2.CO.SH$, is liberated, but it immediately decomposes into carbonyl sulphide and ammonia.

W. C. Zeise[2] prepared **ammonium thiocarbamate,** or *ammonium dithiocarbamate*, $NH_4S.CS.NH_2$, by the action of carbon disulphide on alcoholic ammonia—*vide supra*, ammonium thiocarbonate. H. Debus said that the best yield is obtained by working at 10°–15° with not too conc. soln. E. Mulder passed the gas from 150 grms. of ammonium chloride and 300 grms. of quicklime into 600 parts of 95 per cent. alcohol and 96 grms. of carbon disulphide, and crystallized at about 30°; in this way no crystals of ammonium thiocarbonate were formed. It is also formed when ammonium thiocarbonate is heated. M. Freund and G. Bachrach obtained a 55 per cent. yield by mixing 50 grms. of 10 per cent. alcoholic ammonia dil. with 5 grms. of 96 per cent. alcohol, and 12 grms. of carbon disulphide. G. Inghilleri prepared ammonium dithiocarbamate by heating 6 grms. of carbon disulphide and 8 grms. of ammonium carbonate in a sealed tube for 6 hrs. at 100°–110°: $CS_2+(NH_4)_2CO_3=H_2O+CO_2+NH_2.CS.SNH_4$. Ammonium thiocarbamate furnishes citron-yellow, prismatic crystals. If derived from 95 per cent. alcohol, said E. Mulder, the crystals are but feebly coloured, and with 85 per cent. alcohol, colourless needles are obtained. W. C. Zeise said that when freshly prepared the

crystals have no smell, but after standing in air for some time, they smell of ammonia and hydrogen sulphide; sulphur, water, and ammonium thiocyanate are formed. In moist air, said H. Debus, the crystals give a turbid liquid which consists almost wholly of ammonium thiocyanate. If air is excluded, W. C. Zeise found that the undried crystals pass in some weeks into hydrogen sulphide and ammonium thiocyanate. When heated, the crystals melt with some bubbling; at 150°, much ammonia, probably mixed with cyanogen and nitrogen, is evolved, and carbon disulphide, ammonium thiocarbonate, and thiocyanate are formed; and at 200°, the mass leaves a brown residue. The crystals are readily soluble in water, forming a yellow soln. J. H. Gladstone found a soln. of the salt in 18·71 eq. of water has a sp. gr. 1·091 at 10°, and the refractive indices 1·4171 with the *A*-line, and 1·4254 with the *D*-line. W. C. Zeise, and M. Freund and G. Bachrach found that chlorine, or ferric chloride, converts ammonium thiocarbamate into *thiocarbamide disulphide*, $(NH_2CS)_2S_2$. P. Klason observed that the same product is obtained by the action of a hydrochloric acid soln. of iodine. According to W. C. Zeise, when hydrochloric acid or sulphuric acid, dil. with 8 parts of water, is mixed with the salt dissolved in 12 parts of water, the mixture becomes turbid in a few minutes; the more dil. the soln., the longer is the appearance of the turbidity delayed. If the soln. be allowed to stand in a closed vessel for 12 hrs., carbon disulphide, and an ammonium salt, and probably hydrogen cyanide, are formed. If the aq. soln. be heated, or if the alcoholic soln. be allowed to stand or warmed, carbon disulphide, hydrogen sulphide, and ammonium thiocyanate are formed. For the action of hydrochloric acid, *vide infra*. A. W. Hofmann found that with an alcoholic soln. of iodine, ammonium thiocarbonate furnishes ethyl thiocyanate, and ethylamine, $C_2H_5NH_2$. W. C. Zeise said that ammonium dithiocarbamate dissolves very sparingly in cold alcohol, but is more soluble in warm alcohol. E. Mulder said that the salt is insoluble in alcohol. A. Fleischer found that sulphur separates from the alcoholic soln., and W. C. Zeise observed that ammonium dithiocarbonate, thiocyanate, and thiosulphate are formed when the alcoholic soln. is warmed. The salt is insoluble in petroleum. H. Debus said that when ammonium dithiocarbamate is warmed with potassium hydroxide, potassium thiocyanate and hydrosulphide, ammonia, and water are formed. A. Fleischer said that the salt is desulphurized by mercuric oxide.

According to H. Debus, a soln. of ammonium thiocarbamate with cerium sulphate furnishes colourless needles which contain no cerium; uranium nitrate soln. is coloured blood-red; with soln. of arsenious acid, antimony pentachloride, stannous chloride, or bismuth nitrate, white or yellow precipitates are obtained; mercuric chloride soln. gives a white precipitate—probably mercurous chloride—nickel sulphate soln. gives a yellowish-green precipitate; and platinic chloride a brown precipitate. J. Klein discussed the possible applications of the salt in analytical chemistry. **Cupric thiocarbamate,** $Cu(S.CS.NH_2)_2$, is precipitated as a yellow powder insoluble in water; **zinc thiocarbamate,** $Zn(S.CS.NH_2)_2$, as a white mass; and **lead thiocarbamate,** $Pb(S.CS.NH_2)_2$, as a white mass which blackens when boiled with water. A number of complex thiocarbamates were made by H. Goldschmidt and L. Schulhof, S. M. Losanitsch, A. W. Hofmann, and G. Ponzio. M. Delépine made complexes with sodium, copper, silver, barium, zinc, mercury, lead, cobalt, and nickel thiocarbamates; and L. Compin, with copper, cobalt, and nickel thiocarbamates.

If hydrochloric acid be slowly added to a conc. soln. of ammonium thiocarbamate, cooled below 10°, the free acid—**dithiocarbamic acid,** $HS.CS.NH_2$—separates out in colourless needles which are very soluble in water, alcohol, and ether. The alcoholic soln. of the acid decomposes into carbon disulphide and the ammonium salt; and the aq. soln. when warmed decomposes into hydrogen sulphide, and thiocyanic acid. E. Mulder found that when heated the acid forms the ammonium salt, $HS.CS.NH_2=CS_2+NH_3$; and $NH_3+HS.CS.NH_2=NH_4S.CS.NH_2$.

According to G. B. L. Smith and F. Wilcoxon [3] **azido-dithiocarbonic acid,**

$HS.CS.N_3$, has been prepared by the treatment of conc. soln. of the sodium salt with conc. hydrochloric acid. It is a white or very pale yellow, crystalline solid; it crystallizes in the monoclinic system, has a strong double refraction, and is readily soluble in non-aqueous solvents. It has the characteristic properties of a strong acid, and its strength approaches that of hydrochloric acid. It is easily oxidized by various oxidizing agents, yielding the free halogenoid, **azido-dithiocarbonate** $(S.CS.N_3)_2$. In the solid form, the acid is very sensitive to both shock and to heat. It undergoes spontaneous decomposition at the ordinary temp., in keeping with the laws of unimolecular change. In the dry state, this reaction is catalysed by an intermediate product or by the thiocyanic acid formed, but not in aqueous soln. The decomposition may be represented by the equation $HS.CS.N_3=HSCN+S+N_2$. The solid product formed consists of polymerized thiocyanic acid and free sulphur.


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The chapter on carbon does not include those hydrocarbons and their derivatives commonly but arbitrarily admitted into inorganic chemistry; the cyanides and complex cyanides; nor does it include the combustion of the hydrocarbons. These subjects may later be discussed in a supplementary volume.

# CHAPTER XL

## *SILICON*

### § 1. The History of Silicon

It was the general opinion of the early Greek philosophers that minerals and earths were all formed from water. Thus, about 315 B.C., Theophrastus opened his essay—Περὶ λίθων—*On Stones :*

> Everything formed in the earth has its origin either from water or from earth. Water is the base of all the metals.

Theophrastus' term κρύσταλλος, translated *crystallus* in Pliny's *Historiæ naturalis* (**37.** 9, A.D. 77), is derived from the Greek word for ice ; and it was specifically applied to the mineral now known as *rock crystal* or *quartz* because

> Crystal assumes a concrete form from excessive congelation. At all events, crystal is to be found only in places where the winter snow freezes with the greatest intensity ; and it is from the certainty that it is a kind of ice, that it has received the name which it bears in Greek.

In his *Bibliotheca historica*, Diodorus Siculus made the counter-guess that although rock crystal is formed from the purest water, it is not cold. Rather has the *divinus calor* or solar heat made water so hard and dry that it has become crystal. Pliny's guess, however, was most generally accepted.[1] G. Agricola, for instance, said that " rock crystal is not ice, but a denser product of cold." The idea was combated by A. B. de Boodt,[2] J. J. Becher, and R. Boyle in the seventeenth century. Thus, the last-named said :

> I found the weight of crystal to be to that of water of equal bulk as two and two-thirds to one ; which by the way shows us how groundlessly many learned men, as well ancient as modern, make crystal to be but ice extraordinarily hardened by long and vehement cold, whereas ice is, bulk for bulk, lighter than water (and therefore swims upon it) and (to add that objection against the vulgar error) Madagascar and other countries in the Torrid zone abound with crystal.

The history of the discovery of glass is described later. The ancients knew very well that a clear glass can be made by fusing sand or rock crystal with salts of potassium or sodium. J. B. van Helmont [3] noticed that such a glass can be slowly dissolved in water, and that the addition of aqua fortis to saturate the alkali, precipitates the original quantity of siliceous earth. J. R. Glauber called the aq. soln. of the fused alkali and sand—*oleum silicum*, or *liquor silicum ;* and J. N. von Fuchs, *Wasserglas* (*q.v.*).

The high temp. fusibility and the resistance of silica to chemical reagents has greatly retarded the development of the chemistry of silica. C. W. Scheele's discovery of hydrofluoric acid, in 1771, proved a veritable touchstone to the chemistry of silica, but even then, progress was and is very slow. Silica has been identified with the *terra vitrescibilis* of J. J. Becher [4] (**1.** 1, 15). In 1666, O. Tachenus pointed out that, unlike earths, silica has acidic properties, for it unites with alkalies, and shows no tendency to neutralize the acids. The feebly acidic qualities of silica were emphasized further by J. Smithson, and J. W. Döbereiner. J. J. Berzelius (1811), indeed, showed that silica unites with the bases in definite proportions, forming salts of silicic acid ; and that siliceous minerals are to be regarded as definite salts of this acid. T. Bergman separated silica from siliceous

earths by fusing them with alkali carbonate or hydroxide, and treating the product with dil. acid—insoluble silica, and soluble alkali salts were formed.

Towards the end of the eighteenth and the beginning of the nineteenth centuries, G. L. L. de Buffon,[5] P. J. Macquer, and many other chemists regarded silica as a primitive earth, for it was argued: *la silice est la plus homogène, la plus simple, et la plus élémentaire des terres.* This view was favoured by the infusibility of silica, and the resistance which it offers to attack by reagents generally. Some aluminous earths, however, were confused with silica. J. H. Pott,[6] in his memoir: *Ueber den terris vitrescentibus* (1746), emphasized his belief that the chief constituent of the vitrifiable rocks was a peculiar earth which could not be converted into lime, but which, when fused with alkalies, forms a *terra alcalina* which is precipitated by a small amount of acid, and can be dissolved in an excess of vitriolic acid producing what he called *terra selenitica.* The work of J. H. Pott was extended by A. Baumé, and J. F. C. Meyer. A. Baumé showed that only freshly precipitated silica is soluble in the acid:

> Il faut prendre tandis qu'elle est en bouille, et avant qu'elle ait été séchée; car lorsqu'on l'a fait sécher, les parties se sont réunies et agglutinées entre elles par l'attraction; cette terre alors ne plus se dissoudre.

F. A. Cartheuser, C. W. Scheele, and T. Bergman demonstrated clearly that although precipitated silica could be dissolved in water and acids, it was not an alkaline or calcareous earth. At the end of his essay: *De terra silicea* (Upsala, 1779), T. Bergman concluded that:

> Those earths are called primitive which cannot be resolved into such as are more simple, and derivative earths are those which are composed of two or more primitive earths intimately united. . . . In mineralogy, siliceous earth may be considered to be primitive until by apt experiments, both analytic and synthetic, it be demonstrated that the base of this earth entirely agrees with one already known. . . . If the question be asked whether siliceous earth be altogether simple and homogeneous, the proper answer would be in the negative, for it appears plainly to consist of two principles, namely, fluor acid and something derived from water.

Thus, T. Bergman believed that siliceous earth is primitive, but his confidence was shaken because he added, "but not altogether primitive." This doubt was a result of his repetition of some experiments by C. W. Scheele,[7] who, in 1771, regarded silica earth as a compound of hydrofluoric acid with water because, as A. S. Margraaf had shown in 1768, the gas obtained when fluorspar is heated in a glass retort with sulphuric acid, gives a precipitate of silica when passed into water. It was, however, proved by J. C. F. Meyer that no silica is obtained if the sulphuric acid be heated with fluorspar in a lead retort; and C. W. Scheele, and J. C. Wiegleb then demonstrated that no silica is obtained if the materials used in the preparation of the gas are kept out of contact with any substance containing silica.

In 1787, A. L. Lavoisier [8] assumed silica to be an oxide of an unknown metal. About 1808, J. J. Berzelius mentioned in a letter to H. Davy that in making an analysis of cast iron, he found it contained the metal of silex, and that on oxidation, this metal took up nearly half its weight of oxygen; he also succeeded in decomposing silica by heating an admixture of silica, iron, and charcoal. This product ultimately proved to be an alloy of silicon and iron, namely, *ferrosilicon.* In 1809, H. Davy attempted to isolate the metal by the electrolysis of silica, or by reduction with potassium at a red heat. He said: Had I been so fortunate as to have obtained more certain evidences of the metallic substance I was in search of, I should have proposed for it the name *silicium.* No definite result was obtained by J. Mantell, in 1818, although in 1809, J. L. Gay Lussac and L. J. Thénard heated potassium in the vapour of *le gaz fluorique silice,* and noted that the reaction was attended by the development of much heat and light; a large quantity of the gas was absorbed, and very little hydrogen was produced; the potassium disappeared and there remained *une matière solid dont la couleur est brun rougeâtre* which was not examined further. In 1823, J. J. Berzelius produced the element by reducing potassium

fluosilicate, $K_2SiF_6$, with potassium, and he also determined its chief properties—*vide infra* at. wt. silicon. J. J. Berzelius called his product *Kiesel*, but this term has not been adopted.

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## § 2. The Occurrence of Silicon and Silica

Silicon does not occur free. Silicon is next to oxygen the most abundant element in Nature. It occurs in all silicate minerals, and it is the characteristic element of all important rocks outside the carbonates. F. W. Clarke's estimate of the mean percentage mineralogical composition of about 700 igneous rocks is quartz, 12·0; felspars, 59·5; hornblende and pyroxene, 16·8; mica, 3·8; and accessory minerals, 7·9. According to F. W. Clarke's estimates,[1] 27 per cent. of the earth's lithosphere is combined silicon, and 47·33 per cent. is oxygen. Again, 85·79 per cent. of the earth's hydrosphere is oxygen; and the average in the lithosphere, hydrosphere, and atmosphere is 50·02 per cent. oxygen, 25·80 per cent. silicon. F. W. Clarke further estimates that on the average, 59·79 per cent. of the igneous rocks; 58·10 per cent. of the shales; 78·33 per cent. of the sandstones; and 5·19 per cent. of the limestones in the earth's crust consist of silica—free or combined. The weighted average for the lithosphere is 59·77 per cent. of silica.

Silicon occurs as free silica, silicon dioxide, in the form of **quartz**, and, as such, is one of the most common and most abundant minerals on the earth's crust; it forms whole mountain ranges in Scotland, Ireland, North Wales, Shropshire, and numerous other parts of the earth. Some of the water-worn quartz grains in the river-beds of Minas Geraes (Brazil) are transparent and colourless, and they are used extensively as *Brazilian pebbles* in the manufacture of spectacle and other lenses. Similar pebbles are found in Madagascar. The clear and transparent varieties of

quartz were called *crystal* by the ancient Greeks; and to-day they are known as **rock crystal**—*cristal de roche*, or *Bergkrystall;* while the variety which is white, and translucent or opaque is common **quartz.** Some of the glittering rock crystals are called " diamonds " in particular districts—*e.g.*, *Bristol diamonds*, *Marmaroscher Diamanten*, etc. During the cinquecents period—sixteenth century—transparent and colourless quartz was made into vases, bowls, etc., and elaborately engraved, and this mineral was similarly treated by the ancient Greeks and Romans. Rock crystal was probably the sixth precious stone—under the name *adamas* (diamond)—described in *Exodus* (**28.** 18; **39.** 11) as ornamenting the breast-plate of the high priest of the children of Israel.

Nature furnishes some beautiful specimens of crystalline quartz. A single crystal weighing nearly a ton has been reported at Calaveras (U.S.A.), and some fine crystals have been found in many other places—Dauphiné, Savoy, St. Etienne-la-Varenne, the Apuan Alps, the Alps, Snowdon in Wales, Tintagel in Cornwall, etc. Quartz from different localities often shows differences in colour, translucency, and structure; there are a great number of varieties to which special names were applied before it was known that they belonged to the same mineral species, and composed of the same fundamental substance—silica. Some of these varieties still retain their old trivial names, and some are important gem-stones.

For example, the **amethyst,** *amethystine*, or *amethyst quartz* has a bluish-violet or purple colour. It obtains its name from $\alpha$, not; and $\mu\epsilon\theta\acute{\upsilon}\omega$, to intoxicate, because it was fabled to possess some quality which prevented intoxication by wine drunk from amethyst vessels. A sample from Minas Geraes (Brazil) analyzed by H. Rose [2] yielded 97·5 per cent. of silica; 0·25 per cent. of alumina; 0·5 per cent. of iron oxide; and 0·25 per cent. of manganese oxide. It has been suggested that the colour is due to the last-named oxide, but this has not been definitely decided. C. F. Rammelsberg's analysis of a Brazilian sample showed no manganese, and he assumed that the colour is due to a compound of iron and soda. The colour is not destroyed by heating the mineral to about 300°, but if heated to redness, the colour becomes yellow when cooled. W. Hermann found that smoky quartz, amethyst, and citrine lose their colour when heated in oxidizing or reducing gases, and therefore the tinctorial agent is not an oxide of the heavy metals. T. L. Watson and R. E. Beard, T. H. Holland, regarded the colour as due to fine rutile inclusions; and E. F. Holden, to hydrated colloidal ferric oxide. **Rose quartz** has been stated to owe its rose-red colour to manganese; but this is not certain. The colour becomes paler when exposed to light. J. N. Fuchs [3] attributed the colour to the presence of 1·0 to 1·5 per cent. of titanic oxide; W. Hermann, and E. F. Holden, to tervalent manganese; and R. Brauns, P. Berthier, K. von Kraatz-Koschlau, and T. L. Watson and R. E. Beard, to organic matter. A. Nabl found traces of iron and sulphur in amethysts, and showed that citrine had the absorption spectrum of iron oxide; accordingly, he assumed that the colour was produced by iron thiocyanate, but this is not likely. E. Weinschenck opposed the views that the colouring matter is organic, or titania alone, though he said it might be due to small amounts of sesquioxides of titanium, tin, or zirconium. He obtained a red colour with alumina and titanium. It is not improbable that the colour of the amethyst and rose quartz is really due to manganese. E. F. Holden found a pink crystal to be coloured by hæmatite inclusions of microscopic dimensions. The decolorization of rose quartz by heat was studied by W. Hermann, K. Simon, and E. F. Holden. **Yellow quartz,** or *citrine*, is the colour of topaz, and has hence been called *false topaz*. E. F. Holden found a sample of citrine to be coloured by submicroscopic particles of hydrated ferric oxide. **Smoky quartz,** or *quartz enfumée* or *Rauchquarz*, owes its yellow, brown, or black colour to the presence of organic matter or hydrocarbons. Sometimes the quartz is so rich in organic matter that it has a nasty smell when warmed—*stink quartz* or *fœtid quartz*. K. von Kraatz-Koschlau and L. Wöhler found 0·04 per cent. of carbon, and 0·0073 per cent. of hydrogen in a sample of smoky quartz. R. J. Strutt found smoky quartz to be optically turbid, scattering light very strongly; but C. V. Raman showed that with ultra-red rays, smoky quartz is as transparent as colourless quartz. A. Forster made some observations on this subject. B. L. Vanzetti found some specimens exhibit Tyndall's phenomenon, and the coloration disappears at 300°. The lighter coloured varieties of smoky quartz were possibly those called *mormorion* by Pliny. Cut specimens of yellow and brown smoky quartz from Banffshire are known as *cairngorm*. **Milky quartz,** or *quartz laiteax*, or *quartz en chemise*, or *Milchquarz*, owes its opalescence to the presence of innumerable cavities containing, according to D. Brewster, [4] an oily liquid; sometimes the cavities contain a bituminous fluid and at other times water and air-bubbles.

The colour of common quartz is very varied, and is usually due to the presence of foreign particles enclosed in the crystals. For instance, *ferruginous quartz* or *Eisenkiesel* is coloured either red by ferric oxide, or yellow by hydrated ferric oxide; *aventurine*

*quartz* contains scales of mica or hæmatite which give it a spangled appearance. *Cat's eye, œuil de chat,* or *Katzenauge* is a translucent variety of quartz with numerous fine fibres of asbestos or actinolite arranged parallel to one another, which cause a curious chatoyant reflection from the surface with a play of colours moving across the surface as the stone is turned. Cat's-eye quartz is sometimes called *crocidolite—κροκίς,* woof—but this name is usually reserved for a variety of chrysoberyl.

There are two native forms of crystalline silica, **tridymite** and **cristobalite,** which are quite different from quartz and from each other, so that silica is at least trimorphous. Tridymite is found in the more siliceous igneous rocks which have crystallized from molten magmas, in volcanic lavas, and in some meteorites. Cristobalite is comparatively rare; it sometimes accompanies tridymite. Cristobalite has been found in Cerro San Cristóbal (Pachuca, Mexico), St. Vincent (Martinique lava, 1902–3), Mont-Doré (Plateau Central, France), Olokele Canyon (Kauai, Hawaiian Islands), Rhenish Prussia, Tuscan Springs (Tehama County, Cal.), and Jamestown (Toulumne County), in the obsidian of Yellowstone National Park by A. F. Rogers; [5] and in a meteorite found in Kendall County (Texas) by A. F. Rogers. Tridymite has been found in the trachyte of the Euganean Hills, near Padua; [6] in the trachyte of Drachenfels; in rocks in Scotland, Laacher Sea, Phlegræan Fields, Moezar (Hungary), Auvergne, Demarend (Persia), Aden, Guatemala, New Zealand, etc.

The different forms of quartz can be arranged in three groups: (1) The crystalline group described above; (2) the chalcedonies which were once thought to be amorphous, but which are really partially crystalline—cryptocrystalline—*κρυπτός,* hidden; and (3) the hydrated silicas or opals. The name **chalcedony** is applied to various forms of concretionary silica which appear to be made up of quartz, and hydrated silica of the nature of opal. Chalcedony is translucent or opaque; and either white, grey, yellow, brown, or blue. Although crystalline, chalcedony has not the external form characteristic of crystals, but rather occurs in mammillary, botryoidal, globular, or stalactitic masses.

The amount of water in different varieties of chalcedony varies from less than one up to about five per cent., and this in conjunction with the general relations which chalcedony bears to quartz and to opal, confirms C. Hintze's view [7] that chalcedony is a mixture of crypto-crystalline quartz and a hydrated form of silica related to opal. Assuming that the sp. gr. of opal is 2·15 and of quartz 2·65, the corresponding proportions of these two assumed components of chalcedony can be calculated from the observed sp. gr. Chalcedony can be dyed black, red, blue, green, and yellow.[8] Chalcedony appears to have been named after *Χαλκηδών* or *Καλχηδών,* places in Asia Minor, whence it was once obtained. All the varieties of chalcedony referred to by Pliny and Theophrastus have not been clearly identified with those recognized to-day. The so-called *quartzine* and *lutecite* are varieties of chalcedony.[9]

The mineral *carnelian* is a variety of chalcedony which is translucent and of a red colour, hence the name *caro, carnis,* flesh; *sard*—from Sardes in Lydia, or Sardo the Greek name for Sardinia—is an early name for carnelian, but is now applied to a pale or dark brown translucent chalcedony; *plasma—πλάσμα,* image—is a variety of chalcedony coloured green by enclosures of green earth or chlorite, and it resembles green jasper. *Heliotrope* or *bloodstone* is a form of *plasma,* and is a mixture of earthy chlorite and chalcedony. It is usually green in colour with small spots of iron oxide, blood-red in colour. The derivation of the name—from *ἥλιος,* the sun; *τροπή,* a turning—refers to the old supposition that if the mineral be immersed in water it will change the image of the sun blood-red. Another form of bloodstone is hæmatite, not silica. *Chrysoprase—χρύσεος,* golden; *πράσον,* a leek—is an apple-green or grass-green variety of chalcedony found in Silesia. According to M. H. Klaproth's analyses,[10] the colouring agent is nickel oxide—approximately one per cent. *Agate*—from Achates, a river in Italy where specimens were found and now called the Drillo—is a variety of chalcedony sometimes with alternate zones or layers—light and dark. S. S. Bhatnagar and K. K. Mathur [11] discussed the formation of these rings, and prepared artificially banded silica gel by allowing ferric, cobalt, or nickel salt soln. to diffuse into silica hydrogel—*vide* 1. 10, 6. A translucent, white or bluish-white variety, having included in it metal oxides causing brown, red, or black dendritic forms, is called *moss agate,* or *tree agate,* or *mocha-stone.* The variety of agate called *onyx*

—ὄνυξ, a finger nail—has concentric zones alternately white and dark brown or grey; *sardonyx* is a variety of onyx with white and reddish-brown layers. *Flint*—also called *silex*, or *la pierre à feu*, or *Feuerstein*—is allied to chalcedony. It has a conchoidal fracture, and the colour varies from grey to black. It is of organic origin and often contains sponge spicules. The nodules of flint found by primitive man were shaped into various forms so that they could be conveniently held in the hand, and used as implements or weapons. Man, the tool-maker, thus inaugurated the Stone Age, estimated to have been at least 80,000 years ago. In the earlier stages of the Stone Age—the Palæolithic Period—the flints were roughly shaped by chipping; while in the later stages—the Neolithic Period—the flints were ground and polished. *Chert* or *hornstone* is a compact variety of chalcedony, and, like flint, is of organic origin. *Lydian stone*[12]—also called *lydite*, or *touchstone*—is a grey or velvety-black flinty rock or siliceous slate used by jewellers for testing the purity of gold. The metal under investigation is rubbed on the polished surface of the stone, and the colour of the streak of metal, particularly when touched with acid, enables those experienced in the colour of the streaks to estimate the proportion of gold in the alloy. This stone was employed by the ancients under the name *lapis lydius* or *lapis basanitis* for the same purpose. The stone was formerly obtained from Lydia (Asia Minor), but it is now obtained from other localities. A sample analyzed by J. B. A. Dumas gave:

| $SiO_2$ | $Al_2O_3$ | $Fe_2O_3$ | CaO | MgO | $K_2O$ | $Na_2O$ |
|---|---|---|---|---|---|---|
| 84·40 | 5·25 | 1·15 | 0·43 | 0·13 | 0·69 | 0·70 |

with sulphur and phosphorus about 0·06 each; water, 0·7; and organic matter, 4·65 per cent. *Jasper* is a siliceous rock or hardened clay which occurs in masses mixed with some clay and yellow or red oxide of iron. If the yellow forms be heated, they lose water and become red. Jasper is sometimes striped green and brown, or green and red. In *Egyptian jasper* the bands occur in concentric zones. Jasper is often mentioned by ancient writers, and in the Bible.

Sandstones have been formed by the cementing together of the grains of sand, maybe under great press. The cementing agent may be argillaceous, calcareous, siliceous, ferruginous, barytiferous, etc. Special names are given to particular varieties—*e.g. ganister*, etc. In the so-called **quartzites,** the grains of quartz sand appear to have been cemented together by the infiltration of soluble silica. When thin sections are examined microscopically, the original quartz grains can usually be distinctly seen in the outline within an envelope of unfiltered and crystallized silica.[13] In some cases, the quartz grains have recrystallized. According to T. Graham:[14]

> The formation of quartz crystals at a low temp., of so frequent occurrence in Nature, remains a mystery. I can only imagine that such crystals are formed at an inconceivably slow rate, and from soln. of silicic acid which are extremely dil. Dilution, no doubt, weakens the colloidal character of such substances, and may therefore allow their crystallizing tendency to gain ground, and develop itself, particularly where the crystal once formed is completely insoluble as with quartz.



FIG. 1.—Section of Quartzite from the Lickey Hills (Worcestershire), under polarized light.

Sometimes the silicification of the grains has been so complete that to the naked eye the rock appears as homogeneous and compact as vein quartz, and it requires microscopic examination to reveal the agglomeration of the quartz crystals. A photograph of a thin slice from Lickey Hills (Worcestershire) is indicated in Fig. 1, as viewed under polarized light. Grains of other minerals may be cemented in the rock along with the quartz grains. Some varieties of quartzite contain over 99 per cent. silica. The *flexible sandstone* of Delhi is said by O. Mügge[15] to consist of angular quartz grains which interlock or dovetail into each other so that there is a slight play between the particles. Whatever be the true explanation, the sandstone can be bent in an extraordinary manner without breaking. *La pierre élastique* or *die biegsame Sandstein* also occurs in Itacolumi, Minas Geraes, Brazil—whence the name *itacolumite*—and in several other localities, *e.g.* Pennsylvania, North Carolina, etc.

The non-crystalline hydrated silica called **opal** contains up to 12 per cent. of water. The colour varies from white to yellow, red, brown, grey, or blue; and the gem opal exhibits a beautiful play of iridescent colours. Selected specimens are much admired as gem stones, for they are said to "reflect all the prismatic colours in refulgent tints of indescribable brilliancy." Pliny[16] says the *opalus* is made up of the glories of the most precious gems. It was called παίδερως or ὀπάλλιος by Dioscorides in his Περὶ ὕλης ἰατρικῆς written about 50 A.D. Some have a superstitious dread of the stone, which they suppose *porter malheur*. R. E. Liesegang discussed the hypothesis that the opalescence is due to the presence of colloidal matter.

*Hyalite* is a transparent colourless variety of opal; *hydrophane* is a variety which becomes transparent when plunged in water; and *tabaschir* is a related variety. *Geyserite* is a variety from Iceland, and other geyser localities. Analyses by R. W. Woodward,[17] G. Forchhammer, A. Damour, C. Bickell, J. W. Mallet, A. Petermann, etc., have been recorded by F. W. Clarke, and J. Roth. They run: $SiO_2$, 79·34–94·40; $Al_2O_3$, 0·69–10·96; $Fe_2O_3$, 0·17–2·68; CaO, 0–1·71; MgO, 0–1·06; $K_2O$, 0–1·66; $Na_2O$, 0–3·55; $SO_3$, 0–2·49; volatiles, 1·50–14·50. D. Brewster has written on this subject. The occurrence of hyalite in pitchstone has been noted by J. W. Judd, and A. Scott; and in granite, by P. Grischtschinsky. *Petrified wood* contains much hydrated silica. Numerous other names have been applied to varieties of opaline or hydrated silica, *e.g. fire opal, wax opal, glass opal, milk opal, mother-of-pearl opal, iron opal, jasper opal, randanite, memilite, resinous silica*, etc.

In his dissertation *De aquis Upsaliensibus* (Upsala, 1770), T. Bergman reported the presence of silica in this spring water, and, since then, silica has been found in most river, well, and spring waters. In 1794, J. Black[18] demonstrated the relatively large proportion of silica in the volcanic springs of Iceland; R. Bunsen also made observations on the silica contents of these waters; and F. Sandberger found 0·5097 part and A. Damour 0·5195 part of silica in 1000 parts of water. A. K. Dambergis found 0·05 grm. of silica per litre in the spring water at Edepsos. C. Bickell found 0·1663–0·2373 part of silica in 1000 parts of the spring waters of Raykir; and J. Smith, 0·606 part of silica in 1000 parts of water of Rotomahana. R. Woy found the spring waters at Reinerz, Silesia, contained from 0·04994–0·10037 part of silicic acid, $H_2SiO_3$, per 100 parts. L. Colomba suggested that the silica of the fumarole water at Lipari is derived from the action of silicon fluoride on the water. G. Forchhammer[19] observed the presence of silica in sea-water, and observations on this subject have been made by W. E. Ringer, R. C. Wells, etc. According to J. Murray and R. Irvine, one part of sea-water contains from one part in 220,000 to one part in 460,000; and E. Raben found 0·0002–0·0014 grm. of silica per litre. The necessary conditions for the dissolution of silica in water seem to prevail in deep-seated cavities in the earth. The water rising to the surface is cooled, and the pressure reduced. Some of the dissolved silica is then deposited at the mouth of the spring as a thick jelly. This afterwards changes into a hard white porous mass of geyserite. The Great Geyser of Iceland, for instance, is surrounded by a large mound or hillock of silica with a funnel-like cavity from which the geyser discharges. Geysers also occur in the Hot Springs of New Zealand; Yellowstone Park, U.S.A., etc. Some petrifying springs owe their special character to the silicic acid which they hold in soln. Woody tissue, for example, when immersed in such water, may be replaced by the silica. In many cases—*e.g.*, the mineral springs at Yellowstone Park—the alkalinity of the water seems to facilitate the soln. of the silica. The alkaline silicates are decomposed by the carbon dioxide of the atmosphere and the silica is deposited in the neighbourhood as *geyserite* or *siliceous sinter*.

Silica is a regular constituent of plant ashes; the grasses and *equisetaceæ* are particularly rich in silica. According to J. L. Macie,[20] siliceous concretions called *tabaschir* (*vide supra*) are found in the nodes of the bamboo. F. J. Cohn discussed this product in his memoir *Ueber Tabaschir*. E. Wolff, and A. Vogel reported the ashes of barley to have 17·27–36·73 per cent. of silica; oats, 33·46–55·95; maize, 0–5·54; peas, 0–3·02; the skin of potatoes, 1·93–9·40, and the inside, 0–8·11;

tobacco leaves, 4·51–18·39; and mushrooms, 0·09–15·37 per cent. The rigidity of straw was once supposed to be due to the silica it contains, but F. Sachs [21] found it possible to grow plants furnishing straw free from silica without affecting its rigidity; W. Knop, F. V. Jodin, and F. Höhnel obtained similar results. E. T. von Wolff and C. Kreuzhage found a difference in the progress of grain formation, with and without silica; and A. D. Hall and A. Morrison concluded that the presence of silica increased the assimilation of phosphoric acid. C. J. Schollenberger and O. M. Shedd also noted the stimulating effects of silica on growth in soils deficient in phosphoric acid. O. Lemmermann and H. Wiesmann concluded that in the absence of phosphates, colloidal silica can take the place of phosphate. D. R. Nanjo and W. S. Shaw showed that silica is present in the plant as colloidal silica; and U. Abshagen found that in the silicification of a plant, the leaves are affected first, then the lateral sprouts, and finally the stem. Transverse sections show that the increase in silica content proceeds from within outwards. The function of the silica in the straw of most *gramineæ* is not known.

Certain organisms which abound in sea and other waters probably obtain a large portion of their silica from the fine clay matter in suspension. The so-called *diatomaceous earth*, *diatomite*, or *kieselguhr* appears as a friable powder outwardly resembling chalk or clay, and is virtually a mass of the siliceous skeletons of dead diatoms, which formerly lived on the surface of pools of water, etc., and ultimately settled to the bottom along with decaying vegetable matter. The resulting diatomaceous earth is not uncommonly found in peat-bogs, and marshes on the shores of existing lakes. Some of the older deposits are consolidated—*e.g. tripoli* or *tripolite*, so named from its occurrence in Oran (Tripoli). N. Goodwin has compiled a bibliography of these earths. The skeleton of sponges is a delicate network of glass-like fibres and spicules consisting of hydrated silica analogous to opal—*e.g. Euplectella aspergillum*, or Venus' flower basket. The organisms extract the silica from sea-water. The sponges were gradually covered by accumulations of chalk, and the silica seems to have been dissolved by water percolating in the chalk, and redeposited in other parts of the limestone or chalk about other sponge spicules as irregular nodules of flint, or as bands or veins of *chert*—originally the term "flint" referred to any particularly hard rock (*Deut.* **8**. 15; *Psalms* **114**. 8). The photographs, Fig. 27 (and Fig. 70, **1**. 11, 7), may be taken as evidence of the movement of water with silica in soln. in chalk and limestone rocks. A. M. Edwards observed that "some shells in diatomaceous earth dissolved in fresh spring water" probably from the contained ammonia.

Some parts of animals are almost free from silica, other parts contain appreciable amounts. E. C. F. von Gorup-Besanez found appreciable amounts in animal tissues, feathers, etc. The ash of hen's blood is reported [22] to have 1·24 per cent. of silica; the ash of the feathers of flesh-eating and insect-eating birds, 27 per cent. of silica; fish-eaters, 10·5 per cent.; and grain-feeders, 40 per cent. of silica. H. Schulz found 0·0826 per cent. silica in the ash of man's flesh; and 0·1484 in the ash of the skin. More silica occurs in the same tissues in youth than in old age. J. E. Reynolds, arguing from several analogies between the behaviour of carbon and silicon compounds, said that it may be possible for the plant to construct from silicon compounds, ultimately derived from the soil, something akin to silicon protoplasm for use in its structures. Similar observations apply to the power of sponges to extract silica from sea-water as a part of their normal food supply and use it in cell production. He added:

> All theories of life assume that its phenomena are inseparably associated with certain complex combinations of the elements carbon, nitrogen, hydrogen, and oxygen, with the occasional aid of sulphur and phosphorus. These are the elements of that protoplasm which is the physical basis of life, and by their interplay they form the unstable and complicated groupings of which that remarkable material is composed. All the phenomena we call vital are associated with the change of some protoplasm, and the oxidation of carbon and hydrogen. But it is quite open to question whether the connection of life with the elements first specified is inevitable. We can conceive the existence of similar

groupings of other analogous elements, forming other protoplasms capable of existing within much greater ranges of temp. than any plants or animals now known to us have to withstand. For example, we can imagine a high temp. protoplasm in which silicon takes the place of carbon, sulphur of oxygen, and phosphorus of nitrogen, either wholly or in part. In fact, protoplasm so far as we know it in purest form, always contains some sulphur, and often a little phosphorus, representing a very partial substitution of the kind in question.

The spectra of the sun and of different stars show the presence of silicon.[23] The subject has been studied by J. N. Lockyer and co-workers, H. A. Rowland, J. Lunt, F. W. Dyson, W. M. Mitchell, W. S. Adams, O. Vogel and J. Wilsing, A. de Gramont, etc. G. Rose reported quartz in a meteorite from Xiquipulco; G. P. Merrill, in one from St. Mark's, South Africa; H. Laspeyres, in one from Toluca (Mexico); and E. Cohen, in one from Beaconsfield (Victoria). N. S. Maskelyne reported asmanite (tridymite) in a meteorite from Breitenbach. The occurrence of tridymite in meteorites has been discussed by G. vom Rath, A. Weisbach, C. Winkler, G. Tschermak, E. Mallard, E. Cohen, H. Moissan, and N. H. Winchell. The occurrence of cristobalite was reported by E. Cohen in the meteorite of Kendall Co., San Antonio, Texas. According to H. Moissan, silicon carbide (*moissanite*) has been found in meteorites.


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## § 3. The Preparation of Silicon

The silicon prepared by J. J. Berzelius about 1808, by heating a mixture of silica, carbon, and iron was really not silicon at all, but rather an iron silicide, or ferro-silicon. H. Davy was not very successful in his attempt to reduce silica by electrolysis, or by potassium at a high temp. According to A. Dufour, there are signs that quartz is slightly reduced by hydrogen at high temp., but this reaction is not practicable as a means of preparing silicon. The reduction of silica by carbon, at the temp. of the electric arc, is, however, a satisfactory mode of preparation. Silicon appears to exist in two forms—amorphous and crystalline. According to E. Vigouroux, the difference in the two forms is a question (i) of the degree of purity rather than allotropism; and (ii) of the state of subdivision, the grain of the so-called amorphous form being much finer than the crystalline form. Purified amorphous silicon does not differ from crystalline silicon of the same degree of purity—*leurs propriétés chimiques sont identiques.* P. Lebeau came to a similar conclusion.

For a long time, on the strength of J. J. Berzelius' observations,[1] it was thought that there are two forms of amorphous silicon, the one active amorphous silicon—*vor dem Glühen*—was called *silicon-α*, and the other passive amorphous silicon—*nach dem Glühen*—or *silicon-β*. The latter was obtained by strongly heating the former, and washing the product with hydrofluoric acid. (i) The active form was combustible in air or oxygen, the passive form was incombustible in these gases; (ii) the active form was insoluble in all acids excepting hydrofluoric acid, the passive form was insoluble even in hydrofluoric acid or in a mixture of hydrofluoric and nitric acids; and (iii) the active form was soluble in an aq. soln. of potassium hydroxide, the passive form was insoluble in that menstruum. E. Vigouroux examined the products prepared according to J. J. Berzelius' directions, and concluded that the alleged modifications *ne sont pas des corps simples*, but rather impure forms of silicon; and that the observed differences are due to differences in the composition of the two forms. There are, however, differences of opinion because E. Wilke-Dörfurt showed that the amorphous silicon which is obtained by reducing silicon fluoride with sodium at a dull red heat reacts with sulphuric acid and hot water during the washing. The sulphuric acid is reduced with sulphur as one of the products. The yield of amorphous silicon by this process is therefore very small. On the other hand, the grey powder of amorphous silicon, obtained by treating with acids the metallic regulus, furnished when sodium fluosilicate is fused with sodium and aluminium, is not very active chemically, but when heated with hydrofluoric acid, it forms a brown variety of amorphous silicon which is very reactive, for it is violently attacked by conc. nitric acid, forming a white substance, possibly a nitride, which evolves ammonia when heated with sodium hydroxide. Brown amorphous silicon is transformed into the less active form when heated. If these results be confirmed, it may be necessary to reintroduce J. J. Berzelius' α- and β- amorphous silicons—*vide* Fig. 6. According to L. Cambi, the hydrolysis of black vitreous silicon sulphide, SiS, furnishes soluble silica, and amorphous silicon,

which is a paler reddish-yellow than E. Vigouroux' product. The sp. gr. is 2·08; and, after heating, its colour and properties approach those of E. Vigouroux' amorphous silicon (*vide infra*). L. Cambi regards the different varieties of amorphous silicon as indefinite masses possessing different mol. structures. L. Baraduc-Muller observed peculiarities in the thermal expansion which he attributed to the appearance of an allotropic crystalline form of silicon stable between 700° and 1025°—*vide infra;* and J. Königsberger and K. Schilling observed peculiarities in the electric resistance (*q.v.*), which they attributed to the existence of three allotropic forms of silicon.

H. St. C. Deville [2] claimed to have made what he considered to be a graphitic form of silicon—*graphitoidal silicon*—related to the ordinary crystalline form much as graphite is related to the diamond. W. H. Miller, however, showed that both the black glistening hexagonal plates, and the dark steel-grey six-sided pyramids or needle-like crystals of crystalline or *adamantine silicon* are really octahedral crystals belonging to the same system. H. Kopp did show that the sp. ht. of ordinary crystalline silicon and of the graphitic form are different, and this conclusion was confirmed by C. Winkler. F. S. Hyde obtained silicon in graphitoidal plates by melting raw silicon, aluminium, and cryolite. By treating potassium fluosilicate with impure aluminium at a high temp., H. N. Warren claimed to have made oblique octahedral crystals of silicon different from the ordinary crystalline form. In 1904, H. Moissan and F. Siemens found that molten silver dissolves silicon, which it rejects as the metal solidifies. This form of crystalline silicon is partly soluble in hydrofluoric acid, while the ordinary crystalline form is insoluble. The amount of silicon soluble in the acid diminishes as the amount of silicon dissolved by the silver increases, and this is determined by the temp. of the molten silver as illustrated in Fig. 2. When there is only two per cent. of silicon in the silver, the silicon is nearly all soluble in the acid. The solubility in hydrofluoric acid was the only chemical difference observed between the soluble and ordinary forms of crystalline silicon. P. Lebeau noticed similar phenomena when silicon is dissolved in molten copper; and the preparation of crystalline silicon from a soln. of silicon in copper was investigated by W. Manchot and H. Funk. They examined the products from soln. of silicon in aluminium, silver, lead, and zinc, and concluded that quenching is the essential factor in producing the soluble form; that all crystallized silicon is slowly but completely dissolved by hydrofluoric acid; and that the brown variety which resists hydrofluoric acid is in a *state of passivity* acquired by the occlusion of hydrogen.

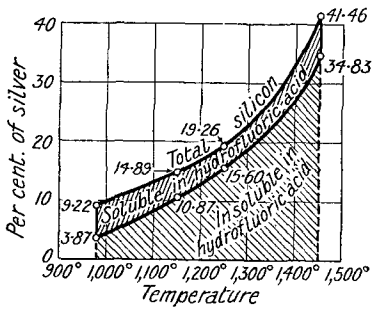



FIG. 2.—Character of Silicon crystallized from Molten Silver.

**The preparation of amorphous silicon.**—Amorphous silicon has been made by reducing silicon halides or oxide with certain metals; by double decomposition of the silicides; and by electrolysis. J. L. Gay Lussac and L. J. Thénard [3] reduced the vapour of silicon tetrafluoride by heated potassium. W. Hempel and H. von Haasy used sodium as the reducing agent, at 400°–500°: $SiF_4+4Na=Si+4NaF$. The mass was allowed to cool in the current of silicon tetrafluoride so that sodium fluosilicate, $Na_2SiF_6$, was formed; this was easily separated from the silicon by extraction with water. A. F. Holleman and H. J. Slijper found that if an excess of sodium fluoride be avoided, there is practically no formation of sodium fluosilicate. When boiled with water and dil. hydrochloric acid, the residue does not, however, consist of pure amorphous silicon, for only about 40 per cent. can be volatilized in a current of chlorine, the remainder consisting principally of silicon dioxide which has been formed in the extraction of sodium fluoride. H. St. C. Deville reduced the vapour of silicon tetrachloride with heated sodium, and added:

The most prolonged washing is not sufficient to remove all the impurities; and as a result the early chemists who occupied themselves with this question—J. L. Gay Lussac and L. J. Thénard, H. Davy, etc.—were prevented from seeing the true nature of silicon.

A. F. Holleman and H. J. Slijper found that the product by this process contained 30 per cent. of silica. In a boiling soln. of benzene, sodium scarcely has any action on silicon tetrachloride.

J. J. Berzelius also reduced silicon tetrafluoride or tetrachloride with potassium, and washed the product first with cold and then with hot water. His product, called *α-silicon—vide supra*—was contaminated largely with hydrogen and carbon; if purified by heating it in a crucible at a red heat, and washing first with hydrofluoric acid and then with water, what he called *β-silicon* was obtained. He also obtained silicon by heating a mixture of potassium and potassium fluosilicate contained in an iron tube, and extracting the potassium fluoride by water: $K_2SiF_6+4K=6KF+Si$. H. Buff and F. Wöhler heated a mixture of sodium fluosilicate with sodium covered with sodium chloride and contained in a fireclay crucible. E. Vigouroux, and W. Hempel and H. von Haasy criticized the methods of J. J. Berzelius, and H. Buff and F. Wöhler. H. Moissan said that the use of alkali metals for the reduction is very liable to give an impure product, because the action is so energetic, and the heat generated during the reduction is so great, that the vessel in which the reaction occurs is much attacked. H. N. Warren reduced silicon tetrafluoride with magnesium, and obtained amorphous silicon and magnesium silicide, but W. Hempel and H. von Haasy found the yield to be poor, and they observed a similar reaction between magnesium and silicon chloride. G. Rauter found that the reduction of silicon tetrachloride by beryllium in a sealed tube is incomplete at 270°–280°; and magnesium and zinc at 390°–400° gave only a little silicon after 64–67 hours' action; zinc-dust after 28 hours' action at 280°–290° gave only a little silicon; better results were obtained with aluminium at 360°–370° after 71 hours' action. E. Lay found that molten sodium amide, $NaNH_2$, partially reduces silicon tetrachloride.

According to R. Bunsen and A. Matthiessen,[4] sodium exerts a reducing action on silicates, glass, porcelain, etc., even at 200°, while calcium and strontium begin to act at a red heat. H. St. C. Deville reduced a mixture of silica with calcspar and potassium carbonate by means of sodium, but the resulting silicon was very impure. T. L. Phipson showed that magnesium reduces silica, and J. Parkinson obtained silicon and magnesium silicate as products of the reduction. L. Gattermann heated with a Bunsen's burner a mixture of quartz sand and magnesium contained in a test-tube, and found the main reaction corresponds with the equation: $SiO_2+2Mg=2MgO+Si$. The reaction is accompanied by vivid incandescence, and if precipitated silica be used, there may be a slight explosion. If an excess of magnesium is employed, the product is mainly magnesium silicide. In any case, the product which remains after washing with hydrochloric acid is not very pure; and C. Winkler claimed a purer product by reducing silica with magnesium silicide in presence of an excess of silica, but, according to W. Hempel and H. von Haasy, the yield is very small. E. Vigouroux investigated the conditions necessary for preparing pure amorphous silicon by the reduction of silica with magnesium. If the exact amount of magnesium strictly necessary for the reduction be employed, the product is a mixture of amorphous and fused silicon, and a small quantity of magnesium silicide. If an excess of silica be used to avoid the formation of magnesium silicide, it will be very difficult to remove all the silica from the product. If magnesia be added to moderate the violence of the reaction, amorphous silicon can be obtained in a high degree of purity. If the materials are imperfectly dried, the materials may be projected from the reaction vessel with explosive violence. E. Vigouroux recommended the following procedure for making amorphous silicon:

Clear transparent quartz is powdered and intimately mixed with magnesium powder in the proportions corresponding with $SiO_2+2Mg=Si+2MgO$, and with 25 per cent. of

purified commercial magnesia. Both the quartz and the magnesia should be separately calcined to drive off the moisture, otherwise a dangerous explosion may occur—particularly if precipitated silica be used instead of quartz. A convenient charge for a fireclay crucible is silica, 180 grms.; magnesium, 144 grms.; magnesia, 81 grms. The crucible and contents are placed in a furnace at a bright red heat. In two or three minutes, the reaction proceeds with vivid incandescence. The crucible is then withdrawn from the furnace and allowed to cool. The contents of the crucible are uniformly coloured maroon. The product is added to hydrochloric acid, and the insoluble residue washed by decantation. It is then treated with hydrofluoric acid, and after the vigorous action has subsided, heated to 100°. The clear liquid is decanted, and the residue again treated with hydrofluoric acid. The washed residue is then added in small portions at a time to sulphuric acid contained in a platinum dish; the mixture is heated for some hours to the b.p. of the acid so as to convert the metal fluorides into sulphates. The cold mass is washed with hot water; then with conc. hydrochloric acid, then with water, and finally heated to redness in a current of hydrogen. The product contains 96–97 per cent. of amorphous silicon. If purified silica and magnesium be employed, and the reduction be performed in a Bohemian glass tube brasqued with magnesia, and traversed by a current of hydrogen, a still purer product can be obtained. He obtained 99·0–99·6 per cent. silicon in this way.

E. Vigouroux found that pulverized aluminium of commerce, washed free from fatty materials by ether and alcohol, can be used in place of magnesium. The reaction commences at about 800°, and corresponds with the equation: $3SiO_2+4Al=2Al_2O_3+3Si$. The product with aluminium is as pure as that with magnesium, but the yield is not so good. F. E. Weston and H. R. Ellis also reduced silica with aluminium; A. Burger, with calcium; and L. Burgess, with the carbon arc.

Amorphous silicon is deposited when a cold plate is held in the flame of burning silicuretted hydrogen. According to V. Köhlschutter,[5] silicon is separated when canal rays and disintegrated aluminium impinge on glass. H. N. Warren passed sparks through silane, and obtained a deposit of amorphous silicon on the walls of the containing vessel. A. Dufour, and H. Moissan and S. Smiles also obtained amorphous silicon by the decomposition of silicon hydrides; and O. Ruff and C. Albert, by the decomposition of silicochloroform, $SiHCl_3$, at 800°. L. Cambi obtained amorphous silicon by the hydrolysis of silicon sulphide. According to W. Hempel and H. von Haasy, the silicon which separates during the cooling of soln. with less than 20 per cent. of silicon in molten aluminium, is in the amorphous state. H. N. Warren also obtained a separation of amorphous silicon from ferrosilicon; and A. E. Jordan and T. Turner found no crystals of silicon were present in iron with less than 10 per cent. of silicon, and the graphite which separates from such iron also contained no silicon. T. Naske said that silicon in excess of $Fe_3Si$ separates when siliciferous iron is cooled. G. J. L. de Chalmont obtained amorphous brown silicon by the action of sulphur on copper silicide at 250°–300°.

M. Junot [6] claimed to have obtained amorphous silicon by the electrolysis of a potassium cyanide soln. of sodium silicate, but A. J. Balard could not confirm this. H. St. C. Deville found that amorphous silicon separates at the negative electrode when a soln. of silica in a molten mixture of sodium and potassium fluorides is electrolyzed with carbon electrodes. F. Ullik obtained amorphous silicon by the electrolysis of a molten mixture of potassium fluosilicate and fluoride. According to G. Gore, a deposit of silicon is obtained when aq. soln. of alkali silicates are electrolyzed with copper electrodes. A. Minet electrolyzed a mixture of sodium chloride, cryolite, and aluminium, and obtained a silicon alloy which was not further investigated. A. Grätzel von Grätz obtained a similar alloy. H. N. Warren electrolyzed an alcoholic soln. of silicon tetrafluoride with a mercury cathode, and on evaporating the mercury from the amalgam, obtained amorphous silicon.

**The preparation of crystallized silicon.**—In 1854, H. St. C. Deville [7] accidentally prepared a lustrous mass of plates of silicon by electrolyzing a double chloride of aluminium and sodium which contained siliceous impurities. The aluminium was removed by hydrochloric acid. He said:

This body possesses *une inaltérabilité encore plus grande*; and has all the chemical properties which J. J. Berzelius attributed to the residue obtained by the incomplete combustion of ordinary silicon. Thus, in order to give an idea of the indifference of the

action of the most energetic reagents, I may say that the new silicon has been heated white hot in a current of pure oxygen without changing in weight.

He also pointed out that the electrolysis of all siliceous materials in fused alkali fluorides furnishes silicon. F. Wöhler obtained a globule of aluminium by fusing sodium and cryolite in a fireclay crucible, and when the aluminium was removed by acid, crystalline silicon remained. The element is nearly always obtained in the crystalline form when a compound of silicon is reduced by magnesium, zinc, or aluminium in the presence of other metals; and, according to J. Robbins, silver and tin behave similarly. H. N. Warren obtained silicon crystals by melting silicon with an aluminium alloy containing 10 per cent. of tin; and W. Hempel and H. von Haasy said that silicon separates in the crystalline form from aluminium containing over 20 per cent. silicon. E. Eggertz found crystals of silicon in many kinds of iron. H. Hanemann studied the formation of silicon when carboniferous iron is heated in contact with fireclay crucibles. L. Troost and P. Hautefeuille found that when amorphous silicon is fused and allowed to cool, crystalline silicon is formed. In H. St. C. Deville and H. Caron's process, potassium fluosilicate was reduced by sodium in the presence of zinc; and F. Wöhler used a mixture of aluminium and potassium fluosilicate. In either case, the zinc or aluminium can be removed by treating the alloy with acids. F. Wöhler's process is as follows:

A mixture of 125 grms. of aluminium and 400 grms. of potassium fluosilicate, $K_2SiF_6$, is heated in an iron crucible. The reaction proceeds tranquilly. After half an hour's heating to about 1400°, the crucible is removed and allowed to cool. The crucible is broken. The metallic button covered by a thin layer of scoria and weighing about 110 grms. is dislodged from the bottom of the crucible. The button has a silvery colour, is very brittle, and has a very crystalline texture. The button is digested in hydrochloric acid, and then boiled in nitric acid; it is finally treated with hydrofluoric acid, washed, and dried. About 50 grms. of crystalline silicon are obtained.

A. J. Kieser analyzed a sample of silicon prepared by F. Wöhler's process, and found 71·81 per cent. of silicon; 0·33 per cent. of silica; 2·51 per cent. of iron; and 25·32 per cent. of aluminium. C. Winkler heated to redness for about 45 mins. a mixture of cryolite, powdered quartz, and aluminium powder, all covered with a layer of sodium chloride. T. Scheerer emphasized the difficulty of removing aluminium from silicon prepared in this manner. L. Weiss and T. Engelhardt recommended reducing potassium fluosilicate with massive aluminium, a better regulus being obtained than when aluminium powder is used. The regulus is crushed and extracted successively with hydrochloric, conc. sulphuric, and hydrofluoric acids. The product, even after repeated boiling in a state of fine powder with hydrofluoric acid, contains 0·3–0·5 per cent. Fe, 0·1 per cent. Cu, and 0·72 per cent. $SiO_2$.

H. St. C. Deville obtained fine needles of silicon by heating aluminium to redness in the vapour of silicon chloride; when silicon fluoride was used, the product always contained aluminium fluoride. H. St. C. Deville found that if aluminium be heated to a high temp. in contact with glass or quartz, the metal always retains some silicon. E. Vigouroux made silicon by heating quartz powder mixed with an excess of aluminium in a carbon crucible in an electric furnace, and obtained silicon with a fine crystalline fracture. The reaction proceeds at a lower temp. in the presence of a flux, and he preferred a mixture of 120 grms. of aluminium, 30 grms. of quartz, and 220 grms. of potassium fluosilicate. A. J. Kieser used a similar process, and obtained silicon with 0·1887 per cent. of alumina. K. A. Kühne used the thermite process with a mixture of 360 parts of silica, and 400 parts of aluminium; he also used a mixture of silica, 36 parts; aluminium, 40 parts; and sulphur, 50 parts in a fireclay crucible. A. F. Holleman and H. J. Slijper used a modification of this process. O. P. Watts recommended using cryolite or felspar as a flux; K. Gröppel, a basic aluminium silicate. W. G. Mixter recommended purifying the silicon by recrystallization from molten aluminium and subsequent treatment with hydrofluoric acid, potassium pyrosulphate, and hot purified sulphuric acid.

E. H. and A. H. Cowles and C. F. Mabery [8] made silicon alloys by reducing silica with carbon in the electric furnace, and H. Moissan made crystalline silicon by reducing silica in a similar way. H. Moissan said :

> When an intimate mixture of carbon and powdered rock crystal is heated in a carbon cylinder closed at one end in an electric furnace, the orifice of the tube is soon covered with snow-like flakes of silica ; lower down are found beautiful crystals of silicon carbide ; lower still are rings of brilliant black crystals interspersed with globules which have been fused. Neither the crystals nor the globules are attacked by a mixture of nitric and hydrofluoric acids. They inflame in fluorine gas forming silicon fluoride. Some of the crystals resemble those obtained by the soln. of silicon in molten zinc. The crystalline dust which collects in the tube contains 28–30 per cent. of crystalline silicon.

K. Gröppel obtained silicon by heating aluminium silicates, silica, and carbon in the electric arc furnace. The final slag had the composition $SiO_2+6–7Al_2O_3$. About 3 per cent. of cryolite renders the slag sufficiently fluid. O. P. Watts found that sodium silicate gives better results as a source of silicon than does silica, glass, or calcium silicate ; he also obtained silicon by reducing silica or silicates with silicon carbide. The reduction of silica by carbon or silicon carbide in the electric furnace has been discussed by G. J. L. de Chalmot, R. Scheid, F. J. Tone, etc. J. Königsberger and K. Schilling electrolyzed silica with carbon electrodes at about 3600°, and the product contained 0·1 per cent. of silica, and less than 0·01 per cent. of carbon.

A. Lampen found that carborundum breaks up into silicon and graphite between 2200° and 2240° ; and W. R. Hodgkinson and F. K. Lowndes, that if a platinum wire be heated white hot in thoroughly dried silicon tetrafluoride, crystalline silicon is formed. J. N. Pring and W. Fielding also obtained small hard crystals when a silicon tetrachloride in the presence of hydrogen is decomposed by a carbon rod heated electrically to about 1700°. Some silicon carbide is formed at the same time ; at 1925°, the whole of the deposit was silicon carbide.

E. W. von Siemens and J. G. Halske [9] found that silicon films or silicon-mirrors could be obtained by placing the surface to be plated in a uniformly heated pipe above the temp. of decomposition of silicon hydride, and passed through the system a current of that gas mixed with hydrogen. The mirror so produced is used in work with ultra-violet rays.

H. Kuzel [10] prepared **colloidal silicon** suspended in water or other liquid, and the process was also used for colloids of elements of high m.p. such as chromium, manganese, molybdenum, uranium, tungsten, vanadium, tantalum, niobium, titanium, boron, thorium, zirconium, platinum, osmium, and iridium. The element is first brought to a fine state of division by grinding and sifting, or by cathodic disintegration, and is then converted into the colloidal state by repeated alternate treatments for long periods with dil. acid soln. and dil. alkaline or neutral soln. under the influence of moderate heat and violent agitation. After each treatment the material is washed with distilled water, or other solvent until completely free from the reagent employed. H. Kugel also showed that gels of these elements are peptonized—or reconverted into colloidal soln.—by digestion with ammonia or amines or with very dil. soln. of alkali hydroxides or carbonates. The peptonized soln. have a powerful agglomerating action on powdered metals.

According to F. Limmer,[11] the amorphous silicon of commerce contains 20–65 per cent. of crystalline silicon, 2–12 per cent. of silica. B. Neumann found commercial silicon prepared in the electric furnace contained 70–97·5 per cent. of silicon ; and a minimum of 2·5 per cent. impurities—0·1–3·5 per cent. iron ; 0·14–0·70 per cent. aluminium as metal or carbide ; 0·22–1·40 per cent. of calcium ; and 1·9–24·0 per cent. of insoluble matters, chiefly ferrosilicon, silica, and silicon carbide. P. F. Spielmann reported that commercial graphitic silicon contained :

| Silicon | Iron | Aluminium | Silica | Alumina |
|---|---|---|---|---|
| 93·91 | 2·75 | 0·41 | 2·65 | 0·46 per cent. |

The preparation of silicon of a high degree of purity has not been successful, and in many cases where the properties have been determined, the (undetermined) degree of purity has been very low. It is therefore probable that statements of some of the properties of silicon will be found erroneous, though they may be right for the impure element. Contradictory statements also appear.


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## § 4. The Physical Properties of Silicon

According to J. J. Berzelius,[1] the **colour** of the so-called amorphous silicon is dark brown, and the tint is darker after calcination than before. Crystalline silicon *en masse* is dark steel-grey, with a reddish tinge in reflected light. Small **crystals** are often transparent and light orange in colour. When it occurs in almost black six-sided plates with a metallic lustre resembling graphite, it is called *graphitoidal silicon*; F. S. Hyde said that the crystals appear to be incomplete octahedra. The *adamantine silicon* appears in steel-grey needle-like crystals, or in hexagonal prisms; when prepared by the zinc process, silicon seems to favour the octahedral habit, and when made by the aluminium process, the crystals are lamellar. The habit is probably largely affected by the rate of cooling. H. de Sénarmont found that the tabular and acicular crystals prepared by H. St. C. Deville were octahedral and sometimes arranged in series (Fig. 3); and often with truncated and trihedral apices. According to W. H. Miller, both the graphitoidal and adamantine crystals are octahedral. They belong to the cubic system. According to P. Groth, the crystals of silicon and carbon are not isomorphous. Although carbon and silicon unite to form a carbide, they do not to mixed crystals, and silicon carbide itself is dissimilar in crystalline form from either of its components. Carbon tetraiodide and silicon tetraiodide crystallize in the cubic system, but further information as to the isomorphism of the two compounds is lacking. As G. Jerusalem has emphasized, no instance is on record in which silicon replaces carbon without a profound modification of the crystalline form. Isomorphism might be expected between the metal carbonates and metasilicates, but none has been observed—*e.g.* lithium carbonate, $LiCO_3$, is monoclinic, lithium metasilicate, $LiSiO_3$, is rhombohedral; nor has any ismorphism been observed between the carbonates and metasilicates or metatitanates of the bivalent metals—$CaSiO_3$, $(Mg,Ca)SiO_3$, $MgSiO_3$, $MnSiO_3$, $MgTiO_3$, $MnTiO_3$, and $FeTiO_3$. According to J. Königsberger, the crystals of silicon may be isomorphous with those of titanium and zirconium.

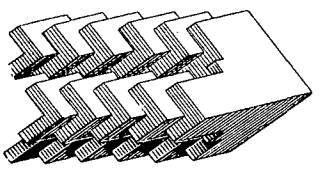


FIG. 3.—Pile of Octahedral Crystals of Silicon.

According to A. W. Hull, P. Debye and T. Scheerer, W. Gerlach, E. C. Bain, W. L. Bragg, L. W. McKechan, and H. Küstner and H. Remy, the space-lattice deduced from the **X-radiograms** is identical with that of the diamond. There are two intermeshed face-centred lattices, one being displaced with reference to the other along a cube-diagonal, a distance of one-fourth the length of the diagonal. The side of the cube is 5·42 A. to 5·43 A., compared with 3·56 A. for the diamond, and the distance between adjacent atoms is 2·35 A. compared with 1·54 A. for the diamond. There are 8 atoms per unit cube. R. N. Pease calculated 1·17 A. for the atomic radii of the atoms in silicon; and W. L. Bragg, and M. L. Huggins, 1·17 A. A. L. Norbury studied the at. vol. of silicon in alloys. P. Debye found no difference in the X-radiograms of amorphous and crystalline silicon, showing that the two forms are structurally the same. M. L. Huggins, L. A. Turner, and H. Collins discussed the electronic structure of the silicon molecule—*vide* silica. H. Moissan and F. Siemens' soluble silica forms yellow translucent plates rather darker in colour than ordinary crystalline silica. H. N. Warren's form was octahedral like ordinary crystalline silica. According to C. Winkler, the crystals are very hard; they scratch glass but not topaz. J. R. Rydberg places their hardness at about 7 when that of the diamond is 10.

F. Wöhler gave 2·490–2·493 for the **specific gravity** of graphitoidal silicon at 10°; A. Harmening gave 2·493; C. Winkler, 2·004–2·197 for specimens obtained from molten zinc; W. H. Miller, 2·337; H. St. C. Deville, 2·493; and K. Honda, 2·399. L. Playfair gave 2·48 as the mean of six determinations of the sp. gr. of adamantine silicon. L. Weiss and T. Engelhardt obtained 2·3013 at 19° as the mean of five determinations of a sample with 1·58 per cent. aluminium, and 97·46 per cent. silicon; and 2·3454 at 19° as the mean of six determinations for samples of silicon with rather less aluminium. The sp. gr. of a sample of amorphous silicon made by E. Vigouroux' process was 2·35 at 15°, and that of the crystalline form a little smaller. L. Cambi gave 2·08 for the sp. gr. of a sample of the amorphous element made by the hydrolysis of silicon sulphide. The different amorphous forms, said he, are not clearly-defined allotropes. H. Moissan and F. Siemens gave 2·30–2·42 for the sp. gr. of crystalline silicon soluble in hydrofluoric acid. P. F. Spielmann gave 1·90 for the sp. gr. of commercial silicon. The **atomic volume** of silicon is 11·4, if the sp. gr. be taken as 2·42. T. W. Richards found the mean change of vol. per 0·987 atm. press. between 98·7 and $5\times98\cdot7$ atm. press. is 0·16. C. A. Edwards found the **hardness** of silicon on Brinell's scale to be 240; and C. A. Edwards and A. M. Herbert gave 89·3 for the **plasticity** number when that of platinum is 116. The coeff. of **compressibility** is $0\cdot32\times10^{-6}$ at 20° between 100 and 500 megabars when the compressibility of mercury is $3\cdot95\times10^{-6}$. E. Grüneisen showed that if $\alpha$ be the coeff. of linear expansion; $v$ the vol. of a gram-atom; and $\beta$, the coeff. of compressibility, then $\alpha v/\beta$ is nearly constant for most of the metals, and for silicon. J. H. Hildebrand and co-workers calculated relative values for the **internal pressure** of silicon and other elements.

According to H. Fizeau,[2] the coeff. of **thermal expansion** is $\alpha=0\cdot00000763$ per degree at 40°, and 0·00000780 at 50°. This makes the coeff. of cubical expansion $3\alpha=0\cdot000023$. According to L. Baraduc-Muller, the mean value of the coeff. between 15° and 1000° is $\alpha=0\cdot00000468$; it is fairly constant between 200° and 700°; it increases rapidly to 805°, decreases to its original value at 835°, again increases slightly to 900° and then becomes small and negative at 970°; it increases and becomes positive at 1000°, and increases slightly up to 1055°. The value of $d\alpha/dt\times10^4$ from 607°–700° is 5·05; 700°–805°, 10·47; 805°–835°, 4·30; 835°–900°, 2·30; 900°–970°, −0·85; 970°–1000°, 2·66; 1000°–1025°, 2·80; 1025°–1055°, 3·31. S. Valentiner and J. Wallot found that the coeff. of expansion decreases with a falling temp., becomes zero at −157°, and is negative at liquid air temp. H. V. Regnault[3] obtained numbers for the **specific heat** of crystalline silicon varying from 0·1673 to 0·1784; and for that of fused silicon, from 0·1557 to 0·1750 between about 12° and 100°. H. Kopp gave 0·165 for the sp. ht. of crystalline

silicon, 0·138 for fused silicon, 0·181 for graphitoidal silicon, and 0·214 for amorphous silicon between 20° and 50°. H. F. Weber gave 0·1964 for the sp. ht. of crystalline silicon at 128·7°, and 0·2029 at 232·4° (*vide* **1.** 13, 12). A Wigand obtained 0·1712 for grey microcrystalline silicon between 0° and 99°. T. W. Richards and F. G. Jackson obtained 0·118 between —188° and 20°; A. S. Russell obtained 0·0861 at —135° for crystalline silicon, and for amorphous silicon, 0·0913 at —135°, and 0·1796 at 27°. C. Forch and P. Nordmeyer found the sp. ht. to increase with rise of temp. Thus:

| | −184° | −39·07° | 43·13° | 71·07° | 100·09° | 212° | 252·03° |
|---|---|---|---|---|---|---|---|
| Sp. ht. . | 0·0876 | 0·1360 | 0·1697 | 0·1833 | 0·1901 | 0·2011 | 0·2029 |

P. Nordmeyer and A. L. Bernoulli gave 0·1234 between —185° and 20°. H. Schimpff represented the sp. ht., $c$, of 99·2 per cent. silicon at the temp. $\theta°$, by $c=0{\cdot}165428(\theta-17)+0{\cdot}0_31584310(\theta-17)^2-0{\cdot}0_63742(\theta-17)^3$; he gave 0·1597 for the true sp. ht. at 0°, and 4·54 for the **atomic heat** at 0°. H. F. Weber gave 5·75 for the at. ht. at 100°. The deviation of the at. ht. from Dulong and Petit's law has been discussed **1.** 13, 12. The at. hts. computed from the results of W. Nernst and F. Schwers below —183·2°; H. Schimpff, between —150° and 0°; and by H. F. Weber between 21·6°, and 232·4° are as follows—the temp. being taken on the absolute scale:

| | 20·1° | 33·7° | 53·7° | 89·8° | 173° | 273° | 323° | 359° | 505·4° |
|---|---|---|---|---|---|---|---|---|---|
| At. ht. . . | 0·031 | 0·152 | 0·548 | 1·524 | 3·21 | 4·54 | 4·96 | 5·38 | 5·74 |

The results are plotted in Fig. 3 in connection with carborundum. The at. ht. was also considered by F. Michaud, and E. van Aubel. A. Magnus represented the thermal capacity of silicon between 0° and $\theta°$ by $Q=0{\cdot}1723\theta+6{\cdot}40\times10^{-5}\theta^2-2{\cdot}575\times10^{-8}\theta^3$. E. D. Eastman gave for the **entropy** of silicon 5·7 cals. per degree at 25°; and G. N. Lewis and co-workers, 4·7 cals. per degree. The **thermal conductivity,** 0·20 cal. per cm. per second per degree, was measured by J. Königsberger and J. Weiss.

According to C. Winkler,[4] silicon can be heated to redness without changing its sp. gr., or losing perceptibly in weight. Both H. N. Warren, and F. S. Hyde said that graphitic silicon is infusible before the blowpipe. C. M. Despretz melted this element, but his observations were made with the impure product obtained by the earlier workers. H. St. C. Deville said that it can be melted in a good wind furnace—*feu de vent*—and he estimated that its **melting point** lies between m.p. of cast iron and steel—say between 1400° and 1500°—and he showed that the molten element can be cast without perceptible oxidation. H. Moissan found that silicon can be readily melted in the electric furnace, and that the molten element is bluish or steel-grey. H. Moissan and F. Siemens said that the m.p. is near 1500°. T. W. Richards gave 1460° for the m.p. G. Arrivant gave 1415°; R. Vogel, 1408°; W. Fränkel, 1412°; H. Giebelhausen, 1425°; R. S. Williams, 1414°; W. R. Mott, 1430°; F. Dörinckel, 1458°; W. Guertler and G. Tammann, 1425°; and K. Lewkonja, 1443°. According to W. Fränkel, molten silicon, like bismuth, expands on solidification.

P. Schützenberger and A. Colson stated that the **volatility** of silicon is not appreciable in the blast furnace, but they found that platinum-foil heated to a reddish-white heat amidst a mass of lampblack contained silicon which presumably was carried as vapour through the lampblack from the crucible. H. Moissan believes that the conclusion is a *non sequitur*, for the vap. of silicon would have been arrested by the carbon. L. Troost and P. Hautefeuille said that silicon appears to be volatile when melted in a stream of hydrogen carrying some silicon tetrafluoride or tetrachloride. This apparent volatilization is attributed to the formation of lower chlorides or fluorides which are stable at a low temp. and at a red heat, but undergo dissociation at intermediate temp. The reaction was discussed by P. Duhem—*vide* hexachlorodisilane. A. Ditte showed that

selenium and tellurium hydrides exhibit a similar phenomenon; C. W. Hasenbach also observed a similar effect with nitrogen trioxide; and H. Debray and A. Joly, with ruthenium oxide. P. Hautefeuille and A. Perrey found that when the vap. of aluminium chloride is passed over aluminium heated at 440° in a glass tube, a deposit is formed of an amorphous substance, which consists mainly of silicon mixed with small quantities of iron and aluminium. It would seem, therefore, that aluminium is retained by silicon heated at 1300°, but is given up when the metal is heated at a temp. much below its softening point. C. Friedel also observed that silicon is volatilized in the electric arc between silicon poles—*vide* iron silicides. A. Dufour noted that the passage of an electric discharge through a vacuum tube filled with silicon hydride immediately causes a deposit of amorphous silicon; if, however, the current is continued for about an hour, the original deposit of silicon gradually disappears and is re-formed in the dark space round the cathode. The final deposit is always formed in the dark space, even if other parts of the tube are cooled to 80°; hence the phenomenon cannot be due to the distillation of the silicon from the hot regions to the colder. The facts can only be explained satistorily by supposing the silicon to recombine with the hydrogen present to form silicon hydride, which is decomposed in the dark space by the impact of the corpuscles, emitted from the cathode. H. Moissan found that silicon can be distilled in the electric arc furnace, and that the vap. condenses as small globules in the cold part of the tube; E. Vigouroux observed that the vapour condensed in the form of lamellar crystals. W. R. Mott gave 1800° for the **boiling point**; and E. Tiede and E. Birnbrauer, 1350°. According to H. von Wartenberg, the vap. is polyatomic, and the latent **heat of vaporization** of silicon is —44,000 cals. per gram-atom for temp. up to 1315°. The conc. of silicon vap. over crystalline silicon when the partial press. of hydrogen is one atm. is $1{\cdot}15\times10^{-3}$ at 1205°, and $3{\cdot}00\times10^{-3}$ at 1315°. J. J. van Laar calculated 4920° for the **critical temperature**; and 1450 atm. for the **critical pressure**. Assuming that the allotropic change from amorphous to crystalline silicon is a real phenomenon, L. Troost and P. Hautefeuille state that the **heat of transition**: $Si_{amorphous} \rightarrow Si_{crystalline} + 8{\cdot}059$ Cals., but H. von Wartenberg believes this value to be much too high, and estimates that the heat of transition is less than 2 Cals. The **heat of combustion** of amorphous silicon was found by H. von Wartenberg to be 195 Cals.; M. Berthelot gave 184·5 Cals., and W. G. Mixter, $Si+O_2=SiO_2+191$ Cals.

H. von Wartenberg [5] gave 3·87 for the **refractive index**, $\mu$, of silicon; and for the absorption coeff., $\mu k=0{\cdot}47$. J. H. Gladstone, A. Haagen, A. Schrauf, and J. Kannonikoff computed the **refraction equivalent**—the product of the at. wt., and $(\mu-1)D$, where $D$ is the sp. gr.—and found values varying from 6·0 to 11·25, showing, as G. Abati emphasized, that the refraction eq. depends on the constitution of the compound in which the element occurs. A. Schrauf, and A. Haagen found that the **molecular rotatory power**, calculated from that of quartz, is 0·27. H. von Wartenberg gave 35·7 per cent. for the **reflecting power** of silicon; and W. W. Coblentz found that the reflecting power of polished silicon is greatest for light rays in the blue part of the spectrum, and falls away rapidly towards the ultra-red. The curves for the percentage amount of light of wave-length $\lambda$ ($\mu$=0·001 mm.), reflected from two samples of polished commercial silicon, are illustrated in Fig. 4. The curves remained horizontal as far as they were examined, viz. to $\lambda=10\mu$. E. P. Lewis and A. C. Hardy found the reflective power of silicon for rays below $\theta$=1860 to be 25–44 (rock salt, 8–9); I. C. Gardner also measured the reflection coeff. of the extreme ultra-violet rays.

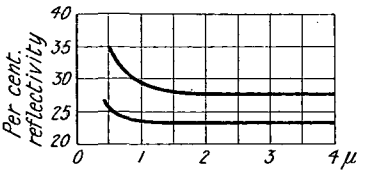


FIG. 4.—Reflecting Power of Silicon.

The **spectrum** of silicon has not yet been made clear. The lines are very numerous, and they occur principally in the ultra-violet. Different bands and lines

are obtained under different conditions, and it is not always clear which are due to silicon and which to compounds of silicon with oxygen, hydrogen, or the halogens. J. Plücker [6] obtained the **spark spectrum** by passing the electric discharge through silicon tetrachloride in a vacuum tube, and other observations on the line spectrum have been made by G. Kirchhoff, J. M. Séguin, A. Mitscherlich, L. Troost and P. Hautefeuille, G. Salet, A. del Campo and co-workers, R. A. Sawyer and R. F. Paton, G. Ciamician, H. A. Rowland, J. M. Eder and E. Valenta, E. Demarçay, J. N. Lockyer and co-workers, A. de Gramont, J. Lunt, W. N. Hartley, K. von Wesendonck, J. Hartmann, F. Exner and E. Haschek, E. B. Frost and J. A. Brown, W. Crookes, G. Stead, A. Hagenbach and H. Konen, W. M. Mitchell, A. Dufour, J. H. Pollok and A. G. G. Leonard, F. W. Dyson, W. S. Adams, C. Fabry and H. Buisson, E. Goldstein, C. Porlezza, etc. G. Salet gave for the most prominent lines in the visible spectrum: 6366, 6341, 5981, 5960, and 5948 in the orange-yellow; 5772 in the yellow; 5708 and 5646 in the yellowish-green; 5057 and 5041 in the green; and 4131, 4126, and 4103 in the violet—*vide* Fig. 5. In the ultra-violet the chief lines, according to C. Porlezza, and

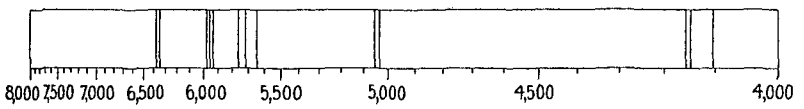



FIG. 5.—Spark Spectrum of Silicon.

J. C. McLennan and E. Edwards, are 2881·73, 2528·60, and 2516·26. The **flame spectrum** of silicon in the oxyhydrogen flame was found by W. Huggins to be continuous. G. Salet observed some bands in the spectrum of the hydrogen flame charged with silicon halides. The chief lines in the spectra of silicon chloride, bromide, and iodide are the same. The flame spectrum has also been studied by A. de Gramont and C. de Watteville. The **arc spectrum** has been observed by J. Hartmann and G. Eberhard, C. Porlezza, F. Exner and E. Haschek, etc. The most intense lines in the ultra-violet arc spectrum are, according to C. Porlezza, and J. C. McLennan and E. Edwards, 3905·70, 2881·70, 2528·60, 2524·22, 2516·20, and 2507·01. G. D. Liveing and J. Dewar, W. N. Hartley, F. Exner and E. Haschek, J. C. McLennan and co-workers, R. A. Millikan and I. S. Bowen, etc., studied the **ultra-violet spectrum.** J. N. Lockyer showed that successive spectra are developed by silicon as the energy of excitation is increased. What he called $Si^{I}$ corresponded with the arc spectrum; $Si^{II}$ with the spark spectrum which is associated with some doublets; $Si^{III}$ is associated with some triplets; and $Si^{IV}$ is associated with a pair of lines in the violet. A. Fowler, in 1914, showed that the enhanced lines of the alkaline earth metals furnished series similar to the arc lines except that the series constant was four times its normal value. According to the electron theory, this means that the enhanced lines are produced by atoms which have lost one electron, and hence it was inferred that atoms which have lost one electron will give a series with $4N$ in place of the normal Rydberg's constant $N$. This is the case with the series in the spark spectrum of silicon which has the constant $4N$ corresponding with $Si^{+}$. The triplets in series III seem to be associated with $Si^{++}$, and the IV-silicon series has a constant of $16N$, which is taken to indicate the existence of radiating atoms which have lost three electrons, $Si^{+++}$. The regularities in the band spectrum were studied by C. Porlezza, W. Jevons, H. Deslandres, R. B. Lindsay, and W. Jevons. A. de Gramount discussed the sensitiveness of the spectrum of silicon in steels. W. J. Humphreys studied the effect of *pressure* on the spectrum of silicon; and J. Chautard, A. Cotton, G. Gerndt, H. M. Reese, P. Zonta, A. Dufour, etc., the effect of a *magnetic field.* The sensitiveness of the silicon spectrum for analytical work has been investigated by A. de Gramont. The sensitiveness with soln. of water-glass is such that with a dilution of 1 : 10,000, six silicon lines between 2578·60 and 2507·01 and the lines 2881·70 can be detected.

F. Haber [7] computed the **vibration frequency** of silicon for the red ray to be $13{\cdot}57\times10^{12}$, and for the violet ray, $3{\cdot}69\times10^{15}$. J. E. P. Wagstaff gave $\gamma=9{\cdot}6\times10^{12}$. E. H. Kurth examined the **X-rays** from silicon. J. C. McLennan and M. L. Clark gave 149·5 for the critical voltage of the *L*-series of **X-rays** from silicon; and A. E. Lindh studied the *K*-series. J. Ewles found the minimum voltage for the excitation of the whitish-yellow **cathodoluminescence** of amorphous silicon to be 1600, and for the red cathodoluminescence of crystalline silicon 2400. H. S. Roberts and L. S. Adams studied the crystal of silicon as a **radio-detector.**

J. J. Berzelius [8] said that "amorphous silicon does not conduct electricity, but this property cannot be regarded as being at variance with the supposed metallic nature of silicon, for this element has hitherto been obtained only in a state of minute subdivision, and finely divided iron, obtained by igniting ferrous oxalate, is likewise non-conducting." H. St. C. Deville said that the **electrical conductivity** of crystalline silicon is like that of graphite. A. C. Becquerel said that fused or crystalline silicon is a very poor conductor, and in consequence it becomes hot when conducting a current. F. le Roy utilized this property to make an electrically heated furnace with agglomerated rods of silicon as the resistance medium. The **electrical resistance** of a rod 40 sq. mm. in cross-section and 10 cms. long was $200\times10^6$ micro-ohms under conditions where a similar rod of carbon had a resistance of $150\times10^3$ micro-ohms, and a similar rod of nickel-brass had a resistance 850 micro-ohms. The temp. coeff. of the resistance is negative, and it is 40 per cent. less at 800° than it is at 0°. F. Streitz attributed the negative temp. coeff. of the resistance of silicon to the presence of minute cavities which close as the temp. rises. According to J. Königsberger and K. Schilling, the absolute electrical resistance per c.c. falls from 0·290 at −189° to 0·0385 at 217° (Fig. 6); it then abruptly rises to 0·162, and falls to 0·85 at 435°; and again rises abruptly to 0·100, and falls to 0·022 at 835°. It is assumed that these changes correspond with the conversion of what they call *α-silicon* to *β-silicon* between 210° and 217°; and with the conversion of *β*-silicon to *γ-silicon* between 435° and 440°. Both changes are reversible. The electrical conductivity of silicon is thus an exception to the general rule that the modification most stable at the higher temp. has the smallest electrical resistance. F. Fischer and E. Baerwind found the sp. gr., and the thermoelectric power of the supposed modifications are independent of the rate of cooling and are not, therefore, likely to belong to allotropes. The negative variety can be converted into the positive form by fusion in a vacuum cathode furnace, and it is not therefore an effect of aluminium. The negative variety is supposed to be a solid soln. of a small quantity of the oxide in silicon. J. Königsberger and J. Weiss gave $12{\cdot}5\times10^{-9}$ ohms for the sp. resistance of silicon at 30°. E. Thomson made some observations on this subject. K. Höjendahl examined the theory of the conductivity of silicon based on the electronic theory. P. W. Bridgman found the resistance of silicon decreases under press., but the press. coeff. becomes less the higher the press. At 0°, the total decrease under a press. of 12,000 kgrms. per sq. cm. was 14·0 per cent., and at 52°, 15·8 per cent.; another sample gave 10·1 per cent. at 0° and 15·3 per cent. at 95°. The average temp. coeff. of one sample was +0·000117 between 0° and 52°; and of another +0·0000615 between 0° and 95°. The temp. coeff. is much more susceptible to impurities than the press. coeff. He estimates that for pure silicon the press. coeff. of the resistance will be of the order −0·000012 when the press. is expressed in kgrms. per sq. cm. This coeff. is high, being nearly

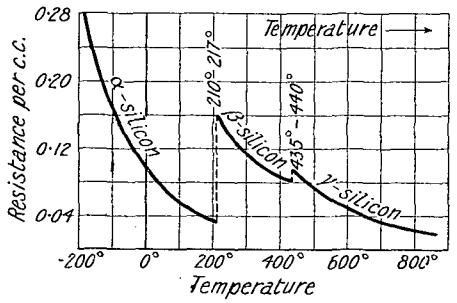



FIG. 6.—The Effect of Temperature on the Electrical Resistance of Silicon.

the same as that of lead. The use of silicon as a crystal detector in wireless telephony—*vide* carborundum, **5**. 39, 18, has been discussed by R. C. Hartsough,[9] L. S. McDowell and F. G. Wick, and F. Fischer and E. Baerwind.

A. Iljeff [10] found the **Thomson effect** at 0° and 100° to be negative; J. Königsberger and J. Weiss found the **thermoelectric force** of silicon against copper to be $478\times10^{-6}$ volt per degree. C. Benedicks found for copper against silicon 608 microvolts, the largest value so far discovered. For F. G. Wick's observations on the silicon-lead couple, *vide* lead. The General Electric Co. patented the Cu–Si thermocouple for pyrometric work; it gave 415 microvolts per degree. F. Fischer and co-workers found that some specimens of silicon are positive to copper, and others as strongly negative, and a thermocouple composed of the two varieties may have a thermoelectromotive force as high as 820 microvolts per 1°. The two varieties do not differ characteristically in electrical conductivity; but the difference is due to the presence of silica. Melting silicon in contact with magnesia, lime, or alumina renders it positive, silica being removed. On the other hand, melting silicon so that a part of it burns and the oxide thus formed dissolves, renders it negative. According to K. Honda, the sp. **magnetic susceptibility** at 18° is $-0{\cdot}123\times10^{-6}$ mass units for a sample of crystalline silicon containing 0·200 per cent. of iron as impurity; and $-0{\cdot}143\times10^{-6}$ for a sample with 0·085 per cent. of iron. These constants were not affected by variations of temp. S. Meyer gave $+0{\cdot}01\times10^{-6}$ at 16°, and for another sample $+0{\cdot}2\times10^{-6}$. A. Duvillier, and B. Cabrera studied the relation between the magnetic properties and the electronic structure of the silicon atom.


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## § 5. The Chemical Properties of Silicon

Silicon, carbon, and boron form a small group of elements which exhibit allotropism, presumably owing to high mol. complexity. This is evident by the low volatility of these elements even at high temp., and by their low chemical activity towards reagents generally. Silicon is feebly electronegative, and has a greater tendency to form compounds with the non-metals than with the metals. Silicon lies next to carbon in the fourth group of elements in the periodic table, but the relationship to carbon is not very close. Silicon behaves as a quadrivalent element, although there are a few cases in which it appears to be bivalent—*vide infra*. According to E. Vigouroux,[1] and E. Wilke-Dörfurt, as previously stated the difference between the so-called amorphous and crystalline silicon is due to the finer state of subdivision of the former. In consequence, the former appears to be more chemically active, but a similar state of activity can be obtained by the mechanical comminution of crystalline silicon. H. Moissan and S. Smiles made a silicon of great reactivity by passing sparks through liquefied silicon hydride. The product, for example, reduces a soln. of cupric sulphate slowly at ordinary temp., and rapidly when boiling; at 50°–60°, it reduces a soln. of mercuric chloride to mercurous chloride; and it reduces a boiling soln. of a gold salt. These reactions are not given by silicon prepared in the ordinary way. X-radiograms of amorphous and crystalline silicon show no difference in structure. The greater reactivity of the pseudo-amorphous form is due to its extremely finely divided state. According to W. Manchot, when rubbed with lead dioxide, the pseudo-amorphous form takes fire, the crystalline form gives no reaction.

According to E. Vigouroux, amorphous silicon readily absorbs **hydrogen** and many other gases, including water-vapour, from which it can be freed only by heating to redness. Both amorphous and crystalline silicon were found by E. Vigouroux, and A. Dufour to react with hydrogen at a high temp., although C. Friedel had previously failed to obtain a positive result at the temp. of the electric arc. J. J. Berzelius said the silicon-$\alpha$ which he made burns with a vivid flame when slightly heated in **air**; only about one-third of the silicon is burnt, however, since the remainder is protected from the air by the silica formed; about two-fifths is burnt under similar conditions in oxygen. On the other hand, the silicon-$\beta$

can be heated white hot before the blowpipe without taking fire. From the evidence, it appears as if the former were really an alloy of potassium and silicon, and that the potassium had been expelled from the latter by ignition in a closed vessel. In either case, probably much silica was also present. J. J. Berzelius continued that silicon which has been rendered coherent by gradual exposure to a white heat does not take fire at a red heat in air or in **oxygen.** W. Hempel and H. von Haasy observed no oxidation in air at 150°. G. Tammann said that he observed no increase in weight after heating crystalline silicon in air for 10 mins.; but after 5 mins. at 1100°, there was a 3 per cent. increase in weight. H. St. C. Deville, and F. Wöhler said that crystalline silicon can be heated to whiteness in oxygen without change. This is not quite right. According to E. Vigouroux, silicon is not changed in warm air, but it is attacked superficially when heated to 400° in oxygen. L. Weiss and T. Engelhardt said that silicon is not oxidized by oxygen at 700°. N. B. Pilling and R. E. Bedworth investigated the oxidation of silicon. E. Vigouroux found that silicon burns in oxygen provided the temp. be raised to the ignition point very quickly before a protective crust of silica has had time to form. In order to do this, there should be a rapid current of dry oxygen, and the silicon finely divided. If the powder be projected into a red-hot crucible, each grain scintillates for a moment, and this also occurs when the powder is passed through Bunsen's flame. This incandescence is due to an incomplete, superficial combustion. The surfaces of the grains become white, and the silica can be removed by washing with hydrofluoric acid. L. Weiss and T. Engelhardt found that **water** at ordinary temp. is decomposed by finely divided silicon; and E. Wilke-Dörfurt observed that silicon is oxidized by water boiling under a reflux condenser, and in an atm. of carbon dioxide. H. Moissan and F. Siemens said that amorphous silicon does not decompose water in a platinum vessel, but in a glass vessel, at 95°, an appreciable decomposition occurs in 6–12 hrs. This is due to the presence of alkali dissolved from the glass, and the action occurs in a platinum vessel if the water contains a trace of alkali. E. Vigouroux found that at a bright red heat steam is slowly decomposed by silicon: $Si+2H_2O=SiO_2+2H_2$; at a higher temp., the decomposition is faster. The reaction is rapidly inhibited by the protective action of the crust of silica formed on the silicon.

H. Moissan found that **fluorine** attacks silicon at ordinary temp., *avec une vive incandescence*, and the heat of the reaction melts the silicon; but H. Moissan and J. Dewar observed that liquid fluorine is without action. J. J. Berzelius found that when ignited amorphous silicon is heated in **chlorine** it ignites and burns completely to form silicon chloride; W. Hempel and H. von Haasy said that silicon unites with chlorine at 340°–350°; L. Gattermann and K. Weinlig worked at 300°–310° in preparing silicon tetrachloride. F. Limmer said that commercial amorphous silicon is attacked by chlorine less readily than crystalline silicon, presumably because the former is contaminated with much more silica. E. Vigouroux said that combustion with incandescence occurs at 450° with chlorine; at 500° with **bromine**; and not at all with **iodine**; but at a red-heat iodine reacts *sans incandescence visible*. P. F. Spielmann found that boiling bromine has no action on graphitoidal silicon; and A. Besson observed that iodine chloride and iodine bromide form the double halides (*q.v.*). In all cases where silicon reacts with the halogen, the corresponding halide is produced. The heats of reaction with crystalline silicon are:

| | $SiH_{4gas}$ | $SiF_{4gas}$ | $SiCl_{4gas}$ | $SiBr_{4liquid}$ | $SiI_{4solid}$ |
|---|---|---|---|---|---|
| Cals. | 24·8 | 239·4 | 121·8 | 71·0 | 6·7 |

According to E. Vigouroux, G. S. Newth, and W. Hempel and H. von Haasy, gaseous **hydrogen fluoride** attacks silicon at ordinary temp., forming silicon tetrafluoride. H. Buff and F. Wöhler, and A. Besson obtained with dry **hydrogen chloride** at a red heat, a mixture of silico-chloroform, $SiHCl_3$, and silicon tetrachloride, $SiCl_4$; L. Gattermann and K. Weinlig worked at 450°–500° for making silico-chloro-

form. E. Vigouroux found that analogous reactions obtain with **hydrogen bromide,** and **hydrogen iodide.** According to A. Duboin and A. Gautier, when a mixture of silicon and alumina is heated with hydrogen chloride, a mixture of silica and aluminium chloride, but not silicon chloride, is formed; and generally, mixtures of alumina with boron, silicon, or carbon behave similarly towards hydrogen chloride. J. J. Berzelius' silicon-$\alpha$ was stated to dissolve in **hydrofluoric acid** with the evolution of hydrogen, while his silicon-$\beta$ was not attacked by this acid. A form of silicon soluble in hydrofluoric acid was prepared by H. Moissan and F. Siemens, W. Manchot and co-workers, and by P. Lebeau—*vide supra.* V. Eggertz found that the silicon which crystallizes from many kinds of cast iron is soluble in hot hydrofluoric acid. H. St. C. Deville, F. Wöhler, and H. Moissan reported that ordinary crystalline silicon is not attacked by hydrofluoric acid. *Aucun acide dissous ou liquide, agissant isolément,* said E. Vigouroux, *n'attaque le silicium amorphe.* Dil. or conc., cold or boiling hydrofluoric acid or **hydrochloric acid** is without action; and under similar conditions neither **sulphuric acid** nor **nitric acid** has any action. J. L. Gay Lussac and L. J. Thénard, and J. J. Berzelius found that amorphous silicon is dissolved by a mixture of nitric and hydrofluoric acids; and H. St. C. Deville, F. Wöhler, and H. Moissan obtained similar results with crystalline silicon. P. F. Spielmann said that commercial graphitoidal silicon is not attacked by a mixture of sulphuric and hydrofluoric acids. E. Vigouroux found that hydrofluoric acid mixed with some oxidizing agents—*e.g.* nitric acid, **potassium chlorate, potassium nitrate,** etc.—or nitric acid mixed with some fluoride—*e.g.* potassium fluoride, etc.—attacks silicon at ordinary temp. A mixture of fuming nitric acid and potassium chlorate has no action on silicon. J. J. Berzelius said that the silicon is not changed by fused potassium chlorate. Probably the violent reaction occurs when the mixture is heated rapidly. Cold aqua regia is without action; at 100° hydrated silicon dioxide is formed. Many of the metal **fluorides, chlorides, bromides,** and **iodides** are decomposed when heated with silicon—*e.g.*, at a red heat, **silver fluoride** gives silver and silicon fluoride; $Si+4AgF=SiF_4+4Ag$, and similarly with lead and zinc fluorides; according to E. Vigouroux and F. Ducelliez, **potassium hydrofluoride** gives a mixture of potassium fluoride and fluosilicate: $Si+4KHF_2=2KF+2H_2+K_2SiF_6$. L. Lévy found that with **titanium chloride,** at a high temp., arborescent crystals of titanium silicide are formed. In other cases, with an excess of silicon, and at a high temp., a silicide may be formed. According to A. Besson, **sulphur chloride,** $SCl_2$, at a red heat forms silicon thiochloride, $SiSCl_2$; and **sulphuryl chloride,** $SO_2Cl_2$, at a red-heat, forms silicon tetrachloride and sulphur dioxide. H. Moissan and P. Lebeau found that **sulphuryl fluoride,** $SO_2F_2$, acts in an analogous manner. A. Ditte found that amorphous silicon reacts with a conc. aq. soln. of **iodic acid** at 250° liberating iodine, and forming hydrated silicon dioxide; crystalline silicon reacts more slowly than amorphous.

J. J. Berzelius said that when silicon is heated in the vapour of **sulphur,** or when sulphur vapour is passed over silicon at a white heat, the combination is attended by incandescence and silicon sulphide is formed. E. Vigouroux said that the reaction begins at 600°; G. J. L. de Chalmot, at 300°. W. Hempel and H. von Haasy studied the reaction. According to E. Vigouroux, **hydrogen sulphide** at 400°–500°, or at the temp. of its dissociation, has no appreciable action on silicon, but at an elevated temp. silicon sulphide is formed. P. Sabatier found that at a dark red heat, **hydrogen selenide** forms silicon selenide. E. Vigouroux did not observe any appreciable reduction of **sulphur dioxide** by silicon at 1000°. For the action of **sulphuric acid,** *vide supra.* E. Wilke-Dörfurt found that at an elevated temp., sulphuric acid is reduced by silicon to sulphur, and silicon dioxide is formed, but E. Vigouroux found that the boiling conc. acid has no action.

According to E. Vigouroux, H. Funk, and P. Schützenberger and A. Colson, **nitrogen** reacts with silicon at about 1000°, forming the nitride. The reaction was studied by L. Weiss and T. Engelhardt, H. Funk, and R. Formals; the former showed that the reaction begins at about 1300°, for the increase in weight, $w$ grm. per

gram, which occurs when silicon is heated in nitrogen at $\theta°$ for 30 mins., is as follows:

| 1240° | 1295° | 1300° | 1310° | 1320° | 1400° | 1480° |
|---|---|---|---|---|---|---|
| 0·0001 | 0·0001 | 0·0001 | 0·0002 | 0·0014 | 0·0049 | 0·0061 |

At a bright red heat, E. Vigouroux found that **ammonia** reacts with silicon, forming the nitride, and liberating hydrogen. Aq. ammonia has no action on silicon. The **nitrogen oxides**—$N_2O$, and NO—are vigorously reduced above 800°. For the action of **nitric acid,** *vide supra.* P. Lebeau said that nitric acid (1 : 1) at 100° does not attack very finely divided silicon; nor did E. Vigouroux observe any reaction with the boiling fuming acid. W. Manchot found nitric acid attacks silicon in a soln. of silicon in silver. The slowly-cooled, insoluble silicon inflames in contact with cold nitric acid. No chemical action occurs when silicon is heated in contact with **phosphorus, arsenic,** or **antimony** at the temp. at which these elements are distilled; and at a red heat, **phosphorus pentoxide, arsenic trioxide,** and **antimony trioxide** are reduced by silicon. L. Kahlenberg and W. J. Trautman observed no reduction with arsenious or phosphoric oxides, but they found antimony trioxide and **bismuth trioxide** were reduced by silicon. M. Wunder and B. Jeanneret found that after 3 hrs.' treatment with **phosphoric acid** of sp. gr. 1·75, at 230°, silicon dissolves, forming a colourless liquid with a gelatinous substance in suspension. Any carbon present remains undissolved.

H. Moissan and A. Stock, E. Vigouroux, and O. P. Watts found that **boron** unites with silicon at a very high temp., forming silicon boride (*q.v.*). J. J. Berzelius said that molten **boric oxide,** or **borax**, has little or no action on silicon. For the action of **carbon** on silicon, *vide* the carbides. H. Moissan found that molten silicon at 1200°–1400° dissolves carbon. K. Nischk studied the affinity of carbon for silicon; and G. Tammann and K. Schönert, the diffusion of carbon in silicon. P. Schützenberger and co-workers found that carbon monoxide is slowly absorbed by silicon at a white heat, forming a silicon carboxide, and if oxidizing gases are excluded silicon carbide is formed. E. Vigouroux found carbon monoxide is not attacked by silicon at 1200°; but **carbon dioxide** is reduced to carbon monoxide at 800°–1000°. P. Schützenberger and A. Colson found that at a white heat carbon dioxide is absorbed by silicon, forming silicon carboxide; they also found that silicon, in an atm. of **cyanogen**, forms silicon carbonitride. A. C. Vournasos found that at a white heat a mixture of carbon and silicon, in an atm. of nitrogen, formed **sodium formate**, which gives nascent hydrogen when heated, does not react with silicon.

Silicon dissolves in many molten **metals,** forming silicides—*vide infra.* In general, the affinity of silicon for oxygen exceeds that of the other metals excepting those of the alkalies and alkaline earths, boron, and aluminium. Accordingly, a great many **metal oxides** are reduced by silicon at a high temp. Some **metal sulphides** behave similarly. E. Vigouroux reduced the oxides of copper, mercury, tin, lead, bismuth, manganese, and iron by heating them with silicon; the reaction is sometimes attended with incandescence. C. Winkler obtained lead silicate by heating lead oxide with crystalline silicon. H. N. Warren also reduced the oxides of lead, chromium, molybdenum, and tungsten by heated silicon. G. Tammann reduced **metatitanic acid** to a lower oxide by means of silicon at an elevated temp.: $2TiO(OH)_2+Si=SiO_2+H_2+H_2O+Ti_2O_3$. Anhydrous **titanic oxide,** $TiO_2$, and the hydrated **oxides of silicon, zirconium, and thorium**, are not affected. H. Moissan found that molten **calcium oxide** reacts with silicon, forming a basic calcium silicate. L. Kahlenberg and W. J. Trautmann, and H. Goldschmidt reduced **barium oxide** by heating it with silicon; but not so with **calcium, strontium, beryllium, magnesium, or aluminium oxides. Lithium carbonate** is slightly reduced. J. J. Berzelius found that a vigorous reaction occurs when amorphous silicon is mixed with **potassium or sodium hydroxide** and heated to

the m.p., hydrogen being evolved ; the reaction is feebler with barium hydroxide, and feebler still with calcium hydroxide. H. St. C. Deville said that crystalline silicon is slowly attacked by fused potassium hydroxide ; C. Winkler said that the attack is rapid. F. Wöhler, and H. Moissan and F. Siemens, and H. Moissan and A. Stock found that a soln. of potassium or sodium hydroxide attacks crystalline silicon in the cold, and when warmed silicon is slowly dissolved with the evolution of hydrogen —*vide* **1.** 7, 2.

According to J. J. Berzelius, when a mixture of amorphous silicon and an **alkali carbonate** is heated, a vigorous reaction attended by incandescence occurs, carbon separates and carbon monoxide is evolved, and the smaller the proportion of alkali carbonate, the lower the temp. of the reaction ; with a large proportion of alkali carbonate, the reaction occurs without incandescence and without the separation of carbon, but with the evolution of carbon monoxide. H. St. C. Deville, and F. Wöhler also found crystalline silicon reacts with incandescence with alkali carbonates when heated, forming carbon, carbon monoxide, and alkali silicate. E. Vigouroux said that amorphous silicon reacts with the alkali carbonates, in aq. soln., or in a molten state, forming silicon dioxide, or silicate. J. J. Berzelius said that amorphous silicon is slowly attacked by fused **potassium nitrate** and gases are evolved ; E. Vigouroux also said that potassium nitrate at its temp. of decomposition reacts with amorphous silicon. P. F. Spielmann said that fused potassium nitrate does not attack commercial graphitoidal silicon. As a rule, mixtures of silicon with oxidizing agents—**lead chromate, potassium dichromate,** etc.—react vigorously when heated to redness. L. Kahlenberg and W. J. Trautmann found that various **chromates** are reduced by silicon ; the **molybdates** and **tungstates** are only partially reduced ; **silver, mercury, chromic, copper, lead, and stannous oxides** are readily reduced ; not so with stannic oxide. **Tungstic and molybdic oxides** are reduced to the lower oxides, but not to the metal ; **lead sulphate** and **lead chloride** are reduced to the metal, **lead borate** reacts with silicon, but no metal globules were formed ; **boric oxide** is not reduced by silicon. E. Vigouroux found **lead sulphate,** and **calcium phosphate** are reduced by silicon when heated. According to P. Lebeau, a 10 per cent. soln. of **cupric chloride, ammonium or potassium cupric chloride, cupric sulphate, chromic acid,** or **ferric or ferrous chloride** does not attack amorphous silicon. L. Kahlenberg and W. J. Trautmann also examined the reactions of silicon with many inorganic salts.


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## § 6. The Atomic Weight and Valency of Silicon

According to D. I. Mendeléeff,[1] " the composition of silica has been the subject of the most contradictory statements in the history of science," and J. C. G. de Marignac could say that *il n'y aucun corps simple dont le poids atomique offre plus d'incertitude que le silicium.* Near the beginning of the nineteenth century, the composition of silica was variously represented :

| | SiO or $Si_2O_2$ | $SiO_2$ | $SiO_3$ |
|---|---|---|---|
| At. wt. (O=16) . . . . | 14 | 28 | 42 |
| Eq. wt. (O= 8) . . . . | 7 | 14 | 21 |

Differences of opinion grouped mainly about $SiO_2$ and $SiO_3$ as the best representative formulæ for silica. J. J. Berzelius' analyses showed that eight parts of oxygen by weight were united with seven parts of silicon, and at first the formula was written SiO. The formula SiO was proposed by T. Thomson, and was supported by J. B. A. Dumas, and J. J. Ebelmen from arguments suggested by the constitution of the silicic esters. No satisfactory guide to the selection of the at. wt. was available before Avogadro's hypothesis had been recognized as a criterion. The significance of J. B. A. Dumas' determination of the vap. density of silicon tetrachloride, made in 1826, was not recognized by J. B. A. Dumas himself even in 1857, for he then gave the formula $SiO_3$, whereas the vap. density of the tetrachloride, 5·94 (air unity), corresponds with 29·7 as the smallest unit of silicon present in this compound. J. J. Ebelmen's work on the ethyl silicates could not be satisfactorily interpreted when the formula of silica was assumed to be $SiO_3$, for the ratio of the oxygen in ethyl oxide to the oxygen in the silica in these compounds is as 1 : 1, 1 : 2, and 1 : 4. J. J. Berzelius' analyses of various silicates showed that the ratio of oxygen in the base to the oxygen in the acid commonly varied from 2 : 1 to 1 : 3, and he accordingly argued that in the trisilicates, where the ratio is 1 : 3, the potassium oxide and alumina are united with silica in the same way that the potassium oxide and alumina are united with sulphur trioxide in the alums. By analogy, therefore, the formulæ for felspar and alum were considered to be similar :

| | |
|---|---|
| Alum . . . . | $K_2O.SO_3+Al_2O_3.3SO_3+24H_2O$ |
| Felspar . . . | $K_2O.SiO_3+Al_2O_3.3SiO_3$ |

The argument is not valid since the trisilicates are not normal salts of silicic acid, but rather acid salts, because they contain the largest proportion of acid to base, and are usually found in nature side by side with free silica. H. Kopp based an argument for the formula $SiO_3$ on the volatile chlorides and bromides. The differences between the b.p. of chloroform, $CHCl_3$, and bromoform, $CHBr_3$, is about 96°; there is a similar difference between the b.p. of phosphorus trichloride, $PCl_3$, and tribromide, $PBr_3$; and between silicon chloride and bromide, hence the formulæ of the latter should be $SiCl_3$ and $SiBr_3$ respectively, corresponding with the system of chemical equivalents then in use, and with $Si_2O_3$ for silica. H. Kopp, however, later showed that evidence of this kind is quite unreliable because the difference of 32° per atom of chlorine displaced by bromine is not general. J. I. Pierre prepared what were regarded as a number of chlorosulphides

by the action of hydrogen sulphide on silicon chloride, and he considered that the results were best interpreted on the asumption that the formula of silica is $SiO_3$, but he mistook silicon trichloro-hydrosulphide, $SiCl_3.SH$, for $SiSCl_2$.

H. Rose studied the action of silica on fused sodium carbonate, and he showed that an eq. of silica displaced an eq. of carbon dioxide if the formula of silica be $SiO_2$, while if the formula be $SiO_3$, 1·5 eq. of carbon dioxide are displaced. The erroneous assumption was made that the eq. of carbon dioxide evolved is equal to the eq. of the silica added. He found the assumption that the formula of silica is $SiO_2$ to give the simpler results. If the same argument were applied to niobic and tantalic acids an erroneous conclusion might be obtained because the amount of carbon dioxide expelled really depends on the temp.; indeed, as showing the unreliability of the argument, T. Scheerer concluded that the formula is $SiO_3$ from his observations on the behaviour of silica towards the alkali carbonates; he considered that the silicates could be better represented by regarding silica as $SiO_3$ than as $SiO_2$. F. von Kobell, in 1871, and F. A. Quenstedt, as late as 1877, supported T. Scheerer in this respect. P. Yorke's experiments led him to conclude that there are at least two silicic acids with different eq. M. A. Gaudin arguing from (i), the vapour densities of silicon chloride and fluoride; and (ii) the analogies which silica bears to titanic and stannic oxides, advocated the formula $SiO_2$. O. B. Kühn, A. Würtz, C. Weltzien, and L. Gmelin favoured the formula $SiO_2$; and P. Einbrodt compared the results obtained by representing the composition of the minerals by silica considered as $SiO_2$ and as $SiO_3$, and claimed that the former gave the more advantageous results. He also emphasized the evidence in favour of this formula derived from the vapour densities of the silicon halides, and from the displacement of carbon dioxide in the carbonates by silica. J. C. G. de Marignac, in his memoir: *Sur l'isomorphisme des fluosilicates et des fluostannates et sur le poids atomique du silicium*, showed that the sp. ht. rule could not be used to estimate the at. wt. of silicon because of the variability of the sp. ht. with temp. and allotropic state. He explained the isomorphism of the fluostannates and fluosilicates, by assuming that the formula for silicon fluoride is $SiF_4$ analogous with $SnF_4$ for stannic fluoride. He later showed that the fluotitanates and fluozirconates should be included in the same isomorphous series. These conclusions were confirmed by the work of C. Friedel and co-workers on the volatile compounds of silicon and carbon —*vide infra* in connection with the silicon hydrides. F. S. Kipping obtained evidence of the formation of a silicon hydrocarbon, $Si(C_6H_5)_2.Si(C_6H_5)_2.Si(C_6H_5)_2.Si(C_6H_5)_2$, in which two of the four silicon atoms may be tervalent.

Silicon is now regarded as a quadrivalent element, and the formula of silica is accordingly represented by $SiO_2$, because of (i) the vapour density of the volatile silicon compounds—Avogadro's law; (ii) the at. ht. determined by H. F. Weber at 232°, approximates to Dulong and Petit's rule; (iii) the isomorphism of the complex fluorides of silicon, titanium, zirconium, and tin—Mitscherlich's rule; and (iv) the position of silicon in the periodic table in the fourth group between carbon and titanium, and in the second horizontal series between aluminium and phosphorus, is particularly suited for an element with the properties possessed by silicon. There are very few compounds in which silicon is said to exhibit a valency lower than that of a tetrad. W. Barlow and W. J. Pope inferred from the absence of isomorphism between silicon and carbon compounds, and the similarity on the morphotropic behaviour of silicon with the bivalent elements, that carbon is unique in possessing a fundamental valency as large as 4, and that silicon is essentially bivalent. G. Jerusalem supports this hypothesis—*vide* **1**. 5, 18.

J. J. Berzelius determined the amount of oxygen required to oxidize the impure amorphous silicon which he had prepared, and from this he calculated that the at. wt. of silicon—translated into modern units—is 19·6; and he later obtained the values 26·3, and 29·0. In a table published in 1814, he gave the at. wt. 32·46; and 1815, 23·11. In 1811, F. Stromeyer, also working with an impure sample of silicon, obtained 27·25. Between 1815 and 1826, J. J. Berzelius analyzed hydro-

osilicic acid, by converting it into the barium salt, and obtained 29·6. He obtained 31·3 to 31·6 as a result of the analysis of aluminium silicate; and 29·63 by the oxidation of a sample of silicon purified by washing with hydrofluoric acid. T. J. Pelouse, J. B. A. Dumas, and J. Schiel decomposed silicon tetrachloride by water; the first two determined the liberated hydrochloric acid by titration with standard silver nitrate, and the last, by precipitation as silver chloride. From the ratio $SiCl_4 : 4Ag$, T. J. Pelouze obtained 28·39, J. B. A. Dumas 28·09, and O. Hönigschmid and M. Steinheil 28·105; while from the ratio $SiCl_4 : 4AgCl$, J. Schiel obtained 27·96. H. St. C. Deville transformed silicon into alkali silicate, and from the ratio $K_2O : SiO_2$, obtained 30·4 for the at. wt. C. Winkler likewise heated silicon with (i) potassium hydroxide, (ii) sodium carbonate, and (iii) an aq. soln. of potassium hydroxide, and obtained values varying from 28·9 to 29·4 for this constant. The above determinations may be considered to conclude the older and less reliable determinations of the at. wt. of silicon. According to T. E. Thorpe and J. W. Young, the only reliable values for the at. wt. of silicon are based upon the analysis of the silicon halides which appear to be the most suitable of all compounds of silicon for at. wt. determinations when suitable precautions are taken; they showed that colloidal silica interferes with the titration of hydrobromic acid in the liquid obtained by the decomposition of silicon tetrabromide in water; and they determined the weight of the silica produced in the reaction, and calculated the at. wt. 28·385 from the ratio $SiBr_4 : SiO_2$. Similarly, W. Becker and J. Meyer obtained 28·225 for the ratio $SiCl_4 : SiO_2$. G. P. Baxter and co-workers analyzed silicon tetrachloride and silicon tetrabromide and obtained consistent values agreeing with 28·063 to about one part in two thousand. In another set based on the analysis of the tetrachloride, 28·111 was obtained. A. Stock and E. Kuss obtained 28·15 by using the reaction $SiH_4+2NaOH=Na_2SiO_3+2H_2$. The International Atomic Weights Committee use 28·3 as the best representative value for the at. wt. of silicon. B. Brauner calculated 28·3 for the best representative value, and F. W. Clarke, 28·25. F. M. Jäger and D. W. Dijkstra found no difference in the general properties of terrestrial and extraterrestrial silicon from meteorites, and hence inferred that the ratio of the isotopes must be the same whatever be the origin of the silicon.

H. von Jüptner found the mol. wt. of silicon dissolved in iron corresponds with a seven-atom mol. The effect of silicon on the f.p. of copper shows that in molten copper the mol. of silicon is possibly monatomic. The formation of silicide may spoil the inferences. E. Rutherford and J. Chadwick [2] obtained evidence of the emission of long-range particles when **α-particles** act on silicon; but G. Kirsch and H. Pettersson obtained evidence of the emission of hydrogen nuclei by bombarding silicon with α-rays; L. F. Bates and J. S. Rogers made observations on this subject. According to F. W. Aston, silicon furnishes three **isotopes,** one of at. wt. 28, and the others of at. wt. 29, and 30. R. S. Mulliken obtained evidence of the two isotopes in the band spectrum of silicon nitride.

S. Brown [3] assumed that the silica in plants is derived from the transmutation of carbon into silicon by the plant; J. J. Berzelius, however, attributed the appearance of this element to the slight solubility of silicic acid in the water taken in by the roots of the growing plants. S. Brown believed that when paracyanogen is heated out of contact with air, alone or in contact with potassium carbonate, platinum, or other substances having a strong attraction for silicon, its nitrogen atoms pass away unchanged, while its carbon atoms unite together and form silicon. G. J. Knox argued that the nitrogen is the source of the silicon in S. Brown's experiment; he regarded nitrogen as a compound of silicon and hydrogen because he obtained silicon under similar conditions to those described by S. Brown, but with substances containing no carbon—*e.g.* potassium amide, $KNH_2$, which he called "ammonia-nitruret of potassium." G. Wilson and J. C. Brown obtained silicon in a number of cases under conditions which they said "preclude the possibility of its being derived as an impurity or accidental ingredient from the vessels or materials or reagents made use of." T. Gross thought that he had transformed silicon into carbon by the electrolysis of an aq. soln. of an alkali silicate between silver electrodes. Subsequent observations by J. D. Smith and R. H. Brett, etc., have failed to establish these results; if no silicon be present in the system, none is formed.

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## § 7. The Silicides of the Alkali and Copper Families of Elements

The binary compounds of silicon with the electropositive elements, more particularly the metals, are called **silicides.** Their chemistry attracted but little attention until H. Moissan investigated their formation in the electric furnace. A few can be prepared at low temp., and many are found as metallurgical by-products. There appears to be a somewhat similar relation between the carbides and silicides to that which subsists between carbon and silicon. Many of the methods of preparation of the carbides can be employed for the silicides; the most important methods depend on (i) the direct union of the elements at a high temp. E. Vigouroux said that the alkali metals, zinc, aluminium, lead, tin, antimony, bismuth, gold, and silver do not combine directly with silicon even in the electric furnace; while iron, chromium, nickel, cobalt, manganese, copper, and platinum combine directly with silicon to form crystalline silicides. (ii) The reduction of the metal oxide by silicon; (iii) the reduction of the metal silicate or a mixture of the metal oxide and

silica by carbon; (iv) the reduction by a metal like sodium, magnesium, or aluminium of a siliceous compound in presence of the free metal or metal oxide; (v) the action of a silicon halide on a metal; or (vi) the dissolution of a metal in copper silicide. Most of the metal silicides readily crystallize; and they are not so active chemically as the carbides. Most of them are fairly stable in contact with water—the silicides of lithium and of the alkaline earths are alone decomposed by water. The metal silicides usually form well-defined crystals with a brilliant metallic lustre; they are usually hard, and possess a high m.p. The silicides are not generally so chemically active as the carbides. At a dull red heat, when heated in oxygen, the silicides may be attacked superficially, or they may resist attack altogether. The chemical properties are of course dependent upon the contained metal; lithium silicide, for instance, is easily oxidized. The aluminium, magnesium, alkaline earth, and the alkali silicides are attacked by dil. acids.

The following monographs deal with the silicides: O. Hönigschmid, *Karbide und Silicide*, Halle a. S., 1914; P. Lebeau, *Le silicium et ses combinaisons artificielles*, Paris, 1899; E. Vigouroux, *Le silicium et les siliciures métalliques*, Paris, 1896; H. Moissan, *Le four électrique*, Paris, 1897; London, 1904.

According to J. J. Berzelius,[1] potassium unites with silicon without perceptible incandescence. The compound containing a larger proportion of potassium than silicon is dark greyish-brown, and dissolves entirely in water evolving hydrogen, and yielding potassium silicate. The compound containing more silicon than potassium is obtained by decomposing silicon fluoride by potassium, and it leaves a residue of silicon when digested in water. If potassium vapour be passed over heated silica, *potassium silicide* and silicate are formed, and dissolve in water without leaving any residue; but if the greater part of potassium be previously expelled by heat, the remaining vitreous mass when digested first in water and then in hydrofluoric acid, leaves a little silicon behind. H. St. C. Deville doubted J. J. Berzelius' inference that he had prepared potassium silicide in these experiments. He also said:

> The many experiments which I have made with sodium have convinced me that any combination of this kind does not exist; at any rate, the silicon can retain only a minute quantity of sodium.

C. Winkler also stated that crystalline silicon does not absorb the vapour of potassium or sodium either when feebly or strongly heated. H. Moissan, however, said that silicon is attacked superficially by the vapour of the alkali metal, forming a little potassium or *sodium silicide* as the case may be; but E. Vigouroux found that when silicon and sodium or potassium are heated together in sealed tubes, no combination occurs at temp. up to that at which the alkali metal volatilizes. No silicide of sodium, potassium, rubidium, or cæsium has yet been prepared. H. Moissan found **lithium silicide,** $Li_6Si_2$, to be formed when silicon and lithium are heated in vacuo for 2 or 3 hrs., and finally at dull redness. The excess of lithium is removed either by treating the product with liquid ammonia which dissolves free lithium as the so-called lithium ammonium, or by distilling off the free lithium at 400°–500° under reduced press. Lithium silicide forms small, lustrous crystals of a deep indigo-blue, has a sp. gr. 1·12, and is decomposed in a vacuum above 600° into lithium and amorphous silicon. Hydrogen, above 600°, yields, with the silicide, lithium hydride and silicon. When warmed in gaseous fluorine, a reaction takes place with incandescence, producing lithium and silicon fluorides; with chlorine, bromine, and iodine, the reaction is similar, but a higher temp. is required before it begins. Heated in air, it burns and melts; in oxygen, much light and heat are developed. It reacts with molten sulphur with great vigour, a lithium polysulphide and a sulphide of silicon being formed; the last-mentioned substance is decomposed by cold water with evolution of hydrogen sulphide. Selenium, tellurium, and phosphorus all attack the silicide with production of incandescence. Arsenic and antimony form crystalline alloys only

slowly attacked by cold water. Lithium silicide reduces the oxides of iron, chromium, and manganese, alloys being produced. When the silicide is placed on sulphuric acid, it becomes incandescent, hydrogen sulphide is evolved, and sulphur formed. With nitric acid, it reacts explosively, producing nitrogen peroxide and silica. With hydrochloric acid, the silicide becomes incandescent and then is coated with hydrated silica; at low temp. or when dil. acid is used, a gas spontaneously inflammable in air is evolved; it burns with a very white flame and deposits amorphous silica; an ethereal soln. of hydrogen chloride has no action on the silicide. The reaction with water is very violent; a spontaneously inflammable gas is evolved, and a soln. of lithium hydroxide containing silica in suspension is obtained. If the reaction is moderated by covering the silicide with glycerol, pure hydrogen is evolved. With aq. soln. of alkali hydroxides, only hydrogen is evolved. It appears that water always decomposes the silicide with formation of hydrogen and a hydrogen silicide, $Si_2H_6$; the latter is decomposed by the alkali hydroxides.

The affinity of silicon for *copper*, said G. J. L. de Chalmot,[2] is small, and is less than it is for iron, manganese, and chromium, nearly the same as it is for silver, and perhaps a little less than it is for zinc; M. Philips also said the affinity of silicon for copper is smaller than it is for hydrogen and carbon, and, added W. Hampe, smaller than it is for fluorine. M. Philips said that the two elements begin to react at about 775°. In 1810, J. J. Berzelius obtained an alloy of copper with 2·3 per cent. silicon, by heating a mixture of silica, carbon, and copper turnings in a closed crucible at a white heat; and in 1823, he made alloys richer in silicon by dissolving silicon in molten copper. According to M. Philips, the production of *cuprosilicon*, as alloys of copper and silicon are called in commerce, from the constituent elements, using an excess of silicon, does not give a homogeneous product, but if an excess of copper is used, homogeneous alloys can be readily obtained. The ready oxidizability of amorphous silicon makes it unsuited for the work. A mixture of 100 grms. of copper and 20 grms. of silicon gave an alloy with 13·28 per cent. of silicon and 85·8 per cent. of copper; and a mixture of 150 grms. of copper and 22·5 grms. of silicon gave an alloy with 87·17 per cent. of copper and 11·96 per cent. of silicon; while a mixture of 100 grms. of copper and 10 grms. of silicon gave an alloy with 90·69 per cent. of copper and 9·02 per cent. of silicon. The copper turnings and powdered silicon were placed with silicon below the copper in a graphite crucible and heated to about 1150°–1250° for about 2 hrs. The mixture was frequently stirred. The mixture during fusion was covered with a layer of equimolar parts of potassium and sodium chlorides; borax was found not to be so good. Alloys were also made from the constituent elements by H. N. Warren, W. Hampe, E. Vigouroux, W. Manchot and H. Funk, H. Behrens, K. Nischk, and E. Rudolfi. H. Goldschmidt obtained cuprosilicon in a thermite reaction between cupric oxide and silicon. C. Heusler fused copper with siliceous pig-iron—ferrosilicon—removed the two upper layers which formed when the molten mass was allowed to stand, and found that cuprosilicon remained at the bottom. A. Sanfourche said that it is impossible to prepare alloys with over 12·10 per cent. of silicon, and that in consequence all formulæ professing a higher proportion of silicon should be deleted from literature.

As indicated above, J. J. Berzelius obtained cuprosilicon by heating a mixture of copper, carbon, and silica; A. Dick used a similar process. W. Feld and G. von Knorre made a mixture of copper—the eq. amount of cupric oxide—kieselguhr, and sodium chloride into briquettes, with tar as a bond; the briquettes were carbonized at a dull red heat, and smelted with a flux of quartz and lime; the resulting alloy contained 8 per cent. silicon; if fluorspar be used in place of sodium chloride, the product has 7 per cent. silicon. E. H. and A. H. Cowles and C. F. Mabery heated copper with an excess of sand and wood charcoal in an electric furnace; and G. J. L. de Chalmot, and G. Kroupa recommended a similar process. W. Rathenau heated in an electric furnace a mixture of copper or copper oxide, lime, carbon, and sand. The products were calcium carbide and cuprosilicon. C. Matignon and R. Trannoy heated a mixture of copper silicate and aluminium;

O. P. Watts reduced copper ore in presence of a silicate by means of calcium carbide or aluminium in an electric furnace; and M. Philips heated an intimate mixture of cupric oxide and silicon carbide for 5 hrs. in a coke furnace; H. St. C. Deville and H. Caron heated together potassium fluosilicate, sodium, and copper turnings and obtained an alloy with 12 per cent. of silicon; and L. Weiller used a mixture—potassium fluosilicate (450), glass (600), sodium chloride (250), sodium carbonate (75), calcium chloride (500), and calcium carbonate (60)—intended to produce its own sodium. E. Vigouroux obtained cuprosilicon by the action of silicon tetrachloride on copper at 1200°; and A. Dufour obtained a red precipitate containing copper and silicon by passing silicon tetrahydride into a soln. of cupric sulphate.

H. N. Warren prepared a cuprosilicon by the electrolysis of molten potassium fluosilicate with molten copper as cathode. He thus obtained a brittle alloy of the two elements. J. Walter electrolyzed molten potassium silicate, at a temp. above the m.p. of cuprosilicon, by using a molten copper cathode, and a carbon anode. The potassium silicate can be fluxed by the addition of potassium carbonate or chloride, sodium silicate, etc. A. G. Betts obtained cuprosilicon as a by-product by electrolyzing a molten mixture of clay, copper, and alumina sat. with cryolite—aluminium formed at the cathode accumulated on the surface of the bath, and cuprosilicon formed at the anode collected at the bottom of the bath.

Partial observations on the constitution of the copper-silicon alloys have been made by E. Vigouroux, P. Lebeau, G. J. L. de Chalmot, W. Hampe, and M. Philips. The equilibrium diagram, Fig. 7, was obtained by M. Rudolfi. He believes that only two compounds are formed, $Cu_3Si$, and $Cu_{19}Si_4$; and that the latter is produced by secondary changes in the solidified alloy. The compounds reported by E. Vigouroux, and P. Lebeau are considered to be eutectic mixtures. The f.p. curve shows a maximum about 855° and 13 per cent. by weight of silicon, corresponding with the compound $Cu_3Si$, two eutectic points at 825° and 9·8 per cent. and 800° and 18·3 per cent. by weight of silicon, and a break at 849° and 7·8 per cent. of the same element. A. Sanfourche believes that $Cu_{13}Si_4$ better represents the formula of E. Rudolfi's tritasilicide.

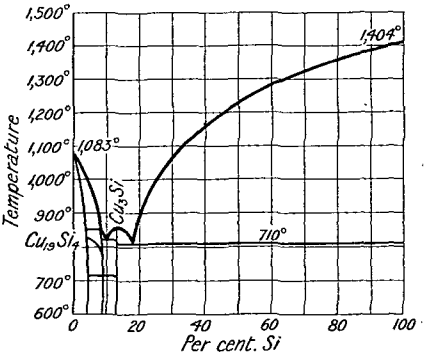



FIG. 7.—Equilibrium Diagram of Silicon and Copper.

Returning to Fig. 7, from 0–4·5 per cent. of silicon, mixed crystals separate; a second series of solid soln. from 7·34–8·3 per cent. of silicon are only stable within narrow limits of temp. Two reactions take place during the cooling of the crystallized alloy: the solid soln. sat. at 7·34 per cent. of silicon decompose at 815°–780° into two other series of solid soln., one of which splits up at 710° into the compound $Cu_{13}Si_4$ and the solid soln. first mentioned. It looks as if there is a misinterpretation of the results in E. Rudolfi's experiments. The results have been criticized by W. Guertler, and A. M. Portevin. K. Bornemann considers the individuality of E. Rudolfi's *copper tetrasilicide*, $Cu_{19}Si_4$, is very doubtful. R. Frilley found no signs of it on the sp. gr. curve of the alloys.

According to P. Lebeau, commercial cuprosilicon contains large and small crystals of silicon, some steel-grey crystals of ferrosilicon and a matrix of **copper tetritasilicide,** $Cu_4Si$, not the hemisilicide, as stated by G. J. L. de Chalmot, and E. Vigouroux in 1896. The latter prepared the tetritasilicide by fusing 17 parts of silicon and 90 parts of copper in a current of hydrogen, and removing any silica from the product by treatment with a 5 per cent. soln. of sodium carbonate. He heated to 1200° in a stream of hydrogen, 81·74 grms. of copper, 28·26 grms. of crystalline silicon, and 200 grms. of lead, bismuth, or antimony. He found that the maximum amount of silicon retained by the copper is about

10 per cent., any in excess is present as free silicon ; this amount of silicon corresponds with the formation of the tetritasilicide ; and in the presence of lead and bismuth, the tetritasilicide rises to the surface, but in the case of antimony it remains disseminated throughout the mass. E. Vigouroux passed silicon tetrachloride over copper at 1200° and obtained cuprosilicon with less than 5 per cent. of combined silicon ; by repeating the treatment, the combined silicon was carried up to about 10 per cent. R. Frilley found no sign of this compound on the sp. gr. curve. Copper tetritasilicide has a metallic silver-white appearance which rapidly darkens, becoming first yellow and then brick-red. It is hard, brittle, and easily powdered ; the fracture is tin-white and fine-grained ; the sp. gr. is 7·48 at 0° ; and that of the fused silicide is 7·58. P. Lebeau gave 850° for the m.p. With water, this silicide develops hydrogen ; chlorine attacks it below a red heat ; it is readily attacked by warm dil. or conc. nitric acid or by a mixture of nitric and hydrofluoric acids ; but hydrochloric, sulphuric, or hydrofluoric acid has scarcely any action on the compound. Hot conc. sulphuric acid is coloured blue and silica separates ; aqua regia attacks the alloy in the cold, and more rapidly when heated. Hot alkali-lye has very little action, and when boiled with a 5 per cent. soln. of sodium hydroxide, the grains of the tetritasilicide are covered with a dirty grey film. H. Behrens said that the silicide is attacked by a mixture of hydrochloric acid and potassium chlorate, and that aq. ammonia preferentially attacks the copper, and a hot soln. of potassium hydroxide preferentially attacks the constituents rich in silicon. According to P. Lebeau, this is the only definite compound of copper and silicon which can be detected by the cooling curves of the alloys ; E. Rudolfi said that, excepting the less definite $Cu_{19}Si_4$, **copper tritasilicide,** $Cu_3Si$, is the only compound shown on the cooling curves. R. Frilley found evidence of it on the mol. vol. curve of the alloys. H. St. C. Deville and H. Caron prepared this compound accidentally in their study of the action of silicon tetrachloride vap. on sodium placed in a copper boat.

M. Philips reported the formation of *copper diheptitasilicide,* $Cu_7Si_2$, to be formed as a residue after treating the tritasilicide with 20 per cent. potash-lye for 5 hrs. on a water-bath. W. Guertler believes this product to be a mixture. M. Philips also reported *copper dipentitasilicide,* $Cu_5Si_2$, to be formed, but this was not isolated. R. Frilley obtained evidence of the existence of this compound on the mol. vol. curve ; and of *copper ditritasilicide,* $Cu_3Si_2$, a point of inflexion on the sp. gr. curve of the alloys. E. Vigouroux, C. Matignon, and G. J. L. de Chalmot prepared what was regarded as *copper hemisilicide,* $Cu_2Si$, by heating copper with an excess of sand and wood-charcoal in an electric furnace, the crystalline mass approximated $Cu_2Si_3$, and when treated with aqua regia gave a residue with a composition $Cu_2Si$. L. Kahlenberg and W. J. Trautmann reported this compound. E. Vigouroux heated a mixture of copper with 10 per cent. silicon in an electric furnace until the excess of copper had volatilized. The steel-grey crystals had a sp. gr. of 6·9 at 18°. R. Frilley found evidence of this compound as a point of inflexion on the sp. gr. curve ; and of *copper silicide,* CuSi, on the mol. vol. curve. E. Rudolfi considers that the alleged compound is really a eutectic. G. J. L. de Chalmot reported the occurrence of *copper trihemisilicide,* $Cu_2Si_3$, in a commercial sample of cuprosilicon. R. Frilley regarded a point of inflexion on the sp. gr. curve as evidence of the existence of this compound ; and on the mol. vol. curve, he found evidence of *copper tetrasilicide,* $CuSi_4$. The chemical individuality of none of these products has been established.

According to W. Hampe, copper with 0·526 per cent. of silicon preserves its colour ; E. Rudolfi said the colour with one per cent. of silicon is like that of brass ; those with 1·5 to 2 per cent. of silicon are yellowish-red, those with 3·5–4·8 per cent. have a pale bronze colour ; and those with about 5 per cent. are pale brass-yellow, or, according to E. H. and A. H. Cowles and C. F. Mabery, greyish-black ; those with 8 per cent. silicon are silver-white ; and those with up to 10 per cent. are silver-white with a bluish tinge. H. St. C. Deville and H. Caron say that those with 12 per cent. silicon have a reddish tinge like bismuth ; and C. Winkler said those with 20–30 per cent. silicon are grey. H. Behrens said that the microstructure of alloys with 0·5 per cent. silicon shows a grey network. W. Hampe said the fracture of an alloy with 3·66 per cent. silicon is compact and lustrous ; with 6 per cent.,

crystalline and pale grey; with 8 per cent., conchoidal; and with 11·7 per cent., glassy. Observations have also been made by E. Vigouroux, A. Dick, S. Bogdan, and M. Philips. A. L. Norbury measured the vol. of the solute atoms in solid soln. of cuprosilicon. The sp. gr. of cuprosilicon alloys have been measured by A. Dick, W. Hampe, G. J. L. de Chalmot, etc.

| Per cent. silicon . . | 9·10 | 12·07 | 13·24 | 20·52 | 40·48 |
|---|---|---|---|---|---|
| Sp. gr. . . . . | 7·810 | 7·034 | 6·764 | 5·966 | 4·998 |

According to R. Frilley:

| Per cent. Si . | 0 | 13·50 | 17·98 | 27·92 | 34·88 | 48·80 | 68·00 | 90·50 | 100·00 |
|---|---|---|---|---|---|---|---|---|---|
| Sp. gr. . | 8·80 | 7·78 | 6·90 | 6·33 | 5·61 | 4·02 | 3·15 | 2·54 | 2·40 |
| Mol. vol. . | 7·21 | 6·97 | 7·35 | 7·35 | 7·85 | 9·75 | 10·27 | 11·77 | 11·66 |

The decrease in sp. gr. is fairly regular with increasing proportions of silicon. The hardness of cuprosilicon at first increases rapidly with increasing proportions of silicon; and afterwards the increase is slower; observations were made by H. St. C. Deville and H. Caron, C. Winkler, G. J. L. de Chalmot, M. Philips, etc. H. Behrens said that the hardness of a 2·1 per cent. alloy is 3·1; of a 3 per cent. alloy, 3·0 for the crystals and 3·3 for the matrix; the numbers are respectively 3·2 and 3·4 for a 5 per cent. alloy; and for a 10 per cent. alloy, over 6 for the graphite-like crystals, 4 for the yellow prisms, and 4·2 for the matrix. E. Rudolfi said that quenching and slow cooling have little influence on the hardness. W. Hampe found the tensile strength of 0·53 and 3·47 per cent. silicon alloys to be respectively 50 and 95·3 kgrms. per sq. mm.; he also found the malleability decreases with increasing content of silicon; the ductility of an alloy with 0·53 per cent. of silicon was like copper, a 2 per cent. alloy could still be drawn readily, but a 3·66 per cent. alloy was difficult, an alloy with 6 per cent. of silicon is brittle, and one with 11·7 per cent. of silicon behaved like glass. E. Wilson found the linear coeff. of thermal expansion to be 0·0000234–0·0000240 for alloys with 1·5–2·0 per cent. of silicon. H. St. C. Deville and H. Caron found alloys with 4·8 per cent. of silicon melted like bronze, and those with 12 per cent. of silicon melted more easily than silver. For E. Rudolfi's observations, *vide* Fig. 7. C. Heusler, and E. H. and A. H. Cowles and C. F. Mabery found that cuprosilicon is a good electrical conductor; W. Hampe said that alloys with 0·53 and 3·47 per cent. of silicon have respectively 28·11 and 6·5 per cent. of the conductivity of purified copper. E. Wilson found the sp. resistance of commercial copper increases by adding 1·5–2·0 per cent. of silicon from $2{\cdot}76\times10^{-6}$ to $3{\cdot}3\times10^{-6}$ ohms, and the temp. coeff. falls from 0·0040–0·0030.

According to W. Hampe, alloys with over 3·47 per cent. of silicon become corroded on exposure to air; other observations were made by M. Philips, who found that hot water decomposes cuprosilicon liberating hydrogen, and forming copper silicate, $Cu_2SiO_3$; the $Cu_7Si_2$ alloys seem to be most readily attacked; the development of hydrogen begins between 46° and 65°, and is quite marked between 70° and 94°. The alloy with 12 per cent. of silicon increased in weight 7·6 per cent. after 48 hrs.' boiling with water. C. Combes found alloys with about 20 per cent. of silicon give with dry hydrogen chloride, copper and silicon chloroform. G. J. L. de Chalmot said that alloys with 39 per cent. of silicon react very slowly with sulphur at 200°–250°; and at 270°–280°, the copper of the alloy is converted into cupric and cuprous sulphides; similarly also with the 10–12 per cent. alloys; the silicon is set free. M. Philips said sulphuric acid or soln. of ammonium chloride liberates hydrogen at comparatively low temp. E. Vigouroux said that nitric acid readily dissolves alloys with 2·5 per cent. silicon, and black crystals remain when the 20 per cent. alloys are treated with this acid. W. Hampe said the 6 per cent. alloy is completely dissolved by the acid, and that with the 11·7 per cent. alloy small shining flecks are separated. G. J. L. de Chalmot said that aqua regia dissolves part of the copper from cuprosilicon. Molten mixtures of the alkali carbonates and nitrates readily decompose the alloy. E. Vigouroux found

that soln. of alkali hydroxide have little or no action on an alloy with 2·5 per cent. of silicon. P. Lebeau found the silicon is displaced from cuprosilicon when it is heated with many metals—silver, zinc, aluminium, and tin. P. Lebeau and J. Figueras obtained chromium silicide; E. Defacqz, molybdenum silicide. M. Philips describes the use of cuprosilicon for deoxidizing copper and bronze; and for toughening aluminium. G. Kroupa discusses the hardening of copper by cuprosilicon. E. Vigouroux found commercial cuprosilicons with 10, 13, and 15 per cent. of silicon; and C. J. L. Leffler analyzed one with 38·9 per cent. of copper, 54·23 per cent. of silicon, 6·71 per cent. of iron, and 0·12 per cent. of carbon.

J. J. Berzelius [3] first noticed that silver alloys with silicon when the two elements are heated before the blowpipe, and he supposed **silver silicide** was formed because when the alloy was dissolved in acid, some silicic acid was formed. He obtained similar results when a mixture of charcoal and finely divided silver was strongly heated under a layer of glass containing only alkaline or earthy bases. F. Stromeyer said that under these conditions, silver unites with both carbon and silicon. J. S. Stas also noted that molten silver or silver vap. reduces silicates and silica *avec formation de silicate et de siliciure d'argent.* C. Winkler melted silver with 3, 10, and with 20 per cent. of silicon under cryolite, and obtained respectively silver-white, dirty grey, and grey-coloured alloys. G. J. L. de Chalmot obtained an argentosilicon alloy by heating sand, carbon, lime, and silver in an electric furnace. Some calcium was also present. F. Wöhler passed silicon hydride into a soln. of silver nitrate and obtained a precipitate which he regarded as a mixture of silver silicide and silver; G. Buchner regarded the precipitate as **silver nitratosilicide,** $Ag_4Si.4AgNO_3$, analogous to the precipitates obtained with arsine and stibine. E. Vigouroux passed silicon tetrachloride a number of times over molten silver but obtained only silver chloride, no silicide. H. N. Warren obtained an alloy by heating a mixture of silver, sodium, and potassium fluosilicate at a high temp. He concluded that silver unites with silicon only when the latter is *in statu nascendi.* J. Percy said that he could find no sign of combination when crystalline silicon is heated in contact with silver; nor did L. Kahlenberg and W. J. Trautmann observe any signs of combination. H. Moissan also noted that molten silver dissolves silicon and gives it up again on cooling. It therefore follows that the claims of F. Wöhler, H. N. Warren, G. J. L. de Chalmot, J. J. Berzelius, F. Stromeyer, and C. Winkler to have obtained alloys which contained silver silicide are invalid; *au contraire,* J. Percy, H. Moissan, and E. Vigouroux claimed that silicon and silver do not unite chemically, and they are probably correct. H. Moissan and F. Siemens measured the solubility of silicon in molten silver at different temp., and expressing the results in parts of silicon, per 100 parts of silver, found:

| | 970° | 1150° | 1250° | 1470° |
|---|---|---|---|---|
| Solubility . . . | 9·22 | 14·89 | 19·26 | 41·46 |

The silicon is rejected as the soln. cools. The results are plotted in Fig. 8.

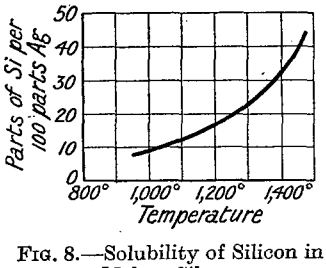



FIG. 8.—Solubility of Silicon in Molten Silver.

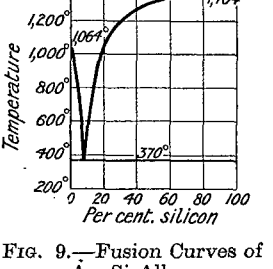



FIG. 9.—Fusion Curves of Au–Si Alloys.

G. Arrivaut found that the liquidus curve of the silicon-silver alloys has two branches, one of which starts from the m.p. of silver, and the other from the m.p.

of silicon, 1415°; the two curves intersect at the eutectic temp., about 800°, at a point corresponding with about 5 per cent. of silicon (*vide* Fig. 9, **3.** 22, 7). The solidus is a horizontal line passing through the eutectic, ranging from 0 to 90 per cent. silicon. No mixed crystals were formed. In the fusions containing 40–60 per cent. of silicon, a small white pearl is formed on the bluish-grey button of slightly oxidized silver. This is attributed to the increase in vol. of silicon on solidification; it contains 4·8 per cent. silicon and 94·85 per cent. silver. The subject was also studied by W. Manchot and co-workers.

C. Winkler [4] obtained alloys of gold with 3 and with 10 per cent. of silicon. He said that the former is dirty yellow, and that the latter is yellowish-grey and brittle. H. N. Warren said that gold *in statu nascendi* unites with silicon much more readily than is the case with silver, and he claimed to have made **gold silicide** by heating gold and sodium with potassium fluosilicate at a bright red heat. E. Vigouroux could not obtain any evidence of the formation of a gold silicide. C. di Capua found gold and silicon to be totally miscible when liquid; to be mutually insoluble in the solid state; and to form no compounds. The eutectic, Fig. 9, contains about 94 per cent. of gold, and solidifies at 370°.


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## § 8. The Silicides of the Calcium Family

F. Wöhler[1] prepared calcium silicide by heating an intimate mixture of dry, warm, anhydrous calcium chloride, silicon, and sodium in a crucible brasqued with dry sodium chloride. The lead-grey crystalline regulus was very impure. Analyses varied from

| Free Si | Combined Si | Ca | Mg | Na | Al | Fe |
|---|---|---|---|---|---|---|
| 6·68–65·65 | 14·55–52·16 | 9·53–34·51 | 0·17–2·48 | 0·39–3·35 | 0·22–3·16 | 0·30–2·19 |

H. Moissan and W. Dilthey heated a mixture of equal parts of calcium oxide and silicon in a crucible of retort graphite in an electric arc furnace. The crucible was removed from the furnace as soon as the mass was melted in order to avoid forming calcium carbide and silicon carbide. The regulus contains some calcium carbide and silicate as impurities. The product is not satisfactory if an excess of silicon be used. G. J. L. de Chalmot made a calcium silicide by heating silica, calcium oxide, and carbon in an electric furnace; R. Frilley, G. Gin, L. Baraduc-Muller, and C. S. Bradley described somewhat similar processes. E. Jüngst and R. Mewes heated silicon with calcium chloride or fluoride in an electric furnace. T. Goldschmidt, and S. Herrmann heated calcium oxide or carbonate with silicon in a crucible at the temp. of molten cast-iron. The calcium oxide is partly reduced to form calcium silicide, and part forms a slag: $3CaO+5Si=2CaSi_2+CaSiO_3$. The reaction can be satisfactorily conducted in an electric furnace, and calcium chloride or fluoride can be used as a flux. In order to avoid the formation of a silicate, La Compagnie Générale de l'Électrochimie employed calcium carbide in place of calcium oxide: $CaC_2+2SiO_2+2C=CaSi_2+4CO$; and $2Si+CaO+C=CaSi_2+CO$. A. Burger heated calcium with silica in vacuo. H. le Chatelier, and N. Caro mention the occurrence in commercial calcium carbide of crystals of what were considered to be calcium disilicide, $CaSi_2$. None of these processes suffice to establish the existence of calcium silicide as a chemical individual.

S. Tamaru prepared alloys of these two elements from calcium and silicon fused in an atm. of nitrogen. The crucibles of carbon or porcelain were lined with magnesia and tar, and then fired. The product always contained some calcium nitride, and some magnesium. He found silicon is practically insoluble in calcium at 900°, but at 990° a reaction occurs. The equilibrium diagram is shown in Fig. 10. The evidence shows that probably **calcium disilicide,** $CaSi_2$, is formed, and may be another silicide. L. Wöhler and F. Müller could not make this compound directly, but obtained it by heating $Ca_3Si_2$ in a stream of hydrogen at 1000°–1010°; if an excess of silicon is present, this reacts with the calcium hydride to form more calcium disilicide. L. Wöhler and O. Bock obtained it from its elements at 1000°–1100° in hydrogen. The heat of formation is $Ca+2Si=CaSi_2$ +208·7 Cals.

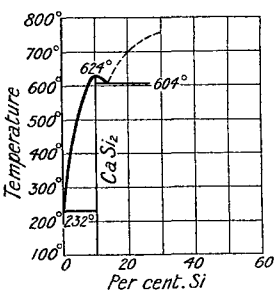


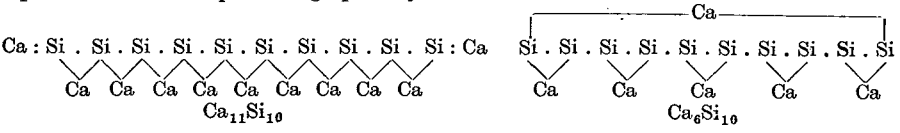

FIG. 10.—Portion of Equilibrium Diagram of Calcium and Silicon.

L. Wöhler and F. Müller also made **calcium monosilicide,** CaSi, or $Ca_2Si_2$, free from the disilicide, by heating a mixture of calcium and silicon in atomic proportions or with excess of silicon up to 100 per cent. in a magnesia boat in an atm. of carbon dioxide at 1050°. After 15 secs., a violent reaction takes

place and the mass becomes incandescent. It must then be cooled rapidly. The mass breaks up readily into small, lustrous, metallic leaflets and larger crystals. L. Wöhler and O. Bock made it from its elements at 1000°–1050° in an atm. of carbon dioxide. The density of the substance, containing a small proportion of uncombined silicon, is 2·346. By dil. acids it is attacked readily with the evolution of a spontaneously inflammable silicon hydride and the formation of hydrated silica; it is only slowly attacked by conc. acids, with evolution of hydrogen, and by cold water; more readily by warm water and by dil. ammonia. By contrast, the disilicide dissolves in hydrochloric acid with formation of yellow silicone and without production of spontaneously inflammable silicon hydride. When, in the preparation of the substance, so large an excess of silicon is used as to prevent the necessary rise in temp. during the reaction, a mixture of mono- and di-silicides is formed. From this it was concluded that the monosilicide is formed endothermically from the disilicide. The heat of formation is $2Ca+2Si=Ca_2Si_2+166·3$ Cals., or $CaSi_2+Ca=Ca_2Si_2-43$ Cals.

R. Frilley obtained no clear evidence of the formation of definite compounds from the sp. gr. curve of the alloys. L. Hackspill made the disilicide by heating to 1000° in vacuo a compressed mixture of 6 grms. of silicon and 4 grms. of calcium filings. O. Hönigschmid said that this silicide is always produced when calcium is heated with an excess of silicon. P. Formhals, and A. Kolb found that when the two elements are heated in the proportions required for $CaSi_2$, some silicon always remains uncombined, and a constant product is not obtained. R. Frilley said that when calcium oxide is reduced by silicon in the presence of carbon, calcium carbide is first formed, and this reacts with the silicon, forming calcium silicide. The reaction between ferrosilicon and calcium carbide is reversible. He also found that the calcium disilicide is obtained when many of the calcium-silicon alloys are digested with a boiling dil. soln. of sodium hydroxide. L. Hackspill claimed to have made needle-like crystals, **calcium ditritasilicide,** $Ca_3Si_2$, by heating silicon with a large excess of calcium, say 1 : 4. The sp. gr. was 1·64 at 14°. L. Wöhler and F. Müller obtained it from its elements at 1000°; they gave 166·3 for the heat of formation, and said that it yields spontaneously inflammable silicon hydride when treated with hydrochloric acid. O. Hönigschmid obtained a similar product. R. Frilley obtained no definite evidence of the individuality of this substance.

A. Kolb, and R. Formhals reported the formation of a silicide, $Ca_{11}Si_{10}$, or $Ca_{12}Si_{10}$, by the action of an excess of calcium on silicon, say 10 : 3. They also reported $Ca_6Si_{10}$ to be formed when calcium is heated with an excess of silicon. The analyses of this substance do not exclude the possibility that impure calcium disilicide is in question. R. Formhals represented these two products graphically:




The formulæ, however, have little meaning so long as their existence as chemical individuals is in doubt.

The calcium-silicon alloy made by H. Moissan and W. Dilthey is a grey crystalline mass with a sp. gr. approximating 2·5; and with a hardness like that of quartz. F. Wöhler's alloy decomposed on exposure to air, forming plates with a metallic lustre and appearance, and it decomposed under water. H. Moissan and W. Dilthey's alloy was fairly stable towards water, and it was decomposed but slowly by cold water. G. Tammann studied the electrode potential and chemical properties of the calcium-silicon alloys. S. Tamaru said that finely divided alloys with 60–91 per cent. of silicon are scarcely affected by water; while those with 38–52 per cent. are attacked with the development of hydrogen. F. Wöhler's alloy was not attacked by heating it to redness in steam. H. Moissan and W. Dil-

they's alloy is not affected when heated to redness in hydrogen ; it is superficially oxidized when heated in air ; and it is incompletely oxidized when heated in oxygen. It readily burns in fluorine gas, forming silicon and calcium fluorides ; chlorine, bromine, and iodine attack it at a dull red heat. F. Wöhler's alloy with conc. hydrochloric acid gives off hydrogen copiously ; dil. sulphuric acid, acetic acid, and hydrofluoric acid behave similarly—with the last-named acid, the silicon is rapidly bleached and dissolved ; with dil. hydrochloric acid, hydrogen is less copiously evolved, and translucent, lustrous plates are formed. When the plates are washed, and dried over sulphuric acid in vacuo, they often ignite when air is introduced, burning to a mixture of silica and silicon. H. Moissan and W. Dilthey obtained silicon-acetylene, $Si_2H_2$, by treatment with dil. hydrochloric acid ; with conc. sulphuric acid, gas was feebly evolved ; conc. or fuming nitric acid oxidizes the alloy very slowly. According to L. Wöhler and O. Bock, the disilicide in nitrogen at 900°–1100° forms $CaSiN_2$ ; and $CaSi_2N_2$. S. Tamaru found that alloys with 60-91 per cent. of silicon are but slowly attacked by dil. acetic, oxalic, or tartaric acid, and likewise with dil. hydrochloric, nitric, or sulphuric acid, giving off hydrogen and spontaneously inflammable silicon hydride ; alloys with 38–52 per cent. silicon are rapidly attacked by dil. acetic, oxalic, tartaric, hydrochloric, nitric, or sulphuric acid, giving off a spontaneously inflammable gas, and forming a white powder which dissolves in alkali-lye with the evolution of hydrogen—*vide* silicone. E. Donath and A. Lissner said that sulphur has no action at a red heat, while hydrogen sulphide attacks the alloy superficially. F. Wöhler found that with an aq. soln. of sulphur dioxide and a little hydrochloric acid, no gas is evolved, but the alloy is transformed into reddish-brown copper-coloured plates ; the brown liquid becomes turbid and there is a separation of sulphur. When the residue which remains when the liquid is poured off is dried in vacuo, and extracted with carbon disulphide, a pale greenish-brown powder remains—*vide* silicone.

This powder smells of hydrogen sulphide, and when heated detonates ; if very gradually heated, hydrogen sulphide is given off, and when no more gas is evolved, the product yields more hydrogen sulphide when treated with water. Ammonia converts the substance into a white mixture of silica and silicon, and hydrogen is at the same time evolved. Analyses correspond roughly with $H_8Si_4S_5$.

A vermilion-red product is formed with selenium dioxide and a little hydrochloric acid ; and tellurium dioxide under similar conditions forms a greyish-black product. A. Geuther, and C. Eichel found that when calcium silicide is heated in nitrogen, calcium nitride is formed and silicon separates out. According to H. Moissan and W. Dilthey, when the calcium-silicon alloy is heated with carbon, it forms calcium carbide, etc. ; it is rapidly dissolved by molten aluminium. The alloy containing some aluminium was found by R. Frilley to be attacked more vigorously the greater the proportion of aluminium. When the carbon-silicon alloy is dissolved by molten iron, it forms iron silicide. Soln. of alkali hydroxide readily decompose the alloy, with the evolution of hydrogen. S. Tamaru said that silicon-calcium alloys are not attacked by alkalies and ammonia. L. Wöhler and O. Bock found that the absorption of nitrogen by heated calcium silicon alloys is accelerated by calcium chloride and fluoride, while the carbonate and sulphate make very little difference. The alloys form ammonia or its equivalent when treated with water, hydrochloric acid, conc. alkali-lye, or fused alkalies. They showed that both *calcium silicocyanamide*, $CaSiN_2$, and *calcium silicocyanide*, $Ca(SiN)_2$, are formed. E. Donath and A. Lissner found that liquid ammonia and organic solvents have no action. S. Tamar found that molten calcium-silicon alloys readily attack porcelain. Calcium-silicon alloy is a strong reducing agent, and, according to C. S. Bradley, and T. Goldschmidt, can be used for removing sulphur and phosphorus from steel ; and, according to W. S. Anderson, as a deoxidizing agent for iron and steel.

C. S. Bradley prepared **strontium disilicide,** $SrSi_2$, by melting together carbon,

silicon, and strontium carbonate or oxide in an electric furnace; E. Jüngst and R. Mewes made it by heating silicon with strontium chloride or fluoride in an electric furnace; T. Goldschmidt, by heating strontia and silicon in an electric furnace; and R. Frilley, by melting a mixture of strontium carbide, silica, and aluminium in an electric furnace. The existence of this compound as a chemical individual has not been established. The alloy is white and crystalline. C. S. Bradley found that it decomposes water with the evolution of hydrogen; and with dil. hydrochloric acid, it gives off a mixture of hydrogen and silicon tetrahydride. It is a strong reducing agent. C. S. Bradley made what he regarded as **barium disilicide,** $BaSi_2$, by a process analogous to that employed for the calcium and strontium disilicides. The product behaved in a similar way. T. Goldschmidt obtained a barium silicide, $BaSi_2$, by reducing barium oxide with silicon, but none was obtained by L. Kahlenberg and W. J. Trautmann. O. Hönigschmid said that barium disilicide is formed when barium is heated with an excess of silicon, and R. Frilley added that the compound is more difficult to make than calcium disilicide. T. Goldschmidt made it by heating baryta and silicon as in the case of the corresponding calcium compound. R. Frilley made it by heating a mixture of silica and barium carbide with either carbon or, better, with aluminium. According to P. Askenasy and C. Ponnaz, barium peroxide and silicon react very violently when the reaction is initiated by means of a fuse. By using coarsely-powdered barium peroxide (50 parts) and silicon (15 parts), a barium silicide with 30 per cent. of barium is obtained. The mixture (with less silicon and a little sodium peroxide) may also be used to fuse iron or copper, or powdered ferro-silicon or titanium silicide may be used in place of silicon. E. Jüngst and R. Mewes likewise prepared what they regarded as **barium hemisilicide,** $Ba_2Si$, by the process which they employed for strontium silicide. The steel-grey mass is decomposed by water and dil. hydrochloric acid, as in the case of the other alkaline earth silicides. According to R. Frilley, it is not attacked by cold chlorine, bromine, or iodine. Soln. of bromine or iodine dissolve it without the development of any gas; hydrofluoric and hydrochloric acids attack it vigorously giving off a spontaneously inflammable gas. Nitric, sulphuric, and phosphoric acids behave similarly but less vigorously. Acetic acid does not give a spontaneously inflammable gas. A soln. of chromic acid behaves like a soln. of bromine; and aq. ammonia has no action.


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## § 9. The Silicides of the Magnesium-Zinc Family

Silicon and beryllium are readily alloyed, and H. Debray [1] said alloys with up to 20 per cent. of silicon are hard and brittle, and can be readily polished. A. Ditte said that up to 1891, beryllium had not been obtained free from silicon. According to P. Lebeau, when beryllia is reduced by silicon in the electric furnace, the resulting **beryllium silicide** is contaminated with silicon carbide. No definite compound has been isolated.

A number of magnesium silicides has been reported, but the existence of only **magnesium hemisilicide,** $Mg_2Si$, has claims to recognition ; the others are probably mixtures of this silicide with magnesium or silicon ; and, according to O. Hönigschmid,[2] this silicide is always formed when the magnesium is heated with silicon and when either constituent is present in excess. T. W. C. Martius noted the occurrence of magnesium silicide in a slag obtained in the preparation of magnesium. F. Wöhler made the alloy by melting together magnesium chloride, sodium, and sodium fluosilicate. Fluorspar can be used as a flux. C. Winkler melted sodium fluosilicate with magnesium, using sodium chloride as a flux ; P. Lebeau and R. Bossuet employed a similar process for alloys with 0–45 per cent. of silicon ; and for alloys with more silicon, they fused magnesium filings, crystalline silicon, and a small quantity of potassium fluosilicate. C. Winkler also obtained what he regarded as *magnesium tripentitasilicide*, $Mg_5Si_3$, and the hemisilicide, $Mg_2Si$, by heating the constituent elements in a stream of hydrogen ; but not by melting the two elements under sodium chloride as a flux. E. Vigouroux, and H. Moissan and S. Smiles also obtained the alloys by melting the two elements in the electric furnace. J. Parkinson, and T. L. Phipson first observed the formation of magnesium silicides in the reduction of silica by magnesium. C. Winkler, and L. Gattermann and co-workers heated silica with magnesium : $SiO_2+4Mg=2MgO+Mg_2Si$. The preparation of magnesium silicide best suited for making the silicon hydrides (*q.v.*) has been investigated by A. Geuther, H. Moissan and S. Smiles, and A. Stock and C. Somiesky. The last-named workers made the silicide by heating calcined silicic acid with twice its weight of commercial magnesium powder at as low a temp. as possible. The product is best if the silica contains less than one per cent. of alkali as impurity ; silica free from alkalies reacts with magnesium too vigorously, producing a high temp. The product is not then readily attacked by acids. M. L. V. Gayler studied the solubility of the hemisilicide in molten aluminium.

A. Stock and C. Somiesky made magnesium silicide by placing 100 grms. of a mixture of calcined precipitated silica with twice its weight of commercial powdered magnesium in an iron crucible of a litre capacity. The crucible was placed in a vessel of cold water. The reaction was started by a fusee and was over in a few moments ; and a stream of hydrogen (washed in sulphuric acid) was sent from a bomb through a tube in the perforated lid of the crucible so that the product cools for half an hour in an atm. of hydrogen. The mass was then broken into coarse fragments not over 0·5 mm. diameter, and the dust which passed through a millimetre-mesh sieve was rejected. The magnesium silicide so prepared has a bluish colour and is markedly crystalline. R. Schwarz and E. Konrad recommended working in an atm. of hydrogen, and mechanically separating the crystals of the silicide from the mixture. The crude product was freed from magnesium by the action of ethyl bromide and anhydrous ether. The purified material is a steel-blue crystalline powder which contains traces of amorphous silicon and iron silicide.

H. N. Warren prepared silicon-magnesium alloys by the action of magnesium on silicon fluoride ; K. Seubert and A. Schmidt, by the action of magnesium on silicon chloride ; and E. Jüngst and R. Mewes, by the action of silicon on magnesium halides in an electric furnace. T. Goldschmidt made the alloy from magnesia and silicon as in the case of calcium-silicon alloys. R. Vogel made a series of alloys directly from the elements heated in carbon tubes in an atm. of hydrogen ; he found

that the molten alloys strongly attack porcelain and magnesia vessels. The f.p. curve, Fig. 11, falls rapidly from the f.p. of silicon to a eutectic at 950° and 42 per cent. of magnesium; it then rises to a maximum at 1102° and 63·2 per cent. of magnesium corresponding with $Mg_2Si$; there is a second eutectic at 645° and 96 per cent. of magnesium. No solid soln. were observed. There is here no evidence of F. Wöhler's *magnesium tritetritasilicide*, $Mg_4Si_3$, or of C. Winkler's tripentitasilicide. According to P. Lebeau and R. Bossuet, under the microscope, polished surfaces (i) of an alloy containing 0·38 per cent. of silicon, show grains of magnesium surrounded by a eutectic, but no crystals of the silicide; (ii) in alloys containing 6–8 per cent. of silicon, well-defined crystals of the silicide appear in the midst of a eutectic very rich in magnesium; (iii) that an alloy containing 40 per cent. of silicon contains that element mainly as crystals of the free silicon; and (iv) crystals of free silicon in alloys containing silicide and a eutectic differing from the former and containing more than 50 per cent. of that element. The pure silicide cannot be isolated by treating the alloys with any aq. reagent, owing to the decomposing action of water, but the magnesium is dissolved away from an alloy containing 25 per cent. of silicon by means of ethyl iodide and ether, leaving brilliant, slate-blue, octahedral crystals of **magnesium hemisilicide,** the analysis of which corresponds accurately with the formula $Mg_2Si$. P. Lebeau and R. Bossuet found that the glistening octahedral crystals of magnesium hemisilicide are slate-blue in reflected light, and in thin layers, by reflected light, they have a reddish tinge. E. A. Owen and G. D. Preston found that the X-radiogram corresponds with a face-centred cube lattice of silicon atoms of side 6·391 A., symmetrically intermeshed with a simple cube lattice of magnesium atoms of side 3·19 A. There are eight magnesium atoms situated within each face-centred cube of silicon atoms, dividing the four diagonals in the ratio 1 : 3 and 3 : 1. The sp. gr. from X-ray data is 1·95+0·05 grms. per c.c. The magnesium atoms are separated by the same distance as in the pure metal; and the sum of the so-called radii of the silicon and magnesium atoms is equal to the distance between these atoms in the compound. The sp. gr. is about 2; and the hardness between that of fluorspar and orthoclase. The m.p., said R. Vogel, is 1102°. A. M. Portevin and P. Chevenard studied the expansion which occurs on heating magnesium-silicon alloys, and found a contraction at about 350° due to the gradual dissolution of magnesium hemisilicide, and conversely an expansion on cooling below that temp. P. Schübel gave 0·2320 for the sp. ht. of $Mg_2Si$ between 18° and 298°; and 0·2445 between 18° and 630°. The alloys are not attacked by atm. air. P. Lebeau and R. Bossuet found that the alloys are easily oxidized and give sparks by friction against a hard substance in air. When heated between 1100° and 1200° in hydrogen or in vacuo, the compound is resolved into its elements. The heat developed by the vigorous combustion which occurs when heated in oxygen is sufficient to fuse the magnesium silicate which is formed. The compound slowly decomposes water at ordinary temp. giving hydrogen but no silicon hydride. Cold hydrochloric acid attacks the alloy vigorously, forming hydrogen and spontaneously inflammable silicon hydride. P. Lebeau said the gas contains silicomethane, silicoethane, and a little silicoethene. For the solid product, *vide* silane.

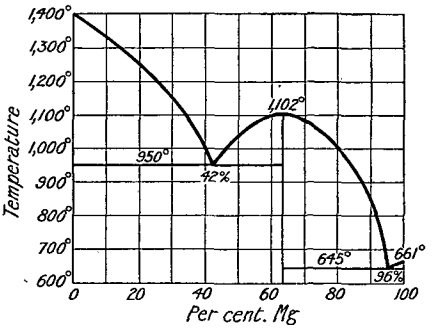



FIG. 11.—Equilibrium Diagram of Magnesium-Silicon Alloys.

According to A. Geuther, when magnesium silicide is treated with hydrofluoric acid, hydrogen is evolved. R. Vogel said that the alloy is slowly attacked by conc. sulphuric or nitric acid, but the attack is rapid with the dil. acids, and hydrogen

is evolved. P. Lebeau and R. Bossuet found the alloy to be a strong reducing agent. A. Geuther found that magnesium nitride and free silicon are formed by heating the alloy at a high temp. in nitrogen, and that a cold aq. soln. of ammonium chloride acts slowly on the alloy: $2Mg_2Si+8NH_4Cl+3H_2O=4MgCl_2+Si_2H_2O_3+8NH_3+6H_2$. The alloy is not attacked by a cold or hot aq. soln. of potassium hydroxide. G. Tammann studied the electrode potential and chemical properties of the magnesium-silicon alloys.

No **zinc silicide** has been isolated. According to H. St. C. Deville and H. Caron,[3] silicon dissolves in molten zinc, and all but a little separates from the soln. during solidification. Similar results were obtained by C. Winkler, and E. Vigouroux. W. Manchot and H. Funk studied this subject. H. Moissan and F. Siemens found the solubility increases rapidly with rise of temp.; and that the solubility in 100 parts of zinc, is:

| | 600° | 650° | 730° | 800° | 850° |
|---|---|---|---|---|---|
| Solubility . . . | 0·06 | 0·15 | 0·57 | 0·92 | 1·62 |

W. Sander and K. L. Meissner studied the ternary system, Zn–Mg–Si. W. Frankel found that when a mixture of zinc sulphide and carbon is heated in a quartz vessel to 1300°–1400° in an atm. of nitrogen, a volatile product is obtained, containing zinc, carbon, and sulphur, which reacts with the silica of the enclosing vessel. The product is also volatile, and corresponds approximately with the composition **zinc sulphosilicide,** ZnSSi. Using a carbon lining to the tube, the vapour nevertheless penetrates to the quartz, and introduces silicon into the mixture. The same compound is also obtained by heating zinc sulphide to 1300° with silicon. It condenses to hard, brown crusts. With acids the sulphur is evolved quantitatively as hydrogen sulphide, and with aq. alkalies, hydrogen is evolved. It may be polished like a metal, and is microscopically homogeneous. The electrical conductivity is less than that of silicon.

No **cadmium silicide** has been prepared, nor has the action of silicon on cadmium been studied. C. Winkler did not observe any signs of the formation of a **mercury silicide** when mercury and silicon are heated in a sealed tube to 100° or to 300°; nor do the two elements unite when allowed to stand in contact under a dil. soln. of sodium hydroxide. He utilized this property to separate aluminium from silicon. H. N. Warren obtained no silicide by the action of mercury on heated potassium fluosilicate. A little silicon amalgam is formed when an alcoholic soln. of silicon fluoride is electrolyzed with a mercury cathode. Silicon remains when the mercury is distilled off. L. Kahlenberg and W. J. Trautmann observed no formation of an alloy when mercuric oxide is reduced by silicon at a high temp.

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## § 10. The Silicides of the Aluminium and Rare Earth Families

For **boron silicide,** *vide* silicon boride. No **aluminium silicide** has been isolated ; *dans tous les cas*, said E. Vigouroux, *il y a simplement dissolution du silicon dans l'aluminium ;* if a third element be present, however, a complex silicide may be formed. H. St. C. Deville [1] stated that :

> Any siliceous material in contact with aluminium at a high temp. is always decomposed ; and if the metal is in excess there is formed an alloy or a combination of silicon and aluminium in which the two bodies may be united in almost any proportions. Glass, clay, and the earth of crucibles act in this way. However, aluminium may be melted in glassware or earthen crucibles without the least contamination of the metal if there is no contact between the metal and the material ; the aluminium will not wet the crucible if put into it alone. However, the moment that a flux facilitates immediate contact (even sodium chloride does this), the reaction begins to take place, and the metal obtained is always more or less siliceous. It is for this reason that I have prescribed in melting aluminium not to add any kind of flux, even when the flux would not be attacked by the metal.

H. St. C. Deville obtained aluminium charged with 10·3 per cent. of silicon. In preparing aluminium, F. Wöhler obtained globules of what he regarded as aluminium silicide containing crystals of silicon, and which, when treated with acids, gave hydrogen and silicon hydride. F. Wöhler treated potassium fluosilicate with aluminium, and obtained an alloy with about 70 per cent. of silicon. C. F. Rammelsberg reduced cryolite with sodium in a porcelain crucible, and obtained an alloy which when treated with hydrochloric acid showed the presence of combined and free silicon. The former changed partly into silica, and partly into gaseous silicon tetrahydride ; while the latter remained as a black residue of graphitoidal silicon.

| Silicon as | $SiO_2$ | $SiH_4$ | Free |
|---|---|---|---|
| Per cent. | 1·85–9·55 | 0·58–0·74 | 0·12–0·17 |

C. Winkler obtained an alloy with 69·34 per cent. of silicon by reducing a mixture of cryolite and quartz with aluminium. J. H. J. Dagger described the production of the alloy by reducing the oxides with carbon in the electric furnace. A. Minet prepared the alloy by the electrolysis of a fused mixture of sodium chloride and sodium fluoaluminate mixed with alumina and silica. R. Frilley used a similar process ; and he also electrolyzed a fused mixture of sodium and potassium fluorides, silica, and cryolite ; and also added silica to the fused mixture employed for preparing aluminium. E. Donath and A. Lissner dissolved calcium silicide in molten aluminium, and found that some aluminium silicide was formed which gave spontaneously inflammable silicon hydride when treated with an acid. E. Kohn-Abrest found that when aluminium is heated in a porcelain boat at 1100° in a vacuum the metal is rapidly volatilized at first, but, after some hours, the loss in weight from this cause becomes negligible. After prolonged heating, the residue is found to be coated with a yellow film, consisting of an alloy of aluminium and silicon. The same results are obtained when boats of pure graphite are employed, but only when these are contained in a porcelain tube. The conclusion drawn is that aluminium

vap. attacks the porcelain, liberating silicon, which is absorbed by the molten aluminium. The porcelain tubes employed are found to be coated internally with a black, crystalline deposit, having the composition *aluminium hemisilicide*, $Al_2Si$, is said to have been isolated. R. Frilley, L. D. Hooper, and E. Viel obtained aluminium hemisilicide by heating china clay in an arc furnace. T. Goldschmidt reduced silica by aluminium in the thermite process, although E. Weston and H. R. Ellis could not obtain a silicide by reducing silica by powdered aluminium; R. Frilley reduced silica by aluminium in the electric furnace and obtained an alloy with 30–96 per cent. silicon. L. Baraduc-Muller heated, to 1700°, a mixture of one mol of alumina with 3 mols of silicon carbide along with lime and magnesia as fluxes, and obtained aluminium-silicon alloys. J. J. Curran examined the influence of sodium on these alloys; M. L. V. Gayler and co-workers, alloys of aluminium, magnesium, copper, and silicon; and W. Sander and K. L. Meissner, alloys of magnesium, zinc, aluminium, and silicon. A binary alloy of aluminium and about 10 per cent. of silicon is called *silumin*. It was studied by G. Masing. T. B. L. Cain, and Z. Jeffries made some observations on these alloys.

For a time, it was thought that the alloy prepared by H. St. C. Deville by the action of silicon tetrachloride on aluminium at a red heat was *aluminium hemisilicide*, $Al_2Si$, and that the specimen prepared by C. Winkler was *aluminium trihemisilicide*, $Al_2Si_3$, but the conclusion was based merely on the analyses. The observation of F. Wöhler and H. Buff that the alloy furnished silicon hydride when treated with hydrochloric acid supported the view that a true compound is formed; and this is confirmed by C. F. Rammelsberg's observation—*vide supra*. E. Vigouroux, and R. Frilley failed in the attempt to make aluminium and silicon unite directly; on the other hand, added E. Vigouroux, if the materials are impure, or if metallic oxides be present, **silicoaluminides** of iron, nickel, cobalt, chromium, molybdenum, tungsten, uranium, manganese, vanadium, and titanium are readily produced. W. Fränkel found that molten silicon and aluminium are miscible in all proportions, but they do not enter into chemical combination. The f.p. curve consists of two branches, Fig. 12; the eutectic mixture contains about 10 per cent. of silicon, and solidifies at 576°. Whether mixed crystals are formed could not be satisfactorily determined; if they exist, those rich in aluminium do not contain more than 0·5 per cent. of silicon, and those rich in the latter element not more than 2 per cent. of aluminium. A. M. Portevin studied the structure of the eutectic; and the changes in vol. on cooling. W. Manchot and co-workers measured the solubility of silicon in aluminium; E. H. Dix and A. J. Lyon, and H. Schirmeister, the tensile strength of the alloys. C. E. Roberts confirmed the observations of W. Fränkel; and H. Sutton described these alloys. J. Czochralsky called an alloy with 11–14 per cent. silicon *silumin* and *alpax*; these other alloys have been described by J. D. Edwards and R. S. Archer, L. Guillet, J. J. Curran, R. E. Search, etc. According to R. Frilley, alloys with up to 10 per cent. of silicon are a little greyer than aluminium alone. The alloys work well. Alloys with 10–20 per cent. of silicon are lustrous and crystalline, more fusible than aluminium alone—*vide* Fig. 12. The alloys with up to 15 per cent. of silicon can be forged. Alloys with 20–38 per cent. of silicon are markedly crystalline, and they readily fracture; they have a bluish tinge. Crystals of silicon appear with alloys with over 38 per cent. of that element. Alloys with 40–55 per cent. of silicon have a matrix of anastomosed crystals. Alloys with over 55 per cent. of silicon look like *silicon fondu*—fused silicon. E. Wetzel found aluminium may have 0·5 per cent. of silicon

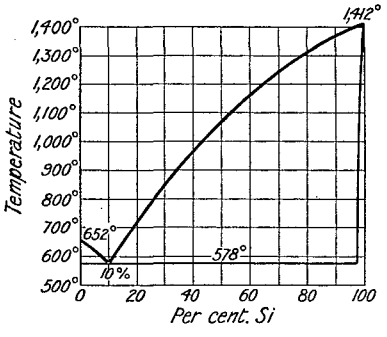



FIG. 12.—Equilibrium Diagram of Aluminium-Silicon Alloys.

in solid soln. at ordinary temp., and one per cent. at 550°. E. C. Bain studied the X-radiograms of the alloys. The sp. gr. of the alloys are :

| Per cent. Si | . | . | 10 | 20 | 30 | 47·5 | 64 | 85·2 | 9·65 |
|---|---|---|---|---|---|---|---|---|---|
| Sp. gr. | . | . | 2·52 | 2·50 | 2·45 | 2·44 | 2·40 | 2·35 | 2·37 |

The sp. gr. curve shows no singularities, and there is no evidence of the formation of definite silicides when silicon and aluminium are fused together; D. R. Tullis also studied the sp. gr. of these alloys. The physical properties have been studied by J. D. Edwards and co-workers, D. Basch and M. F. Sayre, L. Guillet, etc. The alloys are completely soluble in fused alkali hydroxides and carbonates, and in hot conc. soln. of alkali hydroxides. Hydrochloric acid attacks the alloys vigorously, and a deposit analogous to silicone is formed (*q.v.*); hydrofluoric acid behaves like hydrochloric acid; sulphuric acid readily attacks the alloy; nitric acid, hot or cold, attacks the alloys very slowly; and a mixture of nitric and hydrofluoric acids dissolves the alloys vigorously.

R. Frilley melted in an electric furnace a mixture of calcium silicide with aluminium using cryolite or fluorspar as a flux. He thus obtained crystalline alloys corresponding with **calcium trisilicodialuminide,** $CaAl_2Si_3$, and **calcium trisilicotetraluminide,** $CaAl_4Si_3$. Hydrofluoric or hydrochloric acid attacks the alloys vigorously, developing spontaneously inflammable silicon hydride, and leaving as a residue graphitoidal silicon. V. Fuss, and R. Frilley likewise obtained alloys representing **magnesium silicoaluminide.** A. M. Portevin and P. Chevenard studied the vol. changes with alloys of magnesium, aluminium and silicon. V. Fuss, and H. E. Dix and A. J. Lyon studied the physical properties of the ternary alloys silicon-copper-aluminium; S. Daniels, Al-Si-Mg alloys; V. Fuss, the ternary alloys Si-Al-Mg, Si-Al-Fe, and Si-Al-Ni; and W. Sander and K. L. Meissner, the ternary alloys Zn-Mg-Si; Al-Mg-Si; and Al-Zn-Si; and quaternary alloys Si-Al-Zn-Mg. L. Guillet investigated the binary, ternary, and quaternary alloys of aluminium, copper, silicon, and magnesium.

S. Tamaru [2] found that molten thallium and silicon are *praktisch miteinander nicht mischbar*. This is shown by the f.p. curve, Fig. 13. There is no sign of the formation of a definite *thallium silicide*. F. Ullik electrolyzed cerium fluoride and obtained a black powder which was regarded as *cerium silicide* because the analysis corresponded with CeSi. It was not investigated further. J. Sterba prepared **cerium disilicide,** $CeSi_2$, by heating cerium oxide and silicon in an electric furnace. It forms small crystals with a steely lustre; the density at 17° is 5·67. It is only slowly acted on by water; hydrogen is without action on it. Fluorine acts in the cold on it, chlorine, bromine, or iodine only after heating. When heated to redness, it burns in oxygen with a vivid incandescence, and when heated in boiling sulphur or selenium, it burns. Hydrogen chloride acts on it at a red heat. Soln. of hydrochloric and hydrofluoric acids attack it with evolution of hydrogen. Hydrogen sulphide and water are attacked at a red heat. Aq. soln. of alkali hydroxides and ammonia do not react with it in the cold. Only a portion of the thermal diagram has been explored by L. Guillet, and R. Vogel. This is indicated in Fig. 12, **5**. 38, 10. There is a maximum on the curve corresponding with **cerium silicide,** CeSi, of m.p. 1500°. This forms an eutectic with silicon. The eutectic is at 1250° with 46 per cent. Si.

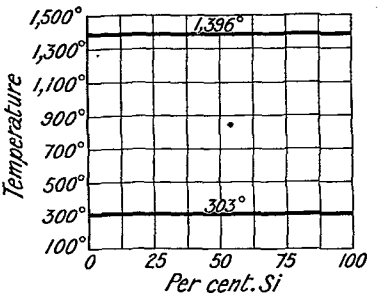



FIG. 13.—Freezing-point Curves of Mixtures of Thallium and Silicon.

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## § 11. The Silicides of the Titanium and Tin Families

For the *carbon silicides*, *vide* silicon carbides. L. Levy [1] treated titanium tetrachloride with silicon and obtained arborescent crystals of **titanium hemisilicide,** $Ti_2Si$, which were not closer investigated. H. Moissan obtained a silicide by heating a mixture of silicon and titanic oxide in the electric arc furnace. L. Baraduc-Muller heated a mixture of titanic oxide, silicon carbide, and carbon with a mixture of lime and magnesia as a flux. P. Askenasy and C. Ponnaz obtained what they regarded as **titanium trihemisilicide,** $Ti_2Si_3$, by heating the constituents in an electric furnace. O. Hönigschmid made **titanium disilicide,** $TiSi_2$, by heating in a fireclay crucible a mixture of 200 grms. powdered aluminium, 250 grms. of sulphur; 180 grms. of fine sand, and either 15 grms. of titanic oxide or 40 grms. of potassium fluotitanate, covering all with a thin layer of powdered magnesium, and igniting with a thermite pastille. Titanium disilicide crystallizes in small, iron-grey, tetragonal pyramids, having a hardness of 4–5 and a sp. gr. 4·02 at 22°. It oxidizes with difficulty, but burns in chlorine at below a red heat. It is insoluble in mineral acids excepting hydrofluoric acid, but dissolves slowly in 10 per cent. potassium hydroxide soln. Fused potassium hydroxide reacts vigorously with it at a red-heat, but potassium hydrogen sulphate is without action under these conditions. H. Moissan said titanium silicide is as hard as the diamond; and G. Gin recommended its use for cutting and polishing gem-stones. P. Askenasy and C. Ponnaz's product behaves like silicon towards barium dioxide—*vide* barium silicide.

E. Wedekind [2] prepared crystals of zirconium silicide by reducing zirconia with silicon in the electric furnace. O. Hönigschmid prepared **zirconium disilicide,** $ZrSi_2$, by a method similar to that employed for titanium disilicide—*vide supra*—and also by heating a mixture of potassium fluozirconate and fluosilicate and aluminium. The compound crystallizes in small, iron-grey, rhombic columns with

a metallic lustre, a hardness approximating to that of felspar, and a sp. gr. of 4·88 at 22°. It is stable in the air, but burns vigorously when its powder is heated on platinum foil. It is not attacked by mineral acids with the exception of hydrofluoric acid, which readily dissolves it, hydrogen being evolved; a 10 per cent. potassium or sodium hydroxide soln. is without action on it, as also is potassium hydrogen sulphate at a red heat. It is decomposed by fusion with potassium hydroxide. According to E. Wedekind, zirconium silicide is readily obtained in the colloidal state.

E. Wedekind and K. Fetzer [3] found that a mixture of thoria and silicon in the electric arc furnace gave a silicide which was washed with hydrochloric acid, and then with a 2 per cent. soln. of potassium hydroxide to remove the uncombined silicon. The m.p. is very high, and the product is decomposed by conc. alkali-lye. O. Hönigschmid prepared **thorium disilicide,** $ThSi_2$, by heating in an electric furnace a mixture of thoria and silicon; a mixture of aluminium, silicon, and thorium; or by the interaction of a mixture of the double fluoride of thorium and potassium, potassium silicofluoride, and aluminium at 1200°, and purified the products from free aluminium and silicon by treatment with potassium carbonate soln. It forms quadratic plates resembling graphite in colour, has a sp. gr. 7·96 at 16°, and when heated combines readily with the halogens, oxygen, sulphur, selenium, or hydrogen chloride, but it is not attacked by hydrogen at a red heat. It is soluble in aq. soln. of the mineral acids, is not attacked by soln. of the alkali hydroxides, but is decomposed on fusion with sodium or potassium hydroxides. For analysis, the compound was dissolved in aqua regia or in a mixture of hydrofluoric and nitric acids, or decomposed by fusing with moist sodium hydroxide.

J. J. Berzelius [4] observed that when tin and silicon are melted before the blowpipe, a ductile alloy is formed, which, when treated with acids, produces some silica. C. Winkler said that silicon can be alloyed with tin. Alloys with 2–3 per cent. silicon were said to be white, and not very malleable; alloys with 10 per cent. silicon were greyish-white and brittle. Warm hydrochloric acid dissolves the tin, and leaves the silicon partly free and partly as silica. E. Vigouroux said that alloys of tin are only mixtures, and contain no *tin silicide.* H. N. Warren obtained crystals of silicon by dissolving the amorphous element in molten tin, and cooling the soln. S. Tamaru found that molten silicon and tin are miscible in all proportions, and, on cooling, pure silicon separates, the eutectic being practically pure tin. The f.p. curve, Fig. 14, falls very slowly until about 80 per cent. tin is reached, and then very rapidly. L. Kahlenberg and W. J. Trautmann observed no formation of tin silicide.

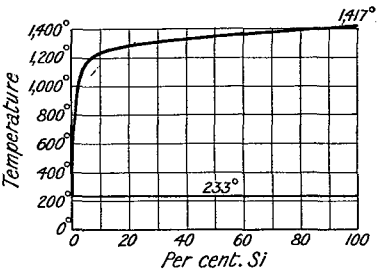



FIG. 14.—Equilibrium Diagram of Alloys of Tin and Silicon.

As in the case of tin, J. J. Berzelius found that silicon dissolves in lead melted before the blowpipe, and forms a malleable alloy or compound. H. N. Warren also said that a brittle *lead silicide* is formed when lead oxide is heated with silicon. H. St. C. Deville and H. Caron could not get the two elements to form an alloy. C. Winkler could not get an alloy at a red heat when the two elements were heated under a layer of cryolite. The silicon floated on the molten lead. He observed no signs of the formation of a lead silicide. A similar observation was made by L. Kahlenberg and W. J. Trautmann. E. Vigouroux observed that no dissolution of silicon in molten lead occurs at 1200°. H. Moissan and F. Siemens found that silicon commences to dissolve appreciably in lead at about 1250°, and that the solubility in 100 parts of lead is as follows:

| | 1250° | 1330° | 1400° | 1450° | 1550° |
|---|---|---|---|---|---|
| Solubility . . | 0·025 | 0·070 | 0·150 | 0·210 | 0·790 |

The solubility thus increases rapidly with rise of temp. The subject was studied by W. Manchot and H. Funk, A. M. Portevin, and L. Baraduc-Muller without obtaining any lead silicide. S. Tamaru found that the cooling curves of different alloys all show two arrests, one corresponding with the f.p. of silicon (1385°), and the other with the f.p. of lead (327°). This corresponds with the separation of the soln. into two layers near the temp. of solidification. Silicon behaves similarly with tin and with thallium.

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## § 12. The Silicides of the Vanadium and Chromium Families

**J. J. Berzelius**[1] observed no sign of the formation of *phosphorus silicide* or *silicon phosphide* when phosphorus vapour is passed over red-hot silicon. O. P. Watts failed to prepare phosphorus silicide by reducing a mixture of phosphoric acid and silica with carbon in the electric furnace ; also by using copper or copper silicide as a flux ; and also by the action of phosphor tin on silicon. C. Winkler found that silicon does not unite directly with arsenic either by heating silicon with arsenic, or arsenic vap. ; nor is arsenic silicide or silicon arsenide formed when silicon is heated with arsine. The silicide was not formed by melting quartz, arsenic, aluminium, and cryolite. **Arsenic pentasilicide,** or *silicon pentitarsenide*, $AsSi_5$, is, however, said to be formed, mixed with arsenic dihydride when zinc silicoarsenide is treated with hydrochloric acid. It was freed from arsenic hydride by heating in a current of hydrogen ; from zinc (and iron) by boiling with nitric acid ; and from silica by a soln. of potassium hydroxide. The dark grey powder consists of microscopic needles ; it can be heated in air without losing arsenic ; acids alone, or aqua regia, are without action ; boiling potash-lye attacks it very slowly, but molten alkali hydroxides or carbonates rapidly form alkali silicate and arsenate. Complex **silicoarsenides** were made by heating the metals with arsenic and silicon under cryolite and sodium chloride as fluxes. Thus, C. Winkler made **zinc silicoarsenide** in this way. The product gave off arsine when treated with hydrochloric acid and, as indicated above, left a residue of arsenic hydride and silicide. E. Vigouroux could get no *antimony silicide*, or *silicon antimonide*, by the action of antimony on silicon in the electric furnace. R. S. Williams found that molten antimony and silicon are completely miscible, and on cooling they form two series of mixed crystals extending respectively from 0–0·3 and from 99–100 per cent. of silicon, Fig. 15 ; there is no evidence of chemical combination. L. Kahlenberg observed that no silicide is formed when antimonious oxide is reduced by silicon. E. Vigouroux found that molten bismuth

dissolves silicon but rejects it again in a crystalline state on cooling; no *bismuth silicide* is formed. R. S. Williams found bismuth is insoluble in fused silicon, but silicon is soluble to the extent of about 2 per cent. in fused bismuth at 1414°,

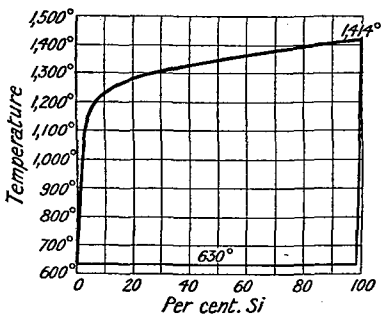



FIG. 15.—Equilibrium Diagram of Alloys of Antimony and Silicon.

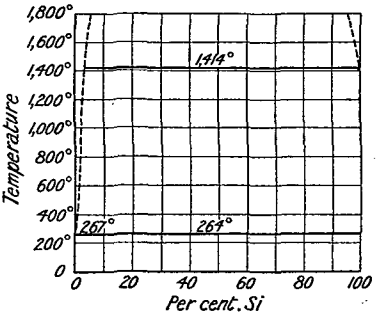



FIG. 16.—Equilibrium Diagram of Alloys of Bismuth and Silicon.

Fig. 16. The two elements form a series of mixed crystals with 0–0·8 per cent. of silicon. L. Kahlenberg and W. J. Trautmann observed no silicide is formed when bismuth oxide is reduced by silicon.

According to J. S. W. Johnston,[2] if vanadium pentoxide in a carbon crucible be heated with silicon to a high temp., a reddish-grey, metallic mass resembling bismuth is obtained. It conducted electricity very well. H. E. Roscoe suggested that the product was vanadium silicide. H. Moissan and A. Holt prepared **vanadium disilicide,** $VSi_2$, by heating an intimate mixture of vanadium trioxide with a little more than five times its weight of silicon for about 2 mins. in an electric arc furnace, and treating the residue successively with potassium hydroxide soln. and conc. nitric or sulphuric acid. It can also be obtained by reducing a mixture of silicon and vanadium trioxide with magnesium; and J. Meyer and R. Backa obtained it by heating a mixture of vanadium pentoxide, silicon, and fluorspar. According to H. Moissan and A. Holt, it forms brilliant prismatic crystals which have a metallic lustre and a sp. gr. of 4·42, scratch glass, and melt and volatilize in the electric furnace. Alkalies and acids, with the exception of hydrofluoric acid, have no action on it, but it burns in fluorine, chlorine, or bromine when heated. Iodine vapour, oxygen, sulphur, and hydrogen sulphide attack it very slowly at the m.p. of glass, but hydrogen chloride converts it into silicochloroform and vanadium chloride. Fused alkali hydroxides decompose the silicide; the action of fused metals depends on whether they combine more readily with silicon or with vanadium. Copper, for example, yields copper silicide and a copper vanadium alloy. H. Giebelhausen found that mixtures of the two elements give a eutectic melting at 1411°, Fig. 17. The maximum on the curve corresponds with $VSi_2$, which furnishes needle-like crystals, melting at 1655°, and harder than silicon. No solid soln. between silicon and the disilicide were observed. H. Moissan and A. Holt also made **vanadium hemisilicide,** $V_2Si$, (i) by heating a mixture of 120 parts of vanadium trioxide and 14 parts of silicon in the electric arc furnace; (ii) by the action of silicon on vanadium carbide, namely, by heating a mixture of vanadium trioxide, silicon, and carbon for 4 mins. in the arc furnace; and (iii) by heating a mixture of vanadium trioxide, silicon, and copper in the electric arc furnace. The hemisilicide is obtained in brilliant prismatic crystals which have a metallic lustre and a sp. gr. of 5·48 at 17°. It fuses at a temp. above the m.p. of the disilicide, and it is insoluble in water,

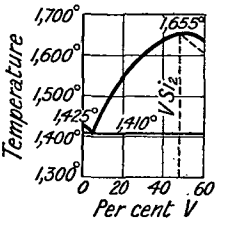



FIG. 17.—Fusion Curves of the Binary System: Si–V.

alcohol, ether, or benzene. Fluorine does not attack it in the cold; with chlorine at a red heat, it gives vanadium tetrachloride and silicon tetrachloride, and with bromine, vanadium tribromide and silicon hexabromide. It is attacked only superficially by water, sulphur, or hydrogen sulphide at a high temp., and ammonia has no action on it. It burns when heated in hydrogen chloride. When fused with an excess of silicon, it gives the disilicide. It is decomposed by molten sodium or copper, but is hardly affected by silver. Hydrochloric, nitric, and sulphuric acids do not attack it, but a mixture of nitric acid with either of the others dissolves it, and it is easily attacked by hydrofluoric acid, even in dil. soln. It is also decomposed by fused potassium hydroxide or a mixture of potassium carbonate and nitrate. O. Hönigschmid prepared **tantalum disilicide,** $TaSi_2$, by a method similar to that employed for titanium silicide. It forms iron-grey four-sided prisms having a metallic lustre resembling that of molybdenum disilicide. The sp. gr. is 8·83 at 0°. The compound is oxidized when heated in oxygen; reacts with fluorine only when heated; also reacts with chlorine when heated, but not with bromine; it dissolves in hydrofluoric acid; it is insoluble in mineral acids including aqua regia; it is soluble in a mixture of nitric and hydrofluoric acids; it is not decomposed by potassium hydrosulphate at a red heat; and it is readily decomposed by fused alkali hydroxides.

H. N. Warren [3] prepared a chromium silicide by heating white hot a mixture of chromic oxide with an excess of graphitoidal silicon. It was easily attacked by hydrofluoric acid. A. Ditte and H. Moissan noted that the two elements unite directly at a high temp. P. Lebeau and J. Figueras stated that when a small quantity of silicon is melted with a mixture of chromium and copper, and the resulting button is digested with nitric acid, prismatic crystals of chromium tritasilicide, $Cr_3Si$, remain; with a larger proportion of silicon, lozenge-shaped, facetted crystals of chromium hemisilicide, $Cr_2Si$, are formed; with a still larger proportion of silicon, chromium ditritasilicide, $Cr_3Si_2$, is formed; and finally, with the silicon in excess, chromium disilicide, $CrSi_2$, is produced. R. Walter made the alloy directly from the elements. R. Frilley made the alloys by heating chromic oxide with silicon carbide, or a mixture of chromic oxide, silicon, and carbon; L. Baraduc-Muller used a mixture of chromic oxide, silicon carbide, and carbon. H. Moissan noted that chromium readily takes silicon from its surroundings—*e.g.* the materials of the crucible; and A. Burger likewise found it to occur when chromic oxide is reduced by calcium in glass or porcelain vessels.

R. Frilley found alloys with up to 10 per cent. of silicon are matte, white, compact, and hard; they have cavities lined with needle-like crystals. Alloys with 10–25 per cent. of silicon are dull and grey; they disintegrate easily, and crystallization is not well defined. Alloys with 25–70 per cent. silicon are well crystallized with cavities lined with crystals; the crystals with alloys up to 30 per cent. of silicon are acicular, those with 35–50 per cent. silicon are prismatic, probably rhombic; and with over 50 per cent. of silicon the prisms are replaced by fine needles. Alloys with over 50 per cent. silicon look like fused silicon. M. François and C. Lormand examined the structure of the crystals. The following are selected from R. Frilley's table of sp. gr., sp. vol., and mol. vol.:

| Per cent. Si | 0 | 10·24 | 23·21 | 35·00 | 51·00 | 61·91 | 70·10 | 89·12 | 100 |
|---|---|---|---|---|---|---|---|---|---|
| Sp. gr. | 6·60 | 6·50 | 5·62 | 5·38 | 4·83 | 3·49 | 3·10 | 2·65 | 2·40 |
| Sp. vol. | 0·151 | 0·153 | 0·178 | 0·189 | 0·207 | 0·286 | 0·322 | 0·381 | 0·416 |
| Mol. vol. | 7·87 | 7·36 | 7·72 | 7·58 | 7·24 | 9·47 | 10·49 | 11·18 | 11·66 |

He says that points of inflexion on the sp. gr. curve correspond with $Cr_2Si$, $CrSi_2$, and a compound *chromium silicide,* CrSi, which has not been isolated; there are also singularities corresponding with $Cr_3Si$, $Cr_3Si_2$, and **chromium trihemisilicide,** $Cr_2Si_3$; the sp. vol. curve shows singularities corresponding with $Cr_3Si$, $Cr_2Si$, CrSi, $Cr_2Si_3$, $CrSi_2$, and chromium heptahemisilicide, $Cr_2Si_7$; and the mol. vol. curve has singularities corresponding with $Cr_3Si$, $Cr_2Si$, $CrSi_2$, and $Cr_2Si_7$. The trihemisilicide was isolated by L. Kahlenberg and W. J. Trautmann. R. Frilley said that all the

chromium-silicon alloys dissolve when fused with alkali hydroxides, carbonates, and nitrates, and in fused sodium dioxide. Soln. of the alkali hydroxides, cold or hot, are without action; likewise also nitric and sulphuric acids. Hydrochloric acid in the cold rapidly attacks alloys with 20–50 per cent. silicon, and is without action on the other alloys; hydrofluoric acid behaves similarly but acts more vigorously; aqua regia acts irregularly on alloys with up to 50 per cent. silicon, and is without action on the others; while a mixture of nitric and hydrofluoric acids easily dissolves these alloys. P. Lebeau and J. Figueras add that the chromium silicides are not analogous to those of manganese, iron, cobalt, and nickel.

G. J. L. de Chalmot prepared **chromium disilicide**, $CrSi_2$, by heating in an electric arc furnace a mixture of chromic oxide, charcoal, and an excess of silica; and P. Lebeau and J. Figueras, by melting copper, chromium, and an excess of silicon. G. J. L. de Chalmot stated that the grey needle-like crystals have a metallic lustre; and sp. gr. 4·393. The compound is not attacked by cold hydrochloric acid or aqua regia; it is soluble in hydrofluoric acid, and in consequence the admixed free silicon can be determined. P. Lebeau and J. Figueras prepared **chromium ditritasilicide**, $Cr_3Si_2$, by heating in an electric arc furnace for 4 mins. a mixture of 100 grms. of 12 per cent. cuprosilicon, and 4 grms. of chromium, and washing the product alternately with 50 per cent. nitric acid, and dil. sodium hydroxide. L. Baraduc-Muller made it by heating a mixture of chromic oxide, silicon carbide, and carbon. E. Vigouroux passed silicon tetrachloride over pulverized chromium at 1200°, and obtained this silicide as a crystalline grey powder. P. Lebeau and J. Figueras said that this silicide crystallizes in long, quadratic prisms, has a sp. gr. 5·6 at 0°, abrades glass, but not quartz, and is stable in moist or dry air at the ordinary temp., but oxidizes superficially at 1100°. The silicide becomes incandescent when placed in chlorine at 400°, forming silicon and chromic chlorides; it reacts slowly with bromine at a red heat, but is not acted on by iodine. It is insoluble in dil. hydrochloric acid, but chromous chloride is formed by soln. of the silicide in the warm conc. acid or by the action of gaseous hydrogen chloride. It is attacked by hydrofluoric but not by sulphuric or nitric acid. Fused potassium chlorate or nitrate does not attack the silicide, but it is converted by fused alkali carbonates into the silicate and chromium sesquioxide, and by fused mixtures of alkali carbonates and nitrates into the silicate and chromate.

H. Moissan obtained **chromium hemisilicide**, $Cr_2Si$, by heating a mixture of silicon and carbon to 1200° in a stream of hydrogen or in a carbon crucible in the electric arc furnace; and also by heating in the arc furnace a mixture of 60 parts of silica, 200 of chromic oxide, and 70 of sugar-charcoal. In each case the product was washed with cold hydrofluoric acid; some silicon carbide was always present as impurity. P. Lebeau and J. Figueras made it by melting together a mixture of 78·22 parts of copper, 12·04 of chromium, and 8·92 of silicon, and treating the product alternately with nitric acid and a dil. soln. of sodium hydroxide. According to H. Moissan, the small prismatic crystals readily scratch quartz and corundum; at a red heat, the compound readily burns in chlorine gas; hydrogen chloride transforms it into silicon and chromium chlorides; nitric acid has no action; aqua regia decomposes the silicide; molten potassium carbonate attacks it slowly, molten potassium nitrate quickly, forming in each case silicate and chromate. According to C. Zettel, when a mixture of 140 parts copper and 140 parts of aluminium is melted in a fire-clay crucible and 200 parts of chromic oxide, previously strongly heated, is added gradually, and after strongly heating for some time a small quantity of aluminium filings, there is a very energetic action. The metallic ingot obtained on cooling contains crystals of a **chromium tritasilicide**, $SiCr_3$, which is separated from the metal by the action of aqua regia. C. Matignon and R. Trannoy heated a mixture of chromic oxide, silica, and aluminium, and found the silicide separated easily from the alumina slag. L. Baraduc-Muller also made this silicide; and P. Lebeau and J. Figueras made the same compound by melting together 84·32–85·63 parts of copper, 10·83–12·83 of chromium, and 1·24–4·36

of silicon, and treating the product alternately with nitric acid and a dil. soln. of sodium hydroxide. Grey prismatic crystals remain. According to C. Zettel, the sp. gr. of the crystals is 6·52 at 18° ; they scratch glass ; they are decomposed by cold aq. hydrofluoric acid, but are not affected by other acids ; they are readily attacked by chlorine and bromine at a red heat, by molten potassium chlorate, and by a molten mixture of potassium carbonate and nitrate ; but fused potassium hydroxide attacks the silicide slowly.

H. N. Warren [4] prepared molybdenum silicide by heating a mixture of the oxide and silicon in an oxy-hydrogen blowpipe furnace. The crystalline mass so obtained was very hard ; it is decomposed by hydrofluoric acid, and by chlorine at a red heat ; but other acids act on this silicide very slowly. R. Walter made the alloy directly from the elements. H. Moissan obtained a crystalline silicide by heating the constituent elements in the electric arc furnace ; and L. Baraduc-Muller, by heating at 1720° for 10 mins., a mixture of 2 mols of molybdic oxide, one mol of silicon carbide, and 3 gram-atoms of carbon, using a mixture of lime and magnesia as a flux. According to E. Vigouroux, **molybdenum trihemisilicide,** $Mo_2Si_3$, is obtained by heating, in a carbon crucible in the electric furnace, a mixture of crystallized silicon and the molybdenum oxides obtained by calcining ammonium molybdate ; the crystalline product is disintegrated by electrolysis in hydrochloric acid, and the mixture of crystalline silicides is treated successively with aqua regia, caustic potash, and hydrofluoric acid ; the removal of carbon silicide is effected by means of cadmium tungstate soln., and the residue consists of molybdenum silicide mixed with more or less iron silicide. When heated in chlorine at 300°, molybdenum silicide becomes ignited, silicon tetrachloride and molybdenum perchloride being produced. O. P. Watts prepared **molybdenum disilicide,** $MoSi_2$, by fusing in an electric furnace a mixture of 70 parts of molybdic oxide, 30 of silica, 50 of boric oxide, 106 of copper, and 120 of aluminium, using cryolite as a flux, and lime to slow down the reaction ; he also made it from molybdenite, silica, and calcium carbide. In either case the product was successively treated with nitric acid, and dil. hydrofluoric acid. The resulting dark-coloured crystals contained a little boron and iron. O. Hönigschmid used a mixture of 10 parts of molybdic oxide, 90 of quartz sand, 100 of aluminium filings, and 125 of flowers of sulphur. E. Defacqz fused a mixture of 90 parts of 50 per cent. cuprosilicon free from iron, and 10 parts of molybdenum for about 1½ mins. in an electric arc furnace ; the product was successively treated with nitric acid, dil. sodium hydroxide, hydrochloric acid, and hydrofluoric acid (on a water-bath), and water. The non-magnetic, grey, microcrystalline plates had a sp. gr. 6·2 at 0° ; O. Hönigschmid gave 5·88 at 0° ; and O. P. Watts, 6·31 at 20·5°. E. Defacqz said that the silicide is not altered by heating in a blowpipe flame and, according to O. Hönigschmid, it is not affected by heating to redness in oxygen. E. Defacqz said that it is not attacked by hydrofluoric, hydrochloric, nitric, and sulphuric acids, by aqua regia, or by fused hydrosulphates. O. Hönigschmid found a mixture of hydrofluoric and nitric acids attacks the silicide vigorously ; and fluorine also acts vigorously at ordinary temp. ; E. Defacqz said that it is acted on by chlorine at 350°–400°, giving silicon chloride and molybdenum pentachloride ; O. Hönigschmid said that bromine has scarcely any action at a red heat. E. Defacqz found that the silicide is attacked by aqua regia containing hydrofluoric acid at the temp. of the water-bath, giving molybdic acid ; and by fused alkali hydroxides or carbonates, or a mixture of these with alkali nitrates or chlorates.

H. N. Warren [5] prepared tungsten silicide by the same process as that employed for molybdenum silicide. The product is harder than molybdenum silicide, and its behaviour towards acids and chlorine is similar. H. Moissan also found that silicon unites directly with tungsten in the electric arc furnace. R. Walter made alloys directly from the elements. The British Thomson-Houston Co. made the alloys by heating mixtures of tungstic and silicic acids and magnesium. R. Frilley said that the general methods of preparing tungsten silicides include (i) The

reduction of tungstic oxide by a mixture of silicon and carbon; (ii) Reduction of tungstic oxide by silicon carbide; (iii) Reduction of a mixture of silica by carbon and tungsten; (iv) Fusion of a mixture of tungsten and 92 per cent. ferrosilicon; and (v) The reduction of tungstic oxide in the electric furnace by an aluminium alloy with 94 per cent. silicon. He said that alloys with 5–10 per cent. of silicon are matte, yellow, and fuse with difficulty. Alloys with 10–20 per cent. of silicon are steel-grey, and are hard enough to scratch glass and agate. Alloys with 20–40 per cent. silicon are more fusible, and easily split into thin plates. Alloys with 40–60 per cent. silicon are granular and have a bluish tinge. Alloys with 60 per cent. silicon look like fused silicon. The sp. gr., sp. vol., and mol. vol. are selected from R. Frilley's table:

| Per cent. Si | 0 | 10·10 | 20·50 | 31·88 | 38·38 | 61·00 | 100·00 |
|---|---|---|---|---|---|---|---|
| Sp. gr. | 18·7 | 13·35 | 10·98 | 8·70 | 7·07 | 3·99 | 2·40 |
| Sp. vol. | 0·054 | 0·075 | 0·091 | 0·115 | 0·141 | 0·251 | 0·416 |
| Mol. vol. | 9·84 | 8·82 | 8·23 | 7·77 | 8·30 | 10·5 | 11·6 |

The singularities in the sp. gr. curve are taken to show the existence of the two silicides, $W_2Si_3$, and $WSi_3$. The singularities in the sp. vol. curve correspond with the same silicides; and those in the mol. vol. curve with the hemi- and trita-silicides but not with $W_2Si_3$. The alloys are attacked only superficially by hydrofluoric acid, but they readily dissolve in a mixture of hydrofluoric and nitric acids. Hydrochloric, nitric, and sulphuric acids are without action. Aqua regia attacks imperfectly alloys with less than 18 per cent. silicon, and has no action on alloys with more silicon. Alloys with 18–35 per cent. of silicon are attacked only with difficulty by fused mixtures of alkali carbonates and nitrates, but alloys with more silicon readily dissolve in fused alkali carbonates. Alloys with up to 18 per cent. silicon oxidize superficially on exposure to air, but alloys with more silicon are not attacked at 1200°. Chlorine attacks the alloys at a red heat; bromine and iodine have no action at 300°.

E. Vigouroux prepared **tungsten trihemisilicide,** $W_2Si_3$, by heating in the electric furnace a mixture of 100 grms. of silicon with 230 grms. of tungsten oxide obtained by heating ammonium tungstate. The heavy, brittle, crystalline product is suspended in dil. hydrochloric acid (1 in 10), and connected with the positive pole of a battery of two or three cells, a carbon plate placed in the liquid being connected with the negative pole. The metal dissolves, and the silicide, which collects at the bottom of the vessel, is treated successively with aqua regia, ammonia, and hydrofluoric acid, and any carbon silicide that may be present is separated by means of methylene iodide. This silicide forms steel-grey plates with a metallic lustre; the sp. gr. is 10·9. It is attacked by chlorine, with incandescence between 200° and 300°; by bromine, without incandescence, below a red heat, and by iodine, without incandescence, above a red heat. In oxygen, it burns very brilliantly at about 500°, and in air it oxidizes below a red heat, but does not burn; nitrogen is without action at any temp. The ordinary acids, including hydrofluoric, have no action even on heating. Aqua regia is practically without action, but a mixture of nitric and hydrofluoric acids attacks the silicide violently, even at ordinary temp. Alkalies in soln. have little action, but fused alkali hydroxides and carbonates decompose the silicide very readily, whilst fused potassium nitrate acts with somewhat less energy. E. Defacqz prepared **tungsten disilicide,** $WSi_2$, by heating copper silicide with amorphous tungsten in an electric arc furnace and washing the resulting product successively with nitric acid, sodium hydroxide soln., warm hydrofluoric acid, and water. The crystals having a lower sp. gr. than 3·4 (principally carbon silicide) were eliminated by washing with methylene iodide. The same product may also be obtained by reducing a mixture of silica and tungstic anhydride with sulphur and aluminium, the crystals being isolated from the button produced by the method already described, nitric acid being replaced by hydrochloric. O. Hönigschmid employed a similar process. This silicide is dimorphous, for when prepared by the second method it occurs in brilliant, bright, grey, prismatic

needles, but when obtained from copper silicide it forms masses of brilliant, grey crystals. The sp. gr. is 9·4 at 0°. O. Hönigschmid gave 9·3 at 0°. The compound is not magnetic, and remains unaltered at 900° in air, is decomposed by copper at 1200°, forming copper silicide and tungsten, and is not affected by sulphuric acid or aqua regia, but is attacked by a mixture of hydrofluoric and nitric acids, yielding tungstic anhydride as a residue. Fused alkali hydroxides or carbonates convert it into the alkali silicate and tungstate, but melted potassium hydrogen sulphate is without action. Dry chlorine attacks the silicide easily at about 450°, yielding a mixture of silicon tetrachloride and tungsten hexachloride, and this reaction can be utilized for the analysis of the compound. According to R. Frilley, **tungsten tritasilicide,** $WSi_3$, is obtained by reducing silica by carbon in the presence of molten tungsten. The resulting alloy is powdered to pass a 100's sieve, washed with conc. hydrofluoric acid to remove ferrosilicon, with a hot conc. soln. of sodium hydroxide to dissolve graphitoidal silicon, and with dil. hydrofluoric acid to remove silica. The small white crystals are attacked by chlorine at a red heat; they are not attacked by hydrofluoric, hydrochloric, nitric, or sulphuric acid; but a mixture of nitric and hydrofluoric acids attacks it vigorously. Molten sodium hydroxide attacks it slowly. A. Pacz described the use of alloys of tungsten with 1–3 per cent. of silicon as filaments for incandescent electric lamps.

E. Defacqz prepared **uranium disilicide,** $USi_2$, from a mixture of 250 parts aluminium, 250 of sulphur, 180 of silica, and 56 of uranium oxide. The mixture after ignition and cooling was treated successively with hot 10 per cent. hydrochloric acid, and dil. sodium hydroxide; then with conc. hydrochloric acid, and hot nitric acid to eliminate any uranium-aluminium alloy; and finally, with dil. sodium hydroxide, dil. hydrochloric acid, and water. The pale grey microscopic crystals belong to the cubic system; and they have a sp. gr. of 8 at 0°. Chlorine attacks this silicide at 500°, giving the chlorides of uranium and silicon. Cold hydrogen fluoride dissolves it readily, whilst oxidizing agents have little action. Although stable in air at a red heat, it burns slowly in oxygen at 800°, and is decomposed on fusion with alkalies, alkali carbonates, or potassium hydrosulphate.


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## § 13. The Silicides of Manganese and of the Iron Family

Manganese silicide was made by C. Brunner [1] by reducing manganese oxide with carbon in the presence of silica ; the regulus contained 6–8 per cent. of silicon. The manganese prepared by C. Brunner by reducing the halide with sodium always contained over one per cent. of silicon, and if the reduction occurred in the presence of silica or potassium fluosilicate, the product contained nearly 10 per cent. silicon. F. Wöhler made a silicide by heating manganous fluoride, cryolite, water-glass, and sodium covered with a mixture of sodium and potassium chlorides in a fireclay crucible ; by melting a mixture of sodium fluomanganite, fluorspar, water-glass, and sodium ; or a mixture of manganous chloride, fluorspar, potassium fluosilicate, and sodium ; or a mixture of manganous chloride, quartz sand, cryolite, and sodium. H. N. Warren heated manganese oxide and silicon to a white heat ; C. Matignon and R. Trannoy used the thermite process with a mixture of manganese oxide, silica, and aluminium ; and L. Troost and P. Hautefeuille found the elements unite directly at a high temp. R. Walter used a similar process. E. F. Price smelted electrically a mixture of manganese, silicon, and carbon. According to P. Lebeau, commercial manganese obtained by the thermite process contains manganese silicide, and commercial manganese silicide is a mixture of $Mn_2Si$ and MnSi with a little iron and silicon carbide, and a trace of calcium. M. A. Sanfourche studied the limiting range of silicon in these alloys.

According to R. Frilley, alloys with 2–10 per cent. of silicon are lustrous and grey, those with 8 per cent. have the appearance of a mass of steel-grey, prismatic crystals. Alloys with 10–30 per cent. of silicon are whiter and more lustrous, and the crystals increase in the alloys with up to 25 per cent. of silicon and form large confused masses. Alloys with 30–45 per cent. of silicon are grey and matte, and spontaneously break up into powder. Alloys with 45–50 per cent. of silicon are very lustrous, and resemble ferrosilicon with 50 per cent. Si. Alloys with over 50 per cent. silicon appear like masses of crystalline silicon. The sp. gr., sp. vol., and mol. vol. of a selection from R. Frilley's table are :

| Per cent. Si | 0 | 8·8 | 20·18 | 33·60 | 45·28 | 59·68 | 82·70 | 100·00 |
|---|---|---|---|---|---|---|---|---|
| Sp. gr. . | 7·40 | 6·17 | 5·80 | 5·35 | 4·65 | 3·62 | 2·74 | 2·40 |
| Sp. vol. . | 0·135 | 0·162 | 0·172 | 0·181 | 0·215 | 0·276 | 0·365 | 0·415 |
| Mol. vol. . | 7·43 | 8·21 | 7·92 | 7·53 | 8·21 | 9·63 | 11·17 | 11·66 |

The sp. gr. curve shows singularities corresponding with $Mn_2Si$, $MnSi_2$, MnSi, and *manganese pentitasilicide*, $Mn_5Si$. The sp. vol. curve shows singularities corresponding with MnSi, $MnSi_2$, but not $Mn_2Si$ ; and with the mol. vol. curve there are singularities with $Mn_5Si$, MnSi, and $MnSi_2$, but not $Mn_2Si$. The alloys are all brittle, and fracture easily. L. Baraduc-Muller studied their coeff. of expansion ; and F. Dörinckel, their m.p. The f.p. curve, Fig. 18, shows two maxima at 21·3 and 33·8 per cent. by weight of silicon respectively, corresponding with the composition of the compounds $Mn_2Si$ and MnSi, as well as three eutectic points at 1075° and 11 per cent., at 1239° and 30 per cent., and at 1135° with 50 per cent. by weight of silicon respectively. Between 50 and 100 per cent. by weight of silicon, microscopic observations indicate the presence of a third compound, the crystals of which are characterized by fine parallel markings, but its composition

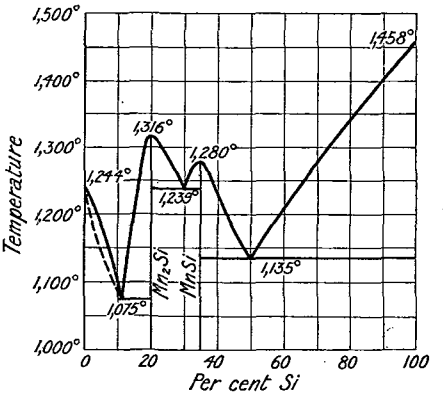



FIG. 18.—Equilibrium Diagram of Manganese-Silicon Alloys.

could not be determined by thermal analysis owing to the slight alteration in the m.p. of the alloy with change of conc. from 45–50 per cent. silicon. The compound in question cannot be $MnSi_2$, which would contain 50·8 per cent. of silicon, whereas crystals of the latter element can be detected in alloys containing only 50 per cent. of silicon. P. Lebeau by treating the alloys with various solvents and analyzing the residues, has arrived at the conclusion that three compounds of manganese and silicon exist, the respective formulæ of which are $Mn_2Si$, MnSi, and $MnSi_2$. From alloys containing 0–10 per cent. of silicon, mixed crystals separate. L. Troost and P. Hautefeuille studied the heats of formation of the manganese silicides. E. Wedekind showed that unlike many other manganese compounds, the silicides are always non-magnetic. G. Tammann measured the electrode potentials.

R. Frilley found that alloys low in silicon are oxidized in moist air at a red heat, being covered by *une pellicule irisée;* those with over 30 per cent. silicon are not oxidized at 1000°. Chlorine, bromine, and iodine readily attack the alloys at a red heat. Hydrochloric acid easily dissolves in the cold, alloys with up to 20 per cent. silicon; with more siliciferous alloys the attack becomes feebler, and is superficial and scarcely perceptible with alloys having over 45 per cent. silicon. Hydrofluoric acid alone dissolves in the cold all alloys with up to 50 per cent. silicon; the residue contains a little carbon present as impurity; the attack with alloys having over 50 per cent. silicon is only partial, and a residue of graphitoidal silicon remains. A mixture of nitric and hydrofluoric acids readily dissolves these alloys. Conc. or dil., hot or cold sulphuric acid is without action; nitric acid partially attacks alloys with less than 20 per cent. silicon, and is without action on more siliciferous alloys. Manganese-silicon alloys are readily attacked by fused alkali hydroxides or carbonates, or better a mixture of alkali carbonate and nitrate. Dil. aq. soln. of alkali hydroxides slowly attack all alloys with over 20 per cent. of silicon, and with a prolonged action, the residue has nearly 20 per cent. silicon. W. Jenge studied the action of soln. of chlorides, bromides, iodides, nitrates, sulphates, sodium hydroxide, sulphuric acid, and hydrochloric acid on manganese silicides. He found that only $MnSi_2$ was non-resistant to acids, and all the silicides were resistant to sodium hydroxide.

P. Lebeau made **manganese hemisilicide,** $Mn_2Si$, by heating in a covered carbon crucible in an electric furnace, a mixture of 10 grms. of crystalline silicon, and 100 grms. of cupromanganese with 22·35 per cent. Mn. The regulus was treated alternately with 50 per cent. nitric acid, and a 10 per cent. aq. soln. of sodium hydroxide; he also heated to redness a mixture of sodium (184 parts), potassium fluosilicate (264 parts), manganese oxide (92 parts $Mn_3O_4$), and copper (100 parts). E. Vigouroux prepared the same silicide (i) by heating silicon with nine times its weight of manganese in the electric furnace and treating the product first with water, then with dil. hydrochloric acid, and finally, and rapidly, with dil. hydrofluoric acid; or (ii) by heating in the electric furnace a mixture of 1 part of silica, 3 parts of manganoso-manganic oxide, and one part of sugar-carbon, and treating the product as above; or better, (iii) by heating silicon with 4 or 5 times its weight of manganoso-manganic oxide in a porcelain dish in an atm. of dry hydrogen up to the softening point of porcelain; (iv) by firing a mixture of silica, manganese oxide, and aluminium, and allowing the flux to cool very slowly, a brittle mass is obtained which, after extraction with dil. hydrochloric acid and then with dil. hydrofluoric acid, consists of crystals of the manganese hemisilicide, $Mn_2Si$, which is decomposed by the action of warm hydrochloric or nitric acid, and in this respect differs from P. Lebeau's compound of the same composition. Attempts to prepare a silicide containing a higher proportion of manganese than the one described above were not successful. Manganese hemisilicide, said E. Vigouroux, furnishes well-defined crystals lustrous and steel-grey; it is hard and brittle; its sp. gr.=6·6 at 15°. P. Lebeau gave 6·20 at 15°. According to E. Vigouroux, it does not alter when exposed to air, and melts at the temp. of the reverberatory furnace. Fluorine attacks it at the ordinary temp., chlorine at about 500°, and iodine and bromine

at higher temp.; oxygen and air attack it at a red heat. Dry hydrogen fluoride decomposes it readily, especially if gently heated, hydrogen chloride below a red heat, and hydrogen iodide at higher temp.; water is without action at 100°, but at a red heat decomposes the silicide, with liberation of hydrogen. Dil. acids attack it readily, and conc. acids, especially hydrofluoric acid, are violent in their action; an aq. soln. of potassium hydroxide is without effect, but the solid substance attacks the finely powdered silicide when heated with it, and fused alkali carbonates or mixtures of carbonate and nitrate oxidize it readily. M. Wunder and B. Jeanneret found that hot phosphoric acid of sp. gr. 1·75 dissolves manganese silicide, forming a clear liquid.

A. Carnot and E. Goutal found that when commercial manganese is dissolved in dil. sulphuric acid with the exclusion of air, an amorphous powder, probably **manganese silicide,** MnSi, remains. P. Lebeau prepared this compound by the process employed for the hemisilicide using 25 grms. of silicon to 100 grms. of the cupromanganese in the one process, and 100 grms. of sodium, 215 grms. of potassium fluosilicate, 23 grms. of manganese oxide, and 50 grms. of copper in the other. This silicide furnishes lustrous tetrahedral crystals of sp. gr. 5·90 at 15°; they scratch topaz, but not corundum. Steam, and oxygen at 1000°, oxidize the silicide only superficially; it is readily attacked by the halogens; the hydrogen halides attack it easily; boiling hydrochloric acid attacks it superficially; hydrogen sulphide has no action at 800°; nitric acid and sulphuric acid, hot or cold, dil. or conc., do not attack the silicide; carbon at a high temp. forms silicon carbide and manganese; and silicon forms the higher silicide. G. J. L. de Chalmot prepared an impure **manganese disilicide,** $MnSi_2$, by melting together manganese oxide (5 parts), wood charcoal (15 parts), quartz (40 parts), and calcium oxide (15 parts) in an electric furnace. P. Lebeau employed the same process in the case of the hemisilicide, but using 14·9 per cent. of copper, 80·43 of silicon, and 3·25 of manganese. The disilicide forms small, dark grey, apparently octahedral crystals having a density 5·24 at 13°; it is not attacked by nitric or sulphuric acid, but is readily soluble in hydrofluoric acid and quickly decomposed by conc. aq. soln. of alkali-hydroxides.

According to G. Gin, when rhodonite is reduced in the electric furnace a crystalline alloy of silicon and manganese is obtained and its analysis indicates that it contains 95 per cent. of crystalline **manganese ditritasilicide,** $Mn_3Si_2$, which forms brilliant, prismatic crystals, sometimes 5 cms. long; the sp. gr. is 6·05 at 15°, and the m.p. 1250°–1300°. The compound is attacked by chlorine with incandescence at a red heat; it is not changed by oxygen at the ordinary temp., but is superficially oxidized at 500°; and it is readily attacked by the gaseous halogen acids, by nitric or hydrochloric acid or aqua regia, or by fused alkali carbonates or mixtures of carbonates and nitrates, whilst sulphuric acid has no action on the compound. P. Lebeau questions the existence of this silicide as a chemical individual.

Near the beginning of the last century, H. Davy [2] found that an iron wire heated electrically to whiteness in contact with silica slightly moistened, and in hydrogen gas, becomes brittle and whiter, and furnishes silica when dissolved in acids. H. Davy here obtained a soln. of silicon in iron. J. J. Berzelius also obtained an analogous product by heating silica and carbon in the presence of iron. He later heated to whiteness a mixture of potassium fluosilicate and iron filings, and washed the iron and potassium fluorides with hot water. The resulting iron silicide dissolves in acids—even in hydrofluosilicic acid. E. D. Clarke exposed silica in contact with iron in a charcoal crucible to the oxy-hydrogen blowpipe flame and also obtained a soln. of silicon in iron, or of iron in silicon. O. Hackl found ferrosilicon in commercial calcium carbide. J. B. J. D. Boussingault fused iron in a fireclay crucible and obtained an alloy with 0·54 per cent. of silicon—presumably derived from siliceous materials of the crucible. He said that the alloy was more difficult to file and to hammer than iron without the silicon. H. St. C. Deville and H. Caron prepared alloys of iron and silicon, and said that a kind of silicon-steel—*fonte siliciée*—is produced which has many properties in common

with the ordinary carbon-steel. C. Winkler confirmed this result without isolating any definite compound. H. Moissan found that if a cylinder of soft iron be embedded in crystals of silicon, and heated at the temp. of a good forge, the silicon penetrates to the centre of the cylinders although the iron does not fuse, and a silicide is formed. This is taken to show that silicon has a distinct vap. press. below its m.p. P. Lebeau found that the combination occurs even at 950°, and says the process resembles the cementation of iron by carbon. L. Grenet, P. Lebeau, J. E. Stead, H. Moissan, and R. T. Haslam and L. E. Carlsmith studied the cementation of silicon in steel; and H. G. C. Fairweather, the alloys of silicon, chromium, and manganese.

Iron-silicon alloys are made commercially and used as a means of introducing specified proportions of silicon into steel, but mainly as a deoxidizer. The alloys were formerly made in a blast furnace, and contained about 14 per cent. of silicon—the maximum was about 20 per cent. To-day, the alloys are made in electric furnaces, with a content 25–30, 45–55, and 75–80 per cent. silicon, and even with 90 per cent. silicon. E. Donath and M. Haissig recommend the term **ferrosilicon** be used for iron-silicon alloys with more than 5 per cent. silicon; W. Pick and W. Conrad have discussed this subject. A. Ledebur says that the term *Siliziumeisen* should be used for iron alloyed with small proportions of silicon, and *Ferrosilizium* for iron alloyed with high proportions of silicon. The name *ferrosilicine* was suggested by C. U. Shepard for a meteoritic iron—iron, 84·00 per cent., silicon, 13·57 per cent.—found at Rutherford (North Carolina). J. W. Mallet suggested that iron silicide was contained in the iron from Staunton (Virginia), and C. Winkler likewise found iron silicide—possibly $Fe_2Si$—in the iron from Rittersgrün (Saxony).

According to R. Walter, the reaction between iron and silicon begins at about 1250°, and owing to the rapid development of heat, the temp. rises to about 1800°. Ferrosilicon is made commercially in several grades determined by the proportion of silicon. The analyses in Table I are selected from the report of S. M. Copeman,

Table I.—Analyses of Commercial Ferrosilicons.

| — | Electric furnace. | | | | | Blast furnace. |
|---|---|---|---|---|---|---|
| | 30 per cent. | 50 per cent. | 75 per cent. | 90 per cent. | 95 per cent. | |
| Silicon | 32·50 | 49·80 | 78·13 | 88·26 | 94·80 | 11·50 |
| Iron | 66·26 | 49·39 | 21·51 | 11·23 | 4·99 | (84·74) |
| Aluminium | 0·51 | 0·40 | 0·17 | 0·12 | 0·10 | — |
| Manganese | 0·28 | 0·11 | 0·06 | 0·08 | 0·08 | 2·25 |
| Sulphur | 0·02 | 0·04 | 0·001 | 0·010 | 0·02 | 0·05 |
| Phosphorus | 0·028 | 0·024 | 0·007 | 0·009 | 0·01 | 0·06 |
| Carbon | 0·26 | 0·13 | 0·09 | 0·07 | 0·00 | 1·40 |
| Calcium | 0·12 | 0·085 | tr. | 0·08 | — | — |

S. R. Bennett, and H. W. Hake. The blast furnace product had 0·06 per cent. arsenic, and the iron was determined by difference. In general, the charge consists of a mixture of steel turnings, anthracite coal, and quartz. The proportion of iron is determined by the desired percentage of silicon in the ultimate product. The mixture is shovelled into the electric resistance furnace, and replenished as often as room is afforded by the melting of that already in the furnace. The molten alloy is removed from the bottom of the furnace by periodical tapping—say every 45 mins.—and run into a bed of sand, and the surface of the molten ingot is skimmed with a piece of green-wood to remove the slag. When the alloy has cooled, it is broken into pieces, and packed for transport. The furnace is circular and built of firebrick, with one vertical graphite cathode suspended over the mouth of the

furnace, and the anode forms a portion of the floor. The anode is made by ramming prepared retort carbon or graphite into an opening in the floor of the furnace. Arrangements are made for raising or lowering the vertical electrode as desired. The temp. of the furnace approximates 2000°. The process is continuous, and the furnaces may be run for over a year without stopping. The electrodes are sometimes water-cooled and they are renewed every few days. In one furnace, a ton of 30 per cent. ferrosilicon required 3500 kilowatt hours; and in another 200 h.p. were needed per ton of 30 per cent. ferrosilicon. The impurities in the final product are determined by the impurities present in the raw materials. There are many modifications in detail.

A large number of patents has been registered—by J. Holloway, E. A. O. Viel, H. Aschermann, B. Scheid, G. Gin, L. d'E. Muller and L. H. Baraduc-Muller, C. A. Keller, E. Straub, M. F. Matt, H. N. Potter, E. F. Price, F. J. Tone, F. Laur, K. A. Kühne, E. Jüngst and R. Mewes, A. Sinding-Larsen, M. von Schwarz, V. C. Bertholus, C. H. Homan, F. J. Tone, W. Conrad, W. Pick, R. Amberg, etc.—for the preparation of ferrosilicon. G. J. L. de Chalmot used a mixture of iron ore, sand, and coke; H. Aschermann used a mixture of iron sulphide and quartz: $FeS+SiO_2=SO_2+FeSi$; W. Rathenau used a mixture of lime, anthracite, silica, and iron, and obtained both calcium carbide and ferrosilicon. W. Borchers and A. Dorsemagen heated ferruginous zinc blende, quartz, iron, and coke in a closed electric furnace and collected the zinc simultaneously given off. G. Gin used barium sulphate, ferric oxide, quartz, and carbon; and represented the reactions $BaSO_4+SiO_2+C=BaSiO_3+SO_2+CO$; and $BaSiO_3+Fe_2O_3+5C=Fe_2Si+BaO+5CO$. E. A. O. Viel and M. Jeantet fused a mixture of clay with iron in an electric furnace.

Silicides with Fe : Si=3 : 1, 2 : 1, 5 : 2, 3 : 2, 3 : 4, 1 : 1, 1 : 2, and 1 : 3 have been reported. **Iron tritasilicide,** $Fe_3Si$, has not been isolated, and it does not appear on W. Guertler and G. Tammann's diagram, Fig. 18; its existence has not been well-established. T. Naske assumed that ferrosilicon made in the blast furnace contained the tritasilicide which he isolated by treatment with dil. sulphuric acid. A. Carnot and E. Goutal found that siliciferous spiegeleisen, with 20 per cent. manganese, contained *manganese iron tritasilicide,* $(Mn, Fe)_3Si$, which they isolated by treatment with dil. sulphuric acid. A. Jouve also found characteristic crystals of the hemisilicide in commercial ferrosilicons. E. D. Campbell and co-workers have studied the heat of soln. of silicon in molten iron and, by analogy with the well-defined iron tritacarbide, $Fe_3C$, compute for the heat of formation $(Fe_3Si)_n=133{\cdot}1$ cals.; and for the reaction $Fe_3C+Si=C+Fe_3Si+17{\cdot}6425$ Cals. H. Hahn described the formation of **iron hemisilicide,** $Fe_2Si$, by melting together iron (40 grms.), silicon (5 grms.), sodium (25 grms.), ammonium chloride (150 grms.), and sodium chloride (80 grms.). According to H. Moissan, the hemisilicide is obtained (i) by heating iron to the softening point of porcelain in a porcelain dish brasqued with silicon. (ii) By heating iron with one-tenth its weight of silicon in a crucible in the electric furnace for four minutes with an arc from a current of 900 ampères at 50 volts. With a higher proportion of silicon, the product is not attacked by acids. (iii) By heating in the electric furnace a mixture of ferric oxide with excess of silicon, silica being volatilized. In all cases, the product is treated with nitric acid dil. with four times its volume of water. The iron silicide forms small, magnetic, prismatic crystals, with a metallic lustre; sp. gr. =7·00 at 22°. Its m.p. is higher than that of cast iron and lower than that of wrought iron. Hydrofluoric acid attacks it readily, and hence it is not identical with the silicide of sp. gr. 6·11 at 23°. H. Hahn said that it is not attacked by this acid. Hydrochloric acid slowly attacks the finely powdered silicide; nitric acid has no action, but aqua regia decomposes it, with formation of silica. The gaseous hydrogen halides attack it at temp. varying from dull to bright redness. Potassium nitrate and chlorate, at their m.p., have no action on it; fused alkali carbonates attack it slowly, and a fused mixture of a nitrate and a carbonate decomposes it

readily. P. Lebeau prepared a hemisilicide by strongly heating iron with twice its weight of commercial copper silicide containing 10 per cent. of silicon, the product being treated with nitric acid (1 : 10) and purified in the usual way. It forms long, brilliant, grey crystals with octahedral terminations. In sp. gr. and chemical properties, it is identical with H. Moissan's silicide ; and it can be isolated from commercial ferrosilicons which contain 10–20 per cent. of silicon and have been prepared at a high temp. E. Vigouroux obtained the hemisilicide by the action of silicon tetrachloride on iron at a dull red heat or at 1100°. A. Carnot and E. Goutal found that spiegeleisen poor in manganese furnishes prismatic crystals of the hemisilicide when treated with very dil. sulphuric acid, and treating the residue successively with a soln. of potassium hydroxide and dil. sulphuric acid. It differs from H. Moissan's hemisilicide in being readily attacked by hot dil. acids. T. Murakami obtained no evidence of the hemisilicide on the equilibrium diagram ; and W. Gontermann regarded it as a sat. solid soln. of iron monosilicide in iron.

A. Carnot and E. Goutal found that when iron is dissolved in dil. hydrochloric acid out of contact with air, the greater part of the silicon is left undissolved in the form of an iron silicide, FeSi. The remainder of the silicon is converted into the hydroxide, $SiO(OH)_2$, and seems to exist in the iron in the form of silicides intermediate between *iron ditritasilicide*, $Fe_3Si_2$, and *iron dipentitasilicide*, $Fe_5Si_2$. When the iron contains manganese, practically the whole of the latter is found in combination with the silicon in the insoluble residue, and it would seem to follow that silicon combines with manganese in preference to combining with iron. J. T. Pelouze and E. Frémy also prepared crystals of what was regarded as *iron ditritasilicide*, $Fe_3Si_2$, in 1864 ; and octahedral crystals are produced by melting together quartz, iron, and carbon ; and G. J. L. de Chalmot by heating the same materials in an electric furnace, and washing the product with dil. hydrofluoric acid. The last-named said that the sp. gr. is 6·36, and that the compound readily dissolves in aqua regia, hydrofluoric acid, and in fused alkali carbonates. A. Jouve doubted the existence of these silicides ; W. Guertler and G. Tammann found no signs of them on the f.p. curve, Fig. 18, but R. Frilley found evidence of $Fe_3Si_2$ of *iron trihemisilicide*, $Fe_2Si_3$, and of *iron tritetritasilicide*, $Fe_4Si_3$, on the sp. gr. curve. There is no other evidence of the existence of $Fe_2Si_3$, and $Fe_3Si_4$.

H. Hahn made crystals of an iron silicide by reducing sodium chloroferrate with sodium in the presence of sodium fluosilicate. The analysis corresponds with $Fe_{10}Si_9$, and he assumed it to be a mixture of iron hemisilicide and **iron monosilicide,** FeSi. The sp. gr. was 6·239 at 19°. E. Frémy made the monosilicide by the action of silicon tetrachloride on red-hot iron. The yellowish-grey octahedral crystals were very hard ; insoluble in aqua regia ; and were decomposed by fused alkali carbonates. E. Vigouroux could not make the monosilicide by E. Frémy's process ; he obtained the hemisilicide $SiCl_4+4Fe=2FeCl_2+Fe_2Si$, at a dull red heat or at 1100°. P. Lebeau produced this silicide by heating iron with an excess of copper silicide. He said that this silicide is sometimes found in geodes in commercial ferrosilicon. A. Carnot and E. Goutal (*vide supra*), and A. Jouve also noted crystals of the monosilicide in ferrosilicon. In the interior of the siliceous mass obtained from an electric furnace in which coke, sand, and lime were heated together at a temp. of about 3000°, B. L. Vanzetti found metallic buttons having a sp. gr. 5·76–6·29, a hardness of about 7 on Mohr's scale, and the composition FeSi—*vide infra* for sp. ht. The chemical characters of the substance point to its being a chemical individual, as also does the absence of magnetic properties. The iron, which occurs to the extent of 3 per cent. as ferric oxide in the coke, doubtless combines firstly with carbon, the latter being subsequently displaced by silicon formed by reduction of the silica present. Similar experiments at a higher temp. than 3000° yielded masses varying in appearance and sp. gr. (3·96–5·54) and more readily acted on by reagents than FeSi. W. Guertler and G. Tammann observed the formation of this compound in their study of the f.p. curve of iron-silicon alloys, Fig. 19 ; and R. Frilley obtained evidence of its existence on the sp. gr. curve.

T. Murakami found evidence of **iron tritadisilicide,** $Fe_3Si_2$, on the equilibrium

diagram; above 1100°, it dissociates into iron and the monosilicide; the trita-disilicide separates primarily at about 1020° in alloys containing over 23 per cent. of silicon, and it is formed by the union of iron with the monosilicide. H. Hahn treated the regulus of iron hemisilicide with dil. hydrofluoric acid and obtained a crystalline residue corresponding with **iron disilicide,** $FeSi_2$; G. J. L. de Chalmot found crystals of this compound, along with $Fe_3Si_2$, in 39–50 per cent. ferro-silicon. He said that since both silicides are attacked by hydrofluoric acid, it is difficult to separate them. The mixture is suspended in water, and the acid gradually added in small quantities at a time. He said that this silicide is brittle, crystalline, and non-magnetic, and has a sp. gr. 4·851. P. Lebeau obtained small lustrous crystals of the disilicide by treating iron with an excess of silicon in an electric furnace; the results with copper silicide and iron were negative. He said that the dark grey crystals have a sp. gr. 5·40 at 15°; their hardness is between 4 and 5. The disilicide is oxidized superficially in oxygen at 1200°; it inflames in contact with cold fluorine, and at a dull red heat in chlorine or bromine; iodine reacts

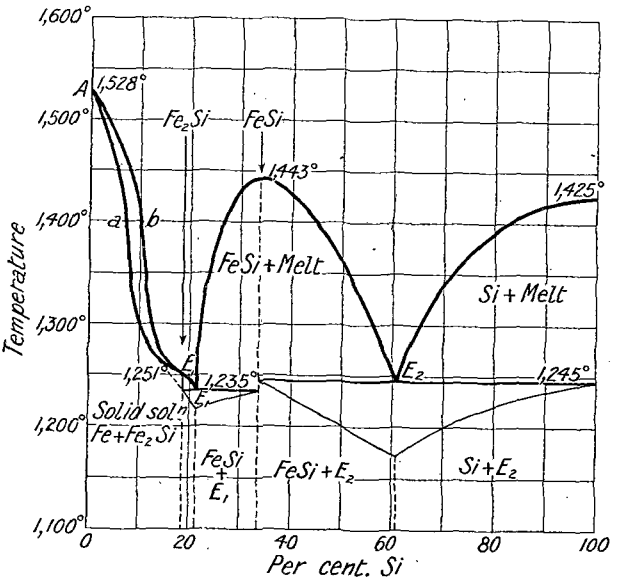



FIG. 19.—Equilibrium Diagram of Iron-Silicon Alloys.

less energetically at a still higher temp. All mineral acids, hot or cold, dil. or conc., are without action, but hydrofluoric acid reacts slowly in the cold and rapidly when heated. Soln. of alkali hydroxides have no appreciable action in the cold, but they act slowly when heated. Molten alkali hydroxides quickly decompose the disilicide. A. Jouve regards the alleged disilicide as a mixture. T. Naske claimed to have isolated *iron trisilicide*, $FeSi_3$, by treating 50 per cent. ferrosilicon with hydrofluoric acid, but the inference has not been confirmed.

The equilibrium diagram, Fig. 19, of the silicon-iron alloys has been worked out by W. Guertler and G. Tammann, A. T. Lowzow, N. Kurnakoff and G. Urasoff, and T. Murakami. According to W. Guertler and G. Tammann, for all alloys with up to about 20 per cent. silicon, solidification begins by the formation of solid soln. of iron and the hemisilicide, $Fe_2Si$, in the region *AabE*; below *AaE*, there is a solid soln. with $Fe_2Si$, forming primary crystallites. Hence, 20 per cent. ferrosilicon is iron hemisilicide melting at 1251°. The microstructure depends on the rate of cooling. Alloys with 20–21·6 per cent. silicon have the f.p. curve $EE_1$; with a portion above 1235° consisting of the hemisilicide and melt, and below

1235°, of the hemisilicide and the eutectic $E_1$. The remainder of the diagram explains itself. M. A. Sanfourche discussed the limiting range of silicon in these alloys. W. Gontermann worked out a more detailed diagram, Fig. 20, for alloys with up to 21·4 per cent. of silicon, where the dotted lines refer to curves not established by experiment. The assumption is made that with less than 15 per cent. silicon two different crystals are formed on cooling, namely, the mixed crystals of iron and silicon containing about 15 per cent. of silicon, and crystals of the composition FeSi. Silicon is soluble to the extent of about 15 per cent. in all the allotropic forms of iron. The effect of silicon on the allotropic forms of iron is also illustrated in the diagram. From the observations of F. Osmond, J. O. Arnold, P. Oberhoffer, and T. Baker, it follows that (i) the transformation $\alpha$-Fe⇌$\beta$-Fe is lowered by 7–8 per cent. of silicon; (ii) the transformation $\beta$-Fe⇌$\gamma$-Fe is not affected by additions up to 2·7 per cent. silicon; and the transformation $\gamma$-Fe⇌$\delta$-Fe is lowered as in the following manner, determined by R. Ruer and R. Klesper:

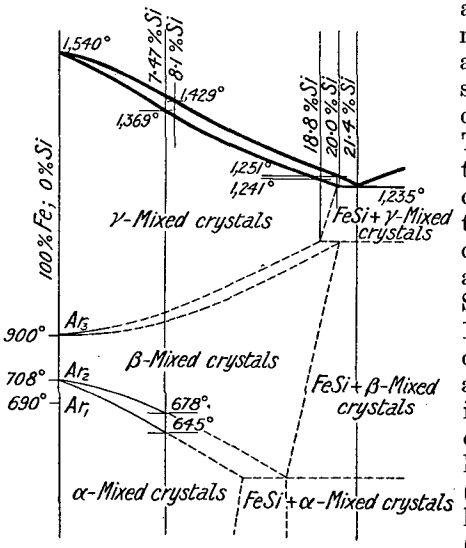



FIG. 20.—Equilibrium Diagram of Iron with up to 20 per cent. Silicon.

| Per cent. Si | 0 | 0·2 | 0·4 | 0·6 | 0·8 | 1·0 | 1·2 |
|---|---|---|---|---|---|---|---|
| Transition temp. | 1401° | 1401° | 1392° | 1385° | 1375° | 1355° | 1335° |

C. Schools studied the effect of silicon on the solubility of iron carbide in $\gamma$-iron. G. J. Snelus, L. L. de Koninck and A. Ghilain, etc., tried to find how the silicon is associated with the iron. E. H. Morton, and L. Troost and P. Hautefeuille, said that the silicon is chemically combined and not mechanically mixed. According to R. Frilley, alloys with 5–15 per cent. of silicon have the appearance of grey steel. Alloys with 15–35 per cent. of silicon are compact, white, lustrous, and are readily fractured under the hammer. Alloys with 35–55 per cent. of silicon are lustrous and grey, and they are not readily fractured under the hammer. Alloys with over 55 per cent. silicon have the colour of fused silicon, and crystals of silicon are often present. Geodes lined with crystals are also present.

The **microstructure** of the alloys has been investigated by M. von Schwarz, F. Osmond, J. O. Arnold, T. Baker, L. Guillet, M. François and C. Lormand, E. Gumlich and P. Goerens, A. B. Albro, P. Paglianti, T. D. Yenson, W. Guertler and G. Tammann, etc. The general results show that with less than 15 per cent. silicon, there is only one kind of crystal present in the alloys; with the low silicon steels when carbon is present, cementite crystals are also present; when over 3 per cent. of silicon is present, carbon separates as graphite and not cementite. According to J. H. Andrew, what W. Gontermann regarded as the $Ar_1$-break in the cooling curve of iron was in reality the $Ar_{2-3}$ break. It is probable that with as much as 10 per cent. of silicon, this point is raised to the temp. of freezing, $\alpha$-iron being formed immediately on freezing and the carbon thrown out of soln. He suggests some modifications in W. Gontermann's diagram to cover the elimination of the Ar-point. W. Gontermann, and F. Wüst and O. Petersen studied the ternary system: Iron-carbon-silicon. They found:

| Per cent. Si | 0·13 | 0·66 | 1·41 | 2·68 | 3·69 | 4·86 | 13·54 | 26·93 |
|---|---|---|---|---|---|---|---|---|
| Per cent. C | 4·29 | 4·05 | 3·88 | 3·56 | 3·32 | 3·08 | 1·94 | 0·87 |
| F.p. | 1138° | 1152° | 1160° | 1185° | 1197° | 1210° | 1233° | 1255° |

The solubility of carbon in iron is diminished by silicon, and carbon is precipitated if sufficient silicon be present—say 4 per cent. The carbon separates as graphite, even when the soln. is rapidly cooled from the molten state. W. Gontermann suggested that the graphite is partly formed by the dissociation of a silico-cementite, and partly as a deposit from a supersaturated soln. of silico-austenite. According to H. Moissan, the fact that the displacement of carbon by silicon is not quite complete is probably due to the establishment of a state of equilibrium between the iron silicide and the iron carbide, the conditions of equilibrium varying with the temp. and with the impurities which are always present in white or grey cast iron. G. Phragmen found that with iron containing above 17 per cent. of silicon, the **X-radiogram** of iron became weak, and at 30 per cent. silicon was entirely replaced by one corresponding with FeSi; at 40 per cent. silicon the lattice of $FeSi_2$ appeared; and at 50 per cent. silicon, this alone existed. No signs of $Fe_2Si$ or of $Fe_3Si_2$ were observed. G. Tammann discussed the space-lattice of iron hemisilicide. G. Tammann and K. Dahl tested the brittleness of the silicide. They found no gliding planes, and noted that the alloy becomes soft 50° below the m.p.

Determinations of the **specific gravity** have been made by F. Stromeyer, who found 7·3241–6·7777 for alloys with 2·2–9·3 per cent. of silicon, H. Hahn, J. L. Smith, T. Turner, R. A. Hadfield, A. T. Lowzow, P. Paglianti, H. Moissan, G. J. L. de Chalmot, P. Lebeau, H. von Jüptner, W. Guertler and G. Tammann, B. L. Vanzetti, J. W. Rothe, L. Weiss and T. Engelhardt, H. W. Hake, M. F. Matt, O. Hengstenberg, M. von Schwarz, E. Maey, S. R. Bennett, etc., also made determinations. The following is a selection from R. Frilley's measurements of the sp. gr., sp. vol., and mol. vol.:

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Per cent. Si | 5·90 | 11·81 | 20·24 | 40·09 | 50·00 | 77·25 | 92·21 | 100·00 |
| Sp. gr. | 6·80 | 6·63 | 6·33 | 5·18 | 4·50 | 2·85 | 2·57 | 2·40 |
| Sp. vol. | 0·146 | 0·151 | 0·158 | 0·193 | 0·220 | 0·351 | 0·389 | 0·416 |
| Mol. vol. | 7·77 | 7·56 | 7·37 | 7·74 | 8·29 | 11·1 | 11·3 | 11·7 |

He added that the curves show five points of inflexion corresponding with $Fe_2Si$, $Fe_3Si_2$, $Fe_3Si_4$, $Fe_2Si_3$, and $FeSi_2$, with a singularity corresponding with FeSi. The sp. vol. curve has singularities corresponding with FeSi and $FeSi_2$; and the mol. vol. curve has one singularity corresponding with FeSi. C. J. B. Karsten observed that iron was hardened by the addition of 0·37 per cent. of silicon; D. Mushet observed that when iron is melted with quartz it becomes harder and more brittle. J. B. J. D. Boussingault, L. Guillet, R. A. Hadfield, W. Mrazek, T. Baker, P Paglianti, W. A. Tilden, W. C. Roberts-Austen, and T. Turner, W. Guertler and G. Tammann, etc., made observations on the **hardness** of iron-silicon alloys. R. Janoyer said that silicon exercises a bad influence on iron, while H. Caron maintained that it has a good influence. G. A. Bisset, C. F. Burgess and J. Aston said that iron with one per cent. of silicon is soft, and it is hard and brittle with 6–7 per cent. of silicon. M. von Schwarz found for the Shore's scleroscopic hardness

| | | | | | | |
|---|---|---|---|---|---|---|
| Per cent. Si | 0·01 | 2·0 | 7·5 | 15·0 | 16·0 | 93·4 |
| Hardness | 24 | 56 | 74 | 64 | 60 | 74 |

Values were determined for intermediate alloys, but the results were considered to be unreliable. When free carbon does not separate, the addition of silicon hardens iron. P. Paglianti found Brinell's hardness increases approximately proportionally with the silicon content. L. Révillon observed that the tensile strength, $T$, and Brinell's hardness, $H$, of a sample of manganese silicon steel to be related as $H=0·389T$; and P. Paglianti gave $H=0·320T$. In 1887, W. A. Tilden, W. C. Roberts-Austen, and T. Turner found that with steels containing 0·10–0·50 per cent. of silicon, the **elastic limit** and **tensile strength** are increased while the **elongation** is diminished. R. A. Hadfield found that ingots could not be forged; he worked with steels having up to 4·90 per cent. of silicon, and carbon varying

from 0·14–0·26 per cent. T. Baker worked with 0·04 per cent. carbon and 7½ per cent. silicon. L. Guillet worked with steels with varying manganese and carbon, and up to 5·12 per cent. of silicon. P. Paglianti worked with a carbon content of 0·10 per cent., manganese 0·22–0·60 per cent., and silicon up to about 6½ per cent. G. A. Bisset said that silicon adds strength to iron comparable with the effect of carbon. T. D. Yensen also investigated the mechanical properties of the iron-silicon alloys. According to T. Turner, increasing the proportion of silicon increases the mechanical qualities of cast-iron until one or two per cent. of silicon has been added when further additions diminish these qualities—*e.g.* the maximum with the crushing strength is about 0·8 per cent.; with the tensile strength about 1·8 per cent.; and with the modulus of elasticity about 1·0 per cent. The general results of the observations show that silicon in quantities up to 4 per cent. increases the strength of steel proportionally with the amount added; if over 4 per cent. be added, the strength decreases rapidly probably owing to the formation of graphite, and the yield point corresponds with the breaking point. The ductility is but little affected by silicon below 2·5 per cent., but above this amount, the alloys become brittle, and with 4 per cent. or more, the elongation and reduction in area are nil. With 7 per cent. or more silicon, the alloys are not forgeable. Unlike carbon, silicon does not confer upon iron the property of becoming hardened when water-quenched. For alloys with 0·15 and 3·40 per cent. of silicon, T. D. Yensen gives respectively 18,500 and 58,000 lbs. per sq. in. for the stress at yield point; 37,000 and 67,500 lbs. per sq. in. for the ultimate strength; 56 and 21 per cent. for the elongation; and 90 and 28·5 per cent. for the reduction of area. P. Schübel gave for the **specific heat** of FeSi, 0·1476 between 18° and 193°; 0·1504 between 18° and 300°; 0·1532 between 18° and 399°; and 0·1583 between 18° and 629°. Observations were also made by M. Padoa, and H. Schimpff. F. O. Osmond, and E. D. Campbell and W. E. Hartman have investigated the effect of silicon on the **heat of solution** of cast-iron in an ammoniacal soln. of cupric chloride. When the proportion of silicon approaches $Fe_3Si$, the product becomes insoluble in that menstruum. L. Troost and P. Hautefeuille, and H. von Jüptner have made thermochemical studies on siliciferous iron.

W. F. Barrett, P. Paglianti, C. F. Burgess and J. Aston, R. A. Hadfield and co-workers, T. D. Yensen, H. le Chatelier, W. Muthmann and co-workers, and W. Guertler investigated the **electrical resistance** of alloys of iron and silicon. M. von Schwarz found:

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Per cent. Si . . | 2·0 | 7·5 | 15·0 | 20·0 | 24·8 | 29·3 | 40·2 |
| Sp. resistance $\times 10^4$ | 0·41 | 0·95 | 1·02 | 1·48 | 3·15 | 8·17 | 14·8 ohms |

In general, silicon increases the electrical resistance of iron by 10–12 microhms per c.c. for each per cent. added. R. A. Hadfield and co-workers studied the **magnetic properties** of silicon-iron alloys. They found that alloys with 2·5 and 5·5 per cent. silicon had a higher maximum magnetic permeability and a lower hysteresis loss than pure iron. This led to the employment of silicon-steel for use in electromagnetic machinery, particularly in transformers. Numerous investigations have since been made on the magnetic properties of these alloys. T. Baker found:

| | | | | | |
|---|---|---|---|---|---|
| Per cent. Si . . . . . | 0·02 | 1·02 | 2·90 | 4·80 | 7·47 |
| Maximum induction ($H=20$) . . | 16000 | 16200 | 15500 | 14750 | 14000 |
| Permeability ($H=4$) . . . | 2325 | 2562 | 2750 | 2665 | 2937 |
| Retentivity . . . . . | 8375 | 8000 | 7325 | 7200 | 9000 |
| Coercive force . . . . | 1·8 | 1·7 | 1·5 | 1·2 | 1·0 |
| Energy dissipated per complete cycle | 10550 | 8798 | 8081 | 6110 | 5613 ergs per c.c. |

G. Dillner and A. F. Engström, unlike other investigators, found that silicon reduced the permeability and increased the hysteresis loss of sheet iron. E. Gumlich and P. Goerens, E. Gumlich and W. Rogowsky, P. Paglianti, S. Guggenheim, C. W. Heaps, J. Hopkinson, T. Murakami, T. D. Yensen, and others have investi-

gated this subject. Carbon in the form of graphite has a smaller damaging influence on the magnetic properties of iron than it has in the dissolved form, or combined as cementite. Silicon precipitates carbon as graphite, and this is an indirect reason why silicon exercises a beneficial effect on the magnetic properties of iron, since iron of a very high degree of purity still retains some carbon. The most favourable proportions vary between 2 and 4 per cent. The eddy-current losses decrease with an increase in the electrical resistance, and from this point of view the silicon content should be as high as possible without loss of the most favourable magnetic properties. T. C. MacKay studied the **Hall effect** in iron-silicon alloys.

A singular property of some samples of ferrosilicon, particularly alloys with approximately 50 per cent. silicon, is their tendency to spontaneous disintegration; *une explication très complète* of the phenomenon is not known. H. Heller said that the effect is likely to occur if over 33·3 per cent. of silicon is present, and that phosphorus and aluminium are directly responsible. It has been attributed to the presence of calcium silicide which is decomposed on exposure to humid air; but R. Frilley could not make the alloys spontaneously disintegrate in this way by purposely adding up to 10 per cent. of calcium. He found aluminium always present in the alloys which disintegrate. This was present either as aluminium silicide, or, as P. Lebeau suggested, as iron silicoaluminide. The disintegration is a serious inconvenience because of the difficulties which attend the use of the powder in some of its metallurgical applications; and also because the material *en poudre* exposes an enormously greater surface to the action of the air than what it does *en masse*. This means that oxidation, etc., by atm. air then becomes serious. To protect the material from oxidation, the lumps of 50 per cent. ferrosilicon are covered with a thin film of paraffin invisible to the naked eye. The resistance of ferrosilicon to chemical agents is to a large extent dependent on its composition. The 50 per cent. alloy is fairly resistant towards oxidizing agents, and this is also true of the different iron silicides. On the other hand, ferrosilicon is largely used in steel manufacture by virtue of its deoxidizing qualities. A fragment of 50 per cent. ferrosilicon is only superficially oxidized when heated in the blowpipe flame, and the film is probably nitride or carbonitride mixed with silica and iron oxide. J. J. Morgan founded a method for the determination of iron in alloys on the ready oxidizability of graphite and silicon; the silicon forms silica which remains as a residue when the oxidized iron is dissolved in acid. M. F. Matt found that ferrosilicon is but incompletely oxidized when heated in oxygen at 1100°. M. von Schwarz heated 50 per cent. ferrosilicon to 1100° in a stream of air for different periods of time, and found the percentage increases in weight to be:

| Time in hrs. . . | 7 | 14 | 21 | 25 | 32 |
|---|---|---|---|---|---|
| Percentage increase. | 0·29 | 11·17 | 12·01 | 12·24 | 12·60 |

similarly in oxygen:

| Time in hrs. . . | 7 | 14 | 26 | 37 | 44 |
|---|---|---|---|---|---|
| Percentage increase. | 11·26 | 13·64 | 16·14 | 18·00 | 19·02 |

Under certain conditions, some ferrosilicons—more particularly those ranging from 30–40 per cent., and from 47–65 per cent. silicon—under the influence of moist air are liable to evolve gases with dangerous and toxic properties. A number of fatalities have occurred during its transit on board ship, or during storage and use in factories. In some cases, passengers on ships or canal boats carrying ferrosilicon have died suddenly; in other cases, workmen have suffered more or less severely from the effects of breathing the fumes evolved from the material; and in a few cases, explosions have occurred spontaneously on handling the containing drums. On account of the accidents which have occurred from time to time, special restrictions are imposed on the transit and storage of ferrosilicon. A record of cases will be found in a report by S. M. Copeman and co-workers. A. Dupré and M. B. Lloyd showed that phosphine may be evolved by the action of water at ordinary temp.

P. Lehnkering also observed that air passed over ferrosilicon may give phosphine but no acetylene. He inferred that some calcium phosphide was present as an impurity in the ferrosilicon. A. W. Cronquist, C. E. Pellew, W. R. Smith, and P. Bruylants and H. Druyts observed phosphine and arsine in the gases. Hydrogen is also produced, but there is no evidence of the formation of silicane or of acetylene. H. W. Hake obtained similar results. According to N. S. Kurnakoff and G. Urasoff, an alloy with about 50 per cent. of silicon is sensitive to water and very dangerous. Alloys with 33·4–100 per cent. by weight of silicon furnish a solid soln. with 55·18–61·5 per cent. of silicon which solidifies at 1245°, and has been called *lebeauite*. The ternary solid soln. of lebeauite with phosphorus or aluminium are stable towards water; but the quaternary solid soln. of lebeauite with phosphorus and aluminium gives off phosphine when treated with water. Ferrosilicon with less than 33·4 per cent. of silicon, and containing $\gamma$-iron, will dissolve respectively 1·7 and 3·0 per cent. of phosphorus and aluminium. Calcium phosphide does not dissolve in liquid or solid ferrosilicon. N. S. Kurnakoff and G. Urasoff also studied the toxic properties of ferrosilicon.

R. Frilley found that hydrofluoric acid in the cold readily dissolves ferrosilicon with up to 50 per cent. silicon; hydrochloric acid attacks alloys with up to 33 per cent. silicon, but has virtually no action on alloys richer in silicon; nitric and sulphuric acids are without action; but a mixture of nitric and hydrofluoric acids attacks *très violemment* all the ferrosilicons. Fused alkali hydroxides or carbonates readily attack the iron-silicon alloys, and the attack is much more vigorous and complete in the presence of potassium nitrate. With alloys containing over 50 per cent. of silicon, the attack by potassium or sodium hydroxide is extremely violent. Cold soln. of sodium hydroxide are without action on alloys with less than 50 per cent. silicon, but beyond that proportion, the attack becomes very vigorous, and a residue, completely soluble in hydrofluoric acid, remains. M. Wunder and B. Jeanneret found that hot phosphoric acid of sp. gr. 1·75 dissolves ferrosilicon, forming a clear liquid; any carbon present remains undissolved. U. Ehrhardt and G. Pfleiderer found crude tar oil containing phenol did not visibly attack ferrosilicon in 4 weeks' time.

Firma Biermann showed that ferrosilicon has an important influence in reducing the tendency of molten steel to become bubbly, "fiery," or frothy during casting. The way the silicon reduces the extrusion of gases from molten steel in the act of solidification has not been established. It is generally assumed that the silicon in steel decomposes iron or other oxides which may be present. The enhanced tensile strength conferred by low percentages of silicon has resulted in the use of silicon steels in making springs, etc. For the use of siliciferous iron in the manufacture of electromagnetic apparatus, *vide supra*. On account of the resistance of the silicon alloys to attack by acids, A. Jouve recommended vessels of ferrosilicon for the manufacture and conc. of sulphuric acid; and N. Terrisse and M. Levy, for acid-resisting alloys. A. Lissner also recommended these alloys as a substitute for platinum vessels in some industries. C. Höpfner recommended ferrosilicon as an electrode material for aq. soln. since it is more durable than carbon, and cheaper than platinum. The 25 per cent. alloy has been recommended for making statuettes, etc., since it polishes well. It is used as a master alloy in making silicon steels. It influences the properties of iron by controlling the condition of the carbon. V. Fuss studied the ternary system Si–Al–Fe.

C. Winkler [3] heated nickel and silicon to a white heat and obtained a sintered not a fused mass; but he obtained a good alloy by reducing nickel oxide with aluminium, quartz, and cryolite. The regulus was contaminated with 12–15 per cent. of aluminium. R. Walter obtained nickel-silicon alloys by heating the component elements to a high temp.; and W. E. Gard obtained a white, homogeneous, fused, non-magnetic regulus in a similar way. E. Vigouroux found that when nickel is subjected to the action of silicon tetrachloride at a high temp. until the *mass fuses* and the loss in weight amounts to 30 per cent., the product consists of

**nickel tetritasilicide,** $Ni_4Si$, which has a metallic appearance, is very brittle and crystalline, and is not attracted by a magnet. By the prolonged action of silicon tetrachloride on the lower silicide, it is converted into the **nickel hemisilicide,** $Ni_2Si$. The same compound is formed when nickel is heated with 10 per cent. of silicon in a current of hydrogen, the crystalline silicide is more fusible than the metal or silicon. Similar results are obtained by heating the silicon and the metal in a crucible in an oxyhydrogen furnace. Heating silicon with the metal oxide does not yield a pure product. The best results are obtained by heating the metal with 10 per cent. of silicon, in a carbon crucible in the electric furnace, until the greater part of the excess of the metal is volatilized. The product is treated with very dil. nitric acid. The hemisilicide is perfectly crystallized, and has a metallic appearance, and a steel-grey colour, and it is stable at the highest temp. The sp. gr. of the nickel hemisilicide is 7·2 at 17°. Fluorine attacks it with incandescence at the ordinary temp., and chlorine has the same effect at a red heat; bromine and iodine are less energetic in their action. Dry hydrogen fluoride and hydrogen chloride attack it at a red heat, and hydrogen bromide and iodide behave similarly. Hydrofluoric acid dissolves it readily, but the other haloid acids act very slowly; aqua regia, however, decomposes the powdered substance completely. Water has no action on the crystals, but water vapour attacks them at a dull red heat. Oxygen or air oxidizes the finely powdered silicide at a red heat. Soln. of alkali hydroxides are without effect, but fused alkali carbonates or mixtures of carbonates and nitrates decompose the silicide readily. W. Jenge studied the action of soln. of chlorides, bromides, iodides, nitrates, sulphates, sodium hydroxide, sulphuric acid, and hydrochloric acid on nickel silicides. The effects were similar to those obtained with cobalt silicides, but NiSi did not resist halogen ions. G. Tammann studied the chemical properties of these alloys.

M. A. Sanfourche discussed the limiting range of silicon in these alloys. W. Guertler and G. Tammann investigated the nickel-silicon alloys by thermal analysis, and controlled the results by microscopic examination of polished sections. They concluded that five silicides exist, $Ni_3Si$, $Ni_2Si$, $Ni_2Si_3$, NiSi, and $Ni_2Si_3$; but they did not confirm the existence of the tetritasilicide of E. Vigouroux. The f.p. curve of the system shows two maxima at 33·3 and 50 at. per cent. of silicon respectively, corresponding with nickel hemisilicide, $Ni_2Si$, and **nickel monosilicide,** NiSi, as well as three eutectic points at 20, 43, and 56 atomic per cent. of silicon respectively. From 0–11·6 and 27·6–33·3 per cent. of silicon, two series of solid soln. separate; if allowed to cool slowly, the sat. crystals interact below 1125° (in alloys containing 11·6–27·6 per cent. of silicon) with formation of **nickel tritasilicide,** $Ni_3Si$; the reaction is a reversible one. A third series of mixed crystals separates from 33·3–37·5 atomic per cent. of silicon; if the cooling is slow, **nickel ditritasilicide,** $Ni_3Si_2$, is formed from these when the temp. falls below 830°. The existence of **nickel trihemisilicide,** $Ni_2Si_3$, is formed on cooling by the interaction of silicon with the fused mass containing 59 atomic per cent. of the latter element. The alloys from 0–20 atomic per cent. of silicon are fairly tough; beyond this point they are brittle and easily powdered. Between the limits of 5 and 20 atomic per cent. of silicon, the alloys are fairly hard, but, contrary to the behaviour of carbon steel, the rapidly cooled alloys are much softer than those allowed to cool slowly. From 20 atomic per cent. of silicon, the hardness gradually decreases, reaches a minimum about 70 per cent., and beyond this point rapidly increases. Alloys containing more than 30 atomic per cent. of silicon are no longer magnetic. L. Baraduc-Muller made these alloys by reducing nickel oxide with carbon silicide, and he confirmed by thermal and microscopic observations the existence of $Ni_2Si$, $Ni_3Si_2$, NiSi, and $Ni_2Si_3$. R. Frilley found that alloys with below 5 per cent. of silicon have a grey colour, and have properties resembling steel with 1·4 per cent. carbon. Alloys with 5–20 per cent. silicon are whiter, and those with 15 per cent. of silicon have a brilliant facetted cleavage. Alloys with 20–35 per cent. silicon are less brilliant, and give a crystalline fracture showing ill-defined octahedral facets.

The crystals with the 32 per cent. alloy are acicular. The fracture of alloys with 35–40 per cent. silicon is matte and dull; alloys with over 50 per cent. silicon appear like fused silicon. M. François and C. Lormand examined the crystal structure. The following are selected from R. Frilley's determinations of the sp. gr., sp. vol., and mol. vol. of these alloys:

| Per cent. Si | 0 | 8·10 | 17·84 | 23·96 | 32·06 | 44·70 | 57·34 | 66·82 |
|---|---|---|---|---|---|---|---|---|
| Sp. gr. | 8·4 | 7·77 | 7·30 | 6·68 | 5·73 | 4·60 | 3·93 | 3·50 |
| Sp. vol. | 0·119 | 0·129 | 0·137 | 0·150 | 0·174 | 0·217 | 2·54 | 0·286 |
| Mol. vol. | 6·98 | 6·94 | 6·73 | 6·95 | 7·56 | 8·57 | 9·34 | 9·80 |

The singularities in the sp. gr. curve correspond with $Ni_2Si$, NiSi, and $Ni_3Si_2$; the sp. vol. curve has singularities corresponding with $Ni_2Si$, and NiSi, but not $Ni_3Si_2$; and the mol. vol. curve has a singularity corresponding with $Ni_2Si$. There are no signs of $Ni_4Si$, $Ni_3Si$, or of $Ni_2Si_3$ on these curves. P. Schübel found for the sp. ht. of NiSi between 18° and 299°, 0·1367; 0·1380 between 18° and 421°; 0·1420 between 18° and 501°; and 0·1454 between 18° and 629°. For $Ni_2Si$, he gave 0·1197 between 18° and 202°; 0·1226 between 18° and 294°; 0·1245 between 18° and 410°; and 0·1285 between 18° and 628°. R. Frilley found that hydrofluoric acid does not attack these alloys; hydrochloric acid does not attack the alloys with a high and a low proportion of silicon, but it does attack those with approximately 32 per cent. of silicon; sulphuric and nitric acids are without action; a mixture of hydrofluoric and nitric acids readily attacks these alloys; aqua regia dissolves in the cold alloys with less than 20 per cent. silicon; and none of the alloys is attacked completely by soln. of alkali hydroxides—cold or hot. Fused alkali hydroxides or carbonates decompose these alloys particularly in the presence of potassium nitrate. V. Fuss studied the ternary system Si–Al–Ni; and M. Pfautsch, Si–Mo–Ni.

C. Winkler found cobalt and silicon behaved like nickel and silicon at a white heat. R. Walter made alloys by heating a mixture of cobalt and silicon to a high temp. According to E. Vigouroux, silicon tetrachloride is reduced by cobalt at the temp. of the electric furnace with the formation of cobalt chloride, which is volatile, and a residue of a cobalt silicide. At 1200° to 1300°, the reaction is complete, and ceases when the cobalt is converted into **cobalt hemisilicide,** $Co_2Si$, which has a sp. gr. 7·28 at 0° and 7·1 at 17°, and differs from H. Moissan's corresponding iron silicide in that it is not attracted by a magnet. E. Vigouroux also prepared the hemisilicide by a process similar to that employed for the corresponding nickel salt, and he found that the general properties were also similar. P. Lebeau prepared **cobalt monosilicide,** CoSi, in the form of prismatic needles by heating for 4–5 mins. in a carbon crucible placed in the electric furnace a mixture of copper silicide and metallic cobalt. The monosilicide melts at 1300° in a current of hydrogen, and has sp. gr. 6·30 at 20°. Cobalt silicide is converted into the fluoride with incandescence when gently heated in a current of fluorine; chlorine reacts only at a dull red heat; hydrogen fluoride or chloride decomposes the substance at high temp., yielding hydrogen and the corresponding haloid compounds of silicon and cobalt. Sulphur has no action on the compound at the softening point of glass; oxygen, nitrogen, ammonia, and steam, under these conditions, decompose the silicide only superficially; hydrogen sulphide, at high temp., gives rise to sulphides of cobalt and silicon. Nitric and sulphuric acids do not attack the silicide; it dissolves, however, slowly in aqua regia, and more rapidly in hydrochloric acid. Cobalt silicide is insoluble in dil. alkaline soln. but is decomposed by the alkali hydroxides, either fused or in conc. soln. Fused potassium nitrate and potassium hydrogen sulphate have no action on the substance; melted potassium carbonate attacks it only slowly. P. Lebeau also prepared **cobalt disilicide,** $CoSi_2$, by heating cobalt mixed with an excess of silicon, or a mixture of cobalt, silicon, and copper silicide, in the electric furnace. It forms dark crystals with a bluish reflection, which often have an octahedral form and seem to belong to the cubic system. It has a sp. gr. 5·3 and hardness between 4 and 5. It is attacked by fluorine, with

incandescence, if gently heated, by chlorine at 300°, and by bromine and iodine at a dull-red heat. Sulphur has no action on it at the softening point of glass, oxygen attacks it superficially at 1200°, and nitric and sulphuric acids, conc. or dil., are without action. Hydrochloric acid, when conc. and boiling, attacks the silicide slowly, and hydrofluoric acid dissolves it rapidly; hot conc. soln. of alkali hydroxides attack it slowly, but the fused hydroxides decompose it rapidly. W. Jenge studied the action of soln. of chlorides, bromides, iodides, nitrates, sulphates, sodium hydroxide, sulphuric acid, and hydrochloric acid on cobalt silicides. Those with less than 32 per cent. silicon were readily attacked by acidic ions, while those with more silicon were resistant. That is, CoSi and the higher silicides behave like silicon, and the other silicides behave like cobalt. G. Tammann found that acids attack those silicides with cobalt in excess of Co : Si= 1: 1 and alkalies those with the ratio 1 : 3.

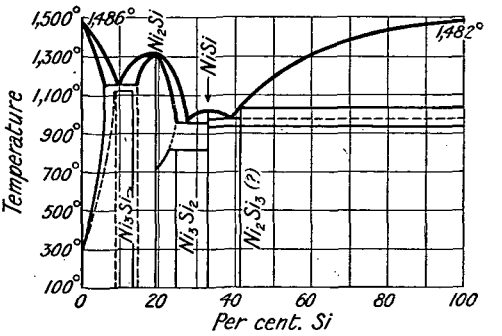



FIG. 21.—Equilibrium Diagram of Nickel-Silicon Alloys.

M. A. Sanfourche discussed the limiting range of silicon in these alloys. K. Lewkonja studied the cobalt-silicon alloys by thermal analysis and controlled the results micrographically. The f.p. curve, Fig. 21, shows that the two elements are completely miscible in the liquid state, and in the solid state the miscibility is confined to alloys with less than 7·5 per cent. and more than 91 per cent. of silicon. Five compounds are shown on the diagram, cobalt hemisilicide, m.p. 1327°; cobalt monosilicide, m.p. 1395°; cobalt disilicide, m.p. 1277°; **cobalt trisilicide,** $CoSi_3$, m.p. 1310°; and **cobalt ditritasilicide,** $Co_3Si_2$, which is formed in the solid state from the hemi- and mono-silicides. The range of existence of these compounds is shown in Fig. 22. Alloys with 0–19·5 per cent. of silicon are magnetizable. These alloys have cobalt in solid soln., and their magnetic intensity increases with the proportion of cobalt.

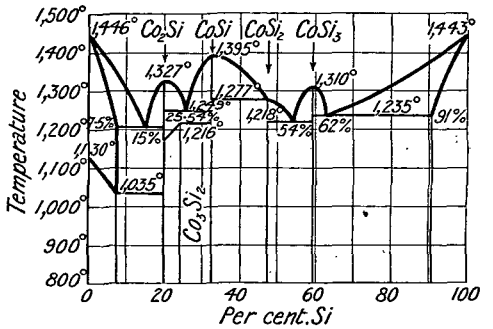



FIG. 22.—Equilibrium Diagram of the Cobalt-Silicon Alloys.

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## § 14. The Silicides of the Platinum Family

J. J. Berzelius [1] stated that if silicon is ignited in a platinum crucible, the two elements do not react, but if silicon fluoride or potassium fluosilicate is reduced by potassium in a platinum crucible, the silicon penetrates into the platinum wherever the latter is touched by the potassium. J. B. J. D. Boussingault found that platinum fuses when embedded in charcoal powder, and exposed to the strongest heat of a forge, at the same time it takes up half per cent. of silicon ; but if covered with lampblack containing no silica, fusion does not occur. C. Winkler, H. St. C. Deville, and P. Lebeau and A. Novitzky observed that silicon readily unites with platinum at a high temp., and a fusible silicide is formed. J. Königsberger and K. Schilling noted that the reaction begins as low as 400°, and at a red heat the reaction with crystalline silicon is quite fast. According to H. N. Warren, a silicide is readily obtained by heating amorphous silicon mixed with platinum black under a layer of potassium fluosilicate in a closed crucible. J. J. Berzelius, and J. B. J. D. Boussingault showed that platinum silicide is also formed when silica or a silicate is heated in contact with platinum under reducing conditions, say, in contact with carbon, not, said the latter, in consequence of the

formation of a carbide as assumed by H. V. Collet-Descotils. The absorption of silicon by platinum in contact with carbon in fireclay crucibles was noted by J. B. J. D. Boussingault, A. Ditte, L. Baraduc-Muller, etc. The formation of a fusible silicide explains how J. J. Prechtl was able to melt platinum in a blast-furnace. The vapour of silicon, said J. B. J. D. Boussingault, may be carried by the furnace gases to the platinum. P. Schützenberger and A. Colson, in the experiment cited in connection with the vaporization of silicon, said that nitrogen and probably also oxygen play a part in the transfer of the silicon to the platinum. M. Lapschin and M. Tichanowitsch found that if an electric current be passed through silica heated in a platinum crucible the metal will be perforated owing to the formation of a fusible silicide. J. B. J. D. Boussingault also found that when platinum is heated with silica in an atm. of hydrogen, some silicide is formed. C. G. Memminger ignited topaz in a platinum crucible placed inside a graphite crucible, and the platinum was converted into a brittle fusible substance with 1·61 per cent. of silicon. According to F. P. Miles, the conditions under which platinum silicide is formed are the presence of reducing gases such as carbon monoxide, of silicon tetrafluoride, and of a basic substance such as magnesia. The silicization of platinum resistance wire coiled round porcelain tubes to form electric tube furnaces, and heated in an atm. of hydrogen, has been discussed by L. Holborn and W. Wien, W. C. Heraeus, W. Ostwald and R. Küch—*vide infra*, action of reducing gases on silica.

According to C. Winkler, platinum which has absorbed 10 per cent. of silicon is greyish-white and fusible at a white heat. J. J. Berzelius found the sp. gr. to be 18·3; J. J. Prechtl, 17·7; and J. B. J. D. Boussingault, 17·5–20·5. According to the last-named, silicized platinum is hard enough to scratch iron and platinum, but it does not become harder by rapid cooling; it is brittle, it readily fractures under the hammer; it is still brittle at a red heat, and its ductility is not restored either by heating it in contact with air, or in contact with manganese dioxide. It dissolves in aqua regia more slowly than does platinum, and gelatinous silica separates. W. C. Heraeus found that the electrical resistance of platinum is increased by silicization.

Five definite silicides have been reported, but they may not be all chemical individuals since analysis is not a satisfactory test. For instance, C. Winkler reported that **platinum dodecasilicide,** $PtSi_{12}$, is formed, as a white crystalline mass, by melting platinum with an excess of silicon under cryolite. A. Colson reported **platinum hemisilicide,** $Pt_2Si$, to be formed when strips of platinum are packed in lampblack, and heated in a fireclay crucible. P. Schützenberger and A. Colson said that the reaction occurs at 1000°. P. Lebeau and A. Novitzky made it by heating platinum monosilicide with tin—*vide infra;* and E. Vigouroux, by heating platinum with 8–10 per cent. of silicon in a carbon-boat contained in a carbon-tube in an electric furnace. The hemisilicide is a white, crystalline, extremely hard, brittle solid, its sp. gr. at 18° is 13·8, it is capable of dissolving silicon, and is attacked, when hot, by chlorine, and by aqua regia; molten alkali hydroxides and hot aq. soln. of alkali hydroxides have but little action. A. Colson obtained a crystalline mass of what he regarded as **platinum ditritasilicide,** $Pt_3Si_2$, by heating platinum with lampblack mixed with 60 per cent. of precipitated silica. The sp. gr. is 14·1; and the m.p. is near the squatting temp. of ordinary glass. A. Guyard made **platinum tritetritasilicide,** $Pt_4Si_3$, by heating a mixture of platinum dust with finely powdered crystalline silicon in the proportion of 2 : 1. Combination takes place at a red heat with some violence, some of the silicon gets thrown out of the crucible, and the remainder combines with the platinum, forming a compound which fuses at a somewhat higher temp. to a bright crystalline mass, metallic in appearance, and very brittle. E. Vigouroux made **platinum monosilicide,** PtSi, directly from its constituents with the silicon in excess, and also by melting a mixture of 24 grms. of platinum black, and 10·5 grms. of silicon in a magnesia boat in a stream of hydrogen for 30 mins. The excess silicon was removed by alkali-

lye, and the silica by hydrofluoric acid. P. Lebeau and A. Novitzky made the same compound by heating for half an hour to a high temp. pastilles composed of a mixture of very finely divided silicon and platinum sponge contained in a carbon crucible. It occurred in the form of a fused ingot with the appearance of silicon. An examination of a polished surface of the ingot reveals the presence of two substances, one of which is silicon, and can be removed by means of a dil. soln. of potassium hydroxide. The residue, which is soluble in aqua regia, has a composition corresponding with the formula SiPt. The same silicide is obtained by heating a mixture of equal parts of platinum and silicon for 5 mins. in an electric furnace. The silicide can be crystallized from fused silver silicide, the latter being afterwards dissolved by successive treatment with sodium hydroxide and nitric acid, and is then obtained in very fine prismatic crystals. The sp. gr. is 11·63 at 15°; and the m.p. about 1100°. This silicide is not attacked by hydrochloric, sulphuric, nitric, or hydrofluoric acid, but is attacked by hydrochloric acid and bromine, and is completely dissolved by aqua regia. When heated with tin, the product contains a mixture of free silicon with prismatic crystals and lamellæ. After washing with potassium hydroxide, this leaves a residue of the hemisilicide. E. Vigouroux found that when the monosilicide is heated with an excess of aluminium, an ingot is obtained which, after treatment with 10 per cent. hydrochloric acid, leaves a residue containing 91·2 per cent. of the silicon from the silicide in a free state. When the free silicon is removed by alkali-lye followed by treatment of the residue with aqua regia, a substance containing only 1·5 per cent. of combined silicon remains. Similarly, when heated with copper (10 grms.), the silicide (1 grm.) gives an ingot which is vigorously attacked by nitric acid (10 per cent.), leaving a residue consisting of platinum containing traces of combined silicon. By heating the copper silicide, $SiCu_4$ (12 grms.), with SiPt (3 grms.), a very brittle, grey ingot is formed, containing 20·6 per cent. of platinum, 67·2 per cent. of copper, and 12·20 per cent. of silicon. This is attacked with difficulty by nitric acid and by aqua regia, but is dissolved by a mixture of aqua regia and hydrofluoric acid. Finally, by heating the silicide, $SiCu_4$ (30 grms.), with platinum (10 grms.), a hard, greyish-white ingot is obtained, which is attacked by 5 per cent. nitric acid, leaving a black residue, from which a dense, grey substance soluble in aqua regia, and having the composition of **platinum copper silicide,** $SiCu_2Pt$, is isolated by levigation.

According to J. B. J. D. Boussingault,[2] when platinum, ruthenium, iridium, or palladium embedded in carbon in a siliceous crucible is heated to redness, the metal is silicized. Palladium, indeed, may take up nearly 4 per cent. of silicon. H. Moissan and W. Manchot prepared **ruthenium monosilicide,** RuSi, by heating a mixture of ruthenium powder and crystallized silicon in a carbon crucible in an electric arc furnace for two or three minutes. The product is crushed and treated with alkali, then with a mixture of hydrofluoric and nitric acids. The silicide is then left in the form of small, white crystals mixed with carborundum, which can be separated by flotation on methylene iodide. If some copper be added to the mixture, the silicide is ultimately obtained in a well-crystallized form. The silicide is white, and has a metallic lustre; at 4°, it has a sp. gr. 5·40 and is very hard. It volatilizes in an electric arc and is very stable. Fluorine easily attacks it, but it is only slowly attacked by chlorine. Bromine and iodine act on it slowly at 600°. When strongly heated, it burns in oxygen, and it is oxidized slowly by fused potassium chlorate or potassium dichromate. Sulphur vapour decomposes it at a red heat, and at the same temp. it is slowly attacked by fused sodium or magnesium. It is not attacked by boiling acids. Fused potassium hydroxide, carbonate, or nitrate only slowly decompose it; but when heated with a mixture of potassium hydrogen sulphate and potassium nitrate, it is decomposed and a perruthenate is formed. Potassium hypochlorite, which acts easily on ruthenium, has no action on the silicide. P. Lebeau and P. Jolibois found that when an intimate mixture of palladium and crystallized silicon is introduced into a porcelain crucible heated by means of a blowpipe, a contraction first occurs, and then, at 500°–600°,

a combination is produced, accompanied by a bright incandescence and sufficient elevation of the temp. to cause complete fusion. The fusion temp. of mixtures of silicon and palladium varies largely with the content of silicon. With an increasing proportion of silicon, the m.p. falls from 1587° for pure palladium to the minimum of 670°, corresponding with 6 per cent. of silicon; it then rises rapidly to the maximum 1400° for 11·76 per cent. of silicon (corresponding with **palladium hemisilicide,** $Pd_2Si$); the m.p. then again falls, reaching a second minimum of 750° for 16 per cent. of silicon, and afterwards rising to a second maximum of 990° for 21 per cent. of silicon (corresponding with **palladium monosilicide,** PdSi). With 25 per cent. of silicon there occurs another minimum at 825°, corresponding with a eutectic, and then the m.p. rises gradually to that of pure silicon. Mixtures containing less than 20 per cent. of silicon show a well-defined slackening in the rate of cooling, followed by a recalescence, the rise in temp. being sufficient to raise the mass to a bright red heat. The increase in incandescence so observed starts at a point in the mass and spreads in a manner similar to the crystallization of a supersaturated soln., and the similarity in the two phenomena is further shown by the fact that the recalescence is prevented by contact of the mixture at the commencement of solidification with a small fragment of a similar ingot previously prepared. The behaviour, on cooling, of mixtures containing more than 21 per cent. of silicon, indicates the presence of the eutectic (SiPd—Si). Ingots which have undergone recalescence have a different structure from the same products, tempered before the appearance of this phenomenon. In the latter case, two homogeneous constituents are always observed, and are very easily distinguished by oxidation. When, however, recalescence has occurred, the more oxidizable constituent is besprinkled with small crystals. The ingots corresponding with the compositions $Pd_2Si$ and PdSi are both homogeneous, but only the latter silicide has been isolated in a crystalline form. When ingots containing above 60 per cent. of silicon are treated with dil. potash-lye, the free silicon dissolves, leaving small, very brilliant, bluish-grey fragments of the monosilicide of sp. gr. 7·31, which, when hot, is attacked by fluorine and chlorine; is superficially oxidized by oxygen at a dull red heat; is attacked by cold nitric acid and aqua regia; but not by hydrochloric or sulphuric acid; and is slowly attacked by alkali hydroxides.

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## § 15. The Hydrogen Compounds of Silicon

Carbon is the dominating element in organic nature, while silicon unquestionably preponderates in the mineral world. The activities of carbon are most marked at comparatively low temp., silicon at high temp. For instance, carbon dioxide can displace silica at ordinary temp., and at high temp. silica can displace carbon

dioxide. Both the carbonates and the silicates are hydrolyzed at ordinary temp., so that aq. soln. of both salts give alkaline hydroxides—carbonic acid is also formed in the one case, and silicic acid in the other. Just as methane can be regarded as the starting-point of that branch of chemistry usually called *organic*, so the analogous silicon hydride can be regarded as the parent of a series of substances called *silico-organic* compounds. In 1863, F. Wöhler [1] emphasized the analogies between the carbon and the silicon compounds, and it would be easy to compile a long list of semblances and another list of dissemblances. For example, the compounds of silicon and hydrogen, the so-called **hydrosilicons,** are in some respects formally analogous with the hydrocarbons, but the analogies cannot really be pushed very far. D. I. Mendeléeff, and J. E. Reynolds argued in favour of the analogies; H. Moissan against. The latter has said:

> Le carbone est seul. Il nous semble, en effet, qu'aucun autre corps simple ne peut lui être comparé, et l'immense développment de la chimie organique semble justifier cette séparation. Malgré il faut bien reconnaitre que les composés dits organiques du silicium ne se rapprochet nullement par leurs propriétés des composés du carbone de même formule.

The number of hydrocarbons is enormous, very few hydrosilicons have been made; the former are usually very stable, the latter unstable. How far does the analogy between silicon and carbon go? Is it only a question of time and trouble for the development of a system of silicon chemistry analogous to that now established in carbon chemistry? Was H. Moissan correct in contesting any deep-seated resemblance between silicon and carbon? According to A. Stock, in spite of the agreement in the maximum valencies of the fundamental affinity units of these two elements, the two elements are distinctly dissimilar. He said that while the affinity of carbon is about equally strong for positive and negative non-metallic elements—hydrogen, oxygen, sulphur, nitrogen, and chlorine—there is an enormous difference between the positive and negative affinities of silicon. The affinity of silicon for oxygen is so predominant that practically all other silicon linkages are broken down by the action of cold water. A further difference is that while the four valencies are symmetrically distributed in carbon, they are not so in silicon. W. Barlow and W. J. Pope emphasized this from the point of view of the valency-volume theory.

The first four members of the homologous series of hydrosilicons, analogous with the methane series of hydrocarbons, have been isolated, and there are indications of the existence of the next two members. P. Lebeau,[2] and A. Besson have obtained evidence of a silicoethylene or silicoethene, $(Si_2H_4)_n$. J. Ogier has described a solid analogous with $(Si_2H_3)_n$; and C. S. Bradley, a yellow solid with a composition, $(Si_2H_2)_n$, analogous with acetylene. There is some doubt about the existence of the unsaturated hydrosilicons. The properties of the analogues methane and silicomethane are totally different. Several substitution products of the silicomethane series have been made in which aliphatic or aromatic carbon radicles have been introduced. F. S. Kipping has also established the existence of dextro- and lævo-rotatory forms of phenylethylpropylbenzylsilicano-sulphonic acid:

$$\begin{matrix} C_2H_5 \\ C_3H_7 \end{matrix} > Si < \begin{matrix} C_6H_5 \\ CH_2.C_6H_4.HSO_3 \end{matrix}$$

The homologous series of saturated hydrides with the general formula $Si_nH_{2n+2}$, is formally analogous with the saturated $C_nH_{2n+2}$ series of hydrocarbons. For example:

| | $Si_nH_{2n+2}$ |
|---|---|
| Silicon tetrahydride, silicane, or silane | $SiH_4$ |
| Disilicon hexahydride, silicoethane, or disilane | $Si_2H_6$ |
| Trisilicon octohydride, silicopropane, or trisilane | $Si_3H_8$ |
| *Tetrasilicon decahydride, silicobutane, or tetrasilane* | $Si_4H_{10}$ |
| Pentasilicon dodecahydride, silicopentane, or pentasilane | $Si_5H_{12}$ |
| Hexasilicon tetradecahydride, silicohexane, or hexasilane | $Si_6H_{14}$ |
| ... ... ... | |

On account of the formal analogy between methane, $CH_4$, and silicon tetrahydride, $SiH_4$, F. S. Kipping proposed the term *silicane* for the latter compound. A. Stock likewise used the termination *-ane* for this series, but he cut out a syllable so that the first member becomes *monosilane* or simply *silane*, and it has the composition $SiH_4$; *disilane*, $Si_2H_6$; etc. In A. Stock's nomenclature, the radicle $SiH_3$, corresponding with methyl, $CH_3$, is called *silyl*; the radicle $Si_2H_5$, *disilyl*; etc. Two $SiH_3$ radicles are designated *bisilyl* or bis-silyl. The bivalent radicle SiO is called *silicyl*. The members of the homologous series $Si_nH_{2n}$, namely, $Si_2H_4$, $Si_3H_6$, $Si_4H_8$, . . ., are distinguished by the termination *-ene*, as is also the case with the formally analogous ethene series of hydrocarbons, $C_nH_{2n}$. For example, $Si_2H_4$ is called *disilene*, $Si_4H_8$, *i.e.* $H_2Si:SiH.SiH_2.SiH_3$ is tetrasilene; etc. Similarly, the members of the homologous series $Si_nH_{2n-2}$, namely, $Si_2H_2$, $Si_3H_4$, $Si_4H_6$, . . ., are distinguished by the termination *-ine*, as is also the case with the formally analogous ethine series of hydrocarbons, $C_nH_{2n-2}$. Thus, silicoacetylene, $Si_2H_2$, becomes *siline*; etc. The radicle $Si_2H_3$ is called *disilenyl*; silicochloroform, $SiHCl_3$, in A. Stock's nomenclature, becomes *trichloromonosilane*; $Si_3Cl_8$, *octochlorotrisilane* or *perchlorotrisilane*; $SiH_3(OH)$, *monosilanol*; $SiH_2(OH)_2$, *monosilandiol*: H.SiO.OH, or *silico-formic acid*, becomes *monosilanic acid*; and $(SiO.OH)_2$, or *silico-oxalic acid*, becomes *disilanic acid*; etc. Compounds with both carbon and silicon have the prefix silico-; thus, $SiH_3.CH_2.CH_3$ is *monosilicopropane*; $Si(C_2H_5)_4$, *silico-nonane*, is called *tetraethylmonosilane*; and $C_3H_7.SiO.OH$, *silicobutyric acid*, is called *propylmonosilanic acid*.

**The preparation of silane.**—The simplest compound of silicon and hydrogen, **silicon tetrahydride,** also called *silicane*, *monosilane*, or *silane*, $SiH_4$, was discovered by H. Buff and F. Wöhler in 1857, and described in their memoir: *Ueber neue Verbindungen des Siliciums* (Göttingen, 1857). They called it *Siliciumwasserstoffgas — siliciuretted hydrogen*. The gas occurred among the products of the action of hydrochloric acid on the impure aluminium silicide which they had made; and it was also made by the electrolysis of an aq. soln. of sodium, ammonium, manganese, or ferrous chloride, using an alloy of aluminium and silicon for the positive pole. In 1858, F. Wöhler made the gas by the action of acids on manganese or magnesium silicide. The gas is spontaneously inflammable in air, and this property can be illustrated by the simple apparatus, Fig. 23, which is filled with dil. hydrochloric acid. Magnesium silicide is dropped into the funnel, and the bubbles of gas rising to the surface of the water in the dish ignite with a flash, and form rings of silicon dioxide.

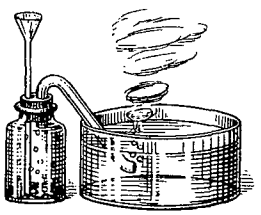


FIG. 23.—The Preparation of Impure Silane.

The gas which is formed by the action of acids on magnesium silicide is a heterogeneous mixture. H. Moissan and S. Smiles say that the gas is essentially hydrogen mixed with 4–5 per cent. of silane, and some silicoethane which can be separated by condensation and subsequent fractional distillation. C. Somiesky found that the 13·7 grms. of silicon in 16·3 per cent. magnesium silicide gave:

| Silicon as | $SiH_4$ | $Si_2H_6$ | $Si_3H_8$ | $Si_4H_{10}$ | Higher Hydrides |
|---|---|---|---|---|---|
| Grms. Si | 1·2 | 0·93 | 0·52 | 0·30 | 0·22—Total 3·17 grms. |

A. Besson also showed that the white solid which is formed is probably silico-oxalic acid. If phosphide or sulphide be present as an impurity in the silicide, the resulting gas will contain hydrogen phosphide or sulphide. H. St. C. Deville and H. Caron obtained the spontaneously inflammable gas by the action of acids on silicized zinc; H. Moissan obtained the gas by the action of acids on lithium silicide; and A. F. Holleman and H. J. Slijper obtained the gas by the action of water on amorphous silicon prepared by using sodium as a reducing agent. The silicon hydride is supposed to have been derived from the sodium silicide present as an impurity.

The preparation of magnesium silicide for making the silicon hydrides has been previously discussed. A. Stock and C. Somiesky noticed that the reaction between the acid and the silicide occurs in two stages. In the cold, there is first a copious evolution of the silicon hydrides, and a brown flocculent substance is formed which decomposes slowly in the cold, and rapidly when warmed, forming the white solid. The yield of silicon hydride is largely determined by the conditions under which the acid attacks the silicide. Hydrochloric acid seems the most suitable because it introduces least disturbing side-reactions. The lower the temp., and the more rapidly the acid attacks the silicide, the better the yield of silicon hydrides, but, since the action of the acid is rather slow in the cold, a temp. of 50° was found to be most suitable for preparing silicon hydride. The yield is also better when the silicide is gradually added to the acid—not too dil.—rather than when the acid is gradually added to a mixture of the silicide and water. For the mechanism of the reaction—*vide* magnesium silicide. A. Stock and C. Somiesky's apparatus for gradually adding the silicide to the acid is illustrated by Fig. 24.

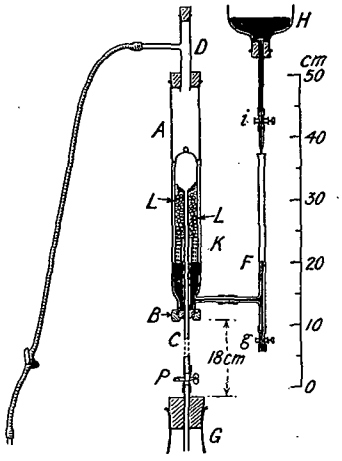



FIG. 24.—Apparatus for gradually Adding Magnesium Silicide to the Acid.

*A* represents a glass tube fitted with rubber-stoppers as shown. The stopper *B* is clamped to the tube to prevent it being forced out by the press. of the mercury. The side-tube *F* is connected to *A* by rubber-tubing, and it is fitted in conjunction with the mercury-holder *H* so that mercury can be introduced into *A* by opening the cock *i*, or removed by opening the cock *g*. A wooden disc *K*, fitted with a glass cylinder *L*, floats on the mercury in the tube *A*; and the wooden disc supports about 100 grms. of granular magnesium silicide contained between the cylinder *L* and the fall-tube *C*, which is 40 cms. long and 0·6 cm. bore. The other end of the tube *C* enters the gas-generating flask. The tube *C* is arranged so that the knocker, of an electric-ball connected with an accumulator, keeps the tube uniformly vibrating. This ensures a steady fall of the magnesium silicide down the fall-tube, as the mercury rising in *C* lifts the

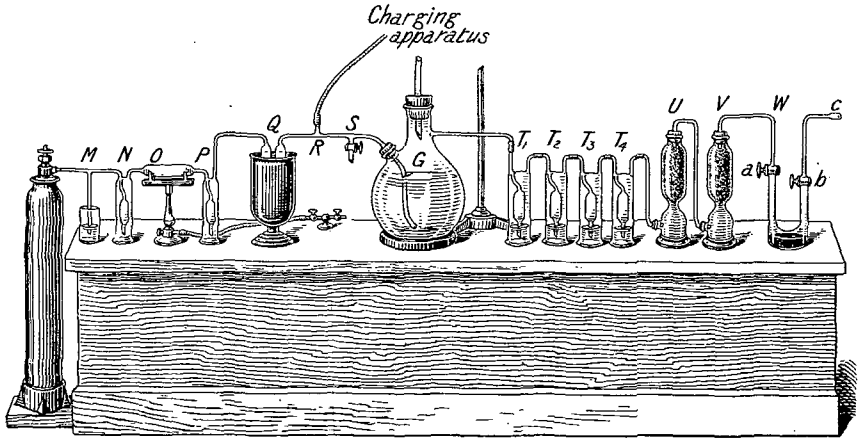



FIG. 25.—Apparatus for the Preparation of the Silicon Hydrides.

silicide above the upper level of *C*. The side tube of *G* is connected by means of a rubber tube with a T-piece fitted to an apparatus supplying hydrogen to the gas-generating flask, *G*.

A four-litre flask, *G*, Fig. 25, containing about 3 litres of a 10 per cent. soln. of hydrochloric acid is fitted to the charging apparatus, Fig. 24, and to the two trains of gas scrubbers shown

in Fig. 25. Hydrogen from a cylinder passes along a tube fitted with a safety-tube *M*; into a sulphuric acid washer *N*; thence through a tube *O* containing platinized asbestos at a dull red-heat; thence through another sulphuric acid scrubber *P*; and then through a U-tube *Q* of about 200 c.c. capacity, cooled with liquid air. The hydrogen then passes *viâ* the bifurcated tube *R* to the charging apparatus, and to the gas-generating flask *G*. A stoppered side-tube *S* allows air-free carbon dioxide to be passed through the apparatus if desired. The hydrogen inlet tube dips below the surface of the acid in the flask *G*; the exit tube is connected by means of rubber with four gas-washers, $T_1$, $T_2$, $T_3$, $T_4$, to remove hydrogen chloride; with a calcium chloride tower *U*; and with a similar tower *V* charged with phosphorus pentoxide and glass-wool. The gas condensing tube, *W*, is cooled by liquid air, and it is fitted with a vacuum stopcock *a*, and ordinary cock *b*, and an end *c* ground to fit the apparatus subsequently employed for fractionating the liquefied gas which collects in *W*. Hydrogen is passed through the whole of the apparatus before any silicide is added to the acid, and it is continued during the two hours which are occupied in adding 100 grms. of silicide to the gas-generating flask *G*. The part *W* is then removed; and the gases are driven from the apparatus by passing a stream of air-free carbon dioxide, *viâ S*.

The condensing tube is now connected with another apparatus fitted with tubes in which it is desired to collect the gas, and so arranged that any tube can be sealed off by the blowpipe flame, or by means of a stopcock. The apparatus is evacuated while the liquefied gases are still cooled by the liquid air. The liquid is then fractioned at the desired temp. The condensed liquid contains about a quarter of the silicon of the added magnesium silicide, in the form of the first six members of the homologous series $Si_nH_{2n+2}$; the remaining silicon appears as silico-oxalic acid. Assuming that the magnesium silicide contains the hemisilicide, the reaction involving the formation of the first member of the series is symbolized: $Mg_2Si+4HCl=2MgCl_2+SiH_4$.

The liquid obtained by cooling with liquid air the gases evolved when magnesium silicide is treated with acid, is distilled in vacuo between −125° and −120°, by using a bath of alcohol rendered viscid by cooling in liquid air. The operation requires 5–10 mins. The fraction can be again condensed by liquid air, and refractioned. The product is silane. The gas can be collected over mercury; 100 grms. of magnesium silicide give 1·6 grms. or 1100 c.c. of silane.

According to C. Friedel and A. Ladenburg, when silico-chloroform, $SiHCl_3$, is treated with absolute alcohol, ethyl silico-orthoformate, $SiH(OC_2H_5)_3$, is produced. The product is also called *triethoxymonosilane*, and when treated with sodium, it furnishes silicane, and silicon tetraethoxide: $4SiH(OC_2H_5)_3 \rightarrow SiH_4+3Si(OC_2H_5)_4$. The function of the sodium is not known.

The triethoxymonosilane is added to a distillation flask—with a bulb 6 cms. diameter and neck 20 cms. long—provided with pieces of sodium. The mixture is gradually warmed over the free flame, and finally heated to the b.p., when about 2 litres of silane will be given off in about 2 hrs. The gas is collected over mercury. The reaction proceeds at lower temp. if potassium be used in place of sodium. Oxygen must be carefully excluded or an explosion may be produced. The gas is almost pure, but not quite free from other silicon hydrides.

O. Ruff and C. Albert found that a small proportion of silane is formed when silicochloroform is decomposed by a soln. of sodium hydroxide. A. C. Vournasos heated an equimolar mixture of anhydrous sodium formate and amorphous silicon, or, better, aluminium silicide, in a graphite tube at 1300°, and obtained a little spontaneously inflammable silicon hydride along with much hydrogen. He also made a little silicon hydride by heating a mixture of sodium formate, sodium hydroxide, and silicon chloride or sulphide in a stream of hydrogen.

As previously indicated, C. Friedel's attempts to induce the direct union of hydrogen and silicon at 1000°, or at the temp. of the electric arc, were not successful. E. Vigouroux, however, said that combination does occur at a white heat if a third element be present; and A. Dufour noted the presence of silane in the gas obtained when hydrogen is passed over silicon heated above its m.p. by the oxyhydrogen flame, or in the electric arc furnace. He said that if an electric discharge be passed through a tube filled with silicane, there is an immediate deposit of amorphous silicon, which, in about half an hour, disappears and is re-formed in the dark space about the cathode, even if the other parts of the tube are cooled to 80°—hence the phenomenon is not due to the distillation of silicon from the hot to the cold

parts of the tube. With arsenic hydride, under analogous conditions, the arsenic is distilled. The equilibrium conditions in the reaction $Si+2H_2 \rightleftharpoons SiH_4$ were studied by H. von Wartenburg. He found that the decomposition is slow below 350°, and it is therefore necessary to employ a catalyst—*e.g.* finely divided nickel. If $p_1$ denotes the partial press. of the silane, and $p$ that of the hydrogen, above 180°, the observed values agree with $\log(p_1/p^2)=8700/4{\cdot}57T-1{\cdot}75 \log T-0{\cdot}7$, where $-8700$ cals. represents the thermal value of the reaction $SiH_4=Si_{solid}+2H_2-8700$ cals. At 380°, for $p$=one atm. the dissociation is almost complete, 99·6 per cent. At 180°, the observed degree of dissociation is 0·90, and at 260°, 0·93, the calculated values are 0·86 and 0·97 respectively. At temp. between 100° and 150°, the press. are higher than those corresponding with the above equation owing to some disturbing influence which H. von Wartenburg suggests may be the reaction: $2SiH_4=Si_2H_4+2H_2$.

**The properties of silane.**—Silane is a colourless gas, and, according to A. Stock and C. Somiesky, a trace of the gas has a faint odour recalling that of stibine, but when more conc., the gas has a repulsive smell, and produces a headache. They found that 83·05 c.c. of the gas at 19° and 750 mm., or 76·62 c.c. at 0° and 760 mm., weigh 0·1103 grm.; consequently, 1 c.c. of the gas at n.p.t. weighs 1·440 mgrms. The density of the gas at 19° is 16·32; and the mol. wt., 32·29. The sp. gr. of the liquid at −185° is 0·68. A. O. Rankine and C. J. Smith found the viscosity of gaseous silane to be 0·0001078 at 8°; 0·0001134 at 15°; and 0·0001436 C.G.S. units at 100°; W. Sutherland's viscosity constant (**1**. 13, 3) is 229; and the mean collision area of the mol. is $0{\cdot}989\times10^{-14}$ sq. cm. J. Ogier first liquefied the gas and found that it remains gaseous at 1° and 200–300 atm. press., and at 0° and 150–200 atm. press., but at −1° it liquefies at 100 atm. press.; at −5°, at 70 atm. press.; and at −11°, at 50 atm. press. The critical temp. is therefore near 0°. K. Adwentowsky and E. Drozdowsky gave −3·5° for the critical temp., and 47·8 atm. for the critical press. H. Moissan found the f.p. to be near −200°; and A. Stock and C. Somiesky found a sharp m.p. for the white solid at −185°. R. Wintgen, and A. Stock and co-workers found the heat of vaporization to be 7·029 Cals., and the molar heat of vaporization at 0° to be 4246·7 cals.; 2782 cals. at $T$° K.; and Trouton's constant, 17·3. The b.p. of the liquid is −112° at 760 mm., and the vap. press. of the liquid is:

| | −160° | −150° | −140° | −130° | −120° | −118° | −114° | −112° |
|---|---|---|---|---|---|---|---|---|
| Vap. press. | 11 | 41 | 102 | 230 | 470 | 530 | 590 | 760 mm. |

R. Wintgen represented the vap. press., $p$, by the equation $\log p=6{\cdot}9961-662{\cdot}6T^{-1}$. Comparing the more important constants of silane and methane:

| | M.p. | B.p. (760 mm.) | Sp. gr. liquid |
|---|---|---|---|
| Methane, $CH_4$ | −184° | −160° | 0·415 (−164°) |
| Silane, $SiH_4$ | −185° | −112° | 0·680 (−185°) |

Silane is quite stable at ordinary temp.; nor is the dry gas decomposed on exposure to light. At a red heat, A. Stock and C. Somiesky found it to be decomposed into silicon and hydrogen; silane, however, is not decomposed so easily as the other silicon hydrides, since when the latter are sent at a low press. through a quartz tube at a dull red heat, some silane is formed; this is also the case when silicochloroform is heated: $4SiHCl_3=SiH_4+3SiCl_4$. J. Ogier said that silane is completely decomposed into its constituents at 400°; the reaction, however, is reversible as indicated by H. von Wartenburg—*vide supra*, where the observations of A. Dufour, and E. Vigouroux are described. J. Ogier found that silane is decomposed by the electric discharge, forming hydrogen, amorphous silicon, and a yellow solid which takes fire on percussion, or when heated in air; it takes fire in an atm. of chlorine; it is but little affected by water; and it is insoluble in alcohol, ether, benzene, chloroform, silicochloroform, and silicon tetrachloride. It contains 2–5 per cent. of silicon, and J. Ogier represented its composition by the

formula $(Si_2H_3)_n$; there is, however, nothing in the analyses to justify its recognition as a chemical individual. J. Ogier also found that if a mixture of equal vols. of silane and nitrogen be sparked, ammonia and a yellow solid are formed; the latter contains nitrogen, because it gives ammonia when treated with water. J. Ogier found the heat of combustion of one gram-eq. of silane in oxygen to be 324·3 Cals., which is less by 24·8 Cals. than the heat of combustion of its constituents; hence he argued that the heat of formation of silane from its elements is 24·8 Cals.—note H. von Wartenburg's measurement above—the heat of formation of methane is 22 Cals.

According to H. Moissan and S. Smiles, the spontaneous inflammability of silane is due to the presence of minute proportions of other silicon hydrides. C. Friedel and A. Ladenberg said that the purified gas at ordinary temp. and press. is not spontaneously inflammable, but it will inflame by slightly raising the temp., or lowering the press.; the purified gas inflames in air if bubbled through warm mercury, or if a hot knife-blade be held in the gas bubbling through cold mercury. The gas inflames if air be bubbled into the purified gas at 100–150 mm. press. A. Stock and C. Somiesky said that small bubbles of the purified gas do not usually ignite in air, but larger bubbles sometimes fire spontaneously with the production of brown flakes; if other silicon hydrides are present, the gas always fires spontaneously in air. To avoid accidents, air should not be allowed to enter a vessel containing silane. K. Heumann said that the spontaneously inflammable gas can be preserved over mercury or over air-free water; but if the water has air in soln., the gas becomes foggy, and loses its spontaneous inflammability. A. Stock and C. Somiesky found that silane is slowly decomposed by water: $SiH_4+2H_2O=SiO_2+4H_2$. After 24 hrs.' exposure at 20° between 5 and 20 per cent. of the gas was decomposed; in about 30 days, decomposition was complete. K. Heumann said that each bubble of the spontaneously inflammable gas entering the atm. bursts explosively into flame, and the white flame emits clouds of silica in vortex rings—Fig. 25; silica and water are formed. The gas issuing from a tube into the atm. burns with a white luminous flame, which in sunlight casts a well-defined shadow. According to H. Buff and F. Wöhler, if cold porcelain be held in the flame, a brown or brownish-yellow film is deposited; and if the tube conveying the gas is heated, a dark brown mirror of amorphous silicon is deposited on the walls of the tube and the issuing gas is no longer spontaneously inflammable. A bubble of air, oxygen, or chlorine introduced into the gas causes a flash of light.

A. Stock and C. Somiesky have studied the oxidation of the silicon hydrides by air, and oxygen. They moderated the violence of the reaction by slowly adding the oxidizing agent to an excess of the hydride under reduced press. and between −70° and −140°. The products of the reaction consist of unchanged hydride (including $SiH_4$ during the oxidation of $Si_2H_6$), nitrogen (and argon) when air or artificial mixtures of nitrogen and oxygen are used (the oxygen is invariably consumed completely), a considerable quantity of free hydrogen, water, and, in certain cases, small quantities of volatile silicon compounds formed during the oxidation. In addition, there is formed a colourless, non-volatile residue which generally contains brown particles, and consists partly of compact crusts formed near the point of entry of the oxidizing agent, partly of a fog in the interior of the reaction vessel, and partly of a uniform, vitreous deposit on the whole wall of the vessel. The colourless components are readily dissolved by very dil. soln. of alkali, and appear to consist of substances such as polymeric prosiloxan, $(SiH_2O)_x$, silicoformic anhydride, $[(SiHO)_2O]_x$, etc.; the brown components contain silicon and possibly highly condensed silicon hydrides poor in hydrogen; they appear to be formed chiefly when the action is accompanied by considerable local heating and a deficiency of oxygen. In spite of variations in the temp. and in the degree of dilution of the oxygen, the reaction proceeds moderately uniform. The oxidation proceeds beyond the stage $SiH_3.OH$, since the presence of $(SiH_3)_2O$ in more than traces could not have escaped detection. The main derivatives of silicon produced during

the oxidation are the polymeric forms of $SiH_2O$, OH.SiHO, $SiO(OH)_2$, etc. The water is supposed to be produced from hydroxylated silicon compounds which become decomposed as the temp. is allowed to become atmospheric, thus $SiH_2(OH)_2 \rightarrow SiH_2O+H_2O$. In those cases in which elementary silicon is deposited, a part of the liberated hydrogen is doubtless due to the thermal decomposition of silane. Its production is not due to a secondary hydrolysis of silane, or its primary oxidation products by water formed during the reaction; but it is rather a primary product of the oxidation: $SiH_4+O=SiH_2O+H_2$; a reaction of this type is unusual and apparently due to the preponderating affinity of silicon for oxygen. The production of hydrogen accounts for the peculiarities observed during the combustion of silicon hydrides, which differs markedly in its violence from similar cases of spontaneous ignition such as the quiet inflammation of phosphorus hydride. The process consists of the following successive steps: inception of oxidation, liberation of hydrogen, formation of a mixture of oxygen and hydrogen, and ignition of the latter when the temp. has been raised sufficiently by the heat of the reaction.

The gas burns in chlorine or in chlorides, which easily part with their chlorine—*e.g.* carbonyl chloride, antimony pentachloride, tin tetrachloride, etc. According to R. Mahn, bromine forms with silane a mixture of $Si_2H_2Br_4$ and $SiBr_4$; G. Buchner said that silane mixed with hydrogen reacts with iodine, forming silicon tetraiodide, and silico-iodoform; iodine chloride reacts feebly and produces the hexachloride, $Si_2Cl_6$, and phosphorus tri- and penta-chlorides, antimony pentachloride, and tin tetrachloride react similarly. T. Wilm and G. Wischin found that carbonyl chloride does not form an acid chloride, but parts with its chlorine. H. Buff and F. Wöhler observed no change when silane is brought in contact with nitrous oxide, nitric oxide, ammonia, dil. sulphuric or hydrochloric acid. A. Stock and C. Somiesky also observed no reaction between silane and dry ammonia, or conc. sulphuric acid. H. Buff and F. Wöhler stated that silane reacts with a soln. of cupric sulphate precipitating what they regarded as brown copper silicide, and possibly some copper and silica; that it does not react with soln. of lead acetate or hydrochloroplatinic acid; that it precipitates palladium free from silicon from soln. of palladous chloride; and that with soln. of silver nitrate, grey silver and black silver silicide are precipitated. G. Buchner stated that with neutral or acid soln. of silver nitrate, a yellowish-brown precipitate is first formed which then becomes black. He represents the reactions: $SiH_4+8AgNO_3=Ag_4Si.4AgNO_3+4HNO_3$; followed by $Ag_4Si.4AgNO_3+4H_2O=8Ag+H_4SiO_4+4HNO_3$. The more stable methane does not reduce like silane. Many of the less stable hydrides—like silicon hydride, hydrogen sulphide, and hydrogen iodide—reduce in virtue of the hydrogen liberated during their decomposition; other hydrides reduce by the direct oxidation of their elements. Thus, with arsenic hydride and silver nitrate, arsenious acid and silver are formed during reduction. H. Buff and F. Wöhler found that soln. of alkali hydroxides decompose the gas in the cold; and, according to A. Stock and C. Somiesky, soln. of alkali hydroxides decompose the gas more rapidly than does water; an alkali silicate is produced: $SiH_4+2NaOH+H_2O=Na_2SiO_3+4H_2$. At room temp. the reaction is complete in 2 hrs. with a 33 per cent. lye; and in 24 hrs. with a 10 per cent. lye.

A small quantity of an aq. soln. of potassium hydroxide was introduced into a eudiometer *containing 2·8 c.c. of silane confined over mercury; 11·1 c.c. of hydrogen* were formed. Hence, one vol. of gas gives 3·96 c.c. of hydrogen. Within the limits of experimental error, this agrees with the empirical formula $SiH_4$; and, since one litre of the gas at n.p.t. weighs 1·4538 grms., the mol. formula may be taken as $SiH_4$.

A. O. Rankine and C. J. Smith discussed the electronic structure of silicane. With dry sodium or potassium hydroxide, a vigorous reaction occurs, and the surface of the hydroxide liquefies. Intermediate products are formed which in contact with water rapidly decompose into hydrogen and the alkali silicate. There is no apparent reaction with alcohol, ether, benzene, carbon disulphide, chloroform, or carbon tetrachloride. The organic liquids dissolve a little of the gas.

**Silicoethane.**—H. Moissan and S. Smiles [3] found that when magnesium silicide reacts with hydrochloric acid, hydrogen containing about 5 per cent. of silicon hydrides is evolved. If the gases be cooled by liquid air or oxygen, the silicon hydrides solidify, and by allowing the solid to liquefy, and fractionating the liquid, **silicoethane,** *disilicane*, or *disilane*, $Si_2H_6$, is obtained as a mobile, colourless liquid. P. Lebeau made the gas in a similar manner. H. Moissan obtained the same compound by the action of hydrochloric acid on lithium silicide. According to A. Stock and C. Somiesky, the liquid which remains after removing most of the silane from the gases obtained in their method of preparing silane (*q.v.*), when distilled between —120° and —115° for about 2 hrs. furnishes a mixture of silane and disilane. The silane can be removed by re-fractionation between —100° and —105°. The yield of disilane is 400 c.c., or 1·1 grms. per 100 grms. of magnesium silicide. A. Stock and C. Somiesky tried unsuccessfully to make silicoethane by the action of alkali metals on monochlorosilane. There are differences in the properties of the products as described by H. Moissan and S. Smiles, and by A. Stock and C. Somiesky, due, say the latter, and also P. Lebeau, to the contamination of the former's product with higher silicon hydrides. For instance, H. Moissan and S. Smiles say that silicoethane at ordinary temp. is a colourless liquid boiling at 52°; but A. Stock and C. Somiesky say that it is a colourless gas, which furnishes a liquid boiling at a much lower temp. Silicoethane can be collected over mercury without perceptible decomposition; and it smells like silane, but is more repulsive. The density of the gas at 21° is 31·75 (theory, 37·1), and the mol. wt. is 64·0 (theory, 62·6); H. Moissan and S. Smiles obtained a density of 2·37 (air unity) at 100°. A. Stock and C. Somiesky found the sp. gr. of the liquid to be 0·686 at —25°; and

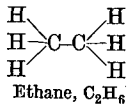
| | —118° | —110° | —90° | —61·15° | —46·8° | —37° | —22° | —15·7° |
|---|---|---|---|---|---|---|---|---|
| Vap. press. | 1 | 2 | 10·5 | 81 | 180 | 290 | 550 | 725 mm. |

R. Wintgen represented the results by log $p$=72578—1133·6$T^{-1}$. The b.p. is —15° at 760 mm.; P. Lebeau gave —7°, and H. Moissan and S. Smiles, +52°, and they said that the m.p. is —138°, while A. Stock and C. Somiesky gave —132·5°. R. Wintgen, and A. Stock and co-workers found the molar heat of vaporization. The mol. heat of vaporization at 0° is 5443·1 cals., and at 5111 cals.; and Trouton's constant, 19·8. Disilane does not decompose at ordinary temp., but at about 300°, it is rapidly decomposed into a liquid and a brown solid which decomposes in contact with alkali-lye with the evolution of hydrogen. The decomposition of disilane at about 500° resembles the cracking of hydrocarbons; in addition to silicon, large vols. of silane are formed, the reaction being dependent on the reducing action of primarily liberated hydrogen on disilane. The higher hydrides are not produced in sufficient quantity to make the method a practicable process of preparation. At higher temp., the fission of the disilane occurs, and hydrogen predominates. Disilane is more stable than the corresponding diborane. H. Moissan and S. Smiles say that when the gas is sparked under reduced press. for 15 mins. it is decomposed into amorphous silicon and hydrogen; the silicon appears as a reddish deposit on the walls of the containing tube, and, added A. Stock and C. Somiesky, the decomposition by sparking is slower than is the case with diborane. Comparing the chief physical properties of silicoethane, diborane, and ethane:

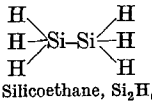
| | M.p. | B.p. (670 mm.) | Sp. gr. liquid |
|---|---|---|---|
| Ethane, $C_2H_6$ | —171·4° | —89·3° | 0·45 |
| Diborane, $B_2H_6$ | —169° | —87° | — |
| Silicoethane, $Si_2H_6$ | —132·5° | —15° | 0·69 |

H. Moissan and S. Smiles say that when silicoethane is exposed to air at ordinary temp., it inflames spontaneously, burning brilliantly and explosively; P. Lebeau said that the spontaneous inflammability is probably due to the presence of silicoethene, $Si_2H_4$, but A. Stock and C. Somiesky state that highly purified silicoethane inflames spontaneously in air. The introduction of air into a flask containing silicoethane produces a vigorous explosion with the separation of white and brown

flecks. Like silicane, silicoethane is slowly decomposed by water at room temp.; in 24 hrs., 20–25 per cent. of the gas was decomposed, and in 13 days only 3 per cent. remained undecomposed. H. Moissan and S. Smiles say that silicoethane is slightly soluble in water, and is slowly oxidized thereby; and, added A. Stock and C. Somiesky, although the gas is not appreciably soluble in water, it is possible that the decomposition in contact with water occurs through the formation of an intermediate product soluble in water, because bubbles of hydrogen are developed in the water during the reaction. They also found that this reaction is largely conditioned by the alkalinity of the glass apparatus, for in quartz vessels, or with slightly acidified water practically no change takes place during several days. According to H. Moissan and S. Smiles, when the gas is bubbled through warm bromine-water, each bubble becomes coated with a layer of silica; nitric acid produces a similar effect; conc. hydrochloric acid is without action; and, added A. Stock and C. Somiesky, dry ammonia and dry hydrogen chloride have no appreciable action in a short time. Conc. sulphuric acid has no action during a short exposure, but, added H. Moissan and S. Smiles, the gas is dried, and it then explodes more violently in contact with air. Silicoethane explodes violently in contact with sulphur hexafluoride; and it is soluble in ethyl silicate. A. Stock and C. Somiesky found silicoethane to be fairly soluble in alcohol, and the soln. to develop slowly a gas, most of the silicoethane being given off unchanged when the alcoholic soln. is dil. with water. Silicoethane is readily soluble in benzene and carbon disulphide—if the silicoethane be mixed with hydrogen they can be separated by the latter solvent. If air has access to the soln. of silicoethane in carbon disulphide spontaneous ignition occurs. H. Moissan and S. Smiles found that silicoethane explodes violently when mixed with carbon tetrachloride, forming hydrogen chloride, carbon, and silicon; and A. Stock and C. Somiesky said that silicoethane reacts vigorously, often with incandescence, when in contact with carbon tetrachloride or chloroform, forming a brown solid. Silane and silicoethane thus behave differently in contact with these reagents. H. Moissan and S. Smiles found that silicoethane is attacked by a soln. of potassium hydroxide liberating hydrogen, and forming an alkali silicate; it reduces aq. soln. of ferric chloride to ferrous chloride, forming a brown precipitate insoluble in hydrochloric acid: a dil. soln. of indigo is decomposed, yielding a green precipitate; acid soln. of both potassium dichromate and permanganate are reduced, and in the latter case, brown manganese oxide is precipitated; soln. of silver nitrate, and auric chloride are reduced; and with mercuric chloride, mercurous chloride is formed. A. Stock and C. Somiesky said that with soln. of cupric sulphate, a copper hydride seems to be precipitated; and soln. of nickel sulphate, chromic chloride, and lead nitrate are not changed. The properties of silicoethane thus differs radically from those of ethane, but resemble in many respects those of silicane. The difference between the hydrocarbon and the hydrosilicon depend on (i) the smaller affinity of hydrogen for silicon than for carbon; and (ii) the readiness with which an oxygen atom can be interposed between the two silicon atoms, but not the two carbon atoms. It is, however, probable that silicoethane and ethane are constituted alike:



Ethane, $C_2H_6$



Silicoethane, $Si_2H_6$

**Silicopropane.**—In A. Stock and C. Somiesky's method of preparing silane, and silicoethane, the residue remaining after the separation of most of the silicoethane from the condensed gas obtained from the action of hydrochloric acid on magnesium silicide, is fractioned at −60°, and re-fractioned at −70°. The product is **silicopropane,** *trisilicane*, or *trisilane*, $Si_3H_8$; the yield is 0·5 grm. for 100 grms. of magnesium silicide. Analysis corresponds with the formula $Si_3H_8$. One c.c. of the gas at n.p.t. weighs 4·18 mgrms. The vap. density at 24° is 46·5 (theory,

46·1). The mol. wt. is 93·7 (theory, 93). The sp. gr. of the liquid is 0·743 at 0°/4°. The liquid freezes to a crystalline solid in liquid air; and it melts at −117·4°. R. Wintgen, and A. Stock and co-workers found the molar heat of vaporization to be 7·13 Cals. The mol. heat of vaporization at 0° is 5443·1 cals.; and Trouton's constant is 20·2. They also found:

| | −70° | −50° | −30° | −10° | −0° | 15° | 40° | 52·6° |
|---|---|---|---|---|---|---|---|---|
| Vap. press. . | 1 | 4 | 18 | 44 | 95 | 180 | 490 | 754 mm. |

The vap. press., $p$, is represented by R. Wintgen by $\log p = 7{\cdot}6764 - 1559{\cdot}2T^{-1}$. The b.p. at 760 mm. is 53°. The vap. press. varies a little with the age of the sample on account of a slight decomposition. Fresh samples at 0° have a vap. press. of 95·5 mm. Comparing the chief physical properties of propane and silicopropane:

| | M.p. | B.p. (760 mm.) | Sp. gr. liquid |
|---|---|---|---|
| Propane, $C_3H_8$ . . . . | below −195° | −45° | 0·54 |
| Silico-propane, $Si_3H_8$ . . . | −117·4° | +53° | 0·743 |

Silicopropane is a light, mobile, colourless liquid much less stable than either silicane or silicoethane. After 18 days' storage at the room temp., a specimen, previously pure, contained less volatile silicon hydrides. Similar relations obtain between diborane and tetraborane. When heated, silicopropane decomposes into silicon and hydrogen, with silicane as an intermediate product. In air, silicopropane immediately inflames with a loud detonation and burns with a clear flame, forming brown and white solids. Silicopropane reacts slowly with water with the development of hydrogen: $Si_3H_8 + 6H_2O = 3SiO_2 + 10H_2$. After 24 hrs.' contact with water, 18 per cent. had decomposed so that the velocity of the reaction is nearly the same as with silicane and silicoethane. Likewise with soda-lye, silicopropane decomposed rapidly; with 33 per cent. lye, 90 per cent. had decomposed in 10 mins. and the calculated quantity of hydrogen: $Si_3H_8 + 6NaOH + 3H_2O = 10H_2 + 3Na_2SiO_3$, was obtained. Carbon tetrachloride acts more vigorously on silicopropane than on silicoethane. The explosive action noted by H. Moissan and S. Smiles, and A. Stock and co-workers was observed only in the presence of oxygen: the merest traces of oxygen suffices to induce the change. A. Stock and P. Stiebeler represent the reaction with chloroform by $Si_3H_8 + 4CHCl_3 = Si_3H_4Cl_4 + 4CH_2Cl_2$, and $Si_3H_8 + 5CHCl_3 = Si_3H_3Cl_5 + 5CH_2Cl_2$, at 50° in the presence of aluminium chloride. Small quantities of methane, and methyl chloride are also produced.

**Silicobutane.**—The liquid residue remaining after the removal of the silicopropane from the liquid condensed from the gases evolved by the action of hydrochloric acid on magnesium silicide, is distilled at a temp. of −25°, and the condensed product re-fractioned at −35°. The product is **silicobutane,** *tetrasilicane*, or *tetrasilane*; the yield from 100 grms. of magnesium silicide is 0·3 grm. Analyses agree with the formula $Si_4H_{10}$. The vap. density is 61·0 (theory for $Si_4H_{10}$, 61·2); the mol. wt. is 122·9 (calculated 123·3). One c.c. of the gas at 0° and 760 mm. weighs 5·48 mgrms. The sp. gr. of the liquid is 0·825 at 0°/4°. The m.p. of the solid is about −90°. R. Wintgen, and A. Stock and co-workers found the molar heat of vaporization to be 9·18 Cals.; and

| | −30° | −20° | −15° | −5° | 0° | +10° | 20° | 25° |
|---|---|---|---|---|---|---|---|---|
| Vap. press. . | 0·8 | 1·0 | 2·8 | 5·8 | 7·8 | 14·0 | 24·0 | 33·0 mm. |

At 0°, the vapour press. of a freshly prepared sample is 7·5 mm. R. Wintgen represented the vap. press., $p$, by $\log p = 8{\cdot}2479 - 2008{\cdot}2T^{-1}$. The b.p. at atm. press. is 109°. The physical properties of $n$-butane, tetraborane, and silicobutane are:

| | M.p. | B.p. (760 mm.) | Liquid sp. gr. |
|---|---|---|---|
| $n$-Butane, $C_4H_{10}$ . . . . | −135° | 0·6° | 0·60 |
| Tetraborane, $B_4H_{10}$ . . . | −112° | 16° | — |
| Silicobutane, $Si_4H_{10}$ . . . | −90° | 109° | 0·825 |

Silicobutane is a colourless liquid, which very closely resembles silicopropane

in its properties. It decomposes fairly rapidly at room temp., and the vap. press. rises quickly on standing. The vap. changes the surface tension and meniscus of mercury. The gas decomposes into silicon and hydrogen when heated—silane is an intermediate product. In water, drops of the liquid acquire a turbid film, and hydrogen is slowly developed. It inflames with a loud detonation when exposed to the air. Silicobutane reacts like silicopropane with chloroform and carbon tetrachloride.

The liquid remaining after the removal of the series from silicane to silicobutane probably contains a small quantity of **silicopentane,** *pentasilicane,* or *pentasilane,* $Si_5H_{12}$, and a still smaller quantity of **silicohexane,** *hexasilicane,* or *hexasilane,* $Si_6H_{14}$. The former has a vap. press. of about 1·5 mm. at 0°, and the latter about 1 mm. No evidence of higher members of the series than $Si_6H_{14}$ was observed. The penta- and hexa-silanes appear to behave like the lower homologue towards air, water, alkalies, etc., and also when heated. The higher members of the series are less stable to light and appear to decompose according to the scheme: $Si_5H_{12} \rightarrow 2(SiH)_x + Si_2H_6 + SiH_4$. The unsaturated hydride, $(SiH)_x$, cannot be obtained in a volatile form of low mol. wt. If obtained by the autodecomposition of the silicoparaffins, by the action of the silent electric discharge on these compounds, by the action of acids on silicides, or by the action of sodium amalgam on silicoparaffins and their chlorides, it always appears in the solid, yellow, associated form; its composition varying between $(SiH)_x$ and $(SiH_{1\cdot3})_x$.

In general, it may be said that silicon has a much smaller affinity than carbon for hydrogen; and silane, the most stable member of the series, is much less stable than methane. The former decomposes at 300°–400°, the latter at very much higher temp. The silane series of hydrosilicons are readily oxidized, and even take fire spontaneously in air; as also do other heavily hydrogenated compounds of silicon—*e.g.* monochlorosilane, $SiH_3Cl$. The members of the silicane series are decomposed by water, and more rapidly by soln. of alkali hydroxides. Similar remarks apply to the organic derivatives of the type $SiHR_3$, where *R* denotes a hydrocarbon—alkyl or aryl—radicle; although C. Pape's [4] tripropylsilane, $SiH(C_3H_7)_3$, is not attacked by alkali-lye. A few alkyl or aryl derivatives of the type $SiHR_3$ are known, but none corresponding with $SiH_2R_2$ or $SiH_3R$ have been made. About fifty tetra-alkylsilanes have been made from silicon tetrachloride or silicochloroform by treatment with magnesium alkyl halides. They range from the simple tetramethyl silane, $Si(CH_3)_4$, to the complex $Si(C_2H_5)(C_3H_7)(C_6H_5)(C_7H_7)$. These compounds are inflammable liquids resembling ligroïn or petroleum; their volatility differs but slightly from that of the corresponding hydrocarbons. They have been halogenated, sulphonated, nitrated, etc. A. Bygdén found the alkyl-silanes to be fairly stable liquids even in contact with water and alkali-lye; they show an asymmetric structure and optical activity; their rotatory power, however, is small in comparison with that of the corresponding hydrocarbons. The tetra-aryl derivatives of high mol. wt. are obtained more readily than the corresponding hydrocarbons—*e.g.* $Si(C_6H_5)_4$ is easily made, whereas M. Gomberg showed that triphenylmethane, $CH(C_6H_5)_3$, is formed under conditions where tetraphenylmethane, $C(C_6H_5)_4$, might have been anticipated. The fact that tetraphenylsilane, $Si(C_6H_5)_4$, and tetrabenzylsilane, $Si(C_7H_7)_4$, can be readily prepared, while tetraphenylmethane, $C(C_6H_5)_4$, can be made only with difficulty, and tetrabenzylmethane, $C(C_7H_7)_4$, is not known, is taken to show that while the affinity of silicon for hydrogen is less than that of carbon, the affinity of silicon for the hydrocarbon radicles is greater than that of carbon. The analogy between the silicon and carbon alkyl and aryl derivatives is perhaps not surprising when it is remembered that carbon *per se* exercises a preponderating influence on these compounds. Corresponding compounds with bismuth, tin, and lead are known.

Compounds with chains of silicon atoms are usually far less stable than the corresponding carbon compounds, and this the more, the longer the chain. Several derivatives of silico-ethane are known—thus, A. Bygdén made *hexamethylsilico-*

*ethane*, $Si_2(CH_3)_6$; C. Friedel and A. Ladenburg, *hexaethylsilicoethane*, $Si_2(C_2H_5)_6$; W. Schlenk and J. Renning, *hexaphenylsilicoethane*, $Si_2(C_6H_5)_6$; and G. Martin made *hexaethoxysilicoethane*, $Si_2(OC_2H_5)_6$. The more complex halides of silicon, or silicon compounds with hydrocarbon radicles, are rather more stable than the corresponding hydrogen compounds. The silicoethane derivatives with organic radicles, hexamethylsilicoethane, and hexaethylsilicoethane, are made from silicon hexachloride by treatment with the respective magnesium alkyl halides; and hexaphenylsilicoethane is made by the same reaction and by treating triphenylchlorosilane, $(C_6H_5)_3SiCl$, with sodium; while hexaethoxysilicoethane is made by treating silicon hexachloride with alcohol.

**The unsaturated hydrosilicons.**—The evidence of the existence of unsaturated derivatives of silicon—*i.e.* compounds with double-linked or triple-linked silicon atoms—is very doubtful. P. Lebeau [5] reported that when the mixed gases formed by the action of hydrochloric acid and magnesium silicide are liquefied, and the liquid fractioned, the first product is a gaseous mixture of silane and silicoethane, and a colourless liquid. The liquid explodes violently in contact with air, and burns with a bright flame. He said that the probable formula is $Si_2H_4$, corresponding with *silicoethene*, or *silicoethylene*. A. Stock and C. Somiesky consider this a mistake; they obtained no evidence of such a compound in their study of the products of the action of hydrochloric acid on magnesium silicide. This is confirmed by A. Besson and L. Fournier's failure to prepare the corresponding chloride, $Si_2Cl_4$. L. Wöhler and F. Müller regarded the gas formed by the action of dil. acids on calcium monosilicide to be silicoethylene, formed in accord with the equation: $Ca:Si:Si:Ca+4HCl=2CaCl_2+H_2:Si:Si:H_2$. W. Schlenk, however, did make *diphenylsilicoethylene*, $(C_6H_5)_2Si:CH_2$, but the corresponding $(C_6H_5)_2C:CH_2$ has not been obtained. J. Ogier's analysis of the product obtained by sparking silicane corresponded with $(Si_2H_3)_n$, but he was probably dealing with a mixture. Similar remarks apply to C. S. Bradley's alleged synthesis of what has been called a polymerized *silicoacetylene*, $(Si_2H_2)_n$, by treating calcium silicide with hydrochloric acid. The yellow crystalline solid is not explosive, and is stable at ordinary temp.; when heated in air, it oxidizes to silica, and when heated in a closed tube, hydrogen is developed and silicon remains. A soln. of sodium hydroxide dissolves it with the development of hydrogen. The alleged silico-acetylene is not formed when strontium and barium silicides are treated in a similar way. The yellow solid is more probably analogous with F. Wöhler's *silicone*, $Si_3H_3O_2$—*vide infra*. For $(SiH)_x$, *vide supra*.

In 1824, J. J. Berzelius reported the formation of a solid silicon hydride by the action of potassium on silicon tetrafluoride, and subsequently washing the product with water, and cold aq. hydrofluoric acid to remove the silica. He assumed that the hydrogen liberated by the action of the excess of potassium on water reacted with the silicon, forming the hydride. He said the substance burns with great splendour when quickly heated to redness in air; and it burns still more brilliantly in oxygen; in neither case is the whole of the silicon oxidized because a protective layer of silica is produced. During the combustion, water is produced even when the hydride has been dried in vacuo at a temp. approaching redness. If this silicon hydride is heated in a covered crucible, a feeble flame is emitted when the cover is taken off. When slowly heated to incipient redness in an open crucible, and then to whiteness in a covered crucible, hydrogen is expelled, and a residuum of silicon, mixed with a little silica, remains. When treated with hot hydrofluoric acid, or potash-lye, a small quantity of silica is dissolved and hydrogen gas evolved. H. St. C. Deville doubted the existence of a hydrosilicon such as that described by J. J. Berzelius. More probably the product was related with F. Wöhler's oxyhydrides.


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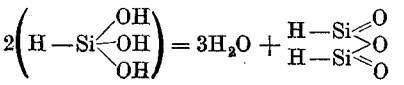
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## § 16. Silicon Suboxides and Oxyhydrides—Siloxanes

The white product, resembling mother-of-pearl, obtained by the action of light and water on the yellow form of silicon was called by F. Wöhler [1] **leucone**—λευκός, white. The change occurs slowly in darkness. F. Wöhler assumed that the silicon decomposed the water, and formed leucone; his analyses of the product ranged between $Si_4H_5O_5$ and $Si_4H_3O_5$. O. Hönigschmid's analyses of the white product obtained by the action of air and light as well as of water on silicon, after washing with alcohol and ether, and drying in vacuo over sulphuric acid, corresponded with $Si_3H_3O_4$; it had a similar crystalline form to calcium silicide. A. Geuther made a substance with a composition $H_2Si_3O_5$, by the action of hydrochloric acid on magnesium silicide. A. Michaelis considered it to be silicoformic anhydride, C. Winkler supposed it to be different. D. I. Mendeléeff gave $SiH_4O_3$ for the composition of leucone, and he regarded it as **trihydroxysilane,** $SiH(OH)_3$, which he assumed to be the first product of the hydrolysis of trichlorosilane or silicochloroform, $SiHCl_3$, a reaction which he symbolized: $SiHCl_3+3H_2O=SiH(OH)_3+3HCl$. He continued: This hydrate, like the corresponding hydrate of phosphorus or carbon, does not remain in this state of hydration, but loses a portion of its water. The carbon hydrate, trihydroxymethane, $CH(OH)_3$, loses water and produces formic acid, H.CO.OH; but trihydroxysilicane loses a still greater proportion of water and leaves $Si_2H_2O_3$, which must be an anhydride, two remaining hydrogen atoms being left from the silane:



This product is, therefore, called **silicoformic anhydride,** HSiO.O.OSiH. H. Buff and F. Wöhler discovered this compound in 1857 ; they showed that it is formed as a voluminous white powder when silicochloroform, silicobromoform, or silicoiodoform is hydrolyzed by water at 0° : $2HSiCl_3+3H_2O=6HCl+Si_2H_2O_3$. C. Friedel and A. Ladenburg recommend the following mode of preparation :

Silicochloroform, boiling between 34° and 35°, is gently distilled into water at 0°. The end of the tube dipping in water has a funnel-shaped end so as to prevent its being blocked by the formation of the solid. As soon as the first bubble has traversed the liquid, the white insoluble compound appears ; and when the operation is ended, the product can be readily separated by filtration, washed with iced-water, pressed between folds of filter-paper, and dried in vacuo over sulphuric acid. After these operations, the product can be dried at 150° without decomposition.

L. Gattermann prepared this compound in a similar manner, but washed it with iced-water, alcohol, and ether. C. Winkler said that the compound is formed by the action of a soln. of ammonium chloride on magnesium silicide—the product is coloured brown owing to the presence of amorphous silicon. F. Wöhler showed that this substance is probably present in the residue which remains after dissolving grey cast-iron, or manganese silicide in hydrochloric acid. According to L. Cambi, silicoformic anhydride is produced when silicon sulphide, SiS, in small pieces is treated with iced-water free from air in an atm. of hydrogen. The product can be washed with cold water, alcohol and ether. He said that *silicoformic acid*, H.SiO.OH, is probably formed first : $SiS+2H_2O=H_2S+H.SiO.OH$, and added : The formation of silicoformic acid is analogous to that of formic acid, which can be obtained from chloroform, carbon monoxide, or compounds containing bivalent carbon, such as the carbylamine derivatives, C : NR ; this analogy can be extended to the corresponding germanium compounds.

H. Buff and F. Wöhler found that silicoformic anhydride is a voluminous, amorphous, white powder which sinks in ether, and floats in water. It is not changed at 300°, but when heated more strongly, hydrogen and silane are evolved, and a mixture of brown amorphous silicon and silica remains. L. Cambi said that in vacuo, at 400°, it splits up into hydrogen, silicon, and silica. O. Hönigschmid said that when leucone is heated in vacuo, the brownish-yellow crystalline residue which remains has the composition of *silicon tetratritoxide*, $Si_3O_4$, and it dissolves in alkali-lye, and in hydrofluoric acid with the evolution of hydrogen. H. Buff and F. Wöhler stated that when silicoformic anhydride is heated in air, it glows with a phosphorescent light, and is finally oxidized to silica ; when heated in oxygen, it burns brilliantly ; when heated in hydrogen, the evolved gas contains silicon hydride ; it is not changed by conc. nitric acid or the other mineral acids, but with hydrofluoric acid, it is vigorously dissolved, and hydrogen, etc., is evolved. L. Cambi said that water oxidizes it at ordinary temp. and hydrogen is evolved : $Si_2H_2O_3+H_2O=2SiO_2+2H_2$. H. Buff and F. Wöhler found that aq. ammonia, and alkali hydroxides or carbonates dissolve it giving off hydrogen, and forming an alkali silicate : $Si_2H_2O_3+4KOH=2K_2SiO_3+H_2O+2H_2$. D. I. Mendeléeff said : " The compound has no acidic properties and there are no acid hydrates of silicon, corresponding with formic acid, which give salts when acted on by alkalies. It must not, however, be forgotten that when formic acid is heated with an alkali, a carbonate and hydrogen are formed: $CH_2O_2+2KOH=K_2CO_3+H_2O+H_2$. Consequently, a similar decomposition is accomplished with silicoformic anhydride as with formic acid, only at the ordinary temp." L. Cambi said that silicoformic anhydride is a strong reducing agent. L. Gattermann found that permanganate soln. are reduced by it, but not chromic acid ; and H. Buff and F. Wöhler obtained

with silver nitrate soln., a brown substance which, when treated with aq. ammonia, forms silver silicate.

H. Buff and F. Wöhler examined the liquid which remained after the separation of silicoformic anhydride by filtration. On standing, or when rapidly heated, or when ammonia is added, hydrogen is evolved. The liquid has strong reducing properties, for it separates sulphur from sulphur dioxide; acidified soln. of selenic or telluric acid deposit selenium or tellurium; mercuric chloride gives mercurous chloride or mercury; potassium permanganate soln. are decolorized; soln. of auric chloride give the metal; soln. of palladous chloride give a black powder; soln. of potassium cupric oxide give hydrated cuprous oxide; and silver soln. give first silver chloride, then a dark brown precipitate which is converted by ammonia into silver silicate. Soln. of chromic acid, indigo, platinum, and iridium salts are not changed.

C. Friedel and A. Ladenburg found that when hexabromosilicoethane, $Si_2Br_6$, is treated with iced-water, hydrogen is evolved, and a white powder is deposited which when washed with water at 0°, and dried at 100°, has the composition: $Si_2O_2(OH)_2$; it is called **silico-oxalic acid.** The air-dried powder has the composition: $(SiOOH)_2.2H_2O$. They also made it by the action of hexaiodosilicoethane, $Si_2I_6$, on absolute alcohol, the ethyl iodide formed at the same time being removed by distillation. L. Troost and P. Hautefeuille obtained the same product by the action of water on hexachlorosilicoethane. L. Gattermann and K. Weinlig made it by exposing purified hexachlorosilicoethane in a platinum dish, cooled with ice, to the moisture of the air until it was converted into a solid, white mass. It was then allowed to remain over lime as long as hydrogen chloride was given off. The product contained 97 per cent. of silico-oxalic acid. The formal relationship between oxalic and silico-oxalic acids is illustrated by the formulæ:

| | |
|---|---|
| O=C—OH<br>O=C—OH | O=Si—OH<br>O=Si—OH |
| Oxalic acid, $(CO.OH)_2$ | Silico-oxalic acid, $(SiO.OH)_2$ |

C. Friedel and A. Ladenburg explain the formation of silico-oxalic acid by supposing $Si_2(HO)_6$ to be first produced, and to become $Si_2O_2(HO)_2$ by the loss of $2H_2O$. Although this substance is the chemical analogue of oxalic acid, it has no acid functions; bases, even the most dil., decompose it with evolution of hydrogen, just as oxalic acid under certain conditions is decomposed by potassium hydroxide. Silico-oxalic acid is said to be a white amorphous powder; and when heated in air or oxygen, it decomposes with incandescence, leaving a residue of silica in proportions agreeing with $2(SiOOH)_2+O_2=2H_2O+4SiO_2$. L. Gattermann and K. Weinlig said that when heated in a test-tube, it decomposes violently with feeble detonation and the evolution of hydrogen. It also explodes when rubbed with a hard substance. When heated with bases, it develops hydrogen: $(SiOOH)_2+4KOH=2K_2SiO_3+2H_2O+H_2$. L. Troost and P. Hautefeuille showed that silico-oxalic acid is a reducing agent; permanganic acid is rapidly reduced, and chromic acid slowly. Cold aq. soln. of selenic acid and of auric chloride are not reduced. Conc. nitric acid is absorbed by silico-oxalic acid, and is not removed by washing or drying in vacuo; and is given off only when heated near the decomposition temp. of silico-oxalic acid. Hydrochloric and sulphuric acids are not taken up in the same way.

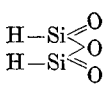
According to L. Gattermann and K. Weinlig, when octochlorosilicopropane, $Si_3Cl_8$, is rapidly decomposed by water, it forms an insoluble acid which is probably **silicomesoxalic acid,** HO.OSi.SiO.SiO.OH. L. Gattermann and E. Ellery made this acid by exposing octochlorosilicopropane in a platinum dish, at 0°, to atm. air. Hydrogen chloride is evolved and silicomesoxalic acid remains. The formal analogy with the corresponding carbon compound is illustrated by the formulæ:

| | |
|---|---|
| O=C—OH<br>HO—C—OH<br>O=C—OH | O=Si—OH<br>HO—Si—OH<br>O=Si—OH |
| Mesoxalic acid. $C_3O_4(OH)_2$ | Silicomesoxalic acid. $Si_3O_4(OH)_2$ |

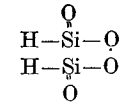
Silicomesoxalic acid is a white powder which does not dissolve in cold water, but is decomposed by hot water giving rise to silica and hydrogen. The acid when dry is extremely unstable and decomposes more violently than silico-oxalic acid. The decomposition often occurs spontaneously and with incandescence. The acid has strong reducing properties, and rapidly reduces a warm alkaline soln. of potassium permanganate.

It is doubtful if silico-oxalic acid and silicomesoxalic acid possess the simple mol. formulæ which characterize their organic namesakes. They are amorphous, non-volatile, and insoluble in water. Silico-oxalic acid decomposes when warmed; and silicomesoxalic acid is liable to decompose explosively with the evolution of hydrogen. D. I. Mendeléeff says that these compounds probably form silica and silicon hydride which decomposes into silicon and hydrogen just as phosphorous and hypophosphorous acids decompose into phosphoric acid and phosphine under similar circumstances. When heated in air they burn, forming silica. They are not attacked by acids, and with alkalies they give off hydrogen and form a silicate. G. Martin has brought forward some evidence to show that in the presence of attached oxygen atoms, say H.O.H—or potassium hydroxide—two directly linked silicon atoms, $\equiv Si-Si\equiv$, are severed with the liberation of hydrogen: $\equiv Si-Si\equiv + H.O.H \rightarrow H_2 + \equiv Si-O-Si\equiv$; and thus one directly linked pair of silicon atoms corresponds with the evolution of one mol. of hydrogen. This agrees with the action of aq. alkalies on, say, hexaethyoxydisilane, $Si_2(OC_2H_5)_6$. Unlike the silicic acids, all the (presumably) hydroxyl groups of silico-oxalic and silicomesoxalic acids are retained in vacuo, over sulphuric acid at 15°, or steam at 100°. G. Martin considers that the greater stability of silicoxalic acid "proves that the silicon atoms which are directly united retain hydroxyl-groups much more tenaciously than do silicon atoms which are united through oxygen atoms," as is presumably assumed to be the case with silicic acid.

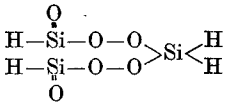
It has been assumed that the easy decomposition of the silico-oxalic acids, their disinclination to form salts, and the evolution of hydrogen when they are treated with potassium hydroxide, show that the hydrogen is probably united directly with the silicon and not indirectly through hydroxylic oxygen as in the case of the silicates. Consequently, the analogy with the oxalic acids, suggested by the names, does not hold good. Formic acid, however, when heated with alkalies does evolve hydrogen: $HCOOH + 2KOH = K_2CO_3 + H_2O + H_2$, and hence the so-called silico-formic anhydride is probably the anhydride of an analogous acid, H(SiO)OH. The graphic formulæ can therefore be represented, *pro tempore*, as:



Silicoformic anhydride, $Si_2H_2O_3$

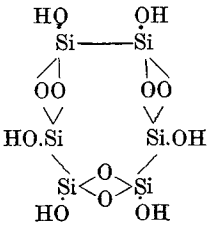


Silico-oxalic acid, $Si_2H_2O_4$

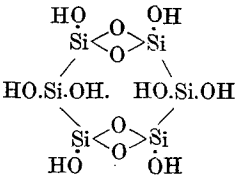


Silicomesoxalic acid, $Si_3H_4O_6$

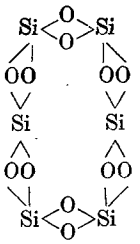
G. Martin argued that (1) the mode of formation of silico-oxalic acid by the hydrolysis of hexaethyoxydisilane, $Si_2(OC_2H_5)_6$, shows that it contains the chain $=Si(OH)-Si(OH)=$; and that the mode of formation of silicomesoxalic acid by the hydrolysis of the octochlorotrisilane, $Si_3Cl_8$, shows that this acid contains the group $=Si(OH)-Si(OH)_2-Si(OH)=$. (2) It is necessary to explain why the action of ammonia gives only one kind of silica by assuming that (i) at least three mols. of hydrolyzed hexachlorodisilane are linked together by oxygen atoms when silicoxalic acid is formed; (ii) at least two mols. of hydrolyzed octochlorotrisilane are similarly linked together to form silicomesoxalic acid; and (iii) when the two silico-oxalic acids are treated with ammonia, each ring loses its hydroxyl groups to form a cyclic or ring compound involving at least $6SiO_2$, which is supposed to represent the mol. of silica. The hypothetical relation between the three compounds in question is illustrated graphically:



Silico-oxalic acid



Silicomesoxalic acid



Silica

Granting that these formulæ for silico-oxalic and silicomesoxalic acid are valid, it cannot be safely assumed that because silicic acid is produced by these reactions, the commonly accepted formulæ are erroneous. The silica actually produced may be the only form which is stable under the conditions of the experiment, just as when water is liberated from all sorts of complex reactions, the equilibrium product is always the same for the same conditions of temp. and press. In order to maintain the proposition that silica is a hexadic ring, it would be necessary to assume a complex change when silica is liberated from hexachlorodisiloxane, etc. In the absence of the mol. wt. and more precise information concerning these and other compounds of silicon, it is possible to weave wonderfully ingenious and subtle patterns, with gossamer threads which have far too fine a texture to bear contact with harsh material facts.

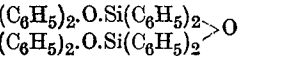
F. Wöhler designated by the term **silicone** a product which he obtained by the action of conc. hydrochloric acid upon calcium silicide. The following is the mode of preparation:

> Calcium silicide in fragments was treated with hydrochloric acid in a vessel surrounded by cold water. Hydrogen was evolved and the calcium silicide gradually converted into silicone. The mixture was left for several hours in a dark place; and agitated until the evolution of gas had ceased. The mixture was diluted with six or seven times its vol. of water, and filtered while protected from light. The product was washed, pressed between filter-paper, and dried in darkness in vacuo over sulphuric acid.

D. I. Mendeléeff called it *chryseone*—χρύσεος, golden. Analysis showed that the alleged silicone contains both hydrogen and oxygen, corresponding approximately with the formula $Si_3H_3O_2$. O. Boudouard obtained a similar product by the action of hot hydrochloric acid on silicon-steel. O. Hönigschmid said that the crystals are dark yellow plates, pseudomorphs after calcium silicide, and that they have a smaller sp. gr. than silicon. The crystals are bleached white by a few minutes' exposure to direct sunlight, and they are gradually decolorized on exposure to diffuse daylight, probably by oxidation. When heated in vacuo, or in an atm. of hydrogen, the product gives off hydrogen and furnishes a greyish-black substance. F. Wöhler said that when heated in a tube to 100°, it develops hydrogen and leaves a mixture of silicon and silica; at 190° in a sealed tube, it is converted into hydrogen and silica. O. Boudouard said that it decomposes if heated above 200°, and that decomposition is complete at 450°; and E. Donath, that silicone is converted into leucone by heat, and light. With water, hydrogen is evolved, and the product becomes white; the reaction is slow in darkness, rapid in light. E. Donath and E. Lissner said that the compound is insoluble in water, alcohol, silicon tetrachloride, phosphorus trichloride, and carbon disulphide. When heated at bright redness in a stream of dry chlorine or hydrogen chloride, it is decomposed with an explosion. It is decomposed very slowly by hydrochloric acid; and fuming nitric acid oxidizes it with incandescence. If suspended in water and then treated with nitric acid, it decomposes with the evolution of nitrogen oxides. The reaction is slow at first, but progresses rapidly later on. The silicone is at the same time oxidized to silicic acid. According to O. Hönigschmid, fuming nitric acid oxidizes silicone with incandescence. Conc.

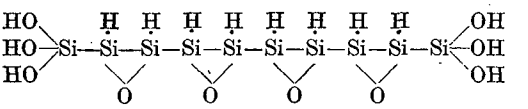
sulphuric acid has no action. The dil. mineral acids act like water. S. Tamaru found that the coloured tabular crystals become white after prolonged contact with hydrofluoric acid. Conc. hydrochloric acid acts similarly.

The fact that the hydrogen in F. Wöhler's product behaves like that in silicon hydride led O. Hönigschmid to assume that the hydrogen is attached directly to the silicon and not to the oxygen. According to O. Hönigschmid, alkali hydroxides or carbonates, ammonia, and pyridine decompose the silicone with the evolution of hydrogen: $2H_3Si_3O_2+12KOH+2H_2O=6K_2SiO_3+11H_2$. The soln. do not decolorize soln. of alkali permanganates or dichromates, and it precipitates the metal from soln. of salts of copper, mercury, silver, gold, and platinum. A. Stock suggested a system of naming the silicon-oxygen compounds containing the group Si.O.Si by calling the parent hydrogen compound *siloxane*, and to specify the number of oxygen and silicon atoms by such terms as disiloxane, disildioxane, etc. Thus $(SiCl_3)_2O$ becomes hexachlorodisiloxane; and the term octophenyltetrasilpentoxane would be applied to:

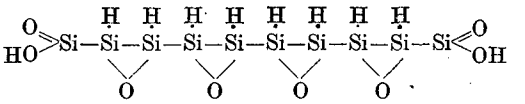


A. Stock believes it to be a mistake to apply the nomenclature of organic chemistry to the above compounds because the radicle —SiO.OH in no way resembles a carboxy-group —CO.OH, and he suggested using the term hydroxyoxo-group.

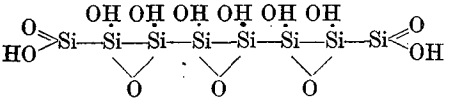
R. Formals, and A. Kolb described a silicone which they obtained by the action of boiling conc. hydrochloric acid on calcium silicide, $Ca_6Si_{10}$. The product washed with water, and dried by treatment with alcohol, and ether had the composition of **tetradecahydrodecasildecoxane,** $H_{14}Si_{10}O_{10}$, or graphically:



and when dried at 120° in a stream of carbon dioxide, furnished **decahydrodecasiloctoxane,** $H_{10}Si_{10}O_8$ or $H_{12}Si_{10}O_8$, or graphically:



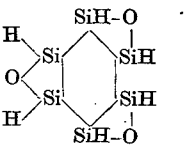
The orange-yellow crystalline mass was insoluble in water, and was bleached white on exposure to light. It is fairly stable in the presence of acids, but not so in the presence of alkalies. By employing the calcium silicide, $Ca_{11}Si_{11}$, in place of $Ca_6Si_{10}$, A. Kolb, and R. Formals obtained a silicone with the composition of **octohydroctosiltridecoxane,** $H_8Si_8O_{13}$, or $H_7Si_8O_{13}$, or constitutionally:



Similarly, by treating the compound $Ca_{11}N_{10}Si_{10}$ with hydrochloric acid, they obtained a yellowish-green slimy silicone with the composition $H_6Si_8O_{13}$, **hexahydroctosiltridecoxane.** The evidence for the inclusion of these products in the list of chemical individuals is not convincing.

K. Kautsky [2] has studied the reaction between cold hydrochloric acid and calcium silicide, and obtained two compounds of different stages of oxidation. By treating this silicide with cold dil. alcoholic hydrochloric acid in the dark, a white, solid substance was obtained, its formation being accompanied by the evolution of hydrogen. It is spontaneously inflammable in air. Its composition corresponds with $Si_2H_2O$, and its properties indicate the constitution $Si_2H.OH$. It has been called *oxydisiline*: $CaSi_2+2HCl+H_2O=H.Si_2OH+CaCl_2+H_2$. It

is a powerful reducing agent, and can be oxidized quantitatively by means of bromine to **silical bromide,** $Si_2OHBr$, the term **silical** being used to signify the radicle $Si_2OH$–. The reaction is symbolized: $H.Si_2.OH+Br_2=Br.Si_2.OH+HBr$. Silical bromide is hydrolyzed by water to form *silical hydroxide*, a red compound, which combines with strong acids, such as hydrochloric acid, to form **silical chloride,** $Si_2OHCl$; with sulphuric acid, to form **silical sulphate,** $(Si_2OH)_2SO_4$; with formic acid, to form **silical formate;** or with acetic acid, to form **silical acetate.** The salts are all yellow to red in colour. The silical compounds are all powerful reducing agents. They, as well as oxydisiline, are decomposed by alkalies with evolution of hydrogen and formation of silica. F. Wöhler's silicone is considered to be oxydisiline contaminated with silical hydroxide. Halogenated hydrocarbons such as carbon tetrachloride, chloroform, or ethyl iodide in presence of traces of water and under the influence of light oxidize oxydisiline to silical compounds. The reaction does not proceed in the dark, but is extremely sensitive to light. It is remarkable that oxydisiline and the silical compounds prepared as described above retain the external crystalline form of the calcium silicide from which they are formed, and the same crystalline form persists when oxidation is carried to the final stage, silica. That the substances have a very open structure is shown by the rapidity with which the reactions proceed in the solid state, and also by the marked absorption of basic dyes by the end-product, silica. Rapid oxidation of the silical compounds, for example, by permanganate, is accompanied by the phenomenon of chemiluminescence in a remarkable degree. H. Kautsky and co-workers prefer to call oxydisiline, $H.Si_2OH$, **siloxene,** and they represent it by $Si_6O_3H_6$ or as indicated in the appended formula which they call **cyclohexasiltrioxene** because the hydrogen atoms can be replaced step-by-step by the halogens, forming a series of halogen siloxenes: thus **siloxene monoiodide,** $Si_6O_3H_5I$, by the action of methyl iodide: $Si_6H_6O_3+CH_3I=CH_4+Si_6O_3H_5I$; **siloxene monobromide,** $Si_6O_3H_5Br$; **siloxene tribromide,** $Si_6O_3H_3Br_3$—*i.e.* silical bromide, *vide supra;* and **siloxene hexabromide,** $Si_6O_3Br_6$. Siloxene does not react with methyl or ethyl iodide in darkness, but does so rapidly on exposure to light, forming the halogen-siloxene and methane or ethane. In the presence of water or amines, hydroxy- or amino-compounds are formed. Bromobenzene, the chloroacetic acids, and other organic halides react with siloxene in a similar manner. H. Kautsky and H. Zocher have investigated the chemiluminescence and photoluminescence of these compounds in some detail; their unsaturated character cannot yet be satisfactorily explained. The silical compounds may be of the oxonium salt type, and a certain similarity of some compounds of bivalent germanium suggests that the silicon in these compounds may be bivalent. Silicalammino-compounds are formed by the action of anhydrous ammonia on the silical compounds, and from these, by the action of alcohols, liquid and solid organo-silicon compounds are formed. These compounds belong to a higher stage of oxidation than the silical compounds.



Cyclohexasiltrioxene

The grey mass obtained by heating silicone in vacuo was considered by F. Wöhler [3] to be a mixture of silicic acid and amorphous silicon. Like silicon, it dissolves slowly in alkali-lye with the evolution of hydrogen, but unlike amorphous silicon, it is completely soluble in hydrofluoric acid. O. Hönigschmid believes that the product is a *silicon suboxide* with the formula $Si_3O_2$, **silicon ditritoxide,** but he says that he is unable to give an *unwiderleglicher Beweis* of the individuality of the assumed analogue of O. Diels' carbon suboxide $C_3O_2$ (*q.v.*). The suboxide reacts with chlorine or hydrogen chloride at a red heat, and much silicon tetrachloride is evolved; white silica remains.

A. Stock and co-workers [4] have prepared a number of siloxanes. They found that when monobromosilane, $SiH_3Br$, is shaken with water, it changes into **disiloxane,** $(SiH_3)_2O$, a colourless, odourless gas, which does not ignite spontaneously but burns with a brilliant light giving a white smoke and a brown

deposit of silicon. The gas can be liquefied and solidified. The m.p. is $-144^{c}$; the b.p. $-15{\cdot}2°$; the sp. gr. of the liquid at $-80°$ is 0·881; the mol. latent heat of vaporization is 5·63 Cals. The m.p. and b.p. are lower than these constants for the parent hydride, $Si_2H_6$, which is the reverse of the relationships between ethane and dimethyl ether. Disiloxane is not sensibly affected when heated to 300°, but at 400° the greater portion of the substance remains unchanged, while a little hydrogen, silane, and polymeric protosiloxane is formed. It decomposes rapidly under the influence of heat when raised to redness. Submitted to a discharge of electric sparks, it slowly yields pure hydrogen. When mixed with oxygen, it inflames or explodes at once, the alteration in volume being in accordance with the equation $(SiH_3)_2O+3O_2=2SiO_2+3H_2O$. It is not appreciably soluble in water, but soon decomposes into hydrogen and insoluble products, like $(SiH_2O)_x$, etc. With sodium hydroxide, however, decomposition is complete, according to the equation $(SiH_3)_2O+H_2O+4NaOH=2Na_2SiO_3+6H_2$, which may be applied in the analysis of the gas. Disiloxane and chlorine react very vigorously at $-125°$; the primary product, hexachlorodisiloxane, may be isolated, but most of it decomposes according to the equation $4(SiCl_3)_2O=2SiO_2+6SiCl_4$, and some brown silicon is even formed as well. Hexachlorodisiloxane has a m.p. of $-33^{c}$ and a b.p. of 137° at 760 mm. Phosphorus pentoxide decomposes disiloxane at atm. temp. giving a little hydrogen, much silane, and polymeric protosiloxane. The initial reaction involves a slight hydrolysis: $(SiH_3)_2O+H_2O=2H_2+2SiH_2O$, followed by a polymerization of the volatile protosiloxane to its non-volatile polymeride; the liberated hydrogen is largely utilized in reducing the disiloxane to silane: $(SiH_3)_2O+2H_2=2SiH_4+H_2O$. The water thus liberated hydrolyzes more disiloxane, and the change continues until it is arrested by the absorption of water by the excess of dry phosphorus pentoxide. The attempts to reduce disiloxane to *disilene*, $Si_2H_4$, were not successful. R. Wintgen gave for the vap. press., $p$, of disiloxane, $\log p=7{\cdot}6864-1232{\cdot}2T^{-1}$; and 5632 cals. for the latent heat of vaporation; 6560·8 cals. for the mol. heat of vaporation at 0°; and 20·0 for Trouton's constant. Disiloxane is the first volatile compound of silicon, hydrogen, and oxygen to have been prepared. Many derivatives, with the same elements, are known, such as silicoformic anhydride, $(O:SiH)_2O$, but these are no doubt polymerides, whereas alkyl, alkoxyl, and similar derivatives of the true monomeric type, for example, $(SiR_3)_2O$ and $[Si(OR)_3]_2O$, have frequently been prepared. Apparently, the compound $SiH_3.OH$, which would be the primary product of the action of water on $SiH_3Br$, is very unstable. It is noteworthy that the alkyl derivatives, $SiR_3.OH$, also change into oxides readily, but the alkyl groups do confer a measure of stability on them, for hexaphenyldisiloxane, $\{Si(C_6H_5)_3\}_2O$, was found by F. S. Kipping and L. L. Lloyd to change back into $Si(C_6H_5)_3.OH$ on boiling with alcoholic potassium hydroxide.

A. Stock and co-workers also found dibromosilane, $SiH_2Br_2$, reacts with water to form hydrogen bromide and a volatile compound, probably **oxomonosilane,** or *protosiloxane*, $SiH_2O$—*vide* magnesium silicide. This compound was obtained as a gas by the action of the required amount of water vapour on dichlorosilane in a very large flask under greatly reduced press. It has an extraordinary tendency to polymerize, much more so than the analogous carbon compound, formaldehyde, in consequence of which the flask must be perfectly clean and smooth. Liquid and solid polymerides are formed immediately on condensation. The liquid polymerides are like benzene, and can be obtained conveniently as a soln. by shaking a benzene soln. of dichloromonosilane with water. These benzene soln. are fairly stable towards water, but reduce silver nitrate in the cold. They correspond roughly with $(SiH_2O)_3$. This polymeride is an amorphous white solid, which is stable at 300° in vacuo, or in contact with boiling water, but inflames in air or chlorine, and reacts with sodium hydroxide, according to the equation $(SiH_2O)_x+2NaOH\rightarrow 2H_2+Na_2SiO_3$. A. Stock and C. Somiesky found that dichlorosilane, $SiH_2Cl_2$, with water also furnishes proto-

siloxane, and this immediately passes into **monoxodioxydisiloxane :** $2SiH_2Cl_2+3H_2O=H_2+4HCl+O.SiH.O.SiH_2.OH$, which, when treated with zinc methyl, forms dimethylsilane, $SiH_2(CH_3)_2$, with a m.p. —150°, and a b.p. —20°.

According to A. Stock and C. Somiesky, the hydrolysis of the halogenated disilanes corresponds exactly with that of the similar monosilanes. Thus monobromodisilane readily reacts with water to yield **tetrasiloxane,** $(Si_2H_5)_2O$, as a colourless liquid, which can be volatilized without decomposition, and when dissolved in benzene, instantaneously reduces a cold soln. of silver nitrate, but not one of copper sulphate. It reacts slowly but quantitatively with a soln. of sodium hydroxide in accordance with the equation : $(Si_2H_5)_2O+8NaOH+3H_2O=4Na_2SiO_3+12H_2$. The solid products obtained by the hydrolysis of dibromodisilane and more highly halogenated derivatives closely resemble silico-oxalic acid, $(HO_2Si.SiO_2H)_x$. They are slowly hydrolyzed further by water; they can be dried in a desiccator without marked decomposition ; they are blackened by silver nitrate soln., owing to the separation of metallic silver; they evolve hydrogen when treated with alkali hydroxide ; and finally they yield a residue of silicate, and explode feebly when heated on platinum foil, evolving gas and becoming discoloured. Evidently the Si–Si linking remains intact in them. Thus, two stages can be clearly distinguished in the action of alkali on $(Si_2H_4O)_x$, namely, a violent evolution of gas with accompanying soln. of the substance, and then a much slower persistent change, which can speedily be brought to an end by warming the soln. The first phase corresponds with the hydrolytic separation of the hydrogen atoms, whilst the second is due to the gradual conversion of **sodium silico-oxalate** into sodium silicate and hydrogen.

C. F. Mabery [5] said that when silica is reduced in the electric furnace, an amorphous greenish substance is formed, and its mode of formation, properties, and composition indicate that it is silicon monoxide, SiO, of sp. gr. 2·893 at 4°. C. Winkler could not prepare the monoxide by reducing silica with magnesium or silicon. At the temp. of the electric arc, however, C. Winkler's reaction, $SiO_2+Si\rightarrow 2SiO$, can be realized. According to H. N. Potter, to effect a partial reduction of silica to silicon monoxide, a mixture of the former with the necessary proportion of carbon is heated electrically in a closed furnace of either the resistance or arc type, provision being made for withdrawing the carbon monoxide gas as it is formed. " This bursting out of the carbon monoxide gas from the point of reaction carries the silicon monoxide with it, but whether in a solid, liquid, or gaseous state is not known " ; in any case, a large portion of it, at least, " is carried out of the region of reaction." Provision is made for trapping the silicon monoxide, as it escapes, in collection chambers. The reduction can be made with carbon : $SiO_2+C\rightleftharpoons SiO+CO$ ; or silicon carbide : $SiO_2+SiC=Si+SiO+CO$ ; and silicon itself can act on carbon monoxide, forming the monoxide : $Si+CO\rightleftharpoons SiO+C$, or the oxycarbide, $Si+CO=SiOC$ (*q.v.*). The reaction between silica and silicon is energetic at about 1800°. The proportion of silica and carbon in the mixture does not influence the composition of the final product, but the yield depends on the proportions of the initial materials. H. N. Potter argues that the so-called silicon monoxide is a chemical individual because its composition remains constant with wide variations in the proportions of raw materials employed ; and the heat of oxidation of silicon monoxide is 200 to 800 cals. higher than that of an eq. mixture of silicon and silica. For commercial reasons H. N. Potter called the monoxide, *monox :* it contains small quantities of silicon carbide and metallic impurities. Monox is an opaque powder, silky to touch and of a yellowish-brown colour. Its sp. gr. is 2·24 ; and its apparent sp. gr. 2·04. It remains solid at 1700°. The vapour should be cooled as quickly as possible in its preparation to prevent as much as possible the dissociation : $2SiO\rightleftharpoons Si+SiO_2$. Monox is a good thermal and electrical insulator ; its thermal resistance is 2500 thermal ohms. When dry and suspended in air, it has a negative electric charge, which depends on its fineness. It can adhere to non-conducting surfaces, such as fibres, and form a screen impervious to solid particles such as

produce tobacco smoke. The chemical properties of monox are often masked by a pellicle of silica which forms on its surface when exposed to air. Monox burns in oxygen. If blown through a flame it is oxidized and whitened, but it still retains its pulverulent form. It decomposes water with the evolution of hydrogen, but the reaction soon ceases because of the formation of a protective layer of silica. Monox dissolves in warm soln. of alkali hydroxides giving hydrogen and the alkali silicates. Hydrofluoric acid attacks it, leaving a residue richer in silicon; and if an oxidizing agent be added to the monox, all is dissolved excepting a small amount of silicon carbide impurity. When mixed with red lead, litharge, or a peroxide, and ignited, monox gives a violent reaction. Monox can be used alone or in combination as a pigment; or pressed into bricks with or without the addition of alumina, magnesia, etc., to form abrasion wheels.

C. Simmonds [6] showed that certain silicates—*e.g.* $PbSiO_3$, $PbSi_2O_5$, and $Pb_2Si_3O_8$—are reduced respectively to $PbSiO_2$, $PbSi_2O_4$, and $Pb_2Si_3O_6$ when heated in hydrogen. No globules of lead were observed; no metallic lead appears when fused with alkali carbonates; boiling nitric acid extracts only a small fraction of the lead. He therefore inferred that virtually no metallic lead is formed but that the lead silicate is reduced to **lead silicite.** The reduction of the more basic silicates furnishes metallic lead. He also found that copper, iron, cobalt, and nickel silicates are similarly converted into **silicites.** It is more likely that the metallic lead is present in the alleged silicites, but in a very finely divided colloidal state analogous to the metallic gold in ruby glass. This lead is reoxidized when the silicate is fused with alkali carbonate; and protected from acid by the silica. W. Mostowitsch could find no evidence of the union of metallic lead with silica.

**Silicon dioxide,** usually called **silica,** $SiO_2$, is produced by the complete oxidation of silicon, but the preparation of the oxide from the element would be a very roundabout and expensive process; nor would the product be very pure because of the difficulty in preparing even moderately pure silicon. Some of the natural varieties of rock crystal and quartz are of a high degree of purity, although contaminations may be derived from the pestle and mortar used in the comminution of the mineral. Some of the white sands—after digestion with hydrochloric acid, washing, drying, and calcination—have a high degree of purity. Anhydrous silica can be easily obtained as a white powder by calcining the hydrated silica or silica hydrogel which is formed in many reactions. For instance, (i) the silica can be separated from a powdered siliceous mineral by fusing it with alkali carbonate; digesting the cold cake with dil. hydrochloric acid; evaporating the soln. to dryness; extracting the residue with hot dil. hydrochloric acid, and then with water; and finally calcining the insoluble residue at a bright red-heat. J. N. von Fuchs [7] precipitated the silica from the alkaline soln.; washed it with hydrochloric acid, then with water; and finally ignited the product. Again, (ii) silicon tetrafluoride, or silicon tetrachloride, is decomposed when treated with water and hydrated silica which is formed is washed by decantation; the washed silica is dried, and calcined at a red heat. This method was recommended by J. J. Berzelius, T. Graham, etc. (iii) One of the most convenient methods is to decompose a soln. of alkali silicate with dil. hydrochloric acid; to evaporate the mass to dryness; to wash the residue with dil. acid, and finally with water until free from chlorides. If further purification be desired, the product can be dissolved in the calculated quantity of soda-lye, and re-precipitated by acid. After thorough washing, the product can be dehydrated by calcination at a bright red heat. The washing of the gelatinous silica is sometimes effected in a dialyzer (Figs. 5—**1**. 13, 7— and Fig. 51). V. Kohlschütter and J. L. Tüscher [8] obtained **colloidal silica,** dispersed in a gaseous medium, by making silicon one electrode of an arc, and oxidizing its vap. by a current of air.

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## § 17. The Preparation of Silicon Dioxide—Quartz, Tridymite, and Cristobalite

At least seven different forms of crystalline silica are known, and possibly there are more. In addition, there are the amorphous and colloidal forms typified by the more or less hydrated opal. There is also fused or vitreous silica or quartz or quartz glass. The forms of crystalline silica stable or metastable at ordinary temp. are quartz, tridymite, and cristobalite. These forms occur in nature, although quartz is alone abundant. Indeed, F. W. Clarke [1] has shown that, next to the felspars, quartz is the most abundant mineral on the earth's crust, and constitutes about 12 per cent. of the entire lithosphere—*vide* the occurrence of silicon.

The $\alpha$-forms of quartz, tridymite, and cristobalite occur in nature ; and a study of the equilibrium diagram, Fig. 26, shows that the two minerals last named are in a metastable condition. When quartz, mixed with a flux, is heated over 870°, it passes into tridymite, and above 1470°, tridymite passes into cristobalite. The transformation of the one form into another is very slow, but the change can be hastened by the use of mineralizers and fluxes. Above 1470°, quartz presumably passes into tridymite, and then into cristobalite. Since both changes are very slow, tridymite may appear under conditions where cristobalite might have been expected, and *vice versâ*. On cooling, the cristobalite may pass slowly back to tridymite, and tridymite to quartz, but the back reaction is so slow that its speed has not been measured, and, at ordinary temp., the speed of the reaction is indefinitely slow. The occurrence of tridymite and cristobalite as natural minerals is evidence of the slowness of the transformation, for they seem to be taking an indefinitely long time to change to $\alpha$-quartz. Some of the alleged syntheses of quartz crystals may really refer to crystals of tridymite or cristobalite, since no test was applied to distinguish which of the three forms of silicon dioxide was produced ; and in some cases, it is even doubtful if the crystals were even those of silicon dioxide.

For example, F. Wöhler, and H. St. C. Deville [2] described crystals of silica-pseudomorphs after silicon—by passing moist chlorine over silicon at a red heat ; E. Frémy obtained pseudomorphs after silicon disulphide by exposing crystals of silicon disulphide to the action

of moist air or water vapour; he also made crystals of silica by passing a mixture of steam and carbon disulphide over briquettes made from lampblack and silica. A. Daubrée made crystals of silica by the action of silicon tetrafluoride or tetrachloride on water-vapour or on beryllia, lime, magnesia, or alumina at a red heat. R. S. Marsden obtained crystalline silica from a soln. in molten silver. F. W. Schweigger-Seidel, and E. Ripetti discussed the formation of quartz crystals in geodes in Carrara marble; T. Bergman reported the deposition of crystals of silica from an aq. soln. of hydrofluosilicic acid, allowed to stand for two years; and L. Gmelin reported that crystals of silica are deposited from an aq. soln. of silicic acid, allowed to stand exposed to air for eight years. In each case, without more evidence, there is an alternative assumption that a silicate was formed—maybe by the action of the silicic acid on the glass containing vessel.

Quartz has been formed in nature under the most diverse conditions having been produced by both igneous and aq. agencies. It occurs as a primary mineral, as a secondary deposition, and as a cementing substance.[3] It is one of the essential constituents of granite, syenite, gneiss, and other acidic or siliceous rocks of igneous origin. This quartz is often peculiarly rich in liquid or gas inclusions. It is found in trachytes, porphyries, etc.; and is the main constituent in quartzite rocks, and sandstones. It permeates all kinds of rocks as an aq. infiltration; it is common in vein-stones of many rocks and in mineral veins; it occurs embedded in various limestones as chert, and flint. It occurs as a foreign mineral in cavities in basalt, limestones, marble, etc. It is the chief constituent of various gravels, sands.

**The synthesis of quartz, tridymite, and cristobalite from molten magma.**—G. Rose [4] fused (i) adularia with microcosmic salt, (ii) amorphous silica with borax and a little sodium carbonate, and (iii) amorphous silica with wollastonite; and in each case obtained tridymite. He also observed that by simple ignition quartz is transformed into tridymite. P. Hautefeuille obtained crystals of quartz by heating a mixture of amorphous silica and lithium or sodium tungstate (or a vanadate) for a long time to a temp. not exceeding 850°, but if the temp. be between 850° and 1000°, crystals of tridymite are formed. He also obtained quartz and felspar by heating above 700° a mixture of silicic acid, alumina, alkali phosphate, and alkali fluoride. P. Hautefeuille and J. Margottet obtained similar results by using a mixture of lithium chloride and oxide as an *agent minéralisateur*; O. Rebuffat used phosphoric acid; F. H. Clews and H. V. Thompson, sodium chloride; A. L. Day and co-workers, a mixture of potassium chloride with 20 per cent. of lithium chloride; F. Parmentier used sodium molybdate; and P. D. Quensel, tungstic oxide. The last-named said that quartz is formed below 1000° and tridymite above that temp.—J. Königsberger said 1050°, and he also found that the presence of boric oxide retards the formation of quartz crystals. N. Parravano and C. R. del Turco studied the effect of ferric, phosphoric, boric, calcium, and tungstic oxides on the conversion of quartz. S. Meunier obtained tridymite from a fused mixture of silica, potassium hydroxide, and aluminium fluoride. K. von Chroustschoff obtained tridymite by fusing rocks rich in silica; and P. D. Quensel, by fusing a mixture of oligoclase, quartz, and tungstic oxide. K. B. Schmutz melted together a mixture of granite, sodium chloride, and sodium tungstate and found crystals of plagioclase, augite, and tridymite in the cooled mass. P. Hautefeuille and A. Perrey obtained tridymite in their experiments on the synthesis of phenacite, and emeralds. K. Bauer obtained tridymite by melting mica-schists with silica, or potash mica with sodium or calcium fluoride, sodium chloride or sodium tungstate. J. Lenarcic obtained no tridymite by fusing mica-schist or gneiss with fluorides, tungstates, or molybdates, but he did obtain crystals of quartz. R. Schwarz obtained crystals of tridymite by fusing sodium silicate with three times its weight of sodium phosphate for 6 hrs. at 1000°; the soluble salts were removed by washing with water on a filter. K. Bauer obtained quartz from fused diorite; and from a mixture of diorite, orthoclase, albite, mica, or hornblende with sodium chloride, potassium tungstate, sodium phosphate, and boric oxide. G. Medanich obtained quartz with glass inclusions by cooling a molten

mixture of granite, sodium hydrophosphate, boric acid, and tin chloride. This subject was also investigated by K. Petrasch. H. E. Benrath observed quartz crystals in a devitrified potash-soda-glass, but F. Fouqué and A. M. Lévy could not confirm this; and J. Morozewicz obtained under similar conditions crystals of tridymite. The last-named said that if an aluminous silicate-magma is supersaturated with silica, the excess separates out on cooling as tridymite and a prismatic modification of crystalline silica. A liparite magma containing one per cent. of tungstic oxide furnished a mixture of quartz, sanidine, and biotite. He said that the function of the tungstic oxide is to liberate silica at a lower range of temp. within which quartz is the stable phase. It will be observed that in the experiments just cited, G. Rose, P. Hautefeuille and co-workers, S. Meunier, K. von Chroustschoff, K. Bauer, R. Schwarz, K. B. Schmutz, J. Lenarcic, G. Medanich, and A. L. Day synthesized tridymite—*vide infra*. H. le Chatelier, and G. V. Wilson observed crystals of tridymite in the devitrification of a lead-glass.

**The synthesis of quartz, tridymite, and cristobalite from solutions.**—C. Schafhäutl [5] synthesized quartz by simply heating a soln. of colloidal silica in an autoclave for 8 days. H. de Sénarmont worked in a somewhat similar way at 200°–300°, but instead of water, he used dil. hydrochloric or carbonic acid. K. von Chroustschoff obtained quartz by heating an aq. soln. of colloidal silica to 250° for several months; and with a mixed soln. of silica and hydrofluoboric acid; at 180°–228°, he obtained cristobalite; at 240°–300°, quartz was formed; and at 310°–360°, tridymite. G. A. Daubrée heated water in a glass tube to about 300°, and obtained crystals of quartz and some silicates by the action of the water on the glass. He also found that quartz crystals are formed when water from the thermal spring at Plombières is heated; and F. Fouqué and A. Michel-Lévy found that some chalcedony is formed at the same time. W. Bruhns heated to about 300° under press., a mixture of powdered glass and a dil. soln. of ammonium fluoride, and obtained quartz; when a mixture of felspar and hydrofluoric acid was similarly treated for 53 hrs., tridymite was formed. J. Königsberger and F. W. J. Müller heated glass and water over 300°, and obtained quartz, tridymite, and soda felspar; the filtered soln. slowly deposited quartz and opal; and the undissolved residue contained both tridymite and felspar. G. Maschke heated a soln. of sodium silicate in a sealed glass tube, and when the temp. was below 180°, he obtained crystals of hydrated silica, but above that temp., quartz crystals were formed. C. Friedel and E. Sarasin obtained quartz by heating nearly to redness a mixture of potassium hydroxide, gelatinous silica, and alumina for 14–38 hrs. in a steel tube. At a still higher temp., crystals of quartz and tridymite were found side by side. E. Baur heated in a steel autoclave at 250°, for 6 hrs., a soln. of silicic acid and potassium aluminate; when the proportion of $SiO_2 : KAlO_2$ was between 5 : 2 and 5 : 25, orthoclase, tridymite and quartz were formed, while with sodium aluminate in place of the potassium salt, crystals of albite and quartz were produced, and with $SiO_2 : NaAlO_2$ as 5 : 25, quartz alone was formed. G. Spezia found that the evaporation of an aq. soln. of silicic acid furnishes opal, and if alkalies are present quartz is produced; if opal be heated with a soln. of an alkali silicate, an aggregate of quartz crystals is formed. A hot dil. soln. of sodium silicate dissolves some quartz, and the latter is re-deposited at a lower temp. He found that the soln. and re-deposition of quartz is not affected by press., but is sensitive to variations of temp. A. L. Day and co-workers obtained fine crystals of quartz by heating to 400°–450° a mixture of magnesium ammonium chloride, sodium metasilicate, and water for 3 days in a steel bomb. It will be observed that in the experiments just indicated C. Friedel and E. Sarasin, K. von Chroustschoff, W. Bruhns, E. Baur, and J. Königsberger and F. W. J. Müller obtained tridymite, and that K. von Chroustschoff also obtained cristobalite.

**The mutual conversion of the different forms of silica.**—H. Rose [6] pointed out that before the discovery of tridymite in nature by G. vom Rath, it had been

actually prepared by G. Rose—*vide supra*. H. le Chatelier observed tridymite was formed by the prolonged heating of quartz in a steel furnace. E. Mallard also observed the development of tridymite, in silica bricks, made from quartz sand mixed with about 2 per cent. of lime, which had been heated for 18 months in a steel furnace at Assially. W. Sokoloff said that in the transformation the flux seemed to dissolve the quartz and reject it as tridymite. Similar changes have been noted in silica bricks by W. Ssokoloff, P. J. Holmquist, K. Endell, A. Scott, etc. C. F. Rammelsberg noted that the calcination of amorphous silica changes it into tridymite. L. Elsner said that rock-crystal is not changed when heated for some days in a porcelain oven (1400°–1600°), but E. Cramer, K. Endell, H. and G. Rose, etc., have noted that under these conditions quartz is changed into tridymite, or a form with a low sp. gr. H. Schulze and A. Stelzner noted the formation of tridymite in the walls of a zinc retort; and A. Lacroix in the bricks of a glass furnace at Clichy. A. Schwantke observed tridymite in roofing slates which had been struck by lightning. C. Vélain found crystals of tridymite, anorthite, and wollastonite in the glass formed by the ashes of wheat and oats during the conflagration of grain mills at Petit-Brie and at Nogentel. E. Mallard also noted that *fibrous tridymite* had accumulated in a cavity in the masonry of a steel furnace; the fibrous silica observed by L. N. Vauquelin in the bottom of an iron smelting furnace was probably tridymite. This form of silica occurs in white silky fibres resembling asbestos and has hence been called *Eisenamianth*—possibly some graphite and titanium cyanide and nitride are also present. C. Schnabel, C. W. C. Fuchs, P. C. Grignon, and F. C. L. Koch also discussed the occurrence of fibrous silica in the masonry of furnaces. According to A. C. Hawkins, a fibrous quartz resembling asbestos occurs in the metamorphic slates at several localities on Rhode Island. A. Brun transformed quartz-glass into crystallized quartz by heating it between 700°–750° in the vapours of alkali chlorides; between 800° and 1000°, tridymite was formed. C. Johns found that quartz-sand was transformed to tridymite at 1500°, and suggested that the inversion temp. was 200° lower. E. Sommerfeldt, and A. Blackie noted the transformation of quartz-glass into tridymite at 1200°–1300°; and M. Herschkowitsch noted the formation of crystals of quartz when quartz-glass is heated over the gas blowpipe flame. A. L. Day and E. S. Shepherd found that quartz and amorphous silica are transformed into tridymite at about 1000°, and in the presence of alkali chlorides the transformation occurs at about 800°, and in the back-reaction occurs at about 750°. For C. N. Fenner's observations, *vide infra*.

Owing to the very small differences in the properties of tridymite and cristobalite, it is more than likely that many of the alleged transformations of silica and quartz into tridymite were really transformations into cristobalite. C. N. Fenner has shown that tridymite is transformed into cristobalite above 1470°. P. J. Holmquist, K. Endell, A. Lacroix, A. Scott, etc., have studied the conversion of quartz or tridymite into cristobalite, and also the formation of cristobalite in silica bricks in high temp. furnaces. F. E. Wright, E. S. Shepherd, and G. A. Rankin found that cristobalite is formed during the slow cooling of molten quartz glass, and C. N. Fenner observed that if a mixture of tridymite and sodium tungstate be heated for 10 hrs. at 1475°, a considerable proportion is transformed into cristobalite, but below that temp. no cristobalite is formed.

There are abrupt changes in the properties of quartz at about 575°, and hence quartz below this temp. is designated $\alpha$-**quartz** and above this temp. $\beta$-**quartz.** The change is reversible. There are also reversible changes in the properties of tridymite at about 117°, and in those of cristobalite at about 270°. H. Steinmetz found the transition point of tridymite to be 115°, and the change is attended by a 0·6 per cent. expansion. The lower temp. forms are called respectively $\alpha$-**tridymite** and $\alpha$-**cristobalite;** while the higher temp. forms are called respectively $\beta_1$- and $\beta_2$-**tridymite** and $\beta$-**cristobalite.** With $\beta_1$-tridymite there is another change at about 163°, and above that temp. $\beta_2$-**tridymite** is formed. The complex series of

changes which occur during the calcination of quartz, tridymite, and cristobalite have been elucidated by the work of C. N. Fenner, K. Endell, W. P. White, J. A. Cunningham, J. Königsberger, A. Scott, P. Braesco, J. B. Ferguson and H. E. Merwin, H. le Chatelier, etc.

The effect of raising the temp. of quartz, tridymite, cristobalite, and vitreous quartz is summarized in Fig. 26, after C. N. Fenner. With quartz, at about 575°, α-quartz changes into β-quartz, and at the same time there is a slight decrease in density. The reverse transformation occurred at 570°. Another change takes place at 870° ± 10°, for β-quartz then changes into what is called $\beta_2$-tridymite; at 1470°+10°, $\beta_2$-tridymite changes into β-cristobalite, which melts at 1625°.

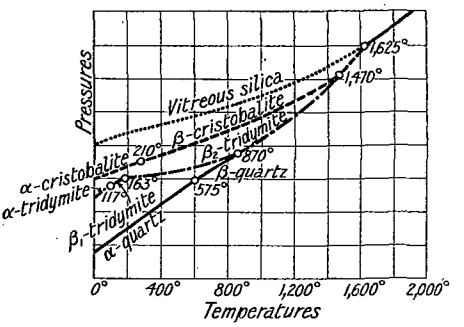



FIG. 26.—The Equilibrium Conditions of Quartz, Tridymite, and Cristobalite.

To summarize, the region of stability of each form lies between the transition points:

$$\alpha\text{-Quartz} \overset{575^\circ}{\backsimeq} \beta\text{-Quartz} \overset{870^\circ}{\backsimeq} \beta_2\text{-Tridymite} \overset{1470^\circ}{\backsimeq} \beta\text{-Cristobalite} \overset{1625^\circ}{\backsimeq} \text{Melt}$$

If α-tridymite be heated on a gradually rising temp., it changes at about 117° into $\beta_1$-tridymite, and at 163°, $\beta_1$-tridymite changes into what is called $\beta_2$-tridymite, which then changes on subsequent heating at 1470° into β-cristobalite, which melts at 1625°. The transition points of α- into $\beta_1$-, and of $\beta_1$- into $\beta_2$-tridymite are shown on the curves, Fig. 26, where the press. are diagrammatic. The $\beta_1$ to $\beta_2$-tridymite transformation is supposed to be analogous with the α- to β-quartz transformation. To summarize, the region of stability of each form lies between the transition points:

$$\alpha\text{-Tridymite} \overset{117^\circ}{\backsimeq} \beta_1\text{-Tridymite} \overset{163^\circ}{\backsimeq} \beta_2\text{-Tridymite} \overset{1470^\circ}{\backsimeq} \beta\text{-Cristobalite} \overset{1625^\circ}{\backsimeq} \text{Melt}$$

According to H. le Chatelier, cristobalite is the metastable phase in relation to tridymite, so that above 1480°, tridymite is more stable than cristobalite; while, according to A. Scott, tridymite is the stable phase up to at least 1550°, since bricks containing 97 per cent. of silica are practically all tridymite after being at this temp. for prolonged periods. C. N. Fenner, however, claimed that in the absence of an *agent minéralisateur* the transformations between tridymite, cristobalite, and quartz are remarkably sluggish, and that because tridymite can be heated in a dry state at temp. exceeding 1480° without transformation is of no importance in drawing conclusions as to stability relations, when under proper conditions it can be converted into cristobalite; and he has again emphasized that at temp. above 1470° ± 10°, quartz, tridymite, and amorphous silica have repeatedly and unequivocally been converted into cristobalite; between 1470° ± 10° and 870° ± 10°, quartz, cristobalite, and amorphous silica have similarly been converted into tridymite; and below 870° ± 10°, tridymite, cristobalite, and amorphous silica have been converted into quartz. J. B. Ferguson and H. E. Merwin also demonstrated that the stability region for cristobalite lies above that for tridymite.

Similarly, if α-cristobalite be heated, it passes into β-cristobalite at about 225°, and this melts at 1625°. The transition temp. 225° is not sharply defined, since in the conversion of α- to β-cristobalite, the observed values ranged between 274·7° and 276·9°; and for the reverse transformation, between 240·5° and 198·1°. To summarize, the region of stability of each form of cristobalite lies between the transition points:

$$\alpha\text{-Cristobalite} \overset{225^\circ}{\backsimeq} \beta\text{-Cristobalite} \overset{1625^\circ}{\backsimeq} \text{Melt}$$

The relationship between these different forms of silica is illustrated diagrammatically in Fig. 26. So far as information is at present available, the more important physical properties of the products of these different mutations of quartz and its polymers are summarized in Table II.

TABLE II.—PHYSICAL PROPERTIES OF THE DIFFERENT MODIFICATIONS OF SILICA.

| — | Crystal system. | Specific gravity. | Index of refraction (sodium light). | Double refraction. | Polarization (sodium light). |
|---|---|---|---|---|---|
| $\alpha$-Quartz . . | Hexagonal | 2·65 | $\omega$, 1·5352 (570°)<br>$\epsilon$, 1·5328 (570°) | +0·0091 (20°)<br>+0·0080 (570°) | 21·7° (20°)<br>24·1° (560°) |
| $\beta$-Quartz . . | Hexagonal | 2·633 | $\omega$, 1·5328 (580°)<br>$\epsilon$, 1·5404 (580°) | +0·076 (590°)<br>— | 2·52° (600°)<br>— |
| $\alpha$-Tridymite . | Rhombic(?) | 2·28 | 1·4775 | +0·0021 | — |
| $\beta_1$-Tridymite . | Hexagonal | 2·30 | — | Feeble | — |
| $\beta_2$-Tridymite . | Hexagonal | — | — | — | — |
| $\alpha$-Cristobalite . | Tetragonal | 2·348 | 1·486 | −0·00053 (?) | — |
| $\beta$-Cristobalite . | Cubic | 2·215 | — | Feeble | — |
| Silica glass . . | Amorphous | 2·21 | 1·460 | Nil. | Nil. |

The form of quartz present in chalcedony shows no signs of the transformation at 575°, and, when fused with sodium tungstate, seems to change directly into $\beta_2$-tridymite at about 870° without showing the 575° transition point. This is possibly an effect of the greater speed at which chalcedony passes into the form with a low sp. gr. C. N. Fenner, however, suggests that the quartz of chalcedony may be another modification of silica different from quartz. A. Wietzel concluded from his observations on the sp. ht., etc., that chalcedony is not a distinct form of silica, but simply microcrystalline quartz; he also studied the stability of the different forms of silica when associated with quartz-glass.

J. Morozewicz [7] reported a prismatic modification of quartz to be formed along with tridymite when an aluminous magma supersaturated with silica is allowed to cool; and F. Fouqué and A. M. Lévy also said that a prismatic form of silica is produced when an excess of silica is fused with augite, enstatite, or hypersthene.

The different varieties of natural quartz have different speeds of conversion.[8] J. W. Mellor and A. J. Campbell found that quartz was transformed much more slowly than flint. If $S$ denotes the sp. gr. of the material after $n$ firings in a pottery oven, they found that with flint, $S(6{\cdot}7-e^{-1{\cdot}05n})=14{\cdot}87$; and with quartz, $S(7{\cdot}8-e^{-0{\cdot}31n})=18{\cdot}096$. J. T. Robson also found that flint and chalcedony changed more quickly than sand and quartz rock. The subject was studied by A. Grün.

**Analyses of quartz, tridymite, and cristobalite.**—J. G. Wallerius [9] did not give an analysis of quartz or *Kiesel* in his description of this mineral in 1750. In 1779, T. Bergman gave for the analysis of a specimen of rock-crystal: Silica, 93 per cent.; alumina, 6 per cent.; and calcium oxide, 1 per cent. M. H. Klaproth, D. L. G. Karsten, and C. F. Bucholz also made analyses of varieties of quartz. Good rock crystal contains 99·5 per cent. of silica. Numerous analyses—F. A. Genth, P. Schweitzer, J. W. Mallet, A. des Cloizeaux, C. F. Rammelsberg, P. Holland, A. Becker, etc.—have been made. Analyses of tridymite have been made by G. vom Rath,[10] N. S. Maskelyne, V. Wartha, A. Koch, C. Winkler, etc. G. vom Rath analyzed cristobalite—*vide supra.*

E. Weinschenk [11] found traces of titanium, iron, and manganese in many varieties of quartz; and manganese was also found in a blue quartz. A. Nabl found iron, sulphur, and nitrogen in amethyst. L. Wöhler and K. von Kraatz-Koschlau found no sulphur. A. Nabl found ferric oxide in citrine quartz. C. F. Rammelsberg said amethyst from Brazil contains 0·01 per cent. manganese,

and a clear quartz had 0·02 per cent. ferric oxide, 0·02 per cent. calcium oxide, and 0·04 per cent. soda; an amethyst had 0·0027 per cent. of carbon. S. Curie and S. E. Gleditsch found traces of lithium in transparent quartz. N. von Fuchs found 1·0 to 1·5 per cent. titanic oxide in rose quartz. A. Forster obtained 0·5 to 0·6 grm. of ammonium carbonate by distilling 4·5 kgrms. of smoky quartz. E. Wülfing found no perceptible loss of weight when smoky quartz is decolorized at 300°—*vide* the occurrence of coloured quartz.

Quartz crystals may show cavities containing **liquid, solid, and gaseous inclusions**—*vide* **1.** 11, 2, Fig. 3. H. Davy [12] found that the cavities in rock crystal contained water with a trace of alkali sulphates, and nitrogen gas. D. Brewster found that the fluid enclosure contained crystals of calcium carbonate. F. Salm-Horstmar found traces of chlorine in quartz, and he assumed this was derived from alkali chlorides present as impurities. H. C. Sorby found cubic crystals contained in the liquid in the cavities of some quartz crystals, and he believed these crystals were sodium chloride. This was confirmed by the observations of F. Zirkel, H. Rosenbusch, E. Warburg and F. Tegetmeier, J. Königsberger, etc. J. Königsberger and W. J. Müller analyzed the inclusion in the cavity of a sample of quartz from Bächistock (Switzerland) and found:

| | $H_2O$ | $CO_2$ | $CO''_3$ | $SO''_3$ | Cl | Na | K | Li | Ca |
|---|---|---|---|---|---|---|---|---|---|
| Per cent. . . | 83·4 | 9·5 | 1·8 | 0·5 | 1·6 | 2·0 | 0·7 | 0·2 | 0·3 |

H. C. Sorby found alkali and calcium sulphates, free acid, and in some cases almost pure water. H. Vogelsang found spectroscopically cavities with an aq. soln. of carbon dioxide, and also with liquid carbon dioxide—the liquid disappears when the temp. is raised above the critical point, 32°. This agrees with the observations of D. Brewster, T. Simmler, W. E. Hidden, J. Bosscha, H. Geissler and H. Vogelsang, etc. C. W. Hawes found so much carbon dioxide under press. in the cavities in a quartz from Brancheville (Conn.), that when broken up with a hammer, some of the cavities burst open with a report; A. W. Wright obtained from this same quartz a gas with 98·32 per cent. carbon dioxide, and 1·68 per cent. nitrogen along with smaller amounts of sulphur dioxide, hydrogen sulphide, volatile hydrocarbons, ammonia, and chlorine; or if referred to the accompanying water, 30·48 per cent. carbon dioxide, 0·50 per cent. nitrogen, and 69·02 per cent. water. From the basis of the ratio of liquid to gaseous carbon dioxide in the inclusions, and other known data, A. Johnsen, and O. Mügge endeavoured to calculate the conditions under which particular specimens have been formed. The quartz is used as a kind of geological thermometer. C. L. Reese, and G. Tschermak reported that petroleum enclosed in the cavities of some crystals from Guntersville (Alabama), and asphaltum in crystals from Herkimer Co. (New York). H. Sjögren found methyl disulphide or ethyl hydrosulphide in quartz from Salangen. J. G. Bornemann found plant remains in the rock crystal from Oberlungwitz and Radowenz in Bohemia. G. Tschermak gave the following list of minerals he had observed included in quartz:

Magnetic pyrites, mispickel, pyrite, argentite, antimonite, molybdenite, zinc blende, anatase, rutile, hæmatite, ilmenite, magnetite, dolomite, calcspar, amphibole, topaz, felspar, tourmaline, muscovite, chlorite, epidote, titanite, laumontite, desmine, and pilinite. G. A. Kenngott, and R. J. G. Beaugey observed anhydrite included in quartz.


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## § 18. The Physical Properties of Silicon Dioxide

The **colour** of quartz has been indicated in connection with the occurrence of this mineral. O. Ruff and P. Schmidt said the vapour at 1900°–2160° is blue. The **crystalline form** of quartz attracted the attention of Pliny, who, in his *Historia naturalis* (**6**. 37, *c.* 77), said that "it is not easy to account for the regular hexagonal shape and smoothness of the crystals and this the more as the pyramidal terminations do not always have the same appearance." Quartz crystals furnished N. Steno (1669)[2] with material for his work on the constancy of the angles of crystals. M. A. Cappeller made a measurement of the angles of the crystals in 1723. In 1783, J. B. L. Romé de l'Isle measured the angles of several varieties of quartz, and showed that *il n'y a qu'une seule espèce de cristal de roche;* that *les masses moins regulières ou moins homogènes prennent les noms de quartz, de grès, d'agate, caillou, jaspe*, etc.; and that amethyst is nothing but rock crystal coloured violet or purple. Observations were also made by R. J. Haüy, C. S. Weiss, H. Dauber, G. Rose, N. von Kokscharoff, W. Haidinger, J. Bindrich, S. Ichikawa, M. Websky, A. des Cloizeaux, G. Sella, F. Hessenburg, F. Leydolt, V. von Lang, etc. The typical quartz crystal is a doubly terminated hexagonal prism (Fig. 27), and it appears as if it were a combination of a hexagonal prism and a bipyramid. Some

typical crystals remaining after the dissolution of the calcium carbonate from some Derbyshire limestones are illustrated by the photograph, Fig. 27. *Confer* Fig. 70, **1.** 11, 7, in some cases the crystals appear as the simple bipyramids. Quartz crystals belong to the hexagonal system. According to A. T. Kupffer, the axial ratios are $a : c = 1 : 1{\cdot}09997$, and the constants of the forms: $r$ {100}, $z$ {22$\bar{1}$}, $m$ {21$\bar{1}$}, are $mr$, 38° 31′, and $rz$, 46° 31′. A. N. Winchell found a rock from a mine near the Iron River, Michigan, contained isotropic quartz. The quartz gave the standard X-radiogram so that the apparent isotropism was attributed to the extremely fine state of subdivision of the mineral.

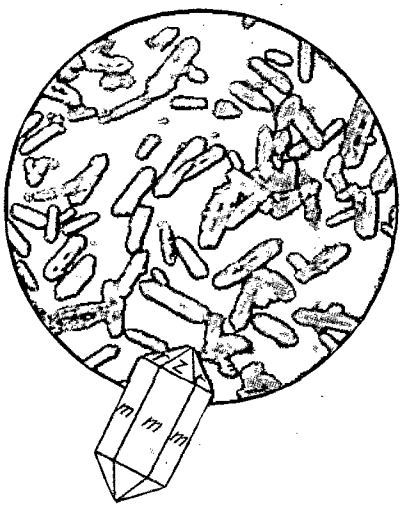


FIG. 27.—Quartz Crystals.

The trigonal symmetry of quartz is illustrated by crystals with three alternate faces of the pyramid larger than the remaining three, showing that the hexagonal bipyramid consists of two rhombohedra; by crystals which are terminated by one rhombohedron, and by crystals which occur as simple rhombohedra. Crystals with certain faces only on alternate corners show that the crystals are trigonal trapezohedra. These crystals possess no centre or plane of symmetry, and they are enantiomorphous, Fig. 27. The two sets of faces may form what are conventionally known as right- and left-handed quartz crystals: a crystal of the one kind is a mirror image of the other. The two kinds are about equally numerous. When complementary right- and left-handed faces occur on the same crystal, it is not a single crystal but an interpenetrant twin. Two right-handed or two left-handed, or a right- and left-handed, crystals may be twinned by interpenetration parallel or perpendicular to the prism edge. The twinning of right- and left-handed crystals frequently occurs in quartz crystals from Brazil, and is hence called *Brazilian twinning;* Fig. 30 is an example; and the twinning of two right- or two left-handed

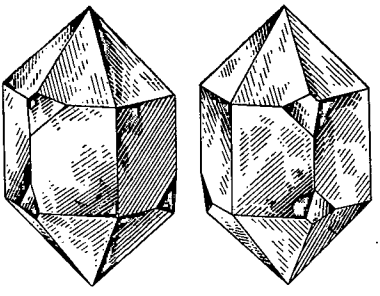

FIG. 28.—Left-handed Quartz.


FIG. 29.—Right-handed Quartz.

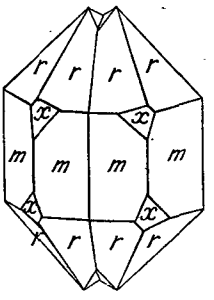


FIG. 30.—Brazil Twinning.

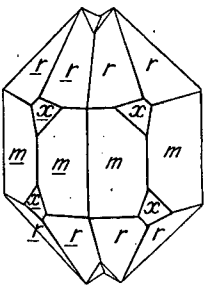


FIG. 31.—Dauphiné Twinning.

crystals is called *Dauphiné twinning*—after Dauphiné, near Bourg d'Oisano. There is also twinning by juxtaposition, forming genicular (Fig. 32), three-rayed, and cruciform (Fig. 33) twins. G. Friedel, and J. Beckenkamp have discussed the twinning laws of quartz. Mis-shapen and distorted crystals with horizontal striations are also found. O. Mügge showed that while $\alpha$-quartz crystallizes in the trapezohedral-tetartohedral division of the hexagonal system, $\beta$-quartz is also hexagonal but has

trapezohedral-hemihedral symmetry. The axial ratios of the two forms are nearly identical. The only crystallographic change which occurs during the passage from $\alpha$- to $\beta$-quartz is a molecular rearrangement, so that the common digonal axes of the $\beta$-form become polar in the $\alpha$-form.

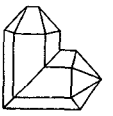


FIG. 32.—Genicular Twin.



FIG. 33.—Cruciform Twin.

Quartz which has been formed above 575° can be distinguished from quartz which has never reached that temp. At ordinary temp. all quartz is $\alpha$-quartz, but if at any time in its history a particular piece of quartz has passed the inversion point and been heated above 575°, it bears ever afterwards marks potentially present which on proper treatment can be made to appear just as an exposed photographic plate can be distinguished at once from an unexposed plate on immersion in a proper developer, although before development both plates may be identical in appearance.

F. E. Wright and E. S. Larsen go further and say that quartz can be used as a geological thermometer, because, if at any time quartz has been heated above 575°, this fact is recorded in its structure by the corrosion figures. Hence also, quartz in any rock must have been formed below 870°, and its peculiarities indicate whether it was crystallized below or above 575°.

During the microscopic examination of some pieces of trachytic porphyry from San Cristobal, near Pachuca (Mexico), in 1863, G. vom Rath [3] found some hexagonal tabular crystals of *eine neue Krystallform der Kieselsäure* which frequently exhibited compound twinning, and since there were usually three individuals in one compound form, he named the crystals tridymite—from τρίδυμος, triplet. The crystals had a sp. gr. varying from 2·295–2·326 (15°–16°), thus corresponding with opal rather than with quartz; and they furnished on analysis: 96·1 per cent. of silica; 1·9, ferric oxide; 1·3, alumina; and 0·66, loss on ignition. G. Rose then showed that if powdered rock crystal or amorphous silica be calcined in a porcelain oven, or if adularia or amorphous silica be heated with microcosmic salt, tridymite is usually obtained. The crystals, Fig. 34, are thin hexagonal plates bounded by the faces $c$ (0001), $m$ ($10\bar{1}0$), and the subordinate faces $a$ ($11\bar{2}0$), and $p$ ($10\bar{1}1$). The crystals may show juxtaposition twins, or trillings; or the twins may be formed by interpenetration, and they may occur in fan-shaped groups, or spherical aggregates. According to R. Brauns, and E. Mallard, the crystals of silica from the Euganean Hills, which A. Lasaulx described as tridymite, are really quartz crystals into which the original tridymite has changed. He found that crystals of tridymite from Cerro San Cristobal, and Mont Doré, are pseudo-hexagonal, but they belong to the rhombic system and have the axial ratios $a : b : c = 0{\cdot}5774 : 1 : 0{\cdot}9405$. There is a change of tridymite into a hexagonal form near 130°, so that silica can exist in two crystalline forms of hexagonal symmetry; one of the forms is quartz, the other tridymite. The axial ratio of $\beta_1$-tridymite at 130° is $a : c = 1 : 1{\cdot}65304$. F. Wallerant regarded tridymite as a monoclinic mineral with rhombic symmetry. The crystals have also been studied by A. Marian, G. Boeris, R. Panebianco, M. Schuster, J. Beckenkamp, E. Billows, F. Sandberger, and F. Zirkel. Tridymite is found in certain acidic volcanic rocks; the primitive rocks on the earth's crust, however, always have their free silica in the form of quartz. N. S. Maskelyne described crystals of a variety of silica which he found in a meteorite from Breitenbach (Bohemia), and which he named *asmanite*—from the Indian term *a-sman*, thunderbolt. M. Schultze showed that asmanite and tridymite are the same mineral species. E. Mallard showed that *lussatite* is a fibrous scaly aggregate of crystals with a weaker double-refraction than that of quartz; and F. Slavik said that lussatite is probably a fibrous variety of tridymite mixed with a little opal.

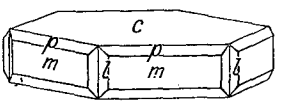



FIG. 34.—Idealized Crystal of Tridymite.

In 1887, G. vom Rath also found as an inclusion in the augite of San Cristobal

another form of crystal different from tridymite and quartz; the analysis was: $SiO_2$, 91·0 per cent.; $Fe_2O_3$ and $Al_2O_3$, 6·2 per cent. He named the crystals cristobalite from the place where they were found. The external form of the crystals can be referred to the regular octahedron. According to E. Mallard, cristobalite is a distinct species and not a mere variety of tridymite, although the sp. gr. are so nearly alike. The crystals which are usually imperfect are pseudo-cubic, but they really belong to the tetragonal system; they are grouped in such a way that the bases of six pyramids represent the six faces of a cube. There is a similar grouping in analcime, and E. Mallard added, that, like analcime, cristobalite is only approximately tetragonal and uniaxial, and ought rather to be regarded as rhombic. At 175°, he says, cristobalite undergoes a reversible change, all birefraction disappears, and the crystals acquire the optical properties proper to their external cubic form. Hence, $\alpha$-cristobalite is regarded as tetragonal, and mimetic cubic; while $\beta$-cristobalite is cubic. J. Beckenkamp, O. Mügge, and P. Gaubert have made observations on this subject.

The crystalline form of chalcedony has not been determined, although C. Hintze [4] said that it is *vielleicht rhombisch*. Chalcedony and flint are usually said to be cryptocrystalline. Chalcedony occurs in mammillary, botryoidal, or stalactitic masses, and lining or filling cavities in rocks. Opal and vitreous silica are amorphous. According to F. Savart, quartz does not admit of cleavage in the ordinary way, but if the prism be made red hot and suddenly cooled, the fractures which occur give rhombohedral pieces. Hence he infers that the primitive form is the rhombohedron like that which would be obtained if the crystal were susceptible of cleavage parallel to the three non-adjacent faces of the prism. E. W. Washburn and L. Navias conclude from their examination of the X-radiograms of quartz, tridymite, cristobalite, silica glass, raw and calcined flint and chalcedony, that calcined chalcedony can be regarded as a kind of silica glass; while calcined flint may be either cristobalite or tridymite. Raw flint and raw chalcedony contain much quartz in a colloidal state. R. Wietzel [5] found chalcedony to be simply microcrystalline quartz.

Lord Kelvin, S. Nakamura, and S. Ichikawa studied the molecular structure of quartz. The **X-radiogram** of quartz has been investigated by W. H. Bragg. He refers the lattice to a set of hexagonal axes, because this gives the simplest explanation of the observed spectra. The value of $a$ is $4{\cdot}89\times10^{-8}$ cm., and there are three mols. of silica, $SiO_2$, associated with each point of the lattice as structural units or crystal mols. The quartz lattice is produced by three interpenetrating hexagonal lattices. These are so related that they can be derived from each other by a rotation of about $\frac{2}{3}\pi$, and a translation of $\frac{1}{3}c$ along an axis parallel to the direction of $c$, Fig. 35, where $a:c=1:1{\cdot}10$. Each hexagonal lattice locates the position of one-third the triplets. Each trigonal axis of the structure has points arranged spirally about it; and, since a spiral can be either left- or right-handed, the enantiomorphism of quartz follows. J. Beckenkamp assumed that the silicon atoms form a rhombohedral lattice instead of a three-point screw as in W. H. Bragg's structure. J. Beckenkamp's lattice of ordinary quartz is in effect a 3-fold triangular prismatic lattice with the trigonal axis vertical, Fig. 36. The solid circles represent one layer of silicon atoms, the second circles another layer, and the open circles a third layer. The fourth layer is like the first, the fifth like the second, etc. The positions of the oxygen atoms represented by small circles in the diagram depend on whether the crystal is right- or left-handed. In right-handed quartz, the oxygen atoms are situated as in the inset of Fig. 36, where the lowest layer of atoms is numbered 1, the next layer 2, the next 3, . . . The pairs of oxygen atoms 1 and 3, 4 and 6, 7 and 9, are associated respectively with the silicon atoms 2, 5, and 8. The series of 9 atoms of three $SiO_2$-triplets thus form a helix rotating to the right. The spiral structure appears only after the introduction of the oxygen atoms, the arrangement of the oxygen atoms is such that the orienta-

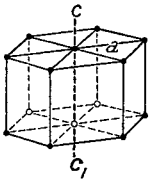



FIG. 35.—Cell of Space Lattice (W. H. Bragg).

tion of the valency directions is the same in horizontal or vertical mol. layers, and the optical rotation perpendicular to the vertical axis is then explained. S. Kyropoulos, C. Mauguin, L. W. McKeehan, E. W. Washburn and L. Navias, H. Haga and F. M. Jäger, and F. Rinne have discussed the X-radiogram of $\alpha$-quartz; S. Kyropoulos found quartz-glass and silicic acid are amorphous. M. L. Huggins, L. W. McKeehan, and R. B. Sosman have suggested a possible structure for the quartz mols.

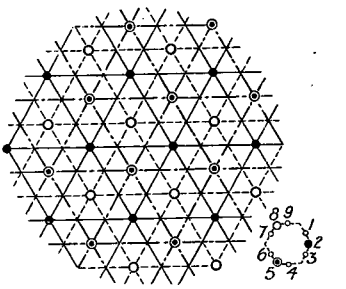



FIG. 36.—Rhombohedral Lattice of Silicon Atoms in Ordinary Quartz; and, in inset, Arrangements of Atoms in Right-handed Quartz.

According to the theory of the electric structure of atoms (**4.** 27, 3 and 4), the silicon atom has a nucleus with a positive charge of 14, and surrounded by 14 non-nuclear electrons; the oxygen atom likewise has a nucleus with a positive charge of 8, and surrounded by 8 non-nuclear electrons. Each atom of both elements has an inner ring of two electrons, and outside the inner ring there is a ring of 6 electrons with the oxygen atom; and with the silicon atom two rings with 8 electrons in the inner ring and 4 in the external ring. Both silicon and oxygen have a tendency to complete a stable external ring of 8 electrons. This tendency causes the combination of silicon and oxygen to form three interlocking systems corresponding with the single mol. of silica, $SiO_2$, Fig. 37. Three such mols. would form a structural triplet unit. The resulting 3-atom mol. is roughly tetrahedral because of the grouping of the electrons of the octet in pairs, and the three are closely assembled with an atom triplet which is approximately trigonal. R. B. Sosman tried to follow in imagination the changes which occur as quartz glass crystallizes; and as the different forms of silica pass through their different inversion points. It is assumed that the atom-triplet $SiO_2$ maintains its individuality in all forms of quartz and silicates (*q.v.*). The union of these triplets furnishes a silica-thread:

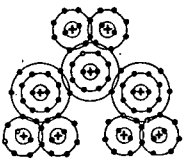
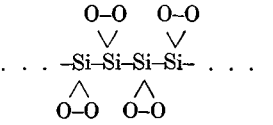


FIG. 37. — Electronic Structure of the Silica Molecule.



These threads are supposed to form in the liquid state or even in the vaporous state. In the liquid they are in a constant state of vibration and movement, with the oxygen atoms in haphazard orientation relative to the thread. On this view, solid silica glass is analogous to a compressed pad of wires. The thread structure is believed to persist in the crystalline state, and the three principal crystalline modifications (cristobalite, tridymite, and quartz) are built up by combining the threads through the oxygen atoms. The high to low inversions ($\alpha$–$\beta$) in all three forms are considered to be due to a change in the state of motion of certain electron orbits resulting from increased thermal vibration of the atoms. These changes produce sudden alterations in the shape of the silica triplet and the relative positions of the two oxygen atoms. In cristobalite, the oxygen atoms of the silica threads are incompletely fixed, some of the threads being capable of rotation about the silica axis. This explains the variable inversion point of this form of silica. F. Rinne, and J. Beckenkamp have made suggestions about the structure of $\beta$-quartz; and J. Beckenkamp, about the structures of tridymite and cristobalite.

The natural and artificial etching of quartz crystals brings out the peculiarities

of twinning, and the enantiomorphism of the crystals. The **corrosion figures** of left-handed quartz are complete mirror images of those of right-handed quartz, as illustrated by Fig. 40. The etching of quartz with *hydrofluoric acid* has been

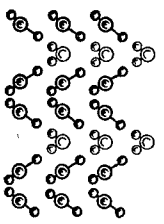


FIG. 38.—Arrangements of Atoms in Right-handed Quartz Crystal.

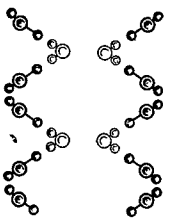


FIG. 39.—Arrangements of Atoms in the Brazilian Twinning of Quartz.

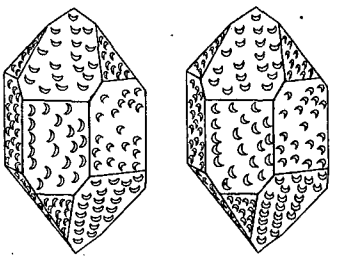


FIG. 40.—Corrosion Figures of Quartz with Hydrofluoric Acid.

studied by F. Leydolt,[6] G. A. F. Molengraaff, J. Beckenkamp, A. Stelzner, F. Gonnard, S. Ichikawa, O. Meyer and S. L. Penfield, A. Bömer, A. C. Gill, F. Salm-Horstmar, etc.; with a soln. of *potassium or sodium carbonate*, by G. A. F. Molengraaff; with a soln. of *potassium hydroxide*, by O. Mügge, H. Baumhauer, and J. Beckenkamp; with a soln. of *sodium silicate* or *sodium borate*, by G. Spezia; with a soln. of borax under press., by G. Lincio; and with *water* under press., by G. Spezia. C. Friedel also examined the corrosion figures produced on $\beta$-quartz by fused *potassium hydrosulphate* at 600°. K. Jimbo, and S. Ichikawa discussed the natural etching of quartz.

In the Arabian *The Book of the Best Things for the Knowledge of Mineral Substances*, by **Abu-r-Raihan**,[7] written towards the end of the tenth century, the **specific gravity** of rock crystal is stated to be 2·50; and another Arabian writer, Al-Khazini, in his *Book of the Balance of Wisdom*, written in the twelfth century, gave 2·88 for the sp. gr. of what is thought to be rock crystal. R. Boyle,[8] in 1690, gave 2·650, and D. G. Fahrenheit, in 1726, gave 2·669. A. le Royer and J. B. A. Dumas gave 2·652 at 4° in vacuo; C. J. St. C. Deville, 2·656; W. H. Miller, 2·65259 at 18°; F. G. Schaffgotsch, 2·653 at 13° (mean of 5); T. Scheerer, 2·653; A. Liversidge, 2·683 at 20°; A. L. Day and E. S. Shepherd, 2·650 at 25°; L. Ahlers, 2·6507–2·6528 at 0°/4°; J. Joly, 2·649–2·652 at about 14°/4°; R. Weber, 2·638; A. S. Herschel and co-workers, 2·54; A. Bartoli, 2·63; and F. C. Neumann, 2·61. F. S. Beudant gave 2·6354 and 2·6541 for the extremes of eleven determinations. L. Ahlers measured the sp. gr. of quartz. H. C. Dibbits gave:

| | 0° | 5° | 10° | 15° | 20° | 25° | 30° | 50° | 100° |
|---|---|---|---|---|---|---|---|---|---|
| Sp. gr. | 2·6507 | 2·6502 | 2·6498 | 2·6493 | 2·6488 | 2·6484 | 2·6479 | 2·6460 | 2·6409 |

A. Breithaupt gave for amethyst, 2·659–2·744; for smoky quartz, 2·651–2·658; for rose quartz, 2·651–2·658; and for milky quartz, 2·618. A. Forster said that the sp. gr. of a sample of smoky quartz was 2·6503 at 0°, and after decolorization by heat, 2·6502. The Earl of Berkeley's values ranged from 2·6484–2·6487 for temp. between 21·24° and 21·95°. A. W. Warrington gave $2{\cdot}650457 \pm 0{\cdot}000013$ at 0°; and the vol., $v$, at $\theta°$, is $v=v_0(1+0{\cdot}0_4336690+0{\cdot}0_731270^2)$, when $v_0$ is the vol. at 0°. For the sp. gr. of tridymite, G. vom Rath gave 2·295–2·326 between 15° and 16°; 2·282 at 18·5°; 2·247 for asmanite; and 2·166 for a sample of tridymite from Csik-Sz-Domokos in Hargitta Gebirge. A. Baltzer gave 2·208 for a sample from Lipari; and A. Weisbach, 2·274–2·278 for a sample from the Rittersgrün meteorite. A. Koch gave 2·43 for the sp. gr. of tridymite. G. Rose gave for artificial tridymite 2·311–2·373; P. Hautefeuille, 2·30 at 16°; and A. L. Day, 2·328–2·326. H. Steinmetz said that when $\alpha$-tridymite changes to $\beta_1$-tridymite

at 115°, its vol. expands 0·6 per cent. According to E. Mallard, the sp. gr. of cristobalite is 2·34, a little higher than the value for tridymite; P. Gaubert gave 2·348; and G. vom Rath, 2·27. The mean sp. gr. of eleven samples of artificial calcined silica was found by F. G. Schaffgotsch to be 2·20 at 12·5°, and F. Ullik gave 2·323. E. W. Washburn and L. Navias gave for the sp. gr. at 25°/25° of raw chalcedony, 2·55–2·61; raw flint, 2·61–2·63; quartz, 2·65; calcined chalcedony, 2·175; calcined flint, 2·25; cristobalite, 2·33; tridymite, 2·27; and silica-glass, 2·194–2·213. C. J. St. C. Deville found that the sp. gr. of crystalline silica, 2·656, fell to 2·22 after fusion. W. A. Shenstone gave 2·21 for the sp. gr. of vitreous silica or quartz glass; A. L. Day and E. S. Shepherd gave 2·213; and F. A. Schulze, 2·22. C. Doelter gave for the best representative values:

| | Quartz | Tridymite | Cristobalite | Opal | Quartz glass |
|---|---|---|---|---|---|
| Sp. gr. . . . | 2·65 | 2·31 | 2·30 | 2·20 | 2·20 |

J. Johnston and L. H. Adams measured the sp. gr. of quartz and concluded that when homogeneous material free from cracks and cavities is powdered, the change of density thereby produced is but little greater than the error of the method of measurement. *E. W. Washburn and L. Navias found the sp. gr. of calcined* chalcedony to be raised about 2 per cent. when the material is very finely powdered. They attribute this to the opening up of pores previously sealed from access by the liquid by which the sp. gr. was determined. It is, however, also probable that the increase is due to contamination from the vessels in which the material was ground. Similar remarks, but in the converse direction, apply to the reduction in the sp. gr. of quartz ground in an agate mortar observed by P. C. Ray. The **hardness** of quartz,[9] tridymite, and cristobalite is 7·0 (the diamond, 10); chalcedony is a little softer. According to F. Auerbach, the hardness of quartz on a face, parallel to the *c*-axis, is in absolute numbers, 308 kgrms. per sq. mm. (2. 20, 7), and if vertical to that axis, 230 (diamond, 2500). H. Rose said that the hardness of quartz glass is fully equal to that of rock crystal; and, according to W. A. Shenstone, the hardness lies between that of felspar and chalcedony. According to M. Herschkowitsch, quartz glass has a hardness of 233 kgrms. per sq. mm. (diamond, 2500). R. Franz gave for the relative hardness (corundum 1000), 667; F. Auerbach, 268; A. Rosival, 176; T. A. Jaggar, 40; and F. Pfaff, 390. The subject was discussed by A. Reis and L. Zimmermann. C. Johns and C. H. Desch showed that silica glass is harder than crystalline quartz. P. J. Holmquist investigated the abrasive hardness with carborundum of different grain-size. He also found that with the (0001)-face as standard for the abrasive hardness, 1000, that for the $(10\bar{1}0)$-face was 900; and for the $(10\bar{1}1)$-face, 840. C. E. Guye and A. Morein studied the viscosity of quartz threads.

The elasticity of quartz with respect to sound-figures was studied by F. Savart.[10] He cut circular plates parallel or perpendicular to the principal axis, and also planes parallel to cleavage faces; he found that the elasticity of all the diameters of any plane perpendicular to the principal axis is sensibly the same; planes parallel to the axis are not the same, but if three planes be taken which form equal angles with each other, the elasticity is the same. According to W. Voigt, the **modulus of elasticity** of quartz is 13,050 kgrms. per sq. mm. at −45°; 10,304 at 0°; 8405 at 45°; and 7853 at 90°. F. Auerbach gave 10,300 at 0°. At ordinary temp., C. E. Guye and V. Fredericksz found the elastic modulus decreases with a fall of temp.; with metals, the reverse usually obtains. On the other hand, A. Perrier and B. de Mandrot found that the elasticity of quartz decreases as the temp. rises to 575°; beyond that, the elasticity at first increases very greatly for small increments of temp., and then gradually diminishes. They gave in kilograms per sq. mm., parallel to the optic axis, 10,480 at 18°; 6960 at 572°; 6510 at 574°; 6320 at 574·5°; 6020 at 575°; 6680 at 576°; 9060 at 577·5°; and 9910 at 1078°; in a direction perpendicular to the optic axis, 8010 at 18°; 3570 at 573°; 3210 at 574°; 9030 at 576°; 10,530 at 585°; and 12,190 at 1140°. A. Blackie found that the samples

of commercial quartz glass had a tensile strength varying from 281 to 902 kgrms. per sq. cm., and in all cases after heating for definite periods to temp. between 1124° and 1353°, the strength fell considerably owing to devitrification by the growth of tridymite. W. Voigt gave for the **tensile strength** parallel to the chief axis, 16·3 kgrms. per sq. mm., and vertical to that axis, 12·6 krgms. per sq. mm.; and for the **crushing strength,** 182 kgrms. per sq. mm., and 160 kgrms. per sq. mm. vertical to that axis. K. Rinne gave 153·64 kgrms. per sq. mm. G. Berndt gave 25,000 kgrms. per sq. cm. for the crushing strength of quartz parallel to the optic axis, and 22,800 kgrms. per sq. cm. perpendicular thereto. F. Stumpf measured the elastic constants of quartz glass; and S. N. Petrenko, the behaviour of quartz glass under compressive tests. F. A. Schulze found the elasticity of quartz glass to be less than that of quartz. A. A. Griffith found the tensile strength of fresh fibres of fused quartz diminishes in a few hours to its normal value. This is explained by the formation of ultra-microscopic cracks. A. Mallock obtained for the elastic modulus of quartz in the direction of the axis $7{\cdot}46\times10^{11}$ dynes per sq. cm.; for smoky quartz, $1{\cdot}207\times10^{12}$; and for agate, $6{\cdot}381\times10^{11}$. W. Voigt also found for the coeff. of torsion of quartz 8405 kgrms. per sq. cm. and 5085 kgrms. per sq. mm. for the **torsion modulus** at 0°, and 3481 at 90°; F. Auerbach gave 6900. F. Auerbach, and F. A. Schulze gave 6970 kgrms. per sq. mm. for the elasticity of quartz glass when the value for quartz crystals is 10,620 kgrms. per sq. mm. when parallel to the principal axis, and 8566 when vertical thereto. F. Horton found the torsion modulus of quartz-glass at 15° is $3{\cdot}001\times10^{11}$ dynes per sq. cm., and at 1060°, almost zero. F. A. Schulze gave 6238 kgrms. per sq. mm. for the elastic modulus; R. Threlfall, 5180; and C. V. Boys, 6000. A. Pazziani and C. E. Guye studied the torsion modulus of quartz-glass fibres, and the effects of annealing. According to R. Threlfall, and C. V. Boys, the rigidity of quartz-glass fibres at 22° is $2{\cdot}8815\times10^{11}$ dynes per sq. cm.; Young's modulus, $5{\cdot}1785\times10^{11}$ dynes per sq. cm.; the bulk modulus, $1{\cdot}435\times10^{11}$ dynes per sq. cm.; and the limit allowable twist is approximately one-third of a turn per cm. in a fibre 0·01 cm. diam. W. Voigt found the **compressibility** coeff. of quartz to be $\beta=2{\cdot}65\times10^{-6}$—about one-twentieth of the value for water; for quartz glass, the value is $1{\cdot}925\times10^{-6}$. A cm. cube could support a weight of 182 kgrms. per sq. mm. parallel to the axis, and 160 kgrms. vertical to the axis, without fracture. E. Madelung and R. Fuchs gave $2{\cdot}66\times10^{-6}$ ($p$=125 atm.); and L. H. Adams, E. D. Williamson, and J. Johnston gave $2{\cdot}31\times10^{-6}$ to $2{\cdot}7\times10^{-6}$ between 0 and 10,000 megabars. A. Schidloff and M. A. Klotz found $1{\cdot}925\times10^{-6}$ for the compressibility of quartz glass; E. Madelung and R. Fuchs gave $2{\cdot}69\times10^{-6}$ ($p$=125 atm.); and L. H. Adams, E. D. Williamson, and J. Johnston, $3{\cdot}1\times10^{-6}$ from $p$=0 to $p$=10,000 megabars. S. Ichikawa studied the lustre and brittleness of quartz.

According to H. Fizeau,[11] the **coefficient of thermal expansion** of quartz for the temp., $\theta$, is $(771{\cdot}1+1{\cdot}712\theta)10^{-8}$ if measured vertical to the $c$-axis, and $(1316{\cdot}2+2{\cdot}526\theta)10^{-8}$, if measured parallel to the $c$-axis. H. Kopp gave 0·000039–0·000042 for the coeff. of cubical expansion of quartz. R. Benoit gave for the coeff. of linear expansion parallel to the chief axis, $0{\cdot}0_5748$, or, at $\theta°$, $\alpha\times10^9=7110{\cdot}7+17{\cdot}12\theta$; H. Fizeau gave $0{\cdot}0_5781$ at 40°; K. Scheel, $0{\cdot}0_5747$; and O. Weigel, $0{\cdot}0_5737$; and perpendicular to the chief axis, H. Fizeau gave $0{\cdot}0_41419$ at 40°; R. Benoit, $0{\cdot}0_40371$ at 20°, or, at $\theta°$, $\alpha\times10^9=13162{\cdot}7+25{\cdot}26\theta$. For the length, $l$, of quartz at $\theta°$ between room temp. and 100°, when the length at 0° is $l_0$, K. Scheel gave $l=l_0(1+7{\cdot}144\times10^{-6}\theta+0{\cdot}00815\times10^{-6}\theta^2)$; H. Fizeau, $l=l_0(1+7{\cdot}10\times10^{-6}\theta+0{\cdot}00885\times10^{-6}\theta^2)$; R. Benoit, $l=l_0(1+7{\cdot}161\times10^{-6}\theta+0{\cdot}00801\times10^{-6}\theta^2)$; and E. Reimerdes, $l=l_0(1+6{\cdot}925\times10^{-6}\theta+0{\cdot}00819\times10^{-6}\theta^2)$; H. McA. Randall represented the coeff. of expansion by $\alpha\times10^8=717{\cdot}0+1{\cdot}620\theta$ up to 250°, and by $\alpha\times10^8=1125{\cdot}0+1{\cdot}65(\theta-250)+0{\cdot}00566(\theta-250)^2+0{\cdot}0000134(\theta-250)^3$, between 250° and 470°. A. Müller gave for quartz parallel to the chief axis, $10^6(l-l_0)/l_0$, $7{\cdot}067\theta+0{\cdot}008362\theta^2$ between 0° and 360°; $3628+13{\cdot}00(\theta-360)+0{\cdot}01852(\theta-360)^2+0{\cdot}0_46721(\theta-360)^3$; and from 500°–540°, $5893+23{\cdot}07(\theta-500)+0{\cdot}1031(\theta-500)^2$.

H. le Chatelier has measured this constant over a range extending from 270°–1060°, and has shown, in his memoir, *De l'action de la chaleur sur le quartz*, that with quartz there is an abrupt change between 480° and 570°, corresponding with a change in the index of refraction. The thermal expansion of quartz in mm. per 100 mm., in passing from 270°–1060°, and starting from zero at 0°, is:

| | 270° | 480° | 570° | 660° | 750° | 910° | 1060° |
|---|---|---|---|---|---|---|---|
| Parallel to *c*-axis | 0·20 | 0·55 | 0·93 | 0·99 | 0·95 | 0·87 | 0·89 |
| Vertical to *c*-axis | 0·42 | 0·86 | 1·45 | 1·59 | 1·59 | 1·57 | 1·55 |
| Mean expansion | — | 1·76 | 1·28 | 1·39 | 1·40 | 1·34 | 1·33 |

If $l$ represents the expansion in unit length then at $\theta°$ below 570°, the expansion of quartz perpendicular to the principal axis is $l\times10^5=1{\cdot}35\theta+0{\cdot}000921\theta^2$; and parallel to the principal axis, $l\times10^5=0{\cdot}711\theta+0{\cdot}000856\theta^2$. R. Benoit gave for the former case $l\times10^5=1{\cdot}316\theta+0{\cdot}00126\theta^2$, and for the latter case, both observers obtained the same result. At 570°, there is an abrupt reversible change of vol. such that unit length becomes 1·0116 perpendicular to the principal axis, and 1·0068 parallel to that axis. Above 570°, there is a contraction such that perpendicular to the chief axis $l=0{\cdot}0162-0{\cdot}0000009(\theta-570)$, and parallel to that axis, $l=0{\cdot}0102-0{\cdot}0000037(\theta-570)$. P. Braesco, A. Müller, and R. Blackie made observations on the thermal expansion of quartz, etc. P. Braesco found that precipitated silica, when dehydrated by heating only to 600°, behaves like silica glass in having only a small coeff. of thermal expansion, and therefore behaves like amorphous silica; but when heated to 1000°–1600° it behaves just like cristobalite. H. le Chatelier's results for quartz, tridymite, amorphous silica, and calcined chalcedony are plotted in Fig. 41, with temp. as abscissæ, and the percentage expansions as ordinates. The abrupt change in the vol. of quartz when it is heated to 575° corresponds with the transition of $\alpha$-quartz into $\beta$-quartz as indicated above. R. Sahmen and G. Tammann gave 500°–550° for the transition temp., and G. Stein, 552°. O. Müggе made observations on this subject. Below the transition temp., the vol. *increases* with a rise of temp.; above that temp. the vol. *decreases* with rise of temp. There are other transition points not shown on this diagram because the speed of the change is so slow, and their existence has been demonstrated by other methods. When a large piece of rock crystal is heated to a high temp. it breaks into small pieces, unless the temp. rises very slowly past 575°, because not only does the unequal expansion in different directions set up strains, but because of the abrupt increase in the expansion coeff. at about 575°. The expansion of tridymite in mm. per 100 mm. is:

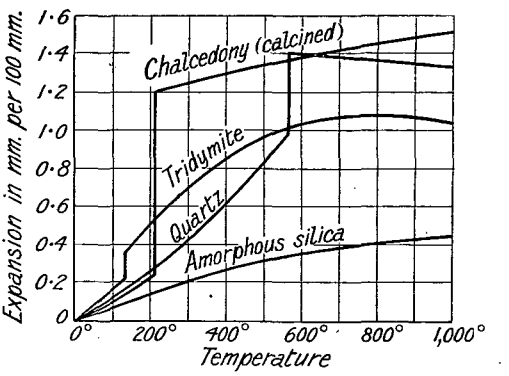



FIG. 41.—Expansion of Different Forms of Silica with Rise of Temperature.

| | 15° | 95° | 130° | 170° | 245° | 480° | 700° | 900° | 1050° |
|---|---|---|---|---|---|---|---|---|---|
| Expansion. | 0 | 0·16 | 0·22 | 0·42 | 0·63 | 0·95 | 0·08 | 0·07 | 0·05 |

The abrupt change, about 130°, according to H. le Chatelier, or between 115° and 120°, according to C. N. Fenner, corresponds with a change from the form, called $\alpha$-tridymite, to the other form, called $\beta_1$-tridymite, which has optically different properties. According to C. N. Fenner, at about 162°, there is another transformation of the $\beta_1$-tridymite into a third form of tridymite, called $\beta_2$-tridymite. H. le Chatelier measured the expansion of quartz which had been calcined in a steel furnace, at 1500°–1600°, when the sp. gr. had fallen to 2·2, and there were no signs

of crystallization in the product; hence he called it *la silice amorphe*. He found for the expansion in mm. per 100 mm.:

| | 15° | 270° | 570° | 660° | 990° |
|---|---|---|---|---|---|
| Expansion . . . | 0 | 0·20 | 0·35 | 0·41 | 0·45 |

The results are plotted in Fig. 41. For calcined chalcedony, he also found

| | 15° | 95° | 170° | 245° | 360° | 650° | 1050° |
|---|---|---|---|---|---|---|---|
| Expansion . . . | 0 | 0·06 | 0·20 | 1·23 | 1·29 | 1·40 | 1·53 |

There is therefore an abrupt change between 170° and 245°, as illustrated by Fig. 41. Measurements with a dilatometer gave 210° for the transition temp. E. W. Washburn and L. Navias found for the cubical expansion, in c.c. per gram per degree, of quartz $0{\cdot}25\times10^{-4}$ near 575°; $-0{\cdot}049\times10^{-4}$ near 570°; calcined chalcedony, $1{\cdot}4\times10^{-4}$ near 220°; calcined flint, $1{\cdot}4\pm10^{-4}$ near 227°; cristobalite, $1{\cdot}5\pm10^{-4}$ near 244°; and tridymite, $0{\cdot}15\pm10^{-4}$ near 117°. B. Bogitch made some measurements on the expansion of silica at temp. up to 1000°.

The coeff. of thermal expansion of quartz-glass is very small. H. le Chatelier [12] gave $0{\cdot}0_6 67$; and L. Holborn and F. Hennig gave 0·00000054 between 0° and 1000°, Fig. 41. F. Hennig found a porcelain rod, one metre long, expanded 4·271 mm. when heated from 16° to 1000°, whereas a quartz-glass rod, under similar conditions, expanded 0·531 mm. K. Scheel found that vitreous quartz between —190° and —46° contracts, not expands, and that the contraction is not overtaken at 16°. He found that two-metre rods, from two commercial samples of quartz-glass, when heated from —190°–16° were less than a metre long, for they appeared to have *contracted* 0·041 mm. and 0·015 mm. respectively, and when heated from 0°–100°, they expanded respectively 0·047 mm. and 0·050 mm. K. Scheel represents the length of a quartz-glass rod at a temp. $\theta°$ between 0° and 100° by $l_0(1+0{\cdot}0000003322\theta+0{\cdot}000000001147\theta^2)$, where $l_0$ represents the length of the rod at 0°. P. Chappius gave $l=l_0(1+0{\cdot}0_6 384741\theta+0{\cdot}0_8 1150\theta^2)$. S. Valentiner and J. Wallot obtained a minimum vol. with silica-glass at —75·4°. G. E. Merritt also found a contraction with rise of temp. from —200° to —70°, and above that an expansion. The following coeff. of thermal expansion show the relation of vitreous quartz to crystalline quartz, to porcelain, and to glass:

| Quartz | | Quartz glass | Ordinary glass | Jena zinc borate glass | White Türingen glass | Berlin porcelain |
|---|---|---|---|---|---|---|
| Parallel *c*-axis | Vertical *c*-axis | | | | | |
| $0{\cdot}0_5 781$ | $0{\cdot}0_4 1419$ | $0{\cdot}0_6 59$ | $0{\cdot}0_5 883$ | $0{\cdot}0_5 336$ | $0{\cdot}0_5 938$ | $0{\cdot}0_5 314$ |

According to G. W. C. Kaye,[13] the maximum density of quartz glass lies near —84°; the sp. gr., at ordinary temp., is near 2·22. When a glass vessel has been heated it does not at once contract to quite its original volume on cooling back to its former temp., but it suffers a slow contraction—*after contraction*, or *Nachwirkung*. This phenomenon is shown by the displacement or depression of the zero after a glass thermometer has been heated, and its gradual restoration after standing some months; and also by the gradual elevation of the zero of thermometers whose scale has been fixed before the glass has had time to season. According to A. Kuhn, quartz-glass does not show this phenomenon.

H. de Sénarmont [14] measured the isothermal ellipsoids in quartz and, expressing the results in mm., found:

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Major axis . | 9·75 | 10·00 | 11·60 | 12·50 | 13·75 | 15·00 | 18·00 |
| Minor axis . | 7·50 | 7·50 | 8·50 | 9·75 | 10·00 | 12·00 | 14·00 |
| Ratio . . | 1·30 | 1·33 | 1·35 | 1·28 | 1·38 | 1·28 | 1·29 |

Measurements were also made by E. Jannettaz, and W. C. Röntgen; the latter showed that the larger the ellipsoidal figure the smaller the ratio of the two axes. D. Forbes' measurements of the **thermal conductivity** were not satisfactory; R. Weber found 0·0158 cal. per cm. per sec. per degree at 0°, and a temp. coeff. of —0·0019. The heat conductivity of quartz is greatest along the chief axis. A. Tuschschmidt's values are 0·0263 unit parallel to the axis, and 0·0160 unit

vertical to that axis at 17°. C. H. Lees obtained 0·030 and 0·016 respectively; E. Griffiths and G. W. C. Kaye, 0·0244 and 0·0147 respectively; and O. S. Buckner, 0·00099 for silica bricks. A. S. Herschel and co-workers obtained 0·0024 unit for the thermal conductivity of flint, and R. S. Hutton and J. R. Beard, 0·00060 for quartz (Calais) sand. Observations were made by M. Smoluchowsky, A. Eucken, and V. von Lang. According to A. Eucken, quartz-glass at 0° has 7·5 times less conductivity than the crystals, and at —190°, 55 times less. R. S. Hutton and J. R. Beard obtained 0·00051 for the conductivity of fused quartz. P. Gilard summarized the literature on the thermal conductivity of silica bricks—*vide* clays. Observations on this subject were made by E. Griffiths, A. T. Green, W. Nusselt, S. M. Marshall, E. Heyn and co-workers, P. Goerens and J. W. Gilles, B. Dudley, Y. Tadokoro, S. Wologdine, G. Dougall and co-workers, R. A. Horning, and G. H. Brown.

F. E. Neumann[15] gave 0·1883 for the **specific heat** of quartz between 14° and 100°; H. V. Regnault, 0·19132 between 13° and 99°; H. Kopp, 0·180–0·190 between 20° and 50°; J. Joly, 0·1881 between 12° and 100°; A. Herschel and co-workers, 0·18 for quartz, and for various sandstones, 0·18–0·28; J. Pionchon, $0·1737+0·000394\theta-0·0_727\theta^3$ below 400°, and 0·305 between 400° and 1200°; R. Ulrich, 0·1909 between 14° and 98°; R. Weber, $0·1754+0·0004\theta$; K. Schulz, 0·1875 for Mamorian quartz between 20° and 100°, and 0·1871 for Brazilian quartz between 20° and 100°; 0·2086 between 20° and 250°; and 0·2253 between 20° and 410°. A. Bartoli gave 0·191 between 23° and 100°; 0·241 between 28° and 312°; 0·308 between 29° and 417°; and 0·316 between 30° and 530°; and H. Stierlin, 0·2030 between 20° and 138°, and 0·2472 between 20° and 609°. A. Magnus, K. Bornemann and O. Hengstenberg, and A. Dannholm made observations on the sp. ht. of quartz and amorphous silica. W. P. White found for the atomic heat (*i.e.* sp. ht. × mol. wt. divided by the number of atoms in molecule) between 0° and

| | 100° | 300° | 500° | 700° | 900° | 1100° | 1300° | 1400° |
|---|---|---|---|---|---|---|---|---|
| Quartz | 3·755 | 4·359 | 4·784 | 5·112 | 5·217 | 5·308 | — | — |
| Quartz glass | 3·708 | 4·272 | 4·627 | 4·870 | 5·049 | — | — | — |
| Cristobalite | 3·784 | 4·689 | 4·876 | 5·042 | 5·163 | 5·276 | 5·351 | 5·388 |

The sp. ht. between 0° and 500° for quartz is represented by $0·1685+0·000194\theta-0·0_611\theta^2$, and for quartz glass, $0·1670+0·000189\theta-0·0_6125\theta^2$. For the at. ht. (sp. ht. × 20·1) at the given temp., W. P. White gave:

| | 0° | 100° | 300° | 500° | 700° | 900° | 1100° | 1300° |
|---|---|---|---|---|---|---|---|---|
| Quartz | 3·37 | 4·10 | 5·10 | 5·90 | 5·46 | 5·66 | — | — |
| Quartz glass | 3·33 | 4·05 | 4·95 | 5·35 | 5·58 | 5·75 | — | — |
| Cristobalite | — | — | — | — | 5·55 | 5·67 | 5·77 | 5·86 |

I. Iitaka found for the sp. ht. of silica-glass:

| | 135° | 180° | 384° | 466° | 493° | 573° | 766° |
|---|---|---|---|---|---|---|---|
| Sp. ht. | 0·197 | 0·199 | 0·220 | 0·224 | 0·230 | 0·247 | 0·258 |

R. Wietzel measured the mean sp. ht. between 0° and $\theta$°; and his data are indicated in Table III. At high and low temp., quartz glass has the greatest sp. ht., as it should have, being the modification stable at the higher temp., but over a wide range it has a lower sp. ht. than quartz and cristobalite, and below 575°, cristobalite has a lower sp. ht. than quartz. The sp. ht. of quartz before the transformation at 575° was 0·2480°, and after the transformation, 0·2527. The at. ht. are indicated in Fig. 42. F. Simon gave for the mol. ht. of quartz glass at 18·9° K. 0·107, and at 287·6° K., 3·454; for cristobalite at 28·6° K., 0·208, and at 116·6° K., 1·560; and A. Perrier and H. Roux, 0·307–0·312 between 428·46° and 510·07°; 0·321–0·337 between 510·07° and 571·00°; and 0·289–0·293 between 581·13° and 651·90°. For the difference in the at. ht. at constant press. and constant vol. calculated from the expansion, W. P. White gave for quartz:

| | 100° | 300° | 500° | 550 |
|---|---|---|---|---|
| $(C_p-C_v)\times 20·1$ | 0·0463 | 0·1313 | 0·862 | 3·832 |

TABLE III.—MEAN SPECIFIC HEATS OF SILICA
(in gram-cals. between 0° and $\theta$°).

| | Quartz glass. | Cristobalite. | Quartz. | Chalcedony. |
|---|---|---|---|---|
| 100° | 0·1850 | 0·1896 | 0·1860 | 0·1965 |
| 200° | 0·2006 | 0·2125 | 0·2031 | 0·2115 |
| 225° | — | 0·2196 | — | — |
| 250° | 0·2068 | 0·2268 | 0·2111 | 0·2170 |
| 400° | 0·2229 | 0·2417 | 0·2288 | 0·2325 |
| 565° | — | — | 0·2470 | — |
| 575° | 0·2366 | 0·2507 | 0·2480 | 0·2510 |
| 600° | 0·2385 | 0·2521 | 0·2530 | 0·2523 |
| 800° | 0·2506 | 0·2601 | 0·2585 | 0·2590 |
| 1000° | 0·2584 | 0·2656 | 0·2630 | 0·2633 |
| 1200° | 0·2621 | 0·2702 | 0·2661 | 0·2695 |
| 1400° | 0·2691 | 0·2737 | 0·2690 | — |
| 1600° | 0·2777 | 0·2763 | 0·2710 | — |
| 1700° | 0·2810 | 0·2770 | 0·2720 | — |

R. Wietzel calculated the free energy of the different phases of silica. The sp. ht. of chalcedony increases more with rise of temp. than does quartz. P. Laschtschenko found the sp. ht. of quartz, at the given temp., to be :

| | 200° | 300° | 405° | 550° | 600° | 700° | 800° | 892° |
|---|---|---|---|---|---|---|---|---|
| Sp. ht. . . | 0·2250 | 0·2255 | 0·2306 | 0·2350 | 0·2400 | 0·2479 | 0·2471 | 0·2476 |

and that of chalcedony at 139° to be 0·1930 ; at 203°, 0·1961 ; at 227°, 0·2039 ; at 330°, 0·2500 ; at 405°, 0·2520 ; at 500°, 0·2515 ; and at 580°, 0·2500. There is thus an abrupt change between 227° and 230° with chalcedony ; and with quartz one between 580° and 600°. K. Schulz gave 0·2054 for the sp. ht. of quartz-glass from Brazilian quartz between 20° and 100° ; 0·2054 between 20° and 250° ; and 0·2204 between 20° and 410°. F. Koref gave 0·0882 for the sp. ht. of quartz-glass between −193·1° and −79·2°, and 0·1471 between −76·3° and 0° ; W. Nernst gave for the mol. ht. of quartz glass 0·637 at −246·75° ; 0·644 at −243·6° ; 0·844 at −237·8° ; 1·33 at −230·4° ; and 3·14 at −189° ; H. Stierlin, for quartz-glass between 18° to 27° and $\theta$° :

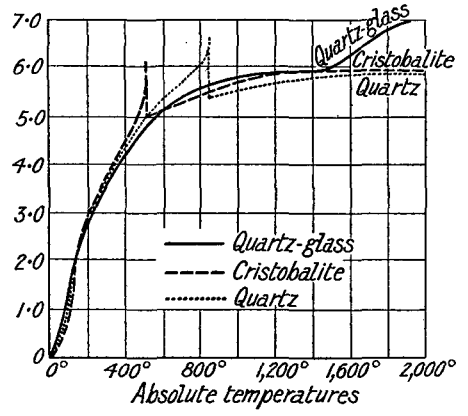



FIG. 42.—The Atomic Heats of Quartz, Cristobalite, and Quartz Glass.

| $\theta$ . . | 77° | 90° | 218° | 314° | 411° | 512° | 704° | 900° |
|---|---|---|---|---|---|---|---|---|
| Sp. ht. . | 0·15283 | 0·19084 | 0·20501 | 0·21418 | 0·22388 | 0·23213 | 0·24243 | 0·25043 |

or $0{\cdot}167851+0{\cdot}0_3352674\theta-0{\cdot}0_6407447\theta^2+0{\cdot}0_9173196\theta^3$. C. Dieterici gave $0{\cdot}16791+0{\cdot}000350\theta-0{\cdot}0_630750\theta^2$ at $\theta$° between 100° and 300° ; and for the sp. ht. between 18° and $\theta$°, $0{\cdot}1676+0{\cdot}00016\theta$ for temp. up to 100°, and $0{\cdot}16791+0{\cdot}000175\theta-0{\cdot}0_61025\theta^2$ for temp. between 100° and $\theta$° up to 300°. Measurements between 0° and 320° were made by J. Heinrichs. Observations on commercial silica bricks were made by E. Heyn and co-workers, Y. Tadokoro, W. Steger, and L. Bradshaw and W. Emery. G. Tammann and H. Dickmann found that, at 105°, superimposed mercury begins to penetrate powdered quartz.

In 1766, J. P. J. d'Arcet[16] melted quartz sand and silica at the highest temp. of a wind furnace. About 1802, R. Hare melted quartz in the flame of the oxy-

hydrogen blowpipe, and A. Marcet, J. Mantell, F. Stromeyer, and E. D. Clarke found that all the different varieties of silica can be fused in the flame of a spirit-lamp fed with oxygen gas, or in the oxyhydrogen blowpipe flame. H. Davy fused it electrically. A. Gaudin showed that fused silica can be drawn out into long threads like molten glass—*vide infra* quartz glass. According to R. Cusack, quartz begins to soften at 1406°, and its **melting point** is 1425°. A. Lampen said that the edges of a piece of quartz are rounded at 1650°, and it fuses at 1700°. A. Brun gave 1780° for the m.p.; W. C. Roberts-Austen, 1775°; W. Hempel, 1685°; and O. Boudouard, 1830°. A. L. Day and E. S. Shepherd, and R. B. Sosman gave 1625° for the m.p. of quartz, but it is not clear to which form this constant refers. A. Wietzel found the m.p. of quartz without conversion to cristobalite, to be between 1600°–1670°. A. Dufour said that before melting, silica becomes viscid; and G. Stein, that at 1600° silica is very viscid, but it becomes much less viscid at 1750°. L. Baraduc-Muller said that silica is not deformed at 1650°, but it begins to soften between 1702° and 1706°. These determinations are extraordinarily divergent. The equilibrium condition of all the different forms of crystalline silica, between 1470° and the m.p., is $\beta$-cristobalite. Hence, the m.p. of quartz cannot be obtained if the temp. be raised slowly enough to allow these different transformations to be completed; under these conditions, the observed m.p. must really be that of $\beta$-cristobalite; and generally, the observed m.p. of quartz must depend on the rate at which quartz is converted into its various transition forms, which, in turn, depends on the rate of heating, and the nature of what might be called impurities which act as mineralizing agents. The heating curve of vitreous silica or silica glass shows none of these changes, and it begins to lose its form about 1625°. If, however, this substance were kept long enough in any particular region of temp. it would probably pass into the form stable at that temp. C. N. Fenner gave 1470° for the m.p. of quartz; and 1625° for the m.p. of cristobalite. K. Endell and R. Rieke gave $1685° \pm 10°$ for the m.p. of cristobalite; N. L. Bowen confirmed this value; A. Wietzel obtained 1696°; and H. le Chatelier, 1780°. O. Ruff and P. Schmidt said silica melts as $\alpha$-cristobalite at $1696° \pm 10°$. C. N. Fenner said that H. le Chatelier's value must be high because cristobalite can be fused to a glass in a platinum crucible, whereas the m.p. of platinum is 1755°. J. B. Ferguson and H. E. Merwin gave $1670° \pm 10°$ for the m.p. of cristobalite and $1710° \pm 10°$ for the m.p. of tridymite. P. D. Quensel gave 1550° for the m.p. of tridymite; and C. Doelter, 1575°–1580°.

C. N. Fenner's values for the **transition temperatures** of the different forms of silica are indicated in Fig. 26. For $\alpha$-quartz$\leftrightharpoons\beta$-quartz, H. le Chatelier gave 575°; F. E. Wright and E. S. Larsen, 575°; R. von Sahmen, 500°–550°; and G. Stein, 552°. C. N. Fenner found the transition point rises 0·01° per atm. rise of press. For the transformation $\beta$-quartz$\leftrightharpoons\beta_2$-tridymite, C. N. Fenner gave 870°; and A. L. Day, 800°. C. N. Fenner estimated that this transition point rises 0·10537° per atm. rise of press. For the transformation $\beta$-tridymite$\leftrightharpoons\beta_1$-tridymite, E. Mallard gave 130°; H. Steinmetz, 115°; F. E. Wright, 120°; and C. N. Fenner, 115°–120°. For the transformation $\beta_1$-tridymite$\leftrightharpoons\beta_2$-tridymite, C. N. Fenner gave 163°. For the transformation $\alpha$-cristobalite$\leftrightharpoons\beta$-cristobalite, E. Mallard gave 175°; F. E. Wright, 225°; C. N. Fenner, 240°–274°; and K. Endell, 230°. For the transformation $\beta_2$-tridymite$\leftrightharpoons\beta$-cristobalite, C. N. Fenner, and N. L. Bowen gave 1470°, the transition temp. with chalcedony is between 170° and 245°, according to H. le Chatelier, and 173°, according to G. Stein. The relation between the m.p. and the transition temp. was studied by R. Lorenz and W. Herz.

The latent heats of the transformations are somewhat uncertain; and the estimates which have been made are the result of indirect computations. J. A. Cunningham [17] calculated the latent **heat of fusion** of quartz to be 135 cals. per gram; and J. H. L. Vogt, 135 cals. E. W. Washburn calculated 6·8 Cals. per mol. for the latent heat of fusion of cristobalite. From D. Tschernobaeff's data for the heats of the reactions $SiO_{2\ sand}+Na_2CO_3=Na_2SiO_3+CO_2-30·4$

Cals., and $10SiO_2+Na_2CO_3=(9SiO_2,Na_2SiO_3)_{glass}+CO_2$ −96 Cals., M. W. Travers obtained −7·3 Cals., and R. C. Ray, 6·95 Cals., for the heat of transformation $SiO_{2cryst.}\rightarrow SiO_{2glass}$; at 900° R. C. Ray's value is 6·50 Cals., and at the m.p. nearly the same as at ordinary temp. C. N. Fenner obtained for the latent heat of transformation α-quartz→β-quartz, 4·0±1·0 cals. W. P. White gave 4·3±1·0 cals. R. Wietzel obtained 2·20–2·35 Cals., and O. Mülert 2·21 Cals., for the heat of crystallization of quartz and chalcedony; and −0·06 for the heat of crystallization of cristobalite.

In 1806, L. N. Vauquelin,[18] and in 1814, J. MacCullogh, reported that silica could be volatilized, while in 1840, J. Jeffreys claimed to have volatilized 100 kgrms. of silica by leading steam into a pottery oven at a temp. higher than the m.p. of cast-iron, but it is not clear if the white dust which was collected had not been carried along mechanically in the current of flue-gas. H. Moissan boiled silica in an electric arc-furnace and obtained a bluish-white vapour which condensed in spherical globules partly amorphous and partly crystalline. According to C. Stein, quartz begins to sublime just over its m.p., approximately 1600°. The sublimate is partly vitreous, partly flocculent silica, and partly tridymite crystals. The volatilization has been noticed at even lower temp. by E. Cramer, P. Schützenberger, E. Hirsch, L. Baraduc-Muller, etc. According to A. L. Day and E. S. Shepherd, silica-glass vaporizes copiously at the m.p. of platinum, 1755°. W. R. Mott gave 3500° for the **boiling point** of silica at 760 mm. O. Ruff and co-workers found silica distils rapidly at 2000° and 15 mm. press.; the vap. press. of silica was also found to be:

| | 1860° | 1900° | 1910° | 2000° | 2055° | 2080° |
|---|---|---|---|---|---|---|
| Vap. press. | 15 | 19 | 25 | 300 | 477 | 761 |

H. von Wartenberg has shown that a reducing gas is always present at these high temp.—free hydrogen, or hydrogen derived from carbon and steam—which reduces the silica locally, and the resulting silicon vap. burns to silica in the cooler parts of the furnace. Silicates behave in an analogous way, for the silica in them is also reduced by hydrogen almost, but not quite, as readily as free silica. The reduction of silica explains how platinum sometimes forms platinum silicide when it is heated in a reducing atm.—not in contact with the silica—presumably owing to the formation of silicon vap. or silicon hydride which attacks the platinum. Silica is also reduced by carbon, and by carbon monoxide, and a similar phenomenon then takes place. F. Kehrmann and B. Flürscheim refer to a loss of silica by evaporating an aq. soln. of an alkali silicate mixed with an excess of hydrochloric acid, but C. Freidheim and A. Pinagel show that the alleged loss by volatilization was probably incurred during filtration, not evaporation.

Crystals of quartz are uniaxial and optically positive. Quartz is doubly refracting in a direction vertical to the chief axis, and singly refracting in directions parallel to that axis; a plate cut at right angles to the chief axis is singly refracting at ordinary temp., but is doubly refracting between 560° and 580°. The **refractive index** of quartz is nearly the same, but rather higher than that of Canada balsam. The refractive index of the ordinary ray for sodium light is $\omega=1{\cdot}54418$, and for the extraordinary ray, $\epsilon=1{\cdot}55328$, showing that the double refraction $\epsilon-\omega=0{\cdot}009$ is low. The value of $\omega$ for smoky quartz is 1·54388, and $\epsilon=1{\cdot}55317$. C. N. Fenner[19] found that artificial crystals, obtained by heating powdered quartz with sodium tungstate for nearly a day below 865°, had the values $\omega=1{\cdot}544$, $\epsilon=1{\cdot}553$. E. Mallard gave 1·4775 for the index of refraction of tridymite with Na-light. P. Gaubert gave approximately 1·486 for the index of refraction of cristobalite for Na-light. Table IV summarizes some of the physical properties of the different forms of silica. The index of refraction is the most useful means of distinguishing these three crystalline forms of silica.

According to C. N. Fenner, the most easily determinable distinctive difference between *tridymite* and *cristobalite* is that between their indices of refraction. When tridymite is immersed in a liquid of refractive index 1·475, tests by the half-shade method or by the Becke-line method show that the index of the material is so nearly matched that the difference

TABLE IV.—SOME PHYSICAL PROPERTIES OF THE DIFFERENT FORMS OF NATIVE SILICA.

| Property. | Quartz. | Tridymite. | Cristobalite. | Chalcedony. | Opal. |
|---|---|---|---|---|---|
| Crystal system . | Hexagonal | Hexagonal | Tetragonal | Rhombic | Amorphous |
| Axial ratios . | $a:c=1:1{\cdot}100$ | $a:c=1:1{\cdot}6530$ | — | — | — |
| Hardness . . | 7·0 | 7·0 | 6·0–7·0 | 7·0 | 5·5–6·5 |
| Sp. gr. . . | 2·65 | 2·28 | 2·348 | 2·6 | 2·1 |
| Mol. vol. . . | 22·8 | 26·3 | 25·7 | 23·23 | — |
| Refractive index | 1·549 | 1·4775 | 1·486 | 1·537 | 1·437–55 |
| Double refraction | +0·009 | +0·0021 | 0·00053 | — | — |

is scarcely appreciable. A similar test may be used for cristobalite, using a liquid of refractive index 1·485. When both are present, a liquid of refractive index 1·480 will serve to show the proportions. In making up immersion liquids for use in this manner, a soln. of potassium-mercury iodide, which is sometimes recommended, is not at all suitable, because of the change in refractive index which is likely to occur while it is being used. It is much better to make use of mixtures of albolene, the index of which ranges from 1·477 to 1·485, with kerosene ($n=1{\cdot}450$) or with $\alpha$-monobromonaphthalene ($n=1{\cdot}658$). Albolene is a petroleum product; and the so-called Russian oil, American oil, etc., are virtually the same. Other distinctive differences between *tridymite* and *cristobalite* are that *tridymite* frequently assumes a lath-like development, and the extinction is then strictly parallel to the elongation. Wedge-shaped twins are common. With cristobalite, the grains are frequently elongated (perhaps an inherited property), but extinction may occur at various angles. A quite noticeable characteristic of cristobalite is the polysynthetic twinning, which gives several narrow stripes, as in plagioclase felspar, or the twinning may resemble the plaid effect of *microcline*. A method of discrimination between tridymite and cristobalite of great value, depends upon the different temp. of the $\alpha\beta$-inversions. This, however, requires the use of special apparatus.

The index of refraction of quartz has been the subject of numerous investigations. Measurements were made by F. Rudberg,[20] V. S. M. van der Willigen, E. Esselbach, E. Mascart, E. Sarasin, L. Mouton, C. Viola, W. Kohlrausch, G. Quincke, E. Abbe, W. Hallock, C. Pulfrich, J. Danker, K. Zimanyl, C. Soret, A. Mülheims, H. Dufet, E. F. Martens, H. C. Sorby, H. Rubens, E. F. Nichols, E. Wülfing, etc. The index of refraction of quartz increases as the wave-length of the light used decreases. Thus J. W. Gifford found:

| Wave-length ($\mu\mu$) . | 670 (Li) | 643·8 (Cd) | 546·1 (Hg) | 480·0 (Cd) | 404·6 (Hg) |
|---|---|---|---|---|---|
| Index of refraction | 1·45607 | 1·45677 | 1·46015 | 1·46357 | 1·46967 |

L. Mouton, H. Rubens, E. F. Nichols, and E. Carvallo made observations in the ultra-red; and E. Sarasin, C. H. Simon and H. Trommsdorff, E. F. Martens, and J. W. Gifford in the ultra-violet. E. W. Washburn and L. Navias found the index of refraction of raw chalcedony to be between 1·533 and 1·538; raw flint, 1·533–1·539; quartz, 1·544–1·553; calcined chalcedony, 1·456–1·470; calcined flint, 1·438; cristobalite, 1·484; tridymite, 1·475; and silica-glass, 1·457–1·460. The effect of temp. has been studied by H. Fizeau, H. Dufet, F. Schlagdenhauffen, G. Müller, C. Pulfrich, E. Reimerdes, J. O. Reed, F. J. Micheli, etc. The index of refraction increases as the temp. rises; thus, J. W. Gifford found that $\omega$ at 18·9° is 1·5441638, and at 25·3°, 1·5441013. H. Dufet gave $-d\epsilon/d\theta=0{\cdot}0_57223+0{\cdot}0_837\theta$ and $-d\omega/d\theta=0{\cdot}0_56248+0{\cdot}0_95\theta$. E. Mallard and H. le Chatelier noticed an abrupt change in this constant at about 570°. F. Rinne and R. Kolb's results with sodium light are illustrated by the curves, Fig. 43. According to A. N. Winchell, hexagonal crystals, exemplified by the *isotropic quartz* from Iron River, Michigan, may be

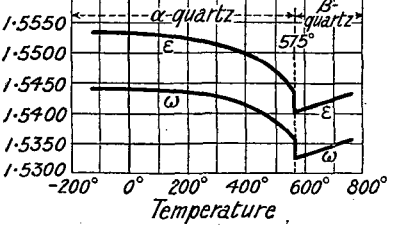



FIG. 43.—The Effect of Temperature on the Refractive Index of Quartz (Na-light).

isotropic, and the mineral furnishes X-radiograms like those of anisotropic quartz. In 1830, D. Brewster showed that quartz-glass is not doubly refracting. The index of refraction of quartz-glass has been measured by C. H. Simon and H. Trommsdorff, H. Dufet, E. F. Martens, M. Herschkowitsch, J. W. Gifford and W. A. Shenstone, and F. A. Schulze. J. W. Gifford found for light of wave-length $\lambda$, the refractive index of quartz-glass is :

| $\lambda$ | 670·8 | 546·1 | 508·6 | 435·9 | 404·6$\mu\mu$ |
|---|---|---|---|---|---|
| Index | 1·4560717 | 1·4601545 | 1·4619030 | 1·4667412 | 1·4696753 |

C. Hlawatsch studied the effect of colouring pigments on the refractive index and found :

| | Colourless quartz | Smoky quartz | Smoky quartz | | |
|---|---|---|---|---|---|
| | | | Light place | Dark place | Calcined |
| $\omega$ | 1·54433 | 1·54388 | 1·54403 | 1·54387 | 1·54436 |
| $\epsilon$ | 1·55305 | 1·55317 | 1·55299 | 1·55289 | 1·55344 |

The **double refraction** of quartz is small. The **dispersion** of the double refraction $\epsilon-\omega$ has been determined by M. de Lépinay, F. Paschen, L. Mouton, E. Ketteler, J. W. Gifford, J. O. Reed, G. Abati, E. F. Martens, E. Aschkinass, F. J. Michali, C. G. Knott, C. Pulfrich, etc. F. E. Wright and E. S. Larsen's data for the double refraction $\epsilon-\omega$ at different temp. are :

| | 15° | 100° | 220° | 535° | 570° | 590° | 1060° |
|---|---|---|---|---|---|---|---|
| $\epsilon-\omega$ | 0·00910 | 0·00902 | 0·00882 | 0·00811 | 0·00797 | 0·00760 | 0·00787 |

The refraction index of tridymite is 1·477, and the double refraction is feeble and positive.[21] In 1884, A. Merian noticed that when biaxial tridymite is warmed, it becomes uniaxial, and on cooling, the crystals again become biaxial. The mean refractive index of cristobalite for yellow light is 1·49. For artificial tridymite, prepared by heating powdered silica with sodium tungstate for about a day at about 875°, C. N. Fenner found for the refractive index parallel to the $a$- and $\beta$-axis 1·469, and for the $\gamma$-axis 1·473 (23°). Similarly, for cristobalite C. N. Fenner obtained for sodium light (at 23°) $\gamma$=1·487, $\alpha$=1·484 for artificial crystals prepared in a similar way, but at a temp. of 1475° instead of 875°. According to P. Gaubert, the double refraction of cristobalite is 0·00053 and negative. On heating to about 230°, there is an abrupt change from the doubly refracting into the isotropic crystalline variety, called $\beta$-cristobalite to distinguish it from normal or $\alpha$-cristobalite. Fused quartz is not doubly refracting. A. Ehringhaus and H. Rose compared the dispersion and double refraction of silicon, titanium, and tin dioxides with the mol. wt.

In 1812, J. B. Biot [22] found that crystals of quartz have the remarkable property of rotating the plane of polarization of light, transmitted in the direction of the principal axis, in such a way that in some crystals the ray is deflected to the right, and in others to the left. The former is conventionally called *right-handed quartz*, the latter *left-handed quartz*. J. B. Biot's convention as to the right- and left-handedness of quartz is now in fairly general use, although some confusion formerly prevailed, because J. Herschel reversed the convention proposed by J. B. Biot. J. Pereira said :

> If, on turning the analyzing prism or tourmaline *from left to right*, the colours descend in Newton's scale, that is, succeed each other in this order—*red, orange, yellow, green, blue, indigo*, and *violet*—J. B. Biot designates the polarization as *right-handed*, or +, or ↗ ; whereas if they descend in the scale by turning the analyzer *from right to left*, he terms it *left-handed*, or —, or ↖. Sir John Herschel, on the other hand, supposes the observer to look in the direction of the ray's motion. Let the reader take a common corkscrew, and holding it *with the head towards him*, let him use it in the usual manner, as if to penetrate a cork. The head will then turn the same way with the plane of polarization as a ray in its progress *from* the spectator through a *right-handed* crystal may be conceived to do. If the thread of the corkscrew were reversed, or what is termed a *left-handed thread*, then the motion of the head, as the instrument advanced, would represent that of the plane of polarization in a left-handed specimen of rock crystal.

J. Herschel, and D. Brewster pointed out that the **optical rotation** discovered by J. B. Biot is related with the structure of the crystals. As in the case of tartaric acid, the crystals are enantiomorphic as illustrated in Fig. 40. The rotating power is also proportional to the thickness of the plate. Observations have been made by O. Broch, V. von Lang, P. Desains, R. Dongier, etc. Lord Rayleigh studied the effect of the earth's motion on the circular polarization of quartz. For sodium light, J. Stefan found the angle of rotation of a plate one mm. thick to be 21·67°, and the angle increases with a rise of temp. from 21·599° at −20° to 25·259° at 840°. The effect of low temp. has been studied by C. Soret and C. E. Guye, J. L. Soret and É. Sarasin, etc. M. G. Levi found that a quartz plate had $\delta=99·25°$ at 12°, and $\delta=102°$ at −180°. The effect of temp. has been studied by V. von Lang, L. Sohncke, D. Gernez, H. Dufet, J. Joubert, etc. According to E. Gumlich, the optical-rotatory power, $\delta$, at the temp. $\theta$ between 0° and 100° for rays of all colours, is $\delta=\delta_0(1+0·000131\theta+0·00000195\theta^2)$, where $\delta_0$ denotes the angle of rotation at 0°. F. Burki gave $\delta=7·1505\lambda^{-2}e^{0·01864\lambda^{-2}}$; and P. Drude, $\delta=12·200(\lambda^2-\lambda_0{}^2)^{-1}-5·046\lambda^{-2}$. The shorter the wave-length of the light, the greater the rotation of the light, so that the angle is smaller for red than for yellow, and so on. Thus, with a plate one mm. thick, H. le Chatelier obtained the results indicated in Table V, and Fig. 44. Fused quartz does not exhibit the phenomenon of circular polarization. P. Zeeman and A. Snethlage measured the Fizeau effect with quartz.

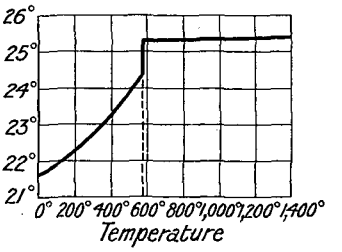



FIG. 44.—Effect of Temperature on the Circular Polarization of Light by Quartz.

TABLE V.—OPTICAL ROTATION OF QUARTZ AT DIFFERENT TEMPERATURES WITH LIGHT OF DIFFERENT WAVE-LENGTH.

| Temp. | Optical rotation with light of wave-length. | | | | | |
|---|---|---|---|---|---|---|
| | 656 Red. | 589 Yellow. | 518 Green. | 500 Green. | 448 Blue. | 279 Ultra-violet. |
| 20° | 17·25° | 21·72° | 28·62° | 30·78° | 39·24° | 114·5° |
| 280° | 18·06° | 22·68° | 29·82° | 32·16° | 40·80° | — |
| 415° | 18·60° | 23·40° | 30·60° | 32·90° | 42·00° | 127° (475°) |
| 560° | 19·38° | 24·30° | 32·04° | 34·56° | 44·10° | — |
| 600° | 20·10° | 25·26° | 33·18° | 35·76° | 45·60° | 131° (650°) |
| 900° | — | 25·82° | 33·24° | 36·00° | 45·84° | 132° |

A. Fresnel,[23] V. von Lang, R. Dongier, A. Cornu, E. Brodhun and O. Shrönrock, R. Brunhes, etc., have discussed the theory of the subject. The production of *Airy's spirals* when two equally thick plates right- and left-handed are superposed and examined in convergent monochromatic polarized light was described by G. B. Airy,[24] J. C. Jamin, B. Hecht, R. Straubel, F. Beaulard, A. Gouy, G. Quesneville, K. Schmidt, R. Ritter, etc. The **optical anomaly** of quartz was investigated by Lord Rayleigh, D. Brewster,[25] H. W. Dove, G. Jenzsch, A. Breithaupt, E. Reusch, H. Böklen, G. Wyrouboff, R. Brauns, E. Schumacher, K. A. Lossen, E. Stecher, C. A. MacMahon, etc. Uniaxial quartz crystals become biaxial when press. is applied at right angles to the optical axis. The effect of *pressure* on the optical properties of quartz crystals was observed by D. Brewster, A. Moigno, F. Pfaff, H. Bücking, M. Sidorenko, E. Mach and J. Merten, F. Pockels, F. Beaulard, H. Monnory, and P. Dongier; the effect of *heat*, by W. Klein, and P. P. Koch; and the effect of an *electrostatic field*, by A. Kundt, W. C. Röntgen,

P. Tschermak, and F. Pockels. Uniaxial quartz crystals in the electric field change in a way analogous to that observed with compression.

In the *magnetic field* there is a simple rotation of the plane of polarization parallel to the axis.[26] The **magnetic-optic rotation** of quartz, that is, the rotation of a beam of polarized light in a magnetic field, expressed in the terms of **E. Verdet's constant** at 20°, decreases from 0·1587 for light of wave-length $\lambda=0{\cdot}22194\mu$ to 0·1079 when $\lambda=0{\cdot}02573\mu$; to 0·04617 for $\lambda=0{\cdot}3609\mu$; to 0·2750 for $\lambda=0{\cdot}4678\mu$; to 0·02574 for $\lambda=0{\cdot}4800\mu$; to 0·02257 for $\lambda=0{\cdot}5086\mu$; to 0·01664 for $\lambda=0{\cdot}5892\mu$; and to 0·01368 for light of wave-length $0{\cdot}6439\mu$ when measured along the *c*-axis. For variations of wave-length from $\lambda=0{\cdot}467\mu$ to $0{\cdot}644\mu$, and a temp. between 20° and 96°, E. Verdet's constant is $1+0{\cdot}00011\ (\theta-20)$ times the value of the constant at 20°. Values were obtained by J. Disch, A. Borel, and T. M. Lowry.

Light passing through a crystal is continuously absorbed as the distance traversed by the light increases. With white light, the different colours are often absorbed at different rates, and the colour of the crystal is due to a combination of the remaining colours. The two rays of a doubly refracting crystal may be absorbed differently so that the colour of the crystal appears different according to the direction in which the light is transmitted. This property is called dichroism when two colours are involved, and the general term used is **pleochroism.** In a polarizing microscope, with the analyzer out, the colour varies as the crystal is turned. An instrument called the *dichroscope* is designed to show the colour of the two rays of the crystal side by side. D. Brewster,[27] and A. Beer showed that amethyst exhibited pleochroism in that the ordinary ray appears pale reddish-violet, and the extraordinary ray, dark bluish-violet; W. Haidinger, that the ordinary ray is more strongly absorbed than the extraordinary ray with crystals from Brazil, Siberia, and from Schemnitz; and H. Baumhauer showed that this applies also with colourless quartz. J. Moreau, C. Ehlers, and P. Ites measured the different absorbing power of quartz for the ordinary and extraordinary rays. E. G. Merritt, and J. Königsberger measured the effect with ultra-red rays; and J. Königsberger, and V. von Agafanoff, the effect with ultra-violet rays.

Quartz is almost transparent to the ultra-violet rays, and, according to C. Doelter, quartz glass is rather more absorbent than the crystals. The transparency for the extraordinary ray is rather larger than for the ordinary ray, and the smaller the wave-length the greater the absorption. Thus, J. Königsberger found for the transparency of a sample of smoky quartz, expressed as a percentage value of the transparency of fluorspar:

| Wave-length | 1·0 | 1·5 | 2·1 | 2·5 | 3·0 | 3·5 | 4·0$\mu$ |
|---|---|---|---|---|---|---|---|
| Ordinary ray | 90 | 88 | 89 | 88 | 81 | 80 | 45 |
| Extraordinary ray | 93 | 92 | 92 | 91 | 90 | 80 | 45 |

E. T. Wherry,[28] and E. F. Holden measured the **absorption spectrum** of rose-quartz. The latter found rose-quartz to be pleochroic. W. R. Ham and co-workers, and G. Joos studied the ultra-violet absorption spectrum of quartz; and W. Jevons, the band spectrum. The transparency of quartz glass for ultra-violet light was studied by H. Trommsdorff, A. Pflüger, H. Kriess, R. Schachenmeister, S. B. Nicholson and E. Pettitt, and C. Schaefer and M. Schubert, J. Königsberger and W. J. Müller, H. Buisson, etc. V. Schumann measured the effect in terms of the time, in seconds, required to affect photographic plates to the same extent.

| | Wave-length | 361 | 275 | 231 | 214 | 199$\mu\mu$ |
|---|---|---|---|---|---|---|
| Time | Quartz glass | 20 | 20 | 20 | 20 | 180 |
| | Air | 18–19 | 16–17 | 12–13 | 11–12 | 1–2 |

According to W. W. Coblentz, the **transmission spectrum** of a plate of clear quartz cut perpendicular to the principal axis and 0·12 mm. thick shows small bands at $2{\cdot}9\mu$ and $4{\cdot}35\mu$, Fig. 45. J. Königsberger with smoky quartz obtained bands at

3·05$\mu$ and 4·05$\mu$ ; and E. G. Merritt, with polarized light, obtained bands at 3·0$\mu$ and 3·6$\mu$ for the extraordinary ray and 2·9$\mu$, 3·75$\mu$, and 4·1$\mu$ for the ordinary ray. With amethyst, J. Königsberger obtained a band at 3·1$\mu$. E. F. Nichols, and C. V. Raman made some observations on this subject.

W. W. Coblentz measured the **reflection spectra** of quartz and quartz glass, and found the one to be entirely different from the other, Fig. 46. The maxima in

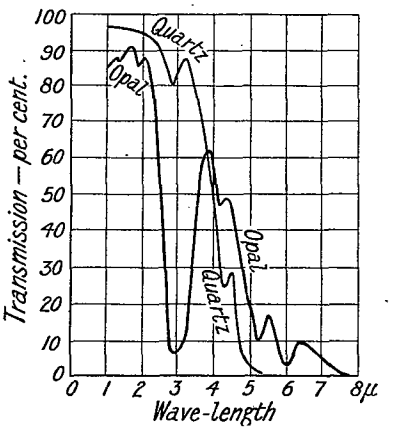



FIG. 45.—Transmission Spectra of Quartz, and of Opal.

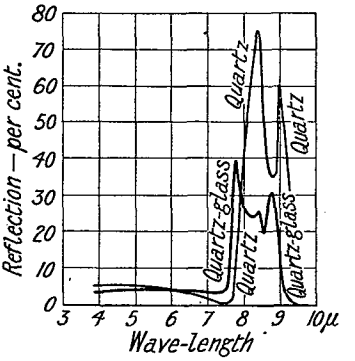



FIG. 46.—Reflection Spectra of Quartz, and Quartz Glass.

the reflection spectra of crystalline quartz occurs at 8·4$\mu$ and 9·02$\mu$ ; and with amorphous quartz, at 7·8$\mu$, 8·4$\mu$, and 8·8$\mu$. The intensity of the maxima of the bands of quartz glass is not so great as those of crystalline quartz, nor does the reflecting power in the region of the spectrum just preceding a reflection band, fall to so low a value as in crystalline quartz. H. Rosenthal made observations on this subject, and measurements of the reflection spectrum in the ultra-violet were made by O. Reinkober. E. P. Lewis and A. C. Hardy found the **reflective power** of quartz, for radiations below $\lambda$=1860, to be 9 to 10 (rock salt, 8 to 9). W. W. Coblentz found the reflecting power for light of wave-length $\lambda$=0·95$\mu$ to be 81 per cent. ; for $\lambda$=4·4$\mu$, 41·5 per cent. ; for $\lambda$=8·8$\mu$, 7·9–13·4 per cent. ; and for $\lambda$=24$\mu$, 9·0 per cent. C. Schaefer and M. Schubert showed that quartz, chrysoprase, hoenstein, and chalcedony have the same quantitative reflecting power, and the maximum at about 9$\mu$ exhibits 90 per cent. of the metallic reflection. With opal and quartz glass, the reflection maximum is in the same proportion as with the other varieties of silica, but the reflecting power is 40–50 per cent. less. This is attributed to a distortion of the space-lattice in the amorphous varieties of silica. It is remarkable that the water maximum, which lies at 3·2$\mu$, is not observed in the case of opal, and it is hence assumed that water is not arranged in the space-lattice of opal. H. E. Ives and co-workers studied the **emissivity** and **illuminating power** of mantles made of silica and heated in the bunsen-flame. H. Rubens and E. Aschkinass measured the transparency of quartz for the so-called *Restrahlen*.

C. F. Kunz,[29] E. F. Holden, and A. Lacroix noted that exposure to **light** lessens the intensity of the colour of rose-quartz. P. Villard found that colourless quartz is darkened by exposure to **cathode rays.** J. Ewles found the minimum voltage for the excitation of the blue cathodoluminescence of silica to be 750 ; E. L. Nichols and D. T. Wilbur also studied this subject. C. Doelter investigated the action of ultra-violet rays on the colour of quartz. J. O. Perrine observed no signs of the excitation of fluorescence by the **X-rays.** According to C. Doelter, quartz is semi-opaque to the X-rays, and its transparency lies between that of corundum and that of calcite. G. T. Beilby, C. J. Salomonsen and G. Dreyer, N. Georgiewsky, and

others found that colourless rock crystals are coloured brown by radium and X-rays, and the colour is removed by exposure to ultra-violet rays or by heating to 200°. C. Doelter and H. Sirk found that the coloration is mainly produced by the $\gamma$-rays, and also by the $\beta$-rays. Observations were also made by N. Egoroff, C. Doelter and H. Sirk, etc. M. Berthelot found that some specimens of quartz were decolorized by radium radiations, and he therefore attributed the positive instances of decoloration to the presence of an impurity. N. Egoroff, O. Hönigschmid, and C. J. Salomonsen and G. Dreyer found that colourless quartz becomes pleochroic by the action of radium rays. Rose-quartz, amethyst, cairngorm, and citrine all become colourless when heated—according to E. Newbery and H. Lupton, rose-quartz requires a red heat; amethyst requires strongly heating directly in the blowpipe-flame; and nearly black cairngorm sometimes becomes colourless when heated in a soft glass tube. They also found that when exposed to **radium radiations** for seven days colourless quartz becomes smoky, and the coloration penetrates a depth of one cm. into the crystal. Rose-quartz decolorized by heat became smoky rather more readily than clear rock crystal, and the pink colour was restored to some extent. Amethyst decolorized by heat did not become smoky, but the purple colour was slowly restored. K. Simon found amethyst is decolorized over 550°. E. Newbery and H. Lupton observed that decolorized cairngorm slowly regained its colour when exposed to radium radiations, and this more rapidly than with the other samples of quartz examined—*vide* **3.** 26, 4. All the recoloured crystals were readily decolorized by moderately heating them, and at the same time a faint **thermoluminescence** appeared. F. Schröter, and E. L. Nichols and co-workers investigated the blue glow which occurs with silica heated in the oxyhydrogen flame. Observations on the action of radium rays were made by A. Ben-Saude and G. Costanzo, C. Doelter, G. O. Wild and R. E. Liesegang, and S. C. Lind and D. C. Bardwell. E. F. Holden concluded that the colour of rose-quartz is not due to radium radiations; and A. Lacroix said that rose-quartz is never associated with radioactive minerals, while smoky quartz is observed with them—a fact also noted by H. V. Ellsworth. Radium radiations may produce an effect like smoky quartz, and also like amethyst. A. Miethe did not observe thermoluminescence when smoky quartz, intensely coloured by exposure to radium radiations, was heated, but G. T. Beilby, E. Newbery and H. Lupton, V. M. Goldschmidt, etc., observed the effect. D. L. Chapman and L. J. Davies, W. E. Curtis, and E. B. Ludlam and W. West found that quartz glass acquires the power of phosphorescing, and thermoluminescing after exposure to the electrical discharge. S. C. Lind and D. C. Bardwell studied the effect of radium radiations on quartz, chrysoprase, moss-agate, and opal. D. Hahn observed that many varieties of rock crystal give a pale yellow thermoluminescence: other varieties give a whitish shimmering glow; and an amethyst glowed with a yellowish light. The phenomenon was also investigated by J. C. y Léon, K. von Kraatz-Koschlau and L. Wöhler, etc. G. F. Kunz and C. Baskerville did not make quartz luminescent by exposure to radium radiations, X-rays, or ultra-violet light. E. L. Nichols and co-workers found that when heated to a certain definite temp. silica emits a blue glow, and the radiation is in excess of that emitted by a black body at the same temp. According to E. Rutherford, a fused quartz tube, after continued exposure to radium emanation, became brittle and cracked, and the whole tube showed a multitude of approximately circular cracks. M. S. Curie also found quartz-glass tubes cracked when exposed to the $\alpha$-rays from a polonium preparation. Hence, quartz glass is very unsuited for enclosing very radioactive preparations. In 1784, G. de Razoumowsky referred to *le phosphorisme des corps du régne minéral par le moyen du frottement*, and included quartz in his list; five years later T. Wedgwood also referred to the luminosity produced in quartz by attrition; and J. H. Pott observed the same phenomenon with flint. M. Trautz observed **triboluminescence** with native quartz, but not with precipitated silica. E. R. Lankester, E. Heron-Allen, J. W. French, W. T. Sollas, C. C. Wilson,

A. Brammall, G. C. G. Damant, and H. S. Allen have studied the luminosity of quartz by attrition. Many varieties of native quartz show **radioactivity,** and they contain some occluded helium and argon gases, as well as some uranium and radium. R. J. Strutt obtained the numbers indicated in Table VI. S. Ichikawa studied the relation between the colour and the phosphorescence of quartz; W. E. Curtis, the phosphorescence of silica-glass.

TABLE VI.—RADIOACTIVITY OF NATIVE QUARTZ.

| Origin of quartz. | Occluded helium per c.mm. | Occluded argon per c.mm. | Radium per 100 grms. Grms. | Uranium oxide per 100 grms. Grms. | Helium per grm. $U_3O_8$ c.c. |
|---|---|---|---|---|---|
| Madagascar . . | 2·4 | 3·16 | $1·39 \times 10^{-11}$ | $4·29 \times 10^{-5}$ | 9·0 |
| Ilfracombe . . | 1·43 | 2·5 | $7·45 \times 10^{-11}$ | $2·31 \times 10^{-5}$ | 10·4 |
| Brazil . . . | 0·74 | 2·0 | — | — | — |
| Quartz sand . . | 0·55 | — | $1·94 \times 10^{-11}$ | $6·00 \times 10^{-5}$ | 6·0 |
| Flint (Norfolk) . | 0·295 | 1·9 | $4·30 \times 10^{-11}$ | $1·33 \times 10^{-4}$ | 0·246 |

When certain crystals are heated in an air bath, and then drawn quickly through an alcohol flame and allowed to cool, a positive charge of electricity collects about the so-called antilogue poles. The phenomenon is called **pyroelectricity.**[30] The charges of electricity can be rendered evident by their effect on other charged bodies; or, according to A. Kundt, by blowing a fine spray of a mixture of equal parts of *powdered sulphur and red-lead on the cooling crystal, the sulphur collects about* the positive poles and the red-lead about the negative poles. The phenomenon with quartz has been investigated by S. Ichikawa, W. G. Hankel, C. Friedel and J. Curie, W. C. Röntgen, A. Kundt, C. F. Naumann, B. von Kolenko, J. Beckenkamp, and P. P. Koch. Electric charges accumulate at certain points on a crystal if it be pressed between the fingers or in other ways. The charges developed are analogous with those developed by heating the crystal, and the phenomenon is called **piezoelectricity.**[31] The phenomenon has been investigated by J. and P. Curie, Lord Kelvin, A. Beckman, F. Pockels, W. G. Hankel, A. Kundt, W. C. Röntgen, P. Czermak, and E. Riecke and W. Voigt. A. Perrier and B. de Mandrot found the phenomenon with quartz disappears at 576°. The elastic deformation of quartz crystals by electric charges has been investigated by J. and P. Curie.[32] C. Marangoni discussed the piercing of quartz plates by a high tension electric discharge.

H. F. Richards[33] measured the electrification produced by the contact of quartz with fluorite, glass, and steel. E. Warburg and E. Tegetmeier showed that a slice of rock crystal cut perpendicularly to the principal axis, and having its ends covered with layers of gold or plumbago, when subjected at a temp. of about 230° to a long-continued e.m.f. of considerable intensity, had its **electrical conductivity** permanently reduced to a small fraction of its original amount. In directions perpendicular to the axis, rock crystal, even at higher temp., has little or no conductivity. The electrical conductivity of rock crystal in the direction of the principal axis is, at high temp., about the same as that of ordinary glass. When a slice cut perpendicularly to the axis is electrolyzed, sodium-amalgam being used as the anode, sodium migrates through the slice, its amount being in accordance with Faraday's law, and the weight of the slice remains unchanged. Even at high temp., rock crystal acts as a good insulator with respect to an e.m.f. in a direction perpendicular to the principal axis. When potassium-amalgam was used in the place of sodium-amalgam, the current had sunk after 40 hrs. to about the hundredth part of its original value, only 2 milligrams of silver in the coulometer were separated, and no potassium could be detected at the cathode, even by means of the spectroscope. It was therefore concluded that the conductivity is due to the presence of sodium, in the form of $Na_2SiO_3$, which was shown by

analysis to be present in the proportion of 1 part in 2300, so that the crystal might be regarded as a very dil. soln. of this salt. The electrolytic character of the conductivity was further confirmed by the fact that a cell giving e.m.f. of from 1·3 to 2 volts could be formed of mercury, a slice of quartz at a temp. of 225°, cut perpendicularly to the axis, and sodium-amalgam. According to the ionic theory of electrolysis, the fact of electrolytic conduction taking place only in the direction of the principal axis, would tend to the inference that in the case of rock crystal not traversed by an electric current, the interchange of atoms between the mols. can only take place, at any rate to a sensible extent, in the direction of the principal axis. E. Tegetmeier showed later that lithium may replace sodium in developing the conductivity of quartz. P. Curie referred the conductivity of quartz to the presence of water or salt soln. in capillary passages oriented parallel to the chief axis; J. Beckenkamp assumed an intramolecular distribution of a fluid so that the ions of the electrolyte are disposed between the crystal mols.; and J. Beierinck assumed that films of opal are distributed within the crystal.

According to P. Curie,[34] the **electrical conductivity** of quartz in the direction of the principal axis is $0{\cdot}844\times10^{-14}$ mho at 20°; $0{\cdot}122\times10^{-11}$ at 100°; $0{\cdot}147\times10^{-10}$ at 200°; and $0{\cdot}179\times10^{-7}$ at 300°—the resistance of mercury at 0° is $1{\cdot}063\times10^{3}$ ohms. K. and F. Exner gave for the conductivity of quartz parallel to the chief axis, $0{\cdot}21\times10^{-9}$ mho at 109°, and $0{\cdot}46\times10^{-8}$ at 148°. G. Wulff measured the electrical conductivity of quartz.

E. Tegetmeier gave for the sp. **electrical resistance** of quartz, referred to that of mercury, as $3{\cdot}55\times10^{10}$ at 0°, $5{\cdot}78\times10^{10}$ at 100°, and $5{\cdot}18\times10^{10}$ at 1600°. E. Warburg and E. Tegetmeier obtained in the direction of the chief axis, $2\times10^{11}$ to $7\times10^{11}$ at 224°. K. and F. Exner obtained a resistance of $4{\cdot}1\times10^{15}$ ohms at 101°, and $0{\cdot}9\times10^{15}$ at 147°; and M. von Pirani and W. von Siemens obtained $4\times10^{4}$ ohms at 1300° when that of porcelain at the same temp. is $1{\cdot}7\times10^{4}$ ohms. C. Doelter obtained perpendicular to the principal axis:

| | 430° | 605° | 780° |
|---|---|---|---|
| Ohms | 61,400 | 4,080 | 6,690 |
| | 890° | 880° | 1180° |
| Ohms | 20,300 | 52,500 | 7,540 |

and parallel to that axis:

| | 930° | 1020° | 1140° |
|---|---|---|---|
| Ohms | 115,000 | 36,512 | 11,970 |
| | 1250° | 1390° | 1400° |
| Ohms | 6,940 | 3,220 | 3,150 |

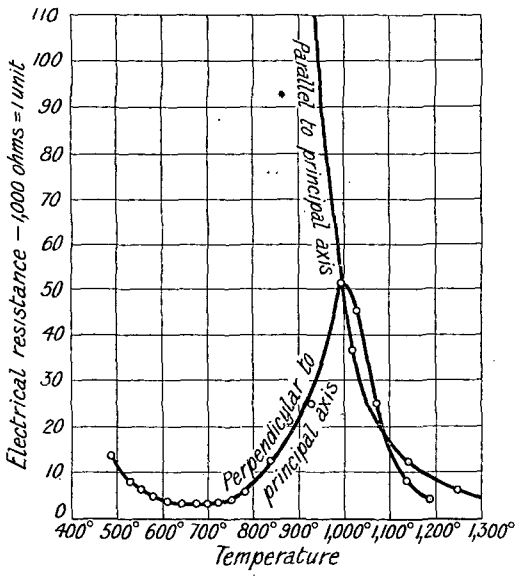



FIG. 47.—Electrical Resistance of Quartz.

Analogous results were obtained with other samples. The results are plotted in Fig. 47. The observed results were represented by E. Rasch and F. Hinrichsen's equation, $\log R=AT^{-1}+C$, where $R$ is the resistance in ohms; $T$, the temp. on the absolute scale; and $A$ and $C$ are constants. This expression has a formal resemblance to the integrated form of J. H. van't Hoff's equation $d(\log R/dT)=-A/RT^2$ (**1**. 12, 9). K. and F. Exner gave $0{\cdot}26\times10^{-11}$ mho for the electrical conductivity of quartz glass at 101°, and $0{\cdot}11\times10^{-10}$ at 147°; and M. von Pirani and W. von Siemens gave $0{\cdot}25\times10^{-4}$ mho at 727°. C. Doelter gave for the sp. resistance of quartz glass:

| | 922° | 988° | 1050° | 1154° | 1207° |
|---|---|---|---|---|---|
| Ohms | 132,800 | 73,330 | 66,923 | 14,291 | 10,000 |

F. Horton found the effect of temp. on the electrical resistance in ohms, and the electrical conductivity in mhos of slabs of quartz-glass to be:

| | 468° | 652° | 703° | 869° | 1013° | 1288° |
|---|---|---|---|---|---|---|
| Ohms | $95\times10^{6}$ | $35\times10^{5}$ | $198\times10^{4}$ | 409000 | 170000 | 65200 |
| Mhos | $1\cdot79\times10^{-9}$ | $4\cdot86\times10^{-8}$ | $8\cdot59\times10^{-8}$ | $4\cdot16\times10^{-7}$ | $1\cdot00\times10^{-7}$ | $2\cdot60\times10^{-6}$ |

There is thus a rapid increase in conductivity with rise of temp. A. Jaquerod and H. Mügeli found the sp. conductivity of silica glass to be $3\cdot1\times10^{-20}$ mhos per c.c. at 60°; $3\cdot16\times10^{-19}$ at 80°; and $3\cdot2\times10^{-18}$ at 100°. A. Joffé showed that the electrical conductivity of quartz is increased by exposure to radium radiations, X-rays, or ultra-violet light, and the effect is greater on the conductivity parallel to the principal axis than on the conductivity perpendicular to that axis. A. Schaposchnikoff found that the electrical conductivity of quartz follows Ohm's law only with electric fields of moderate intensity; with over 4000 volts per cm. there are marked deviations. A. V. Henry measured the electrical resistance of silica refractories between 400° and 1100°.

Quartz at ordinary temp. is an electrical insulator. The **dielectric constant**—determined by M. Romich and J. Nowak,[35] E. Schott, P. Curie, R. Fellinger, W. Schmidt, L. Ebert, W. Voigt, F. Paschen, H. Starke, E. S. Ferry, etc.—parallel to the axis lies between 4·6 and 5·057; and at right angles to that axis, 4·32–4·695. W. M. Thornton found 4·6 parallel to the principal axis, and 4·5485 perpendicular to that axis. F. Hasenöhrl found that at a temp. $\theta°$, the dielectric constant parallel to the principal axis is $4\cdot926\{1-0\cdot00110(\theta-10)-0\cdot000024(\theta-10)^2\}$; and perpendicular to that axis, $4\cdot766\{1-0\cdot00099(\theta-10)\}$. The insulating properties thus decrease with rise of temp. The dielectric constant of quartz is greater than the value computed from the refractive indices; this is also the case with fluorspar, and calcspar. M. Faraday, L. Boltzmann, and H. A. Rowland and E. L. Nichols discussed the dielectric polarization of quartz. F. A. Schulze found the dielectric constant of quartz-glass to be between 3·2 and 3·4; and A. Coehn and A. Curs, 3·2–3·5. A. Jaquerod and H. Mügeli studied the anomalous charging and discharging currents in silica-glass used as the dielectric of a condenser. They also examined the effect of dissolved gases—hydrogen, and helium—on the residual currents in silica-glass. W. F. Powers measured the temp. coeff. of frequency of quartz resonators. All kinds of quartz are diamagnetic. O. Tumlirz[36] found quartz to be diamagnetic perpendicular to the principal axis, and W. König, E. Stenger, etc., have measured the **magnetic susceptibility.** P. Curie found between 18° and 430°, $-0\cdot44\times10^{-6}$ mass units; S. Meyer, $-0\cdot07\times10^{-6}$ to $0\cdot17\times10^{-6}$ mass units; J. Königsberger, and W. Voigt and S. Kinoshita obtained $-1\cdot2\times10^{-6}$ vol. units at 20°. B. Bavink, and G. Wistrand have studied the magnetic properties of quartz. W. Voigt found quartz to exhibit **piezomagnetism.**


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## § 19. The Chemical Properties of Silica

The general chemical properties of the different varieties of crystalline and amorphous silica are very similar; and the same remark applies also to the hydrated forms. The main difference turns on the different speeds of reaction. From this point of view the hydrates are the most active, and quartz, the least active. According to R. Schwarz,[1] amorphous silica (silica glass) is more active than cristobalite, cristobalite is more active than tridymite. and tridymite is more active than quartz. F. W. Clarke said that in all probability tridymite, cristobalite, and quartz are polymers of the fundamental mol., $SiO_2$; and tridymite and cristobalite are the less complex, and therefore more stable at high temp. They are, moreover, less dense than quartz, and quartz-glass, with a still lower density, probably approximates more nearly to the simple mol., $SiO_2$. J. A. Hedvall observed that the precipitated and amorphous forms of silica react faster with the alkaline earth oxides than cristobalite, and this in turn faster than quartz—*vide infra*.

E. Wolff [2] examined the loss on ignition of quartz. The catalytic effect of quartz on the union of hydrogen and oxygen has been previously indicated (**1**. 9, 9); and the effect of silica gel at 150°, 250°, and 350° on the esterification of alcohol was found by C. H. Milligan and E. E. Reid to be twice as great as that of titanic oxide. According to P. Villard, if a tube of silica-glass attached to a manometer be exhausted and heated by a gas-flame, the press. inside rises owing to the passage of

**hydrogen** through the walls of the tube. M. Berthelot said that hydrogen passed through quartz-glass at 1300°, and Z. von Hirschberg, at 1000°. The permeability increases as the temp. is raised. J. B. Johnson and R. C. Burt found the diffusion of hydrogen through quartz-glass starts at 300°, and with nitrogen at 600°. H. Briggs studied the adsorption of hydrogen and nitrogen by silica. G. A. Williams and J. B. Ferguson found that one c.c. silica-glass of sp. gr. 2·22 and at 515°, dissolved 0·0095 c.c. of hydrogen (at n.p.t.) with the press. 750–760 mm. and at 445°, 0·00989 c.c. With helium, 0·0101 c.c. was dissolved at 515°, and 0·0103 at 445°. The solubilities of the gases bear no relation to the rates of diffusion through silica-glass. O. A. Hougen and B. L. Miller found that the siliconizing of platinum wires in silica-tubes in a reducing atm. above 900° is due to silicon vapour produced by the reduction of silica. A. Jaquerod and F. L. Perrot found that **helium** diffuses perceptibly through silica-glass at 220°, and very rapidly at 1100°. The rate of diffusion is proportional to the press. G. A. Williams and J. B. Ferguson found the permeability of silica-glass for helium at 180° can be measured, and at 500°, it is about 22 times that of hydrogen. A. Piutti and E. Boggio-Lera found that at 480° helium is unable to traverse plates of *l*-quartz or *d*-quartz plates only 0·3 to 1·0 mm. thick, and cut parallel or perpendicular to the optic axes, but quartz-glass is permeable at this temp. O. W. Richardson and R. C. Ditto found **neon** to be rather less diffusible than helium. M. Berthelot, and Z. von Hirschberg reported that quartz-glass is permeable to **oxygen, nitrogen,** and **methane,** at 1300°. A sealed quartz-glass tube of 5 c.c. capacity, was filled with hydrogen at 0·2 atm. press. and heated for an hour at 1300°. The contents of the tube were then eq. to 0·68 c.c. of hydrogen or to 0·12 c.c. measured at atm. press. Fused-silica tubes with walls 0·7 mm. thick are not permeable to hydrogen at the ordinary temp., but become so at 800°, whilst at 1300° the diffusion is very marked; **hydrogen chloride** does not begin to diffuse through the walls of a quartz-glass tube below 1400°, neither does **carbon dioxide** below 1300°; the diffusion of nitrogen is feeble at 1000°, but becomes appreciable at 1300°–1400°, whilst oxygen diffuses more readily; relative experiments on the rates of diffusion of these two gases show that at 1400° under a press. of 1·2 atm. one-sixth of the initial vol. of nitrogen or one-third of the initial vol. of oxygen diffuses during one hour. The quartz-glass tubes suffer a permanent distension from the effect of the increased internal press. at the high temp. It was found that tubes of ordinary white glass or of Jena glass are permeable to hydrogen, oxygen, and **carbon monoxide** under the same conditions as were observed with tubes of fused silica, but at a lower temp. It was assumed that the permeability of the walls of glass or fused silica vessels to gases is similar in character to the passage of gases through caoutchouc or animal membranes. C. Belloc regarded the phenomenon at high temp. as an effect of incipient devitrification. E. C. Mayer found a transparent vitreous quartz vessel to be impervious to hydrogen and oxygen at ordinary room temp., and atm. press., but was pervious to hydrogen at temp. higher than 330°, and at press. ranging between 26 cms. above and below atm. press. No leakage was detected with oxygen or nitrogen for press. below atm. Nitrogen did not escape until about 430°. In all cases, at constant temp., the leakage increased with an increase of press.—hydrogen leaked fastest, nitrogen slowest of the three gases in question. G. A. Williams found the permeability of silica glass for hydrogen becomes appreciable above 300°; and at high temp. it is proportional to the gas press., and is an exponential function of the temp. Observations on the diffusion of hydrogen were made by T. des Coudres, M. Bodenstein and F. Kranendieck, W. Watson, and H. Wüstner. The last-named found the coeff. of diffusion of hydrogen, in c.c. per sq. cm. per sec., to be:

| | 300° | 400° | 500° | 600° | 700° | 800° | 900° | 1000° |
|---|---|---|---|---|---|---|---|---|
| Coeff. . . | $0{\cdot}0_6 73$ | $0{\cdot}0_5 16$ | $0{\cdot}0_5 21$ | $0{\cdot}0_5 24$ | $0{\cdot}0_5 24$ | $0{\cdot}0_5 42$ | $0{\cdot}0_5 76$ | $0{\cdot}0_4 103$ |

with the hydrogen at 800–900 atm. press. He also made some observations on nitrogen and oxygen, but found the rate of diffusion to be very slow—particularly

in the case of oxygen. H. Wüstner also measured the absorption coeff., $\beta$, of hydrogen, and obtained:

| 300° | 400° | 600° | 700° | 800° | 900° | 1000° |
|---|---|---|---|---|---|---|
| 0·005483 | 0·005669 | 0·00819 | 0·009858 | 0·01092 | 0·01098 | 0·01029 |

so that the value at about 700° is the same as that of hydrogen in water at ordinary temp. H. von Wartenberg discussed the reduction of quartz by hydrogen above 1200°. R. S. Willow and H. T. George studied the absorption of gas in quartz discharge tubes; and A. F. Benton, the absorption of carbon dioxide, carbon monoxide, oxygen, and hydrogen by silica—*vide infra*, silica gels. E. E. Schumacher found that quartz is wetted by mercury when the adsorbed air is removed from the quartz.

The adsorption of **water** vapour by quartz has been studied by I. Ihmori,[3] A. von Dobeneck, M. Guichard, W. Skey, H. E. Patten, R. E. Wilson and T. Fuwa, L. Vignon, and L. J. Briggs. The last-named found that quartz, like glass, is capable of condensing a water film upon its surface from an unsaturated atm. A part only of this film is liberated when the vap. press. is reduced to zero at 30°. The weight of the water film condensed on the surface of quartz at 30° in an atm. within one per cent. of saturation is 26·6 mgs. per sq. metre determined by drying at 110°. This corresponds to a calculated thickness of the water film of $2{\cdot}66\times10^{-11}$ cm., assuming the density of the film to be uniform and equal to unity. The results obtained with washed quartz do not support the conclusion that adsorption is due to the presence of soluble substances on the surface of the solid. H. E. Patten and F. E. Gallagher found that finely powdered quartz in an open dish over water adsorbed 0·23 per cent. of moisture at 23°; 0·11 per cent. at 43°; 0·05 at 62°; 0·03 at 80°; and 0·02 at 97°. A. von Dobeneck found that 100 grms. adsorbed 0·023 grm. of carbon dioxide at 0°, and virtually the same amount at 10°, 20°, and 30°. B. von Ammon found that quartz powder absorbed 0·295 per cent. of ammonia at 20°. G. R. Paranjpe measured the effect of press. at —190° on the adsorption of hydrogen by quartz. The condensation of water vapour on the quartz appears to be due to the attraction of the solid for the mol. of the vapour, in accordance with the theory of J. W. Gibbs (**1.** 13, 22) as applied to the adsorption of dissolved substances. G. Schwalbe, and C. J. Parks have investigated the Pouillet effect with quartz and amorphous silica—*vide* **1.** 9, 9.

In his *Meteorology*, Aristotle, 320 B.C., said that water is improved for drinking purposes by filtration through sand; and in his *Sylva sylvarum*, F. Bacon wrote of a method of obtaining fresh water from sea-water, by filtration through earth. S. Hales also mentioned that when sea-water is filtered through stone cisterns, the first pint that runs through will not taste of the salt, but the water afterwards collected will be as salt as usual. G. Matteucci also found that the first runnings of soln. of various salts, when filtered through sand, are free from salt. The phenomenon is here probably not altogether an adsorption effect, but is partly due to the more rapid passage of water as shown to be the case by S. Krakoff, and L. J. Briggs with soils. J. N. Mukherjee showed that silica adsorbs acids, although A. F. Joseph and J. S. Hancock could not confirm this. According to L. Vignon, quartz adsorbs the alkali hydroxides or carbonates, but not sodium chloride or magnesium chloride. Other chlorides, nitrates, and sulphates of the alkalies and silver nitrate are adsorbed from aq. soln. The adsorption with carbonates is rather less than with hydroxides; but the results with the alkalies are in some doubt because of the possible chemical action between soln. and solid. R. E. Wilson and T. Fuwa studied the humidity equilibria of silica. The adsorption of water vapour by the so-called amorphous silica is smaller the higher the temp. at which the silica has been calcined. E. Berl and W. Pfanmüller studied the effect of the flotation process on quartz.

Quartz is considered to be insoluble in water at ordinary temp. and press.

The solubility of silica in natural waters has been discussed in connection with the occurrence of silica—*vide supra* corrosion figures. It was also pointed out that J. H. Pott,[4] A. Baumé, J. C. F. Meyer, and C. J. B. Karsten knew that the gelatinous precipitate from *liquor silicium* remains in soln. when treated with an excess of acid. Gelatinous silica, precipitated when silicon tetrafluoride is passed into water, was reported by J. N. von Fuchs to be slightly soluble in water—100 parts of water dissolving 0·013 part of silica. A. E. Delesse found an appreciable solubility at 160°. C. Struckmann found the water dissolved 0·021 part of silica which had been precipitated by carbon dioxide from a soln. of an alkali silicate; and O. Maschke obtained a soln. with 0·09 part of silica after many days' digestion. In these old measurements, the influence of alkalies derived from the solvent action of water on glass does not seem to have been excluded. E. Jordis showed that the solubility is influenced by the presence of acid or alkali in the water. The same remark applies to T. Graham's statement that 100 parts of water dissolve 0·02 part of silica precipitated from a one per cent. soln.; and 0·01 part of silica precipitated from a 5 per cent. soln. E. Ludwig found 100 parts of water dissolved 0·0037–0·0042 part of silica. A. E. Delesse showed that quartz is slightly soluble in water at 160°; and W. Skey stated that hydrated silica dissolves in water. H. Leitmeier found that 0·22 part of opal dissolves in 100 parts of boiling water, and that quartz and chalcedony are not so soluble. Observations on the solubility of silica in water have also been made by E. Manzella, J. Davy, J. Persoz, C. Viola, E. Nicholson, R. Biedermann, C. G. C. Bischof, A. M. Edwards, G. C. Wittstein and R. Pribram, A. Souchay, C. Mieneke, C. Winkler, C. Matignon and M. Marchal, P. Jannasch and O. Heidenreich, G. Gore, F. Meissner, W. Spring, G. B. Ercolani, M. Bellati and L. Finazzi, etc. S. Calderon found that 100 parts of water dissolve 0·01 part of silica, and that the solubility is increased in the presence of oxygen, carbon dioxide, nitric acid, sulphuric acid, and humic acids. H. W. F. Wackenroder found traces of silica in strong brines. Many other observations have been made. T. Graham thought that the solubility depended upon the degree of hydration, and that dehydrated silica is insoluble in water. This, however, is not the case. V. Lenher showed that the action of water on silica is that of a solvent, and this action is accelerated by the finer grinding of the silica, and by raising the temp. and the press. The water converts the silica into the gel form, which then passes into the sol condition. F. Seemann studied the solubility of silica in water and in soln. of ammonium carbonate, sodium chloride, and carbonic acid. R. Schwarz made a clear sol with 0·3 per cent. silica by evaporating a soln. of silicic acid in aq. ammonia slowly over conc. sulphuric acid.

V. Lenher and H. B. Merrill have shown (i) that gelatinous silica attains a state of equilibrium fairly quickly in water—about 24 hrs. suffice—and the solubility is 0·016 at 25° per 100 c.c. of water, and 0·0214 at 90°—the solubility is the same no matter how the gel is prepared; and (ii) that the solubility of ignited silica appears less than that of gelatinous silica because of the length of time required to saturate the soln. They say that in all probability the true solubilities of the ignited and gelatinous forms of silica are the same. The presence of carbon dioxide has no effect on the solubility of silica in water at 90°. The solubility is augmented by press. F. Pfaff found that at 18° and 290 atm. press., 100 parts of water dissolved 0·0213 part of silica. According to G. Spezia, the action of water on polished plates of quartz cut vertical and parallel to the chief axis in terms of the loss of weight in milligrams per sq. cm. of surface suffered in 30 days is illustrated by the results shown in Table VII. G. Spezia infers that press. plays but a subordinate rôle, and that temp. is the most important factor in determining the solubility of quartz in water. The solubility is greater in the direction of the chief axis than it is at right angles thereto.

It might be anticipated that **persilicates** analogous to the percarbonates could be prepared by evaporating silica gels with 30 per cent. **hydrogen dioxide.** A. Komaroosky[5] did obtain a gelatinous residue which liberated chlorine from

TABLE VII.—EFFECT OF TEMPERATURE AND PRESSURE ON THE SOLUBILITY OF QUARTZ IN WATER.

| Parallel to principal axis. | | | Perpendicular to principal axis. | | |
|---|---|---|---|---|---|
| Temp. | Press. atm. | Mgrms. silica dissolved per sq. cm. | Temp. | Press. atm. | Mgrms. silica dissolved per sq. cm. |
| 153° | 1161·0 | 0·067 | 182° | 1322 | 1·62 |
| 175° | 8·8 | 0·11 | 207° | 18 | 3·53 |
| 207° | 1·8 | 1·31 | 231° | 18 | 5·05 |
| 224° | 24·0 | 2·32 | — | — | — |
| 231° | 28·0 | 2·63 | — | — | — |
| 268° | 52·0 | 7·74 | — | — | — |
| 323° | 122·0 | 11·87 | — | — | — |

hydrochloric acid, and iodine from hydriodic acid; it gave ozone when treated with conc. sulphuric acid, and decolorized soln. of potassium permanganate. Hence, it was inferred that either a **persilicic acid,** $H_2SiO_4.1\frac{1}{2}H_2O$, or a **hydrogel of persilicic acid,** $H_2SiO_3.H_2O_2.\frac{1}{2}H_2O$, was formed. A. H. Erdenbrecher found that by triturating anhydrous or crystalline sodium metasilicate with 82 per cent. hydrogen dioxide and alcohol or ether, a porous mass containing up to 15 per cent. of active oxygen is obtained. It absorbs carbon dioxide and moisture from air, and evolves water and oxygen when heated.

According to H. Moissan,[6] **fluorine** is the only halogen which attacks silica, and silicon tetrafluoride is formed even in the cold. If the silica be mixed with carbon, then, at a red heat, H. C. Oersted showed that **chlorine** furnishes silicon tetrachloride; and G. S. Sérullas, that **bromine,** gives silicon tetrabromide. H. Moissan found that **iodine pentafluoride** reacts vigorously with silica, forming silicon tetrafluoride. Quartz is scarcely affected by acids, excepting **hydrofluoric acid** which reacts with it, forming a volatile silicon fluoride. According to H. Rose, powdered quartz dissolves quietly in hydrofluoric acid; but silica of sp. gr. 2·2 dissolves with more violence. According to R. Schwarz, the amounts of the different modifications of silica dissolved by hydrofluoric acid during a period of 30 hrs., are as follows:

| | Quartz. | Tridymite. | Cristobalite. | Quartz glass. |
|---|---|---|---|---|
| One per cent. acid | 5·2 | 20·3 | 25·8 | 52·9 per cent. |
| Five per cent. acid | 30·1 | 76·3 | 74·3 | 96·6 „ |

On the assumption that compounds are less attacked by hydrofluoric acid the more condensed the mol., J. B. Mackintosh assumed that the mol. of quartz is more condensed than that of opal because with dil. hydrofluoric acid, opal lost 77·28 per cent., while quartz lost only 1·56 per cent. The illustration is poor, because one is a hydrated and the other an anhydrous compound—*vide supra*, corrosion figures. According to J. Thomsen, the heat of soln. of hydrated silica in hydrofluoric acid approximates 48 Cals. per mol. of silica when the eq. of 12 mols. of hydrogen fluoride, HF, is used per mol. of silica; and 13·64 Cals. when 2·46 mols. of hydrofluoric acid are used. According to O. Mulert, the thermal value of the reaction with finely-powdered quartz in 20 per cent. hydrofluoric acid is 29·93 Cals. per mol. of silica, $SiO_2$; 32·14 Cals. per mol. of fused-silica, $SiO_2$. R. Wietzel found that with 35 per cent. hydrofluoric acid, the heat of soln. per mol. of quartz-glass is 35·97 Cals.; with rock-crystal, 33·65 Cals.; and with cristobalite, 35·37 Cals. Similarly, with fuming hydrofluoric acid, and quartz-glass, the heat of soln. is 38·83; rock-crystal, 36·48 Cals.; and chalcedony, 36·72 Cals. G. Tammann has also shown from measurements of the electrical conductivity that the soln. obtained in both cases is the same. Consequently, the heat of transformation of amorphous silica to crystalline quartz is about +2·21 Cals. The mol. ht. of soln. of quartz in hydrofluoric acid was found by P. C. Ray to be raised 2·17 Cals. by 15 hrs.' grinding;

this is taken to correspond with the conversion of 31·2 per cent. of quartz to the vitreous state. O. Mulert has shown that the heat of soln. of hydrated silica depends on the degree of hydration of the silica. It rises rapidly from 32·14 with amorphous anhydrous silica to 35·51 Cals. with silica with about 3 per cent. water, and then falls to about 33·5 Cals. with silica having about 10 per cent. of water; after which, the heat of soln. remains constant. The curve is illustrated in Fig. 48. The increase is supposed to indicate that the first 3 per cent. water absorbed by the silica is in a state of compression, and the energy compressing the water is liberated as heat; and when the silica is associated with more water, the compression diminishes and consequently less heat is liberated.

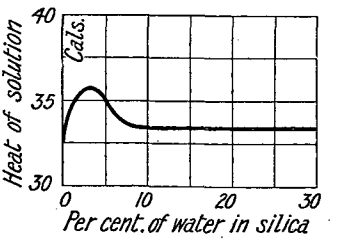



FIG. 48.—Heat of Solution of Hydrated Silica in Hydrofluoric Acid.

G. Gore found that liquid **hydrogen chloride** has no action on silica. According to M. Wunder and A. Suleimann, when gelatinous silica is digested for 2 hrs. on a water-bath with 1 : 2 **hydrochloric acid,** 0·12 grm. of silica per litre passes into soln., and 0·03 grm. of silica per litre after 12 hrs.' digestion at 18°; with 1 : 1 acid, the results were respectively 0·14 and 0·03 grm. of silica per litre; and with 2 : 1 acid, 0·331 and 0·05 grm. per litre. C. Struckmann, O. Masche, and G. C. Wittstein made observations on this subject, *vide supra*. V. Lenher and H. B. Merrill found the solubility in grms. per 50 c.c. at 90° to be:

| Per cent. HCl | 0 | 2·0 | 5·4 | 7·8 | 10·0 | 15·4 | 18·7 |
|---|---|---|---|---|---|---|---|
| $SiO_2$ . . | 0·0212 | 0·0198 | 0·0152 | 0·0114 | 0·0091 | 0·0046 | 0·0028 |

and at 25°:

| Per cent. HCl | 0 | 3·0 | 6·4 | 12·0 | 18·9 | 25·1 | 34·9 |
|---|---|---|---|---|---|---|---|
| $SiO_2$ . . | 0·0081 | 0·00665 | 0·0044 | 0·0023 | 0·0008 | 0·0006 | 0·0004 |

The results are plotted in Fig. 49. J. M. van Bemmelen found that 0·81, 2·27, and

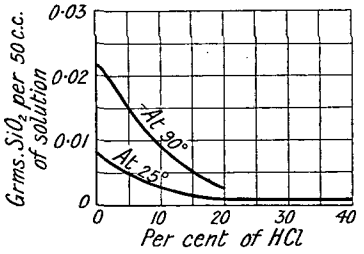



FIG. 49.—Solubility of Silica in Hydrochloric Acid per 50 c.c. of Solution.

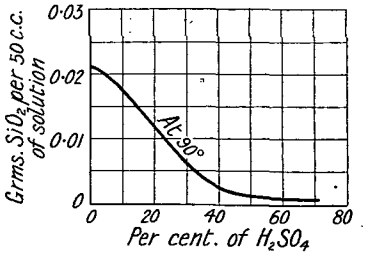



FIG. 50.—Solubility of Silica in Sulphuric Acid per 50 c.c. of Solution.

4·2 mgrms. eq. of hydrochloric acid were absorbed by 10 grms. of gelatinous silica dried at 100° from 100 c.c. of soln., containing respectively 20, 50, and 100 mgrms. eq. He assumed that the water in the silica was replaced by acid. C. J. B. Karsten discussed the action of acids on silica; and G. C. Wittstein, of aqua regia. E. Jordis and E. H. Kanter assumed from conductivity measurements that when hydrochloric acid is added to colloidal silica, combination occurs. C. J. B. Karsten also assumed that a compound of silica and hydrochloric acid can be formed. This was supported by F. Mylius and E. Groschuff. J. Meyer inferred that the amount of hydrogen chloride retained by silica after 4 hrs.' ignition at 1000° is inappreciable. T. Bauer has referred to the difficulty of getting rid of the last traces of hydrochloric acid from silica.

According to F. Koref,[7] and A. Gautier, silica at 800°–1100° is attacked by the

vapour of **sulphur, hydrogen sulphide** or of **carbon disulphide,** forming silicon sulphide (*q.v.*). R. D. Hall said that **sulphur chloride,** $S_2Cl_2$, has no action on heated silica; F. Bourion found that a mixture of chlorine and the vapour of sulphur chloride has virtually no action on precipitated silica at 575°; and at a dull red heat, C. Matignon and F. Bourion found that silicon tetrachloride is readily formed. W. B. Schmidt found that **sulphurous acid** has but a slight action on silica. According to M. Wunder and A. Suleimann, dil. sulphuric acid (1 : 2 dissolves 0·02 grm. and 0·04 grm. of silica per litre when digested on a water-bath and at 18° respectively. L. Wöhler and co-workers studied the action of silica in the contact process for sulphuric acid. V. Lenher and H. B. Merrill gave for the solubility of gelatinous silica in sulphuric acid in grams per 50 c.c. at 90°:

| Per cent. $H_2SO_4$ . | 0 | 3·9 | 7·3 | 11·5 | 25·4 | 55·6 | 71·0 |
|---|---|---|---|---|---|---|---|
| $SiO_2$ . . . | 0·0214 | 0·0211 | 0·0184 | 0·0144 | 0·0058 | 0·0005 | 0·0004 |

The results are plotted in Fig. 50. Observations were also made by S. Calderon. J. M. van Bemmelen found that 1·1, 2·17, and 4·0 mgrms. eq. of sulphuric acid were absorbed by 10 grms. of gelatinous silica dried at 100° from 100 c.c. of soln. containing respectively 20, 50, and 100 mrgms. eq. of sulphuric acid; the acid was assumed to replace the water in the hydrated silica, forming a kind of combination.

H. Funk[8] studied the action of **nitrogen** on silica during which a nitride (*q.v.*) is formed. C. J. B. Karsten found that aq. **ammonia** readily dissolves freshly precipitated silicic acid, but a soln. of ammonium carbonate dissolves very little. G. C. Wittstein also found that calcined silica is soluble in aq. ammonia, and if a soln. of water-glass, mixed with an excess of hydrochloric acid, be treated with ammonia, the flecks first formed are dissolved when more ammonia is added. According to R. Pribram, 100 parts of 9·75 per cent. aq. ammonia dissolve 0·714 part of gelatinous silicic acid, 0·303 part of dried silicic acid, 0·377 part of dehydrated silicic acid, and 0·017 part of quartz. A. Souchay found 100 parts of aq. ammonia dissolve 0·382 part of silica dried at 100°, 0·357 part of calcined silica, and 0·00827 part of quartz. H. Kühn, and J. Persoz also observed the ready solubility of silicic acid in aq. ammonia. The phenomenon is complicated by the action of alkalies derived from the glass containing vessel. C. Struckmann found that 100 parts of 19·2 per cent. aq. ammonia dissolved 0·071 part of silica, and 100 parts of a 1·6 per cent. soln., 0·0986 part of silica. Observations were also made by W. Skey, A. M. Edwards, etc. L. J. Briggs found that if the conc. of an aq. soln. of ammonia after absorption be represented by $C$ mols per litre, and the total adsorption by 100 grms. of quartz powder of surface area 100,000 sq. cms. be represented by $A$ mols per litre, then:

| $C$ . . | 0·0008 | 0·0032 | 0·0102 | 0·0344 | 0·1052 |
|---|---|---|---|---|---|
| $A$ . . | $0·55\times10^{-4}$ | $0·74\times10^{-4}$ | $1·04\times10^{-4}$ | $2·94\times10^{-4}$ | $7·68\times10^{-4}$ |

According to R. Schwarz, the peptizing action of the ammonia makes itself noticeable at a conc. of $0·001N$; for $3N$-ammonia the amount of dissolved silicic acid lies between 63·4 per cent. and 67·4 per cent. for different specimens of the gel. Between the conc. $3N$- and $6N$-ammonia the solubility does not change materially, and from this conc. upwards the solubility decreases.

H. Rose observed that silica may be completely volatilized as silicon tetrafluoride when heated with two or three times its weight of **ammonium fluoride**—J. B. Mackintosh, K. Daniel, F. Leydolt, and F. von Kobell have made observations on this subject. When heated with **ammonium chloride,** artificial silica becomes denser and less readily attacked by reagents. L. J. Briggs found that if the conc. of an aq. soln. of **ammonium carbonate** after adsorption be denoted by $C$ mols per litre, and the total adsorption by 100 grms. of quartz of surface area 100,000 sq. cms. be represented by $A$ mols per litre, then:

| $C$ . . | 0·0022 | 0·0063 | 0·0208 | 0·063 |
|---|---|---|---|---|
| $A$ . . | $0·09\times10^{-4}$ | $0·45\times10^{-4}$ | $0·45\times10^{-4}$ | $1·8\times10^{-4}$ |

A. W. Titherley found that when a mixture of silica and an **alkali amide** is heated between 300° and 400°, ammonia is evolved, and at still higher temp., ammonia, hydrogen, and nitrogen are given off. The residue contained the alkali silicate and silicon nitride. When gelatinous silica is digested with dil. **nitric acid** (1 : 2; 1 : 1; and 2 : 1) on a water-bath for 2 hrs., respectively 0·10, 0·08, and 0·04 grm. of silica per litre passes into soln., and when digested for 12 hrs. at 18°, respectively 0·02, 0·03, and 0·03 grm. of silica per litre dissolves. S. Calderon made some observations on this subject. J. M. van Bemmelen found that 0·86, 2·17, and 4·0 mgrms. eq. of nitric acid were adsorbed by 10 grms. of gelatinous silica dried at 100° from 100 c.c. of soln. containing respectively 20, 50, and 100 mgrm. eq. of nitric acid. The water of the silica is replaced by nitric acid which forms a kind of compound with the silica. G. C. Wittstein also tested the solubility of silica in **aqua regia.**

Silica has in a marked degree the power of forming complex acids. The silicophosphates, silicotungstates, silicomolybdates, silicovanadates, silicotitanates, and the silicostannates can be cited in illustration. A. V. Bleininger and P. Teetor [9] obtained no evidence of the formation of a compound in their study of the glasses obtained by fusing mixtures of silica and boric oxide. The action of soln. of phosphoric acid, of fused sodium phosphate, of phosphorus pentoxide, and fused metaphosphoric acid is discussed in connection with the silicon phosphates, *vide infra.* A. Daubrée found that **phosphorus trichloride** converts silica into silicon tetrachloride; R. Weber obtained a similar result with phosphorus pentachloride; and A. Simon showed that **phosphorus trifluoride** yields silicon tetrafluoride. The action of **carbon** and of **calcium carbide** on silica has been discussed in connection with silicon carbide. Reports as to whether the presence of **carbon dioxide** in soln. in water exercises any influence on the solubility of silica are discordant. C. Struckmann [10] said that the solubility is diminished; V. Lenher and H. B. Merrill said that at 90°, the effect of carbon dioxide on the solubility of silica in water is *nil.* F. Seemann, O. Masche, and S. Calderon made some observations on the subject. C. Matignon and G. Marchal examined the corrosive action of water on quartz in the presence of carbon dioxide under 10 atm. press. during 3 years' action. S. Medsforth studied the action of silica on nickel as a catalyst in the reduction of carbon monoxide and dioxide by hydrogen. A. Findlay and W. H. Harby found that colloidal silica exercises no influence on the solubility of carbon dioxide in water. A. Simon found that **carbon tetrafluoride** converts silica into silicon tetrafluoride; and E. Demarçay said that **carbon tetrachloride** slowly converts red-hot silica into silicon tetrachloride, and H. E. Quantin found that silicates also yield silicon tetrachloride, and this the more readily the greater the proportion of combined alumina in the silicate. *Au contraire,* L. Meyer, and P. Camboulives said that silica is not attacked when heated in a stream of the vap. of carbon tetrachloride, and the latter applied the fact to the analysis of complex minerals. For instance, a separation of free and combined silica in bauxite can be effected in this way, since aluminium silicate is transformed into the chlorides of aluminium and silicon, whilst uncombined silica is not attacked. P. Sabatier and A. Mailhe found that silica acts catalytically on the decomposition of formic acid into carbon dioxide, water, and formaldehyde; and J. B. Senderens, and A. Kling, that silica acts catalytically on the thermal decomposition of alcohols. D. Konowaloff found silica acts catalytically on the decomposition of amyl acetate vapour; C. H. Milligan and E. E. Reid, on acetic acid, and ethyl alcohol vap.; and M. Bodenstein and F. Ohlmer, on the oxidation of carbon monoxide. E. Berl and W. Pfanmüller, W. Suida, E. Dittler, and L. Pelet-Jolivet studied the action of silica, quartz, etc., on organic dye-stuffs. The basic dyes are adsorbed particularly when the grain-size is approximately 10$\mu$. It has been affirmed by F. Verdeil and E. Risler [11] and denied by A. Petzholdt that silica is soluble in a soln. of sugar. J. Weisberg found that calcined silica is much less soluble in saccharine soln. than partially dried silica.

J. J. Berzelius [12] found that at a white-heat silica and **potassium** form potassium silicate and silicide; and that a mixture of silica and carbon, in the presence of **copper, silver,** or **iron,** at a white heat, forms carbon monoxide and a silicide of the metal. J. S. Stas also noted that silica is attacked and reduced by molten silver or silver vap. G. A. Faurie made some observations on this subject. J. B. J. D. Boussingault also found that when a mixture of silica and carbon with **platinum, palladium, ruthenium,** or **iridium** is heated, a metal silicide is formed. R. Bunsen and A. Matthiessen, and H. Moissan found that **calcium** and **strontium** reduce silica at a red-heat. A. Burger also studied the action of calcium. F. Krafft found that these metals, freed from the oxide, can be distilled in quartz vessels; and A. Schuller showed that under diminished press. in quartz vessels, silver can be volatilized at a temp. below its m.p.; a deposit of lead was observed when commercial silver was employed; copper can be sublimed when heated in quartz vessels; **gold** volatilizes very slowly at about its m.p.; **tin** can be distilled somewhat more easily than gold. For the action of the various **metals** on silica, *vide* the silicides.

L. J. Briggs [13] measured the adsorption $A$ by 100 grms. of surface area 100,000 sq. cm. of powdered quartz in mols, when the conc. of the soln. after adsorption was $C$ mols per litre, and found with **sodium hydroxide :**

| | | | | | |
|---|---|---|---|---|---|
| $C$ . . | 0·0007 | 0·0026 | 0·0078 | 0·028 | 0·0866 |
| $A$ . . | $0·42\times10^{-4}$ | $0·79\times10^{-4}$ | $1·48\times10^{-4}$ | $3·45\times10^{-4}$ | $8·10\times10^{-4}$ |

and with **potassium hydroxide:**

| | | | | |
|---|---|---|---|---|
| $C$ . . | 0·0009 | 0·0021 | 0·0063 | 0·0235 |
| $A$ . . | $0·33\times10^{-4}$ | $0·91\times10^{-4}$ | $1·63\times10^{-4}$ | $3·3\times10^{-4}$ |

The adsorption curves for ammonium and the alkali hydroxides are similar in form. The amount adsorbed is not directly proportional to the conc., but is relatively greater in very dil. soln., so that the ratio of the amount adsorbed to the conc. of the soln. decreases as the conc. is increased. The apparent adsorption of potassium hydroxide by quartz when in equilibrium with a tenth-normal soln. is $1·66\times10^{-5}$ gm. mols. per sq. metre, which is eq. to about 0·6 mg. of potassium hydroxide per square metre of surface. The adsorption of potassium hydroxide by a fine quartz sand from a tenth-normal soln. amounts to only 1 per cent. of the salt contained in a vol. of soln. sufficient to saturate the sand. R. E. Hall and co-workers discussed the solubility of quartz in hot alkaline waters. For the action of fused alkali hydroxides, *vide infra,* alkali silicates.

According to C. F. Rammelsberg,[14] quartz is but slightly attacked by a soln. of potassium or sodium hydroxide; hydrated silica is fairly soluble in this menstruum; while the opals, and chalcedonies are readily attacked. Thus, H. Leitmeier found that with different samples of chalcedony, a variety of chalcedony (or opal), called *cacholong,* and quartz, the attack by a 2 per cent. soln. of potash-lye at 85° for 5 hrs. was related with the amount of water associated with the chalcedony, as indicated in Table VIII. Many other observations on this subject have been

TABLE VIII.—ACTION OF POTASSIUM HYDROXIDE ON QUARTZ.

| Variety of silica. | Sp. gr. | Water. Per cent. | Quartz dissolved. Per cent. |
|---|---|---|---|
| Quartz (Rauris) . . . | 2·613 | 0·22 | 7·23 |
| Chalcedony (Farœ). . . | 2·591 | 1·02 | 42·30 |
| Cacholong (Farœ) . . . | 2·370 | 1·35 | 54·49 |
| Chalcedony (Weitendorf). . | 2·608 | 1·50 | 76·02 |

made—*vide supra,* corrosion figures. It is not possible to estimate accurately the proportion of opal and quartz, in a sample of chalcedony, flint or chert, from the

amount dissolved in alkali-lye in a given time, because fine-grained quartz is attacked at the same time. The attack by alkali-lye depends on the conc. of the soln., the grain-size of the mineral, the temp., and time of action. Contradictory results have been published for the effect of, say, 10 per cent. soln. of alkali-lye on quartz because the effect of the size of grain has been overlooked. J. W. Mellor[15] showed that with a sample of clear rock crystal, and a sample of flint from Dieppe, with a 15 per cent. soln. of potassium hydroxide :

| | | |
|---|---|---|
| Average diameter of grain . . | 0·165 mm. | 0·032 mm. |
| Rock crystal dissolved . . . | 0·96 | 6·40 per cent. |
| Flint dissolved . . . . | 2·52 | 12·10 „ |

G. Lunge and M. Schochor-Tscherny found with a sample of powdered quartz after 2 hrs.' action, the percentage amount of quartz dissolved was:

| | Potassium hydroxide soln. | | Sodium hydroxide soln. | |
|---|---|---|---|---|
| | 10 per cent. | 5 per cent. | 10 per cent. | 5 per cent. |
| Quartz dissolved . . . | 21·36 | 16·84 | 19·80 | 16·20 |

In 32 hrs. all was dissolved by a 15 per cent. soln. of potash-lye, and soda-lye required 2 hrs. longer under similar conditions. F. Mylius and F. Förster confirmed the conclusion that the action of a soln. of potassium hydroxide on silica is quicker than that of sodium hydroxide.

J. A. Hedvall[16] found precipitated silica was the only form of silica which reacted appreciably with **calcium oxide** at 1000°, though silica glass acts slightly ; the formation of a silicate occurred at 1400° with cristobalite, while quartz did not act so rapidly. The formation of a silicate with **barium oxide** was appreciable with precipitated silica at 900°, and increased slowly with rise of temp. No sign of reaction was observed with **magnesium oxide** at 900°. According to E. Jordis and E. H. Kanter, aq. soln. of the **hydroxides of the alkaline earths** react slowly with finely divided quartz, forming the corresponding hydrated silicates ; the systems were not in equilibrium after standing 16 days. The reaction is much faster with lime than with baryta or strontia—*vide* calcium silicates. According to K. Hebbeler, if kieselguhr be shaken up with water ; allowed to settle ; the clear water decanted off and replaced by lime-water ; and the lime-water be renewed daily 14 times, the sediment expands to nearly three times its vol. in water. No calcium silicate is formed, but calcium hydroxide is deposited about the kieselguhr, and can be removed by repeated extraction with water. The action of lime-water on silica was studied by J. W. Döbereiner, A. Petzholdt, etc.

In making the so-called *sand-lime bricks*—used for building purposes—sand is mixed with milk of lime ; pressed into the desired shape ; rapidly heated to 80° or 100° ; and then heated under a press. of from 5–10 atm. for 8 hrs. in an autoclave. The lime and quartz are thus bound together by a product which F. Rinne believed is analogous with *plombierite*, $CaSiO_3.2H_2O$, found by A. Daubrée in the deposits from the thermal springs of Plombières. M. Glasenapp found that in any case, from 3–10 per cent. of the silica becomes soluble in acid, and this the more the higher the press. in the autoclave. The action of lime on silica in mortars has been studied by A. Petzholdt.

L. J. Briggs[17] showed that the general behaviour of soln. of the alkali carbonates resembles that of soln. of the alkali hydroxides, but adsorption is more marked with the hydroxides than with the carbonates. Using $A$ and $C$ with the same meanings as before, with **sodium carbonate** :

| | | | | | | |
|---|---|---|---|---|---|---|
| $A$ . . . | 0·0004 | 0·0012 | 0·0032 | 0·0106 | 0·0356 | 0·108 |
| $C \times 10^4$ . . | 0·06 | 0·18 | 0·97 | 1·13 | 1·65 | 1·95 |

and with **potassium carbonate :**

| | | | | |
|---|---|---|---|---|
| $A$ . . . . . | 0·0029 | 0·0093 | 0·0302 | 0·0910 |
| $C \times 10^4$ . . . . . | 0·45 | 0·76 | 1·65 | 2·4 |

There have been differences of opinion as to the action of the alkali carbonates, but

here again the result is largely due to differences in the grain size of the powders submitted to the reagent. G. Lunge and M. Schochor-Tscherny found with a given sample after 2 hrs.' action :

| | Potassium carbonate soln. | | | Sodium carbonate soln. | | |
|---|---|---|---|---|---|---|
| | 15 per cent. | 10 per cent. | 5 per cent. | 15 per cent. | 10 per cent. | 5 per cent. |
| Quartz dissolved . | 9·10 | 6·96 | 6·36 | 10·92 | 8·52 | 3·10 |

With coarser powder the action is very considerably reduced. R. Schwarz found that with powdered quartz and tridymite, of similar grain size, half an hour's boiling with a 5 per cent. sodium carbonate soln. dissolved 2·11 per cent. of quartz, and 2·77 per cent. of tridymite—*vide supra*, corrosion figures. The action of soln. of alkali carbonates on silica has been studied by G. Forchhammer, F. Pfaff, L. Doveri, T. Scheerer, O. Maschke, etc. J. W. Cobb found that mixtures of silica and sodium carbonate begin to react at about 700°, nearly 150° below the m.p. of the more fusible constituent of the mixture. For the action of fused alkali carbonates, *vide infra*, alkali silicates.

J. W. Cobb found that **sodium sulphate** begins to react with silica between 1120° and 1130°. J. M. van Bemmelen [18] investigated the adsorption of soln. of salts by silica, 10 grms. of gelatinous silica dried at 100° in contact with a soln. of 20, 50, and 100 mgrms. eq. of salt per 100 c.c. of soln., adsorbed respectively 1·0, 2·5, and 4·56 mgrms. eq. of **potassium sulphate ;** and with soln. containing 20 and 50 mgrms. eq. of salt per 100 c.c., respectively 0·9 and 2·14 mgrms. eq. of **potassium nitrate,** and 0·85 and 2·16 of **potassium chloride** were adsorbed. The quantity adsorbed is roughly proportional to the conc. of the soln., but with the more conc. soln. the amount adsorbed is less than corresponds with this relation. The 10 grms. of silica employed by J. M. van Bemmelen contained the eq. of 5·5 c.c. of water, and he noted that the amount of salt adsorbed corresponds to a bodily removal of from 4–4·5 c.c. of the soln. This suggested that when the silica was put into a soln., the water it contained was replaced by an equal vol. of the soln. G. C. Schmidt obtained results with potassium chloride in agreement with those of J. M. van Bemmelen, and he concluded that dissolved substances are taken up by precipitated silica mainly in the form of solid soln. rather than through adsorption processes. A. Schuller found that **sodium chloride** may be sublimed under reduced press. in quartz vessels. F. Seemann, J. W. Mellor, V. Lenher and E. Truog, and A. F. Joseph and J. S. Hancock studied the effect of sodium chloride on the solubility of silica. J. W. Mellor suggested that the solubility of silica in soln. of sodium chloride is due to the formation of a sodium silicate. This suggestion was confirmed by A. F. Joseph and J. S. Hancock. H. C. McNeil noted the solubility of silica in fused **barium chloride.**

G. Spezia [19] found that a 5 per cent. soln. of **borax** dissolved about 74 mgrms. per sq. cm. in 4 days from a polished plate of quartz between 290° and 315° under a press. of 76–106 atm. ; but virtually none was dissolved in 20 days between 12° and 16° and 6000 atm. press. The action of borax soln. was also investigated by E. Schweizer, and L. Doveri—*vide supra*, corrosion figures. G. Spezia also found analogous results with a soln. of **sodium silicate,** under a press. of 6000 atm. —there was virtually no action between 18° and 20°, and an appreciable action between 165° and 160°—*vide supra*, corrosion figures. C. Doelter [20] has studied the solubility of quartz in certain **fused silicates**—sanidine, albite, and labradorite—and C. Friedel found that fused **potassium bisulphate** slowly attacks quartz, and produces corrosion figures which change their symmetry at a temp. corresponding with the optical mutations at 570°. P. Hautefeuille studied the solubility of silica in fused **sodium tungstate**—*vide supra*.

A. Schuller [21] found that **silver sulphide** and **lead sulphide** are readily sublimed in quartz vessels under reduced press. L. Troost and P. Hautefeuille found that **aluminium chloride** and **zirconium chloride** have no action on heated silica. According to W. Skey, finely divided, feebly calcined silica decomposes aq. soln.

of **chromic, cupric, or ferric acetate,** and precipitates the hydroxide. Quartz also decomposes ferric acetate soln.

In 1664, J. R. Glauber, in his *Novum lumen chymicum* (Amstelodami, 1664), noted the reaction between sand and any alkali salt; and in 1809, J. L. Gay Lussac and L. J. Thénard [22] observed that silica and **sodium chloride** react to form hydrogen chloride and sodium silicate; but in the absence of moisture, no reaction occurs even at a white heat. C. F. Schönbein made a similar observation. As previously indicated—**2.** 20, 13—sodium chloride is readily dissociated by steam at an elevated temp. F. de Lalande and M. Prud'homme, and H. Schulze noted that chlorine is also formed with dry oxygen; and A. Gorgeu observed that there is a reaction between heated sodium chloride and silica in dry or moist air. The reaction has been further discussed by R. A. Tilghman, W. Gossage, R. Lieber, A. Blanc and T. P. Bazille, T. Williams, G. Fritzsche, H. Grüneberg and J. Vörster, H. H. Lake, C. F. Claus, and A. Ungerer—**2.** 20, 28. According to F. H. Clews and H. V. Thompson, silica and sodium chloride when strongly heated interact to give, in dry air, sodium silicate and chlorine; in moist air, sodium silicate, hydrochloric acid, and a small quantity of chlorine; in moist nitrogen, sodium silicate and hydrochloric acid. The lower temp. limit of the reaction is about 600°, and the extent of the reaction is still very small at 1000°. A rise in temp. and the presence of moisture increase the velocity of the reaction. The results obtained by varying the proportions of sodium chloride and silica indicate that the area of contact is more important than the composition of the mixture, unless the proportion of salt falls much below 50 per cent. H. V. Thompson, W. J. Rees, L. M. Wilson, and A. E. Findley, have studied the reaction from the point of view of the resistance of silica bricks to the fumes of alkali and ammonium chlorides when salty coals are employed in coke ovens, and vertical gas-retorts. The temp. in the former case is comparatively low, but the action is prolonged month after month, so that drastic changes can be produced under conditions where the effects are inappreciable in ordinary laboratory experiments. According to F. H. Clews and H. V. Thompson, quartz is more reactive than precipitated silica or tridymite at 1000°. This does not agree with observations made in other directions. W. Lowenstein measured the solubility of silica in molten **calcium chloride,** and found:

| | 800° | 850° | 900° | 950° |
|---|---|---|---|---|
| Per cent. $SiO_2$ . . | 2·5 | 3·8 | 5·4 | 7·6 |

and he calculated the heat of soln. to be —19,225. There is a reaction, $SiO_2+CaCl_2=CaSiO_3+Cl_2$. G. Marchal found that silica begins to react with **calcium sulphate** at 870°.

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## § 20. The Uses of Silica

As previously indicated, quartz was fused in the flame of the oxyhydrogen blowpipe by R. Hare,[1] in 1802; and later by E. D. Clarke, and others—*vide supra*, the melting of silica. In 1839, A. Gaudin noticed that the glass obtained by melting quartz does not exhibit double refraction, and he also showed that the molten quartz can be worked like glass, and he made threads of fused quartz over a metre long. A. Gautier exhibited spiral threads of fused quartz in 1878. C. Despretz, and C. A. Parsons fused silica by passing an electric current through a carbon rod embedded in sand, and thus obtained a hard fused silica tube. No industrial use for quartz-glass had been found until C. V. Boys, in 1889, showed that the low coeff. of thermal expansion, and the toughness of quartz-glass fibres rendered it a valuable means of suspending the magnets and mirrors of galvanometers. In 1901, R. S. Hutton, and W. A. Shenstone prepared quartz-glass, and laid the foundation of an industry for the manufacture of vessels of vitreous quartz. Various names are applied to the vitrified quartz—thus, *quartz-glass, vitreous-silica, fused quartz, silica-glass, vitreosil*, etc. Vessels made of this material—tubes, flasks, retorts, dishes, etc.—can now be used for various apparatus required in laboratory or factory.

The manufacture of vessels of quartz-glass offers many difficulties. For example, the elimination of air entangled between the grains during fusion is not easy. In W. C. Heraeus'[2] process the quartz is first heated to nearly 600° so as to shatter it up into small pieces. The fragments are then fused in crucibles—made from iridium, or a mixture of alumina and zirconia. Small quantities of the material can be worked in the oxyhydrogen flame like glass in the ordinary gas blowpipe. In another type of silica ware, an electrode of the desired shape is embedded in good quartz sand, and heated electrically. The material near the electrode is sintered together; that furthest away is not fused. The electrode is removed when the furnace cools, and a vessel with an internal shape like the electrode remains. The vessel can be dressed by grinding, etc., and the inner surface can be vitrified by the oxhydrogen blowpipe. This ware is translucent or opaque, and permeated with numerous air-bubbles. In order to eliminate air-bubbles the British Thomson-Houston Co. fuses the quartz in vacuo, and compresses the plastic mass.

The trade name for a product obtained by fusing silica with 0·1–2 per cent. of zirconia is called *Z-siloxide*; and if titania is used, *T-siloxide*. F. Thomas[3] states that these products are less liable to devitrification than vitreosil, or quartz-glass, but A. C. Michie denies this, and claims that these additions make quartz-glass more liable to devitrification. F. Thomas also claims that the siloxides resist attack by alkalies and molten metals better than quartz-glass.

In virtue of its very small coeff. of thermal expansion, vessels made from quartz-glass can be rapidly cooled or rapidly heated without cracking; for instance, a flask made of quartz-glass can be heated red-hot in the blowpipe, and immediately plunged into cold water without fracture—ordinary glass under the same conditions would shatter into fragments. The softening temp. approaches 1600°,

although long pyrometer tubes, if not adequately supported, will bend if heated to 1200°. This might be anticipated since quartz-glass—like ordinary glass—is an under-cooled fluid, which, at ordinary temp., is viscid enough to be rigid and hard, but which, on heating, becomes less and less viscid. Lord Rayleigh detected evidence of a crystalline structure in a specimen of quartz-glass. The absence of a definite m.p. also explains the discrepancies between the different reports of the m.p. of quartz-glass.[4] Quartz-glass has no real melting temp. If heated for long periods—say at 1200°—quartz-glass devitrifies owing to the formation of crystals of cristobalite or tridymite (Fig. 26). The glass then becomes opaque, brittle, and doubly-refracting. Vessels made of quartz-glass also cease to be gas-tight.[5] The crystallization introduces tremendous strains in the body owing to the contraction which takes place about each centre of crystallization. The sp. gr. of the opalescent or devitrified glass approaches 2·3. The properties of quartz-glass—physical and chemical—have been described in connection with those of silicon dioxide.

Sandstone and quartzite are used for building stones, grinding stones, whet-stones, runners and pavers for grinding pans, etc. In making firebricks, ground sandstone, ganister, quartzite, or a similar rock is intimately mixed with a little milk of lime so as to add a total of say 2 per cent. of calcium oxide. The mixture is moulded into bricks, and fired to 1300°–1500°. The resulting *ganister bricks*, *silica bricks*, or *Dinas bricks* are highly refractory—in some cases withstanding furnace temp. approximately 1700°. This is higher than the fusion temp. of the bricks. The bricks maintain their form because the high temp. affects only the face of the brick; the bricks are cooler a short distance from the face. Instead of lime, other binding agents are used—*e.g.* clay, basic slag, etc. The siliceous rock may be associated with enough clay to render further additions unnecessary. If the silica bricks are inadequately fired, they may expand inconveniently in use; this is due to the slow conversion of quartz into forms of silica with a low sp. gr. A little expansion is not a bad thing, for it may help to keep the joints of flues, etc., tight. Quartose sands, ground flint, ground quartzites, and the like are also used in the manufacture of soaps, white paints, polishing powders, soluble glass, cements, enamels, glazes, glass, and in the ceramic industries.

Many of the gem varieties of quartz are shaped into ornaments and gem-stones. Diatomaceous earth or kieselguhr—wrongly called *infusorial earth*—is used as a polishing powder, and in the manufacture of soaps as a substitute for pumice-stone. The absorbent properties of kieselguhr are utilized for the preparation of solid disinfectants by the absorption of liquid antiseptics for the dry dressing of wounds; and for the absorption of bromine, sulphuric acid, and nitroglycerol. Kieselguhr soaked in nitroglycerol is called *dynamite*. The poor heat-conducting qualities of diatomite make it a valuable insulating and fireproof packing for heating furnaces, powder magazines on board ships, cold storage rooms, etc. Diatomite bricks are also very light and porous, and are poor conductors of sound. K. Hebbeler [6] has discussed the increase in vol. which occurs in sedimented kieselguhr when the water is replaced by lime-water—*vide supra*. Silica was found by C. H. Milligan and co-workers [7] to be a better catalyst than either thoria or titania for esterification reactions in the vapour phase. W. A. Patrick described the preparation of silica hydrogels as catalysts when fortified with various metal colloids as promotors; and J. N. Pearce and A. M. Alvarado, the effect of silica as a catalyst in esterification.

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## § 21. Silicic Acids or Colloidal Silica

Colloids and crystalloids appear to belong to different worlds of matter, and give occasion to a corresponding division of chemical science. The distinction between these kinds of matter is that subsisting between the material of a mineral and the material of an organized mass.—T. GRAHAM.

The natural forms of amorphous hydrated silica are classed as opals—*vide supra*, the occurrence of silica. The gelatinous masses obtained by treating with acids soluble alkali silicates, zeolites, and many other natural silicates, are sometimes called silicic acids. The history has been discussed by P. Walden,[1] and R. Frühling. According to L. Doveri,[2] when hydrochloric acid is added drop by drop to a soln. of an alkali silicate, the greater part of the contained silica is precipitated as hydrate, but if the same quantity of acid be added at once, very little of the silica is deposited. T. Graham prepared the **hydrogel of silicic acid** by pouring conc. hydrochloric acid into a conc. soln. of sodium silicate containing about 25 per cent. of silica, $SiO_2$, and washing the precipitated silica free from soluble salts. H. A. Fells and J. B. Firth said that the removal of the sodium chloride before or after heating makes no material difference to the adsorption capacity of silica gel for water. The hydrate was made by F. C. Kuhlmann, F. Üllik, P. Rohland, E. Jordis, W. Kühne, J. M. van Bemmelen, F. Bayer, W. A. Patrick, P. G. Somerville and E. C. Williams, F. X. Govers, B. Kühn, J. H. Frydlender, etc. E. Jordis said that the precipitate is finer and more flocculent the greater the dilution of the soln., and that in this state it can be readily washed. The following process may be employed:

Dissolve 50 grms. of commercial precipitated silica in a soln. of 12 grms. of sodium hydroxide and 50 c.c. of water. Dil. the soln. to 200 c.c. and heat the liquid to about 100°; add hydrochloric acid. Wash the precipitate on a Büchner's funnel with hot water. Again stir up the hydrogel with hot water, and wash on the funnel until free from chlorides. Sodium salts are more easily washed from the silica than potassium salts.

J. J. Berzelius obtained the gel by treating silicon tetrafluoride with water. C. Langlois used silicon tetrachloride; J. J. Ebelmen, ethyl orthosilicate; E. Grimaux, methyl silicate. B. Kempe considered the hydrolysis of ethyl ester to be too slow a process. A. C. Becquerel also observed the formation of gelatinous silica about the positive pole when a soln. of potassium silicate was electrolyzed; and M. Kröger found that by the electrolysis of a 1·5 per cent. soln. of water-glass between a mercury cathode and a platinum anode a clear hydrosol of silicic acid which did not gelatinize for 4 weeks collected in the anode compartment; the sol from a 6 per cent. soln. of water-glass gelatinized immediately it was formed; and with a 30 per cent. soln., silica was deposited on the anode. J. F. Spencer and K. Proud made orthosilicic acid by the electrolysis of a 50 per cent. soln. of sodium silicate in a divided cell with a heavy anode current-density. A platinum dish served as cathode, and a coil of platinum wire in a porous pot served as anode. The glass-like deposit on the platinum wire was entirely insoluble in water, and stable in air. H. C. A. Holleman [3] described the manufacture of silica gel for use as an adsorbent.

By adding 100 c.c. of a mixture of equal parts of conc. hydrochloric acid and water, slowly, drop by drop, and with constant stirring, to a soln. of water-glass, or to a soln. of 60 grms. of sodium metasilicate in 200 c.c. of water, **silica hydrosol or soluble silica** is formed. The silica hydrosol remains in soln. along with the excess of hydrochloric acid and the sodium chloride formed in the reaction: $Na_2SiO_3+2HCl \rightleftharpoons H_2SiO_3+2NaCl$. The hydrochloric acid and the sodium chloride can be separated from the hydrosol by dialysis (Fig. 51). T. Graham found that after four days' dialysis, the liquid in the dialyzer was no longer rendered turbid by a soln. of silver nitrate. E. Jordis, on the contrary, maintained that the chlorine is a constitutive part of the silica in soln., but R. Zsigmondy and R. Heyer confirmed T. Graham's conclusion that the chlorine can be all removed by dialysis; and, in order to ensure rapid dialysis, the dialyzer illustrated in Fig. 51 can be used in place of the simpler form used by T. Graham. In the improved apparatus a current of water is kept circulating about the outside of the dialyzing membrane. The dialyzing surface is also relatively great, so that the operation is much quicker than before. The liquid in the dialyzer is protected from dust by a plug of cotton wool. Acetic acid (E. M. Plessy), oxalic acid (E. Monier), and sulphuric acid (S. Meunier) have been used in place of hydrochloric acid. Hydrosols of silica have been obtained in many other ways. The dialysis of colloidal silica has been discussed by R. Zsigmondy. E. Grimaux prepared the hydrosol by heating 8 grms. of methyl orthosilicate with 200 grms. of water in a flask fitted with a reflux condenser; concentrating the liquor to about three-fourths its vol.; and evaporating off the alcohol. The preparation of silica hydrosols has been investigated by W. Spring, E. Ebler and M. Fellner, etc. E. Jordis studied the formation of hydrosols by the peptization of the hydrogel. E. Frémy reported the formation of a hydrosol of silica by the action of water on silicon sulphide, $SiS_2$; hydrogen sulphide gas is evolved at the same time: $SiS_2+2H_2O=2H_2S+SiO_2$. J. J. Berzelius made the sol by the action of silicon fluoride on crystallized boric acid, and removed the boron and fluorine compounds by treatment with a large excess of aq. ammonia. J. Bradfield removed the excess of precipitant used in making silicic acid by means of the centrifuge; F. Bayer, by pressure; and G. Bruni, and B. L. Vanzetti, by freezing. R. Schwarz prepared sols of silicic acid by evaporating a soln. of silicic acid in ammonia over dil. sulphuric acid.

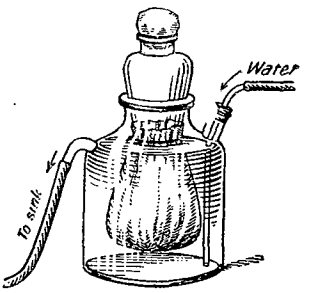


FIG. 51.—B. Proskauer's Dialyzer.

The hydrosol of silica obtained by dialysis has about 5 per cent. of silica, and it can be conc. by boiling in a flask until it contains about 14 per cent. of silicic

acid, but if boiled in an open flask a ring of insoluble silica forms round the margin of the liquid, and this soon causes the whole to gelatinize. The pure silica sol so prepared is a limpid colourless liquid which gelatinizes, or assumes the hydrogel condition, on standing a few days. The longer the sol has been dialyzed the longer it may be kept without gelatinizing. The passage of silicic acid from the sol to the gel condition is retarded by the presence of a little hydrochloric acid, or alkali hydroxide, and is accelerated, by a little sodium carbonate, or by contact with powdered, inert solids, say, graphite. Dialyzed or soluble silicic acid does not give a luminous beam with Tyndall's optical test, showing that the dissolved particles are not large enough to scatter light. J. H. Bechhold filtered the sol through the so-called colloid filter of biscuit earthenware. The first sign of the coagulation of the soln. appears as a feeble opalescence in the track of the beam, and this gradually increases in intensity. C. F. Böhringer obtained highly dispersed sols of silica by treating silica or other silicon compounds with ammonia to form ammonium silicate and subsequently expelling the ammonia by heat. The coarser particles can be removed by ultrafiltration or dialysis. M. Kröger described the preparation of silica hydrosol.

Silicic acid gels were prepared by H. N. Holmes [4] by the action of various acids on soln. of sodium silicate of different conc. He measured the effect of temp. and the effect of the conc. of the acid on time of gelatinization. While W. Flemming found the rate of gelatinization depends on the conc. of the silicic acid, the temp., and the catalytic effect of acids or alkalies, H. N. Holmes showed that the dehydrating influence of non-ionized molecules of the acid is of importance. It may happen that precipitates of gelatinous silica prepared in a particular way, or dried at a particular temp., have a definite composition, but each of the compounds so reported represents an arbitrarily selected point on a continuous curve. Thus, according to O. Maschke, if the precipitate be dried in air, it contains from 13 to 36 per cent. of water—the two extremes thus approximate with $2SiO_2.H_2O$ and $SiO_2.2H_2O$ respectively; and, according to E. Jordis, silica precipitated from dil. soln. of water-glass contains about 94 per cent. of water. F. Ullik dried gelatinous silica in air and found that it approximated to $SiO_2.H_2O$. R. Meldrum said that only the hydrate dried over conc. sulphuric acid has a definite composition, viz. $3SiO_2.H_2O$. J. N. von Fuchs found a sample precipitated by passing silicon tetrafluoride into water, contained 9·1–9·6 per cent. of water after drying over sulphuric acid for 30 days, and thus corresponded with $3SiO_2.H_2O$; and E. Frémy found that when dried in vacuo, the hydrate corresponded with $3SiO_2.2H_2O$. V. Merz found that the freshly prepared, and aged silicic acid lost water at different rates. Thus, the percentage water-contents at different temp. was:

| | 60° | 70° | 80° | 90° | 100° | 130° | 160° | 260° |
|---|---|---|---|---|---|---|---|---|
| Aged | 8·96 | — | 7·46 | 6·90 | 6·24 | — | — | 3·37 |
| Fresh | — | 5·93 | — | 4·64 | 4·26 | 3·5 | 3·0 | — |

J. Gottlieb found that after 4 to 5 weeks' drying in a current of air at 100°, a sample contained 4·47 per cent. of water; after drying in an air-bath between 180° and 200°, 4·19 per cent.—this result was taken to correspond with the hydrate $6SiO_2.H_2O$; L. Doveri also found that the product, dried slowly in air at 100°, contained 8·3–9·4 per cent. of water; at 120°, only a trace of water. J. W. Mellor showed that the rate of dehydration of silica precipitated by acid from conc. and dil. soln. of sodium silicate, is faster in the latter case:

| Time at 800° (min.) | 2 | 10 | 20 | 30 |
|---|---|---|---|---|
| Loss $H_2O$ from conc. soln. | 1·60 | 4·25 | 5·72 | 6·18 |
| Loss $H_2O$ from dil. soln. | 4·49 | 6·45 | 8·72 | 10·04 |

L. Doveri's product dried over quicklime in vacuo was represented by $3SiO_2.2H_2O$; W. K. Sullivan's product, obtained by adding hydrochloric acid to a soln. of basic potassium silicate and drying the gelatinous mass in vacuo, or in dry air, was also represented by the same formula; when dried at 100°–120°, $3SiO_2.H_2O$ was said

to be formed. A. Souchay, J. J. Ebelmen, and H. Rose also made observations on this subject. E. Jordis said that the silicic acid which separates from dil. water-glass soln. contains 94 per cent. of water. Most, if not all, of these hydrates are but arbitrarily selected states in a continuous series between the sol of silicic acid and dehydrated silica, and are represented by arbitrarily selected points on a continuous drying curve. According to T. Carnelley and J. Walker, the dehydration or time-temp. curve shows a terrace just below 100°, but is otherwise continuous. A similar terrace is characteristic of many other colloids. B. L. Vanzetti dehydrated silica gels by evaporation and freezing. There was no evidence of the formation of definite hydrates. The composition of the product depended on the initial conc. of the soln. and the age of the gel, and not on the temp. of freezing down to —200°. R. Schwarz and F. Stöwener inferred from their observations on the effect of ammonia on silica gels, that the ageing consists of a dehydration of primary particles which originally held much water, and in a strictly chemical sense, it is probable that dehydration or polymerization also occurs.

In analysis, the soln. containing the silica which separates when the silicate is treated with an acid, is evaporated to dryness with the object of making it insoluble, and the product is baked at 110°. The product is digested with water or dil. acid, and the soluble matters containing calcium, magnesium, and aluminium oxides, etc., filtered off. The residue, silica, is washed and dried. The higher the temp. and the longer the time of drying, the less the amount of silica which passes into soln. There is a limit to the temp. of desiccation on account of the recombination of silica with the bases. W. F. Hillebrand, for instance, showed that magnesia and silica, under these conditions, combine at about 120°. A second evaporation of the soln. is therefore recommended to recover that which passes into soln. in the extraction after the first evaporation. This subject has been fully discussed by J. W. Mellor.

According to T. Graham,[5] C. Roberts, etc., if a clear soln. of dialyzed silicic acid be evaporated in vacuo at 15°, a clear transparent jelly is obtained which, when dried over sulphuric acid, has approximately the composition $H_2SiO_3$, that is, $SiO_2.H_2O$, or $SiO(OH)_2$, and it has been called **metasilicic acid.** According to V. C. Butzureanu, an acid of the same composition is obtained by treating gelatinous silicic acid with absolute alcohol. W. K. Sullivan made this hydrate by exposing hard, semi-translucent silica to dry air for some months; and J. J. Ebelmen made it as a glass-like mass by exposing silicic ether to moist air. D. Hayes obtained a crystalline mass, approximating $SiO_2.6H_2O$, in the evaporation of sugar soln.; but C. Doelter observed no signs of crystallization after shaking the hydrogel for many months. T. H. Norton and D. M. Roth obtained a hydrate approximating to the composition of **orthosilicic acid,** $H_4SiO_4$, that is, $SiO_2.2H_2O$, or $Si(OH)_4$, by washing gelatinous silicic acid successively with dried ether and benzene, and by squeezing the product between folds of filter-paper. The product loses water when exposed to air, and also in contact with absolute alcohol, or some other absorbent medium. H. Hager claimed to have prepared microscopic crystals of the hydrate $SiO_2.3H_2O$, or $SiO_2.4H_2O$, by the action of conc. hydrochloric acid on a siliceous limestone. C. Struckmann also reported the formation of crystalline needles of a hydrated silica. These results have not been confirmed; the nearest approach which F. Cornu could make was to produce "regularly oriented cracks" when gelatinous silica, derived from many zeolites, contracted on drying. E. Grimaux assumed that the hydrosol was orthosilicic acid which when gelatinized passed into a more complex mol. Nothing is known which precludes the existence of definite crystalline forms of silicic acid, although their existence has not been established by unimpeachable evidence. Like sulphurous and carbonic acids, if the silicic acids are formed, they probably dissociate so readily into water and silica that, as emphasized by V. Lenher and others, there is no satisfactory evidence for assuming the existence of definite hydrates. In any case, it is almost certain that in the hydrogel, the water is not chemically combined with the silica, and the so-called silicic acids are to be regarded as adsorption products. Be this as it may,

a large number of compounds of silica with bases—**silicates**—are known—a large number occur in nature as distinct mineral species, and many others have been prepared artificially. These salts can be referred to unknown silicic acids, derived by condensation and dehydration from orthosilicic acid, and called by A. Wurtz [6] *les acides polysiliques*.

Many of these silicates are salts of orthosilicic acid. E. Martin has assumed that in the normal *silicon hydroxide*, $Si(OH)_4$, two of the hydroxyl groups are basic, and two are acidic at low temp., while at higher temp. all are acidic. Combination between molecules of silica may occur through oxygen, but never directly. With these hypotheses, E. Martin has explained the behaviour of silicic acid, prepared in different ways, towards acids, water, and alkalies. He claimed that there is a tendency to form groups of $5SiO_2$. When calcium silicate, made by heating at 1200°, a mixture of calcium carbonate and silica (2 : 1), is dissolved in acetic acid, and the lime removed by ammonium oxalate, there remains a soln. of *silicic acetate*. This slowly hydrolyzes, forming a hydrated silica, $5SiO_2.4H_2O$, if dried in a desiccator, or $5SiO_2.2HO_2$, if dried at 100°. Hydrated silica prepared by treating calcium silicate with hydrochloric acid, has the composition $5SiO_2.2H_2O$, if dried in a desiccator, and $5SiO_2.H_2O$ if dried at 100°. He also reported $10SiO_2.5H_2O$, or $(H_2Si_2O_5)_5$, and $5SiO_2.5H_2O$, or $(H_2SiO_3)_5$. R. Schwarz and E. Menner [7] have dehydrated silicic acid by means of acetone and shown that **metasilicic acid,** $H_2SiO_3$, is stable below 15°. Silicic acid made by the action of 80 per cent. sulphuric acid on sodium rhetasilicate at 10°, shows definite breaks in the drying curve at 20°, corresponding with **mesodisilicic acid,** $H_2Si_2O_5$, and **mesotrisilicic acid,** $H_4Si_3O_8$; the former is indicated below under the name datolitic acid, and the latter as garnatic acid. Mesotrisilicic acid is not stable above 32°. There were also indications of the possible existence of two hydrates, $12SiO_2.10H_2O$, or **mesohexasilicic acid,** $H_{10}Si_6O_{17}$, and $12SiO_2.9H_2O$, or **mesotetrasilicic acid,** $H_6Si_4O_{11}$. For the nomenclature, *vide infra*, Table X.

F. Rinne found that the silicic acid obtained by treating zeolites with acids has a definite structure, and is doubly refracting; while E. Jordis showed that the silicic acids derived from the different alkaline earth silicates have different tendencies to pass into the sol condition. According to G. Tschermak, different silicic acids—**G. Tschermak's silicic acids**—are obtained by treating certain natural silicates with hydrochloric acid, and these acids may be regarded as the fundamental acid of the particular silicate in question. G. Tschermak prepared these acids by treating the powdered silicate with hydrochloric acid at about 60°; washing the liberated silica hydrates; and allowing the product to dry slowly in air. The slope of the curve, showing the relation between the loss of weight and time, changed abruptly at a certain temp. which G. Tschermak supposed represented a transition from the evaporation of adsorbed water to dehydration by the loss of chemically combined water. G. Tschermak further supposed that at the transition temp. the composition of the hydrated silica corresponded with that of the mineral regarded as a salt of the acid. The supposed acids were further distinguished by their behaviour towards methylene blue—*A. Suida's reaction*—for those acids richest in water were found to be coloured more intensely than acids with less water. V. Iskyul studied the solubility of silica in many minerals. According to G. Tschermak:

(1) *Orthosilicic acid*, $H_4SiO_4$, is obtained by the decomposition of silicon tetrachloride by water, and by the action of hydrochloric acid on orthosilicates—natrolite, diplase, scolezite, willemite, monticellite, calamine. Its sp. gr. at 17° is 1·576, and it is coloured bluish-black by methylene blue. (2) *Metasilicic acid*, $H_2SiO_3$, is obtained by the action of hydrochloric acid on anorthite, olivine, or lievrite. Its sp. gr. is 1·813, and it is coloured prussian-blue by methylene blue. (3) *Datolitic acid*, $H_8Si_4O_5$, is obtained from datolite, gadolinite, euclase, and homilite (*vide supra*). It has a sp. gr. of 2·197 and forms a light prussian-blue tint with methylene blue. (4) *Leucitic acid*, $H_4Si_2O_6$, is a polymer of metasilicic acid obtained from leucite. Its sp. gr. is 1·834, and it is coloured pale prussian-blue by methylene blue. (5) *Serpentinic acid*, $H_2Si_2O_{12}$, a polymer of leucitic acid, is

obtained from serpentine, bowenite, or antigorite. Its sp. gr. is 1·809, and it forms a light prussian-blue tint with methylene blue. It does not gelatinize like metasilicic acid. (6) *Garnitic acid*, $H_4Si_3O_8$, derived from grossular, epidote, zoisite, or prenitè (*vide supra*). It has a sp. gr. 1·910, and it is stained pale or light blue by methylene blue. (7) *Albitic acid*, $H_2Si_3O_7$, is obtained from albite. It has a sp. gr. 2·043, and it is not coloured by methylene blue. (8) *Pectolitic acid*, $H_2Si_3O_9$, is derived from pectolite or wollastonite. It is not stable when isolated. Its sp. gr. is 1·810–1·816. It forms a deep prussian-blue tint with methylene blue. (9) *Sepiolitic acid*, $H_8Si_3O_9$, is obtained from meerschaum. Its sp. gr. is 1·763, and it forms a prussian-blue tint with methylene blue. (10) *Chrysotylic acid*, $H_{10}Si_4O_{13}$, is derived from chrysotyle or serpentine asbestos. Its sp. gr. is 1·725 (17°), and it forms a prussian-blue tint with methylene blue. (11) *Harmotomic acid*, $H_8Si_5O_{14}$, is derived from harmotome, and it forms a pale blue with methylene blue. (12) *Heulanditic acid*, $H_{10}Si_6O_{17}$, is derived from heulandite, and it forms a pale prussian-blue with methylene blue.

J. M. van Bemmelen doubted if these silicic acids are chemical individuals; and H. le Chatelier said that no change in the appearance or consistency of gelatinous silicic acid could be detected after heating 6 hrs. at 320°; and he concluded that silica, like chromic trioxide, does not form hydrates, but on account of its insolubility remains in an extremely fine state of subdivision when precipitated. According to E. Jordis, the work of J. M. van Bemmelen on the vap. press. of the gels of silica shows that the amount of water in a gel is proportional to the partial press. of the water in the surrounding atm. O. Mügge has shown that the differences in the rates of drying observed by G. Tschermak depend on the temp.; and the observed changes cannot be supposed to differentiate between absorbed water and chemically combined water, and they give no basis for the deduction of the formulæ arbitrarily assigned by G. Tschermak. As J. M. van Bemmelen has shown, silica hydrogels are colloidal absorption compounds of indefinite composition, and changes in the rate of dehydration, and the effects on methylene blue are probably due to changes in the mechanical structure of the hydrogel brought about by the gradual removal of water. J. Splichal found that the character of the silicic acid depended on the nature and conc. of the acid employed for decomposing the silicate. P. Pascal found that the silicic acids behave magnetically like mixtures of the anhydrous oxide and water, and lend no support to the assumption that definite silicic acids exist. J. S. Anderson obtained no evidence of the formation of definite hydrates in his study of the adsorption and evolution of liquids from silica gels. H. N. Holmes studied the formation of gel silicic acids. Consequently, the real existence of G. Tschermak's acids has not been satisfactorily established, but the idea may have some uses in developing a system of classification of the silicates.

F. Mylius and E. Groschuff [8] have shown that if, at 0°, the eq. of two mols of hydrochloric acid be added to a soln. containing one mol of sodium silicate, $Na_2Si_2O_5$, with the eq. of 2 grms. of silica per 100 c.c., the resulting **α-silicic acid** does not precipitate albumen from a soln. containing the white of an egg; but on standing some time, or on warming, the α-silicic acid acquires the property of precipitating albumen. It is therefore considered that α-silicic acid passes into **β-silicic acid**. The β-acid is also precipitated by methylene blue and by sodium hydroxide. The electrical conductivity and the lowering of the f.p. change in the passage of α-silica to the β-acid. The α-acid gives results which correspond with a mol. wt. of 155; the β-acid with a mol. wt. approaching 49,000. Consequently, the transformation is considered to be due to a polymerization of the α-acid. T. Graham concluded that *the molecular weight of colloidal silica* must be very great because its acidity is neutralized by such small proportions of alkali, and A. Sabanejeff concluded from the lowering of the f.p. that the mol. wt. of silicic acid must exceed 30,000. The attempt to determine the mol. wt. of colloidal suspensions by osmotic press. phenomena is quite illogical because the whole argument on which the methods are based, is alone applicable to homogeneous soln. and not to homogeneous suspensions. R. Schwarz and O. Liede conclude from the behaviour of silica gel when slowly dried at ordinary temp., that the ageing process consists in the condensation of $(SiO_2)_x$ to $(SiO_2)_{2x}$, and that this occurs

without any change in the appearance of the gel; further changes in the system $SiO_2$-$H_2O$ then occur, leading to the formation of $(SiO_2)_{3x}$, which is indicated by the incipient formation of cloudy particles in the colourless, transparent mass. Precisely similar phenomena are observed when the gel is dehydrated by being heated, but, for some unexplained reason, a much greater loss of water appears to be necessary in this case before the end-point is reached. A. Schwarz and O. Liede obtained $\beta$-silicic acid by passing silicon tetrafluoride into boiling water. The product dissolved less readily in hydrofluoric acid, sodium hydroxide soln., or aq. ammonia than the ordinary $\alpha$-silicic acid. From the conductivity of the ammoniacal soln., they regarded it as a polymerized form analogous to $\beta$-stannic acid.

T. Graham [9] said that the hydrosol is coagulated on standing, and this the more quickly, the more conc. the sol, or the higher the temp. This was confirmed by W. Flemming. T. Graham found that a 12 per cent. sol at ordinary temp. was coagulated in a few hours, while 5–6 per cent. sol required 5–6 days, a 2 per cent. sol required 2–3 months, and a 1 per cent. sol required 2 or more years. According to O. Maschke, the coagulation of the sol in glass vessels is largely determined by the dissolution of alkalies, etc., from the walls of the containing vessels. According to E. Jordis and co-workers, T. Graham's observation that the longer the silicic acid is hydrolyzed the more stable the product, is explained by the increase in the amount of alkali derived from the glass. The contradictory reports are in some cases due to the presence of unsuspected impurities. E. Jordis and co-workers concluded that T. Graham's hydrosol is contaminated by acids or bases, and E. Grimaux's hydrosol is contaminated with organic matter. When the sol is dried over sulphuric acid in vacuo, T. Graham found that the insoluble residue contained 21·99 per cent. of water; and C. Roberts, 24 per cent. of water. W. Kühne found that T. Graham's hydrosol is not coagulated by alcohol, glycerol, sugar, gum, or caramel; alumina hydrosol, ferric oxide hydrosol, gelatine, albumen, and casein were found by T. Graham to coagulate silica hydrosol. W. Kühne, and B. Kempe found that silica hydrosol is not gelatinized by salts with an alkaline reaction, by alcohol, ammonia, sugar, albuminose, glycerol, peptone, and alkali albuminates, but it is gelatinized by glue, and by neutral salts. F. Dienert and F. Wandenbulcke discussed the effect of dissolved salts on the colloidal silica in natural waters, and sea-water.

According to L. F. Werner, acids have a very powerful peptizing effect upon the hydrosol of silicic acid. In the case of the strong acids, this effect is most marked at a medium conc. Alkalies also have a strong peptizing influence; the effect is greatest for medium and low conc. for the highly ionized bases, and in the case of the slightly ionized bases the effect is great in all but the lowest conc. tried. Salts have no effect in presence of acids, but in the presence of bases the congealing effect is hastened. Potassium salts of several negative radicles decreased the time required for gelation. The chlorides of various metals, with the exception of ferric and cupric chlorides, decreased the time of gelation. Sodium hydrophosphate and dihydrophosphate have strong congealing powers, but normal sodium orthophosphate has the opposite effect. The di- and tri-sodium citrates accelerate the setting greatly, the effect decreasing with the conc.; but, in the case of the monosodium salt, the time for setting is the same for all conc. The acetates of the various metals have the greatest congealing effect (excepting that of mercury). Inorganic salts produce but little effect. The alkali salts of the organic acids produce powerful accelerating effects, except the carbonates and hydrocarbonates, which have a peptizing effect in soln. of medium to low conc. F. Diénert and F. Wandenbulcke found that alkali carbonates accelerate the flocculation of colloidal silica, and salts with an acidic reaction like aluminium sulphate hinder the change. J. Amar found the velocity of coagulation to be proportional to the lowering of the surface tension by the coagulant.

According to W. Flemming, silica hydrosol is coagulated by graphite powder, and by alkali and alkaline earth carbonates; hydrogen and hydroxyl ions have a

catalytic effect on the rate of coagulation, for as the conc. of hydrogen ions increases, the coagulation is first retarded and then accelerated; as the conc. of hydroxyl ions increases, the coagulation is first accelerated and then retarded. As shown by T. Graham, silicic acid is readily peptized by sodium hydroxide and ammonia, but it adsorbs lime from suspended calcium carbonate; is precipitated by calcium hydroxide, and basic dyes; and is coagulated by soln. of carbonates of the alkalies or alkaline earths. T. Graham said that his sol was coagulated by carbon dioxide, while H. Kühn said that this agent does not coagulate the silica sol derived from silicates; nor was E. Grimaux's hydrosol coagulated by carbon dioxide. The reaction has also been studied by W. Flemming, E. Jordis, etc. H. Kühn found that the sol is coagulated by the electric current or by freezing, and by alcohol, or sulphuric acid. A. Löttermoser, and N. N. Ljubavin also found the hydrosol precipitates most of the contained silicic acid when frozen. F. Hoppe-Seyler showed that the sol is coagulated by schizomycetes fungi. N. Pappadá and C. Sadowsky found that the speeds of coagulation and gelatinization of silica hydrosols follow the same laws. The coagulation of silicic acid sol was studied by O. M. Smith, etc. According to N. Pappadá, soln. of non-ionized organic substances do not coagulate silica sol, but soln. of ionized salts coagulate negative colloidal silicic acid, and, with a given family of salts, the action is all the more marked the greater the at. wt. of the salt—*e.g.* the cations $Cs^{\cdot}$, $Rb^{\cdot}$, $K^{\cdot}$, $NH_4^{\cdot}$, $Na^{\cdot}$, and $Li^{\cdot}$ act with decreasing intensity in the order named; similarly, the action is more marked the greater the electrical charge on the ion, thus tervalent ions are more active than bivalent ions, and these in turn more than univalent ions. Thus, W. B. Hardy found aluminium sulphate acted immediately; copper sulphate or copper, cadmium, or barium chloride acted in 10 mins.; magnesium sulphate in 2 hrs.; and potassium or sodium sulphate in 24 hrs. The gelatinization seems to be independent of the nature of the anion. S. Glixelli found the acidity of silica is increased in the presence of uni- or bi-valent ions of neutral salts. The protective action of tervalent iron salts on a sol of silicic acid was investigated by E. Guerry and E. Toussaint. H. W. Foote, S. R. Scholes, and R. W. Langley have discussed the precipitation of ferric and aluminium hydroxides along with colloidal silica so as to form solid soln. P. Rohland found that silica hydrogel derived from clay adsorbs colloids—*e.g.* soap, starch, and dextrin—complex dyes—*e.g.* aurin, fluorescein, and cochineal—carbonate-ions, hydrocarbonate-ions, tetraborate-ions, and phosphate-ions. Organic substances containing oxygen—*e.g.* alcohol and acetone—are adsorbed. Silica gel is impermeable to organic substances which do not contain oxygen, and sat. hydrocarbons—*e.g.* toluene, and carbon disulphide. E. Dittler, and H. Rheinboldt and E. Wedekind studied the adsorption of organic colouring matters by hydrogels of silica; L. Berényi, and J. McGavack and W. A. Patrick, the adsorption of sulphur dioxide; L. Berényi, L. Y. Davidheiser and W. A. Patrick, ammonia; W. A. Patrick, sulphur dioxide, ammonia, and carbon dioxide; H. Briggs, hydrogen and nitrogen at low temp.; P. C. Ray, nitrogen peroxide; and A. B. Ray, and H. Briggs, organic vapours; W. A. Patrick and D. C. Jones, formic, acetic, butyric, and benzoic acids, and iodine, from various solvents; nitrobenzene and benzene from kerosene; and acetic acid from carbon disulphide; D. C. Jones, acetic acid from gasoline; W. A. Patrick and J. S. Long, butane. N. K. Chaney and co-workers showed that while carbon adsorbs benzene and rejects the water from a mixture of benzene and water, silica gel adsorbs water and rejects the benzene. C. M. Faber and co-workers measured the variation in the efficiency in the adsorption of water, benzene, nitric acid, and nitrogen peroxide with use. There is a promising field of application for silica gel as an absorbent for condensable vapours from gases; and as a refining agent for liquids, particularly petroleum oils. It also has uses in the recovery of benzene hydrocarbons from coal gas, or coke-oven gases for use as a motor oil. The adsorption of benzene and other vapours has been discussed by E. C. Williams, R. Furness, E. B. Miller, F. Meyer, and N. K. Chaney; and of sodium fluosilicate, and potas-

sium metasilicate, by M. A. Rakuzin. According to E. M. Faber and H. G. Olsen, carbonyl chloride and nitrogen peroxide are absorbed by silica gel. According to J. N. Mukherjee, precipitated silica adsorbs acetic, citric, hydrochloric, and nitric acids, but A. F. Joseph and J. S. Hancock stated that purified silica has no effect on a soln. of an acid, and that the reported effects are due to the use of inadequately purified silica; the effect of silica on a soln. of an electrolyte is to produce free acid and a complex silicate of low solubility and alkaline reaction. W. Bachmann showed that the amount of adsorption of water, benzene, chloroform, ethyl iodide, and acetylene tetrabromide by silica gel is proportional to the density of the liquid; W. A. Patrick and J. S. Long found that the adsorption of *n*-butane is greatest with silica gel with about 2 per cent. of water; and J. McGavick and W. A. Patrick found 7 per cent. of water to be most favourable for the adsorption of sulphur dioxide between −80° and 100°. D. C. Jones studied the effect of the dispersibility of the silica gel on its adsorptive power. J. H. Frydlender, F. Meyer, W. Paulsen, E. B. Miller, R. Furness, N. K. Chaney, and E. C. Williams discussed the use of silica gel as an absorbent for industrial purposes. Their uses, said H. N. Holmes and J. A. Anderson, include solvent recovery, the drying of air for blast furnaces, and for vacuum ice machines; the recovery of sulphur dioxide and nitrogen oxides; removing offensive odours from air; removing sulphur compounds from petroleum fractions; decolorizing certain liquids; the recovery of gasoline from natural gas, etc.

E. Jordis and E. H. Kanter [10] inferred that because the electrical conductivity of silica hydrosol increases to a maximum by the successive additions of small quantities of hydrochloric acid, then falls to a minimum, and again increases, hydrochloric acid and silica unite chemically. F. Mylius and E. Groschuff likewise assumed the formation of an intermediate chloride in the hydrolysis of silicon tetrachloride by water. J. Meyer, however, believes that the obstinate retention of hydrochloric acid by silica gel is an adsorption phenomenon, not chemical combination. The washing has also been discussed by E. Jordis, R. Zsigmondy and R. Heyer, etc. According to J. M. van Bemmelen, the amount of a substance which is absorbed from a soln. by a given quantity of a silica gel (dried at 100°) depends on the temp. and conc. of the soln., as well as on the nature, physical state, and previous history of the absorbent gel. The amount absorbed increases with the conc. of the soln., but not proportionally since relatively more is absorbed from dil. soln. than from conc. soln., so that the ratio of the amount of salt absorbed to the conc. of the soln. decreases as the conc. increases. Alkalies are strongly adsorbed, and soln. of salts of the feeble acids are decomposed and part of their alkaline base is selectively absorbed by the silica—*e.g.* alkali carbonates, phosphates, borates, and calcium carbonate. Absorption thus appears as a kind of incipient combination. When the absorption has progressed far enough, the silica gel may pass into the sol condition, as was observed by T. Graham in an experiment where one part of sodium hydroxide in 10,000 parts of water at 100°, converted 200 parts of anhydrous silica into the sol state. The absorption or adsorption with quartz is much less than with amorphous silica, but it follows the same general law—*vide* the chemical properties of silica. R. Schwarz and H. Stock found silicic acid sols act as a positive catalyst on the photochemical decomposition of silver bromide; and E. O. Holmes and W. A. Patrick, on acetone, acetic acid, and nitric acid.

J. S. Anderson [11] found the sp. gr. of silica gel sat. with water to be 1·500; of the dried gel, 1·980; and of the gel substance, 2·048. E. Berl and W. Urban found the sp. gr. of silica gel dried at 25°, is 2·465; dried at 300°, 2·390; dried at 1000°, 2·271; evaporated with hydrochloric acid and ignited, 2·627. The sp. gr. of the opals ranges from 1·9 to 2·5—the gem opals have a sp. gr. 2·1–2·2. The sp. gr. of hydrated silica which has been dried lies between 1·7 and 1·9. According to F. Auerbach, the hardness of opal lies between 5 and 6. An opal from Mexico had a coeff. of elasticity of 3,880,000; and a torsion coeff. of 1,829,000. In their study of the musical tones produced by vibrating silicic acid gels, H. N. Holmes

and co-workers found that these gels vibrate as rigid solids. The vibration frequency varies inversely as the diameter of the column of gel, and tension exerts an influence; the vibration frequency varies directly as the conc. of the silicic acid, increases with an excess of mineral acids, and decreases with an excess of organic acids. According to H. Kopp, and J. Joly, the sp. ht. of hyalite is 0·2033, and of opal 0·2375.

The separation of aq. soln. from highly hydrated gels—the so-called *syneresis*—increases with increased conc. of silicic acid, increases with excess of mineral acids, and decreases with excess of organic acids. Neither J. Thomsen nor G. Bruni and N. Pappada could detect any thermal change during the coagulation of silicic acid sols, but others have noted an appreciable thermal effect. T. Graham, for instance, noted a rise of temp. during the coagulation of the hydrosol of silica. The heats developed during the coagulation of a 3 per cent. soln. of silicic acid prepared from potash water-glass and a 2·4 per cent. soln. of silicic acid from soda water-glass, are:

| | Sol with 3 per cent. silicic acid from potash water-glass. | | Sol with 2·4 per cent. silicic acid from soda water-glass. | | |
|---|---|---|---|---|---|
| Per cent. aluminium sulphate soln. | 3·4 | 6·8 | 1·7 | 6·8 | 13·6 |
| Heat of coagulation | 15·8 | 27·1 | 17·9 | 30·7 | 32·8 Cals. |

Observations on this subject have been made by F. Dörinckel, E. Wiedemann and C. Ludeking, O. Mulert, L. Kahlenberg and A. T. Lincoln, etc. Similar results were obtained by coagulating the sol with a 6·8 per cent. soln. of alkali sulphate. J. Spichal found that the hydrosols of alumina and silica mutually precipitate one another, and the precipitation is most rapid, and the viscosity greatest, when the molar ratio $Al_2O_3 : SiO_2$ is as 1 : 3. M. Kröger found that the gelatinization of a mixture of silica and tungstic hydrosols proceeds so that the time-tungstic acid curve passes first through a minimum, then as the conc. of the tungstic acid increases, it passes through a maximum and then falls continuously. A. W. Thomas and L. Johnson discussed the mutual precipitation of colloidal soln. of ferric oxide and silica.

The process of gel-formation in silicic acid and the gelatines has been studied ultra-microscopically by W. Bachmann. The amplitude of the Brownian movements of the ultra-microscopic particles diminishes and the size of the particles increases by flocculation during the ageing of the gel; the structure gradually becomes less distinct, and at last ultra-microscopically homogeneous owing to the close-packing of the jelly elements. The supposed foam structure is a diffraction phenomenon. Gel silicic acid obtained by dialysis, with a collodion membrane, and dried over sulphuric acid, polarizes light feebly, thus indicating a very minute heterogeneity. The index of refraction of the opals is low. According to A. des Cloizeaux,[12] the index of refraction for red light varies from about 1·442–1·450; and, according to A. K. Zimanyi, for the yellow sodium light, from 1·4536–1·4580 between 21° and 28·5°. A hydrosol from soda water-glass with 0·4134 grm. of silica per 31·3630 grms. of soln., has a sp. gr. of 1·004923 at 241° (water at 24·1°=0·99730), and an index of refraction for sodium light, 1·33389; and for the $H_\alpha$-line, 1·33205; the $H_\beta$-line, 1·33800; and the $H_\gamma$-line, 1·34139 (water for $H_\alpha$=1·33080). Observations were made by C. Abbati, F. Cornu, M. Lazarevec, etc. According to W. W. Coblentz,[13] quartz has small absorption bands between 2·9$\mu$ and 6·65$\mu$, and the group of atoms characteristic of quartz maintains its characteristics, more or less sharply defined, in the mineral silicates. In opal, the bands characteristic of water are superposed upon those for quartz, and since opal shows no signs of crystallization it is inferred that the water is in a state of solid soln., since the contained water is a function of the vap. press. The absorption spectra of opal, selenite, and the zeolites are alike as regards the position and intensity of the water bands. C. Wissinger studied the absorption spectrum of silica hydrogel. Opal is a non-conductor of electricity. The hydrosol of silica conducts electricity. F. Mylius and E. Groschuff[14] found the conductivity in

presence of sodium chloride changed from $14032\times10^{-6}$ mhos when freshly prepared to $14081\times10^{-6}$ mhos after standing 6 days at a temp. of 16°. Silica hydrosol resulting from the action of 40 grms. of silicon tetrachloride on 2 litres of water had a conductivity of $6{\cdot}2\times10^{-6}$ mhos; after 14 days' hydrolysis the conductivity altered to $3{\cdot}2\times10^{-5}$; and after 22 days' hydrolysis, $1{\cdot}7\times10^{-5}$ mhos.

A. C. Becquerel,[15] and W. Spring found that an alkaline soln. of silica hydrogel acquires a positive charge, and when an electric current is passed through the soln., the gel collects on the cathode. W. B. Hardy, however, showed that with distilled water, the thoroughly washed hydrogel is iso-electric, and with the smallest trace of free alkali in the water, it becomes electronegative. S. E. Linder and H. Picton, N. Pappadá, and A. Löttermoser also found that dialyzed silicic acid collects on the anode. W. Biltz, and W. R. Whitney and J. C. Blake made observations on this subject. O. Lösenbeck measured the electrical conductivity of silica sols. He found the conductivity of hydrochloric acid soln. of conc. up to $\frac{1}{100}N$-HCl is reduced by the presence of silicic acid soln. The magnitude of the change decreases with time, being at first rapid, and then slows off to a limiting value. The particles of silicic acid are negatively charged, and the charge is steadily reduced by the addition of hydrochloric acid until the isoelectric point is reached. With further addition of acid the sign of the charge changes, and the charge increases until the positive value is greater than the original negative value. The contact potential of the particles in different conc. of the same preparation is dependent on the conc. of the sol, in the sense that the isoelectric point of different sols lies at greater conc. of hydrochloric acid the greater the conc. of the sol. The observed results are explained by assuming that the silicic acid particles are sat. with hydrochloric acid, like a sponge, and that this acid is taken up slowly. The hydrogen-ions are expelled from these sponges with a definite tension, so that the contact potential between particle and soln. may be approximately represented by W. Nernst's formula. W. Grundmann studied the electrical properties of sols of silicic acid, and showed that the charge in a hydrochloric acid soln. changes on keeping, becoming at first more negative, reaches a maximum, and then changes in the opposite direction. Colloidal silica in dil. acid and alkaline soln. is electronegative, and during electrolysis accumulates about the anode, and J. Billitzer showed that in alkaline and feebly acid soln.—say, up to 0·1$N$-HCl—the gel is electronegative; with a greater conc. of acid—say, $\frac{1}{2}N$-HCl—the gel is electropositive; and somewhere between these limits an isoelectric point occurs where the liquid is electrically neutral.

These facts have been applied industrially by B. Schwerin to remove impurities from clays, etc. When soln. of chlorides are added to water with the clay in suspension, certain impurities settle readily, others remain in suspension. If the added salt also changes the electrical state of certain impurities so that, say, free silica becomes electropositive while the clay remains electronegative, the passage of a current through the soln. will enable the electronegative clay to collect about the anode, while the electropositive impurity accumulates about the cathode. W. R. Ormandy has discussed the application of the process.

The great variations in the proportion of water in different varieties of opal, and in the same varieties from different localities, prevents the application of a definite formula—$SiO_2.nH_2O$. Thus, E. Frémy [16] found that after drying in vacuo, hyalite opal contained 1·5 per cent. of water; a gem-opal from Mexico, 6·3 per cent.; and a sample of opaque and glassy geyserite, 12·1 per cent. Attempts to find if the dehydration curves of the opals show any signs of breaks or singularities, have given negative results. It is therefore inferred that *opals are not definite hydrates of silica.* In 1877, J. B. Hannay gradually heated a sample of opal with 8·24 per cent. of water at 100° in a current of dry air, and determined the water lost every 5 mins. and later every 20 mins. G. d'Achiardi confined seven different samples of Tuscany opal in desiccators, and found the loss of weight after definite intervals of time extending over 200 days. The results with a sample of kieselguhr

from Castel del Piano, Monte Amiata; a sample of black opal from San Piero, Campo; a milk-white opal from Fundorte; and a water-clear opal from San Piero, Campo, are plotted in Fig. 52; there is here no evidence of any discontinuity in the curves. G. d'Achiardi also obtained the same conclusion by measuring the amount of water lost during definite intervals of temp. rising from 80° to 320°. G. Tammann kept samples of hyalite and opal in desiccators over sulphuric acid of different conc. so as to allow the dehydration to occur in atm. of definite humidity, Table IX.

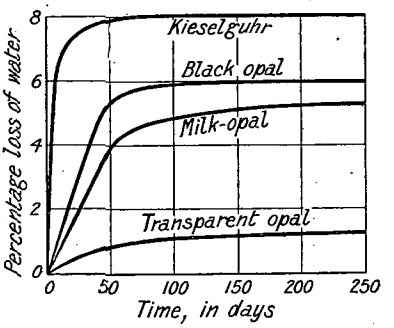



FIG. 52.—The Dehydration Curves of Some Varieties of Opal Confined over Sulphuric Acid.

According to J. M. van Bemmelen,[17] the gel of silica hydrate under the microscope appears to have a cellular structure and to be composed of a kind of network—*Wabenstruktur*—formed by two soln.—the *one more conc. forms the walls of a mass* of cells which enclose the other more dil. soln. O. Bütschli also noticed that a mesh-like structure appears at a certain stage in the drying of gelatinous silica, and dis-

TABLE IX.—LOSS OF WATER BY OPALS IN ATMOSPHERES OF DIFFERENT HUMIDITY.

| Conc. of sulphuric acid per cent. | Vap. press. of sulphuric acid in mm. at 25°. | Time in days. | Percentage loss in weight. |
|---|---|---|---|
| 20·3 | 21·24 | 6 | 2·96 |
| 29·2 | 18·33 | 9 | 3·90 |
| 40·6 | 13·15 | 7 | 9·95 |
| 50·1 | 8·77 | 6 | 10·75 |
| 60·4 | 4·32 | 6 | 11·60 |
| 70·3 | 1·74 | 8 | 12·09 |
| 85·1 | 0·18 | 22 | 13·30 |

appears at a later stage of the drying. He also found that the natural opals exhibit a very fine cellular structure which requires the very greatest magnification to be rendered visible—hydrophane, for example, with a magnification of 2090 diams., shows the cellular structure and is very little different from gelatinous silica. The two are illustrated side by side in Fig. 53. W. Biltz and W. Geibel studied the ultra-microscopic structure of silica hydrogel. According to O. Bütschli, a gel with 30–40 mols. of water can be separated by cutting; with 20 mols. it is somewhat stiff; with 12 mols. it is brittle; and with 6 mols. it can be triturated to form a dry powder. There is a stage in the dehydration where the gelatinous silica begins to lose its transparency and become turbid. This temp. depends on the nature of the gel, its mode of preparation, the rate of dehydration, the age of the specimen, etc. The vol. of the gel shrinks very little if dehydrated further, since the gel now forms empty spaces which gradually fill with air, and produce the turbidity; or, as R. Zsigmondy infers from his ultra-microscopic examination of the phenomenon, the turbidity is produced by the accumulation of liquid separated by films of air. By prolonged

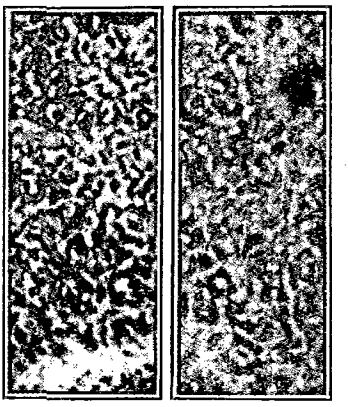


FIG. 53.—The Cellular Structure of Opal (left) and of Partially Dried Gelatinous Silica (right).

heating, the gel gradually loses its air-spaces, and at the same time its absorptive power for water, *e.g.* the amounts of moisture adsorbed by precipitated silica calcined at different temp. are:

| | 110° | 600° | 700° | 800° | 900° | 1200° |
|---|---|---|---|---|---|---|
| Adsorption . . | 18·35 | 15·93 | 15·34 | 12·85 | 3·96 | 0·00 per cent. |

J. Duclaux assumed that reversible gels contain (i) a liquid—water or a solvent; (ii) an insoluble solid, forming with the liquid an irreversible gel or sponge-like structure of ultra-microscopic cells; and (iii) a soluble solid dissolved in the solvent of the gel. The mols. or miscellæ of this substance, which may be either crystalloid or colloid, are too large to be able to escape from the cellules of the sponge, but they are small enough for their soln. to have a certain osmotic press. in relation to the pure solvent. This soln. is the "plasm" of the gel, and its swelling and expansion in a solvent are due to the osmotic press. of the plasm. The limit of expansion is reached when equilibrium is attained between this osmotic press. and the cohesion of the cellular structure of the gel. If the osmotic forces are strong enough, continued inflation of the cellules may result in the dissolution of the gel, and the separation of the soluble and insoluble constituents.

P. P. von Weimarn [18] argued that many of the so-called amorphous powders probably have a crystalline structure, for they may really be so fine-grained that, under the microscope, the form of the crystalline grain appears to be rounded owing to diffraction and other phenomena. The crystalline nature of such precipitates must be proved in other ways since the fineness of the grain prevents the satisfactory application of the microscope. Under the microscope, these precipitates exhibit various characteristics peculiar to crystalline structures—*e.g.* they have a network, honeycomb, rayed, or dendritic structure unless they are formed of detached granules. Hence, says P. P. von Weimarn, such formations are to be regarded as a result of an orientation of the finest granules. R. Schwarz and F. Stöwener studied the *ageing of silica gels*, and showed that during the ageing water is lost even though the gel be under water; the dehydration is regarded as a preliminary stage in the formation of crystals.

The vap. press. of hydrated silica varies continuously and regularly with the conc. of the contained water, so that the solid silica and the water really form a univariant system with only one component—water—and two phases—vap., and water of hydration. If the water vap. be in equilibrium with the water of hydration at a vap. press. $p$, and some water is removed, the solid loses some water of hydration, but the vap. press. is not restored to $p$ since it acquires a lower value $p_1$. If a definite hydrate were in question, the vap. press. would remain at $p$ until all the hydrate had been decomposed.

Partially dehydrated silica hydrate is very hygroscopic. The silica remaining when the organic derivatives of silicon have been submitted to combustion analyses are sometimes very hygroscopic, thus, J. A. Meads and F. S. Kipping report [19] that the product from diphenylsilicanediol on exposure to air, had a constant weight only after the absorption of 16·2 per cent. of moisture. Silica hydrate which has been dried in air becomes warm when moistened with water. Silica obtained by calcining the hydrate at about 500°, can take up about 14 per cent. of water, and silica which has been calcined at a higher temp. can take up only 2 per cent. The water is more easily driven from the rehydrated silica heated to, say, 100° than from the original hydrate. If silica hydrate which has been heated to 200° be exposed to a moist atm., water is again absorbed, and the vap. press. of the hydrate is greater than that of the original hydrate of the same composition. This has been taken to show that the water is less firmly retained by the product of the rehydration of partially dehydrated silica hydrate.

J. M. van Bemmelen [20] has determined the equilibrium conditions of the hydrogel of silicic acid. He started with a freshly prepared sample containing the eq. of $SiO_2+100H_2O$; portions were placed in desiccators over sulphuric acid of different

conc., and accordingly also of different vap. press. Under these conditions, equilibrium occurs when the vap. press. of the gel is equal to the vap. press. of the sulphuric acid over which the gel is confined. The dehydration curve follows the direction of the arrows along *ABCD*, Fig. 54. While *AB* is a continuous curve representing

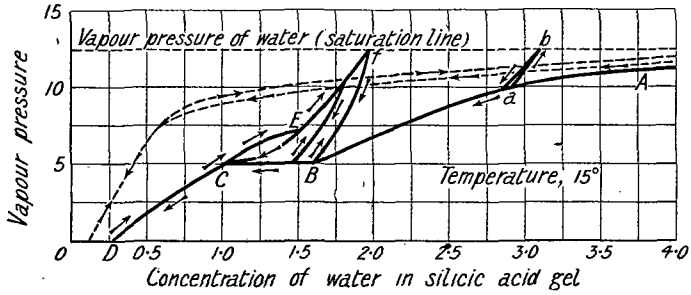



FIG. 54.—Curve of the Dehydration and Rehydration of the Hydrogel of Silicic Acid.

the equilibrium press. during dehydration, rehydration does not follow along the same path in the reverse direction, but rather strikes a shorter course, say, *ab*, to reach the saturation curve representing the vap. press. curve of water at 15°; subsequent dehydration follows nearly along the same path, *ba*, but a little to the left. Returning to the first dehydration curve *AB*, this passes to *BC*, which is nearly horizontal, showing that here the removal of water has very little influence on the vap. press. of the hydrate. As the gel, previously clear and transparent, loses water along *BC*, it begins to develop an opalescence in its interior, owing to the formation of small bubbles of air or water vap. where previously liquid water was present. The opalescence gradually spreads outwards until the whole mass appears yellow by transmitted, and blue by reflected light. As the dehydration continues, the gel at *C* becomes white, and, travelling along *CD*, it becomes opalescent, and finally as clear as glass. The *CD*-curve represents a reversible reaction in that rehydration *DC* and dehydration *CD* follow the same track. At *D*, the gel has about the eq. of $SiO_2+0.2H_2O$. If the gel between *B* and *C* is dehydrated, it takes a short cut to the saturation curve, for after travelling along *DC*, it will pass from *C* to *E* to *f*; on dehydration at *E*, the curve travels as indicated by the arrow so that the process is not reversible. Dehydration from any particular state is represented by arrows directed downwards and to the left, and rehydration by arrows directed upwards and to the right. The curves dotted in the diagram represent, in the same way, the dehydration and rehydration of the hydrogel of silicic acid ten months old. J. Amar measured the speed of dehydration; and J. S. Anderson, the adsorption and evolution of moisture by silica gels. The two curves do not coincide, but show a decided hysteresis in the sense that water is evolved at a lower press. than that at which it is adsorbed. Similar results were obtained with alcohol and benzene. J. S. Anderson also measured the rates of adsorption and evolution of these three substances. E. Berl and W. Urban measured the hygroscopicity of silica gels. W. A. Patrick and F. V. Grimm found the heats of wetting of silica gel in Cals. per gram of gel to be 19·22 for water; 22·23 for ethyl alcohol; 11·13 for benzene; 8·42 for carbon tetrachloride; and 17·54 for aniline.

The net result of the interesting work of J. M. van Bemmelen is to show that **the hydrogel of silicic acid is an unstable system of the general composition $SiO_2.nH_2O$, where the value of $n$ is determined by the physical conditions, and the previous history of the gel.** M. Guichard investigated the adsorption of water by silica gels in relation to time, temp., and age. Similar phenomena were observed with the hydrogels of magnesium, beryllium, aluminium, manganic, ferric, chromic, cupric, zirconium, and stannic hydroxides—with variations, of

course, in individual cases. According to R. Zsigmondy, the peculiar dehydration curves obtained by J. M. van Bemmelen are best explained by assuming that the vap. press. of the retained water is diminished by the presence of fine capillaries. If the capillary formula holds for pores down to $5\mu\mu$, the vap. press. would be depressed 6 mm. The difference between the curves for dehydration and subsequent rehydration are explained by assuming the liquid fails to wet the walls completely in the second case owing to the absorbed air. The irreversibility of the changes is due to the union of the amicronic particles to form larger particles —probably crystalline. J. S. Anderson, from his experiments on the evolution and adsorption of moisture by silica gels, inferred that the gel is made up of pores of varying sizes which are largest where the hysteresis on the drying curve begins, and smallest where it ceases. He measured the lowering of the vap. press. of water, alcohol, and benzene produced by the presence of fine capillaries in the gel, and hence calculated the radius, $\rho$, of the pores from $\log_e(p_0/p)=2\sigma D_v/D_l p_0 \rho$, where $\rho$ represents the radius of the pore; $\sigma$, the surface tension of the liquid at the temp. of the experiment; $D_l$, the sp. gr. of the liquid; $D_v$, the sp. gr. of the vap.; $p_0$, the vap. press. of the liquid in the atm.; and $p$, the vap. press. of the evaporating liquid. The results are in harmony with those of R. Zsigmondy. The last-named found that when silica gel is immersed in a hydrosol of silver or ferric hydroxide, etc., it acts as an ultra-filter; water penetrates into the gel, and a layer of colloid is formed on its surface. E. M. Faber and H. G. Olson studied the repeated activation of the gel. T. Graham found that sulphuric acid can displace the water and form **silica sulphatogel,** if the hydrogel be first placed in dil. sulphuric acid (1 : 3), the product transferred to a stronger acid, and finally to conc. sulphuric acid.

H. N. Holmes and J. A. Anderson [21] prepared mixed ferric oxide-silica gel by treating a soln. of sodium silicate with one of ferric chloride; and similar mixed gels were made with aluminium, chromium, calcium, copper, or nickel oxide in place of ferric oxide.

**Organogels of silicic acid.**—T. Graham [22] prepared sols and gels of silica with fluids other than water—*e.g.* hydrochloric, nitric, sulphuric, formic, acetic, and tartaric acids, sugar-syrup, glycerol, benzene, carbon disulphide, alcohol, ether, and fixed oils. These liquids can displace more or less water without gelatinizing the dissolved silica. If alcohol be added to a hydrosol, containing not more than one per cent. of silica, and the water be removed by drying in vacuo over a desiccating agent; or if mixture of alcohol and silica hydrosol be dialyzed in a jar of alcohol, the water and a soln. of silica alcohol remain; it is **silica alcosol.** The alcosol is gelatinized by a slight increase in conc.; the liquid gives no evidence of the presence of a silicic ether. The corresponding **silicic alcogel** is also made by placing silicic hydrogel with 8–10 per cent. of silica, $SiO_2$, in absolute alcohol, and changing the latter repeatedly until the water of the hydrogel is replaced by alcohol. The product contains 11·64 per cent. of alcohol. Silica alcogel passes into the hydrogel when placed in water, and compounds with other liquids—ether, benzene, carbon disulphide, etc.—miscible with alcohol—are obtained by placing the alcogel in the desired liquid. The ether of the **silica etherogel** can be replaced by fixed oils, by placing the gel in the required liquid. W. Kühne found that glycerol, like alcohol, displaces water from the hydrogel, forming **silica glycerogel.** S. P. Kramer studied the preparation of oil emulsions by the aid of silica gel. W. A. Patrick made silica gels impregnated with metallic oxides by mixing soln. of sodium silicate with a soln. of a metallic salt easily hydrolyzed—*e.g.* ferric chloride—after the gel had set, it was washed free from chlorides. B. S. Neuhausen and W. A. Patrick could not remove *all* the water from silicic acid gels by anhydrous alcohol, acetone, or benzene.

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## § 22. The Silicates and the Aluminosilicates

A good formula indicates the convergence of knowledge; if it fulfils that purpose it is useful, even though it may be supplanted at some later date by an expression of still greater generality. Every formula should be a means towards this end, and the question whether it is assuredly final is of minor importance. Indeed, there is no formula in chemistry to-day of which we can be sure that the last word has been spoken.—F. W. Clarke (1914).

Silicic acid at ordinary temp. is one of the feeblest of the inorganic acids. The acid is precipitated from aq. soln. of its alkali salts by carbon dioxide. Observations on the lowering of the f.p., and the electrical conductivities [1] of aq. soln. of the alkali silicates show that they are almost completely hydrolyzed: $Na_2SiO_3+H_2O=2NaOH+SiO_{2colloid}$, when the dilution is approximately 0·02 mol. per litre. The ready hydrolysis of the alkali silicates is in agreement with the difficulty which attends the preparation of the ammonium silicates—*vide infra.*

Although chemically inactive at ordinary temp., silica acts as a powerful acid anhydride at high temp., combining with the bases and many metallic oxides to form more or less fusible silicates. When silica is melted with sodium carbonate, carbon dioxide is expelled with effervescence. The reaction: $Na_2CO_3+SiO_2 \rightleftharpoons Na_2SiO_3+CO_2$, resembles the action of sulphur dioxide on the same salt at ordinary temp.: $Na_2CO_3+SO_2 \rightleftharpoons Na_2SO_3+CO_2$. When sodium silicate is dissolved in water it is decomposed by sulphuric acid, silicic acid is liberated: $Na_2SiO_3+H_2SO_4=Na_2SO_4+H_2SiO_3$. The two compounds can be separated by dialysis. Sodium silicate thus behaves like other salts, and silica is therefore regarded as an acid anhydride, **silicic anhydride,** $SiO_2$, in the same sense that sulphur dioxide, $SO_2$, is sulphurous anhydride. The powerful acid character of silica at high temp. turns on the fact that most of the acid anhydrides—$SO_3$, $P_2O_5$,

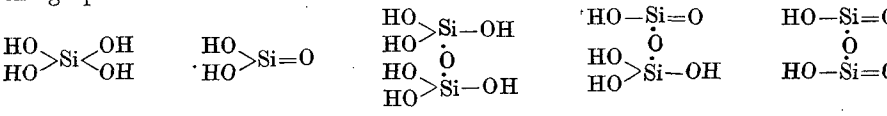
etc.—volatilize at much lower temp., and consequently, as soon as ever so little is displaced, the volatile anhydride passes away and ceases to compete with the silica for the base. At low temp. sulphur trioxide or carbon dioxide rapidly displaces silica from the bases when competing under equal conditions. The igneous rocks on the earth's crust contain silicates rather then carbonates, because at the high temp. of their formation, carbon dioxide could not compete successfully with the silica. Ever since that time, however, the weathering of these rocks has been proceeding slowly and continuously transforming the silicates into free silica, carbonates, and oxides or hydroxides.

Early in the nineteenth century, J. J. Berzelius,[2] J. W. Döbereiner, and J. Smithson expressed the idea that the silicate minerals are salts of silicic acid. A. Laurent proposed to represent the mineral silicates as salts of a series of imaginary silicic acids. The suggestion appeared more feasible after E. Frémy had established the existence of the related stannic acid in 1856; and the work of J. J. Ebelmen, C. Friedel, and J. M. Crafts, L. Troost and P. Hautefeuille, and A. Wurtz on the alkyl silicates, had shown the possible existence of a number of polysilicic acids and of *l'existence d'innombrables silicates que leur mode de génération est fondée, d'une part, sur le principle de l'accumulation des radicaux polyatomiques et de l'autre celui de la hydration successive.* The subject was further developed by the work of T. S. Hunt, W. Odling, C. Weltzien, P. Groth, E. J. Chapman, F. W. Clarke, K. von Haushofer, C. Boedeker, L. Bombicci, P. Groth, G. Städeler, V. Wartha, A. Safarsik, C. Simmonds, A. Streng, N. Lawroff, etc. Examples will be given in connection with the individual silicates. The silicates can be regarded as salts of silicic acid and its various condensation products. The general formula of all the silicic acids is $(n+m)H_2O.nSiO_2$, or $H_{2m}Si_nO_{2n+m}$, where $n$ denotes the number of silicic atoms, and $m$, half of the hydrogen atoms per mol. The silicic acids can be named by starting from the *orthosilicic acids*, the acids formed by the loss of one mol of water per mol of acid can be called *protosilicic acids*, or, as is more usually the case, *metasilicic acids;* the loss of two mols of water gives *deuterosilicic acids* or *mesosilicic acids;* the loss of three mols of water gives the *triterosilicic acids* or *parasilicic acids;* the loss of four mols of water gives the *tetrerosilicic acids*, and the loss of five mols of water gives the *penterosilicic acids*. These acids are illustrated in Table X, which can be extended to the right and downwards if occasion should

TABLE X.—NOMENCLATURE OF THE SILICIC ACIDS AND SILICATES.

| Type. | | 1 mono- | 2 di- | 3 tri- | 4 tetra- | 5 penta- |
|---|---|---|---|---|---|---|
| Ortho- | $H_{2n+2}Si_nO_{n+1}$ | $H_4SiO_4$ | $H_6Si_2O_7$ | $H_8Si_3O_{10}$ | $H_{10}Si_4O_{13}$ | $H_{12}Si_5O_{16}$ |
| Meta-(proto-) | $H_{2n}Si_nO_{3n}$ | $H_2SiO_3$ | $(H_4Si_2O_6)$ | $(H_6Si_3O_9)$ | $(H_8Si_4O_{12})$ | $(H_{10}Si_5O_{15})$ |
| Meso-(deutero-) | $H_{2n-2}Si_nO_{3n-1}$ | — | $H_2Si_2O_5$ | $H_4Si_3O_8$ | $H_6Si_4O_{11}$ | $H_8Si_5O_{14}$ |
| Para-(tritero-) | $H_{2n-4}Si_nO_{3n-2}$ | — | — | $H_2Si_3O_7$ | $H_4Si_4O_{10}$ | $H_6Si_5O_{13}$ |
| Tetrero- | $H_{2n-6}Si_nO_{3n-4}$ | — | — | — | $H_2Si_4O_9$ | $H_4Si_5O_{12}$ |
| Pentero- | $H_{2n-8}Si_nO_{3n-4}$ | — | — | — | — | $H_2Si_5O_{11}$ |

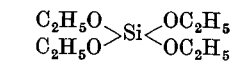
arise. Each member of a horizontal row differs from the one which precedes by the addition of $H_2SiO_3$; and each member of a vertical column differs from the one which precedes by the removal of $H_2O$. The various metasilicic acids are polymers of one another; and those formulæ enclosed by brackets in the table are polymers of some other member of the series. The following are illustrations of the graphic formulæ:



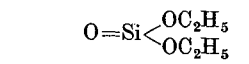
Orthosilicic acid, $H_4SiO_4$. Metasilicic acid, $H_2SiO_3$. Orthodisilicic acid, $H_6Si_2O_7$. Protodisilicic acid, $H_4Si_2O_6$. Deuterodisilicic acid, $H_2Si_2O_5$.

Formulæ for silicates like those of C. Simmonds, which represent the silicon atoms as being joined directly to one another, and not through intermediate oxygen atoms, are considered to be improbable, because, as R. Wegschneider has emphasized, (i) compounds with silicon atoms directly united are unstable reducing agents, and (ii) if the silicon atoms are directly united, oxygen atoms must also be directly united, and this again indicates an unstable oxidizing agent. The union of the strongly reducing group Si.Si with the strongly oxidizing group O.O gives extremely unstable combinations in marked contrast with the stable polysilicates.

Although the existence of the ortho- and meta-silicic acids has not been definitely established, there is less doubt about the alkyl salts of orthosilicic acid, typified by ethyl orthosilicate, and ethyl metasilicate with the respective formulæ:



Ethyl orthosilicate, $Si(OC_2H_5)_4$.

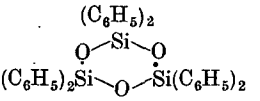


Ethyl metasilicate, $SiO(OC_2H_5)_2$.

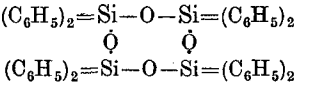
These compounds are formed by the action of the corresponding alcohols on silicon fluoroform, $SiHF_3$. Thus, **methyl orthosilicate,** $Si(OCH_3)_4$, has a sp. gr. of 0·9676 (0°), and it boils at 165°; **ethyl orthosilicate,** $Si(OC_2H_5)_4$, has a sp. gr. of 1·0589 (0°), and boils at 166°; **propyl orthosilicate,** $Si(OC_3H_7)_4$, has a sp. gr. of 0·905 (0°), and boils at 522°; and **amyl orthosilicate,** $Si(OC_5H_{11})_4$ has a sp. gr. of 0·870 (0°), and boils at 323°. Quite a large number of mixed alkyl orthosilicates have been prepared. **Ethyl metasilicate,** $SiO(OC_2H_5)_2$, boiling at about 360°, is said to have been prepared by J. J. Ebelmen[3] in 1846, although there is some doubt whether or not Ebelmen's metasilicates are not really impure orthosilicates. L. Troost and P. Hautefeuille have made a polymer of the metasilicate, *viz.* $(C_2H_5)_2SiO_3$. Ethyl orthosilicate can be regarded as the terminal member of a series of derivatives.

| | B.p. | Sp. gr. (0°) | Formula. |
|---|---|---|---|
| Tetra-ethylsilicon | 152·5° | 0·8341 | $(C_2H_5)_4Si$ |
| Tri-ethylsilicon ethylate | 153° | 0·8403 | $(C_2H_5)_3Si(OC_2H_5)$ |
| Di-ethylsilicon diethylate | 155·8° | 0·8752 | $(C_2H_5)_2Si(OC_2H_5)_2$ |
| Ethylsilicon triethylate | 159·5° | 0·9207 | $(C_2H_5)Si(OC_2H_5)_3$ |
| Silicon tetraethylate | 165·5° | 0·9676 | $Si(OC_2H_5)_4$ |

If tri-ethylsilicon ethylate be treated with acetic anhydride, and the resulting acetic ether—**triethylsilicon acetate,** $(C_2H_5)_3Si(OC_2H_3O)_2$—be hydrolyzed with potash-lye, it yields **triethylsilicon hydroxide,** $(C_2H_5)_3Si(OH)$, which has a constitutional analogy with the carbon derivative—triethyl carbinol, $(C_2H_5)_3C.OH$. Acetyl chloride converts diethylsilicon diethylate into **diethylsilicon dichloride,** $(C_2H_5)_2SiCl_2$, which boils at 148°, and is transformed by water into **diethylsilicon oxide,** $(C_2H_5)_2SiO$, which has a constitution analogous with diethyl ketone, $(C_2H_5)_2CO$. Ethylsilicon triethylate is transformed by acetyl chloride into a fuming liquid, **ethylsilicon trichloride,** $C_2H_5SiCl_3$, which boils at about 100°, and is transformed by water into **ethyl silicic acid,** $C_2H_5SiO.OH$, which is a white amorphous powder with a formal analogy to propionic acid, $C_2H_5CO.OH$, and is accordingly sometimes called *silicopropionic acid*, or *silicipropionic acid*, the corresponding **methylsilicic acid,** $CH_3.SiO.OH$, is called *silico-acetic acid*, on account of its formal analogy with acetic acid, $CH_3.CO.OH$. Silico-acetic acid has been made by the action of conc. hydriodic acid on methylsilicon triethylate, $CH_3.Si(OC_2H_5)_3$. Similarly, **phenylsilicic acid,** $C_6H_5.SiO.OH$, is called *silico-benzoic acid* on account of its formal analogy with benzoic acid, $C_6H_5.CO.OH$; and **benzylsilicic acid,** $C_7H_7.SiO.OH$, is called *silicotoluic acid* on account of the resemblance of its formula with toluic acid, $C_7H_7.CO.OH$. These two compounds are formed during the hydrolysis of the trichlorides of phenylsilicon or tolylsilicon respectively. F. S. Kipping[4] has made a number of acids and anhydrides of the silicic acids—*e.g. diphenylsilicanediol*, $(C_6H_5)_2Si(OH)_2$; *anhydrobisdiphenylsilicanediol*, $HO(C_6H_5)_2.Si.O.Si(C_6H_5)_2OH$; as well as the anhydrides and some derivatives with three and four atoms of silicon in closed rings:



Trianhydrotridiphenylsilicanediol.



Tetranhydrotetrakisdiphenylsilicanediol.

The rings in these compounds appear to be opened by hydrolysis with an alcoholic soln. of potassium hydroxide. J. A. Meads and F. S. Kipping specially remarked that "no closed chain compound has yet been obtained which contains in its mol. more than four atoms of silicon, and four atoms of oxygen."

Suppose that two mols. of orthosilicic acid unite or condense with the elimination of one mol. of water, the sexivalent *orthodisilicic acid*, $H_6Si_2O_7$, would be formed. Although the free acid is not known, several alkyl salts have been prepared. For example, C. Friedel and J. M. Crafts [5] found **hexa-ethoxyorthodisilicate,** $(C_2H_5O)_3Si.O.Si.(OC_2H_5)_3$, among the products of the action of aq. alcohol on silicon hexachloride, $Si_2Cl_6$. The liquid of sp. gr. 1·0196 (0°), boils between 233° and 238° (760 mm.); the corresponding **hexamethoxyorthodisilicate** has a sp. gr. 1·441 (0°), and boils between 201° and 202·5°. Lists of the compounds of silicic with organic radicles, and of other so-called organo-silicon compounds, will be found in the standard works on Organic Chemistry.

J. J. Berzelius [6] classified the silicates according to the *oxygen ratio*, that is, the ratio of the number of oxygen atoms in the base to the number in the acid. Thus, the silicate, $R_4SiO_4$, is regarded as a compound of $2R_2O.SiO_2$ with the oxygen ratio 1 : 1; $R_4Si_3O_8$, as $2R_2O.3SiO_2$, with the oxygen ratio 1 : 3; orthoclase, $NaAlSi_3O_8$, as $Na_2O.Al_2O_3.6SiO_2$, with the oxygen ratio 1 : 3. J. J. Berzelius here regarded the alumina as a base. F. W. Clarke also regarded aluminium as a tervalent base furnishing aluminium orthosilicate, $Al_4(SiO_4)_3$; and by various substitutions obtained formulæ corresponding with numerous mineral silicates. It is, however, well known that alumina is an amphoteric oxide, for it sometimes acts as an acid, and sometimes as a base. It is therefore probable that in some compounds alumina, together with silica, acts as a complex acid, and in other compounds it acts as a true base. Accordingly, a number of different views have been adopted as to the constitution of the aluminium silicates.

In 1869, C. F. Rammelsberg [7] suggested that the aluminium silicates are really *double salts* of aluminium silicate and of a silicate whose basic element is stronger than aluminium. The two salts are united by a kind of residual affinity as is supposed to be the case with the alums. This view was adopted by D. A. Brauns, and V. Goldschmidt. They regarded leucite and beryl as compounds of $R_4SiO_4$ and $Al_2Si_3O_9$; nephelite and sodalite as compounds of $R_4SiO_4$ and $Al_2Si_3O_{12}$; and mica as a compound of $R_6S_{13}O_9$ and $Al_2Si_5O_{12}$; etc.

Another set of hypotheses assumes that many aluminium silicates are *solid solutions* or *isomorphous mixtures* of silicates and aluminates. For example, G. Tschermak,[8] E. Bauer, W. Vernadsky, and J. Morozewicz have elaborated theories that a very great number of silicates are not really so complex as is suggested by their empirical formulæ because they are really mixtures of two or more simpler silicates. This hypothesis has been applied to explain the structure of pyroxene, scapolite, mica, chlorite, etc. For instance, the scapolite minerals can all be regarded as mixtures of two terminal members, meionite, $Al_6Ca_4Si_6O_{25}$, and marialite, $Al_3Na_4Si_9O_{24}Cl$. It is probably true that many aluminium silicate minerals are isomorphous mixtures or solid soln. of two or more aluminium and other silicates.

From another point of view, the aluminosilicates can be regarded as *salts of basic radicles with complex alumino-silicic acids*, analogous to the complex silicotungstic or silicomolybdic acids of W. Gibbs.[9] These complex aluminosilicates are no more closely related to the silicates proper than the ferrocyanides are related to the cyanides. The acidic character of some or all the alumina in the aluminosilicates

was indicated by P. A. von Bonsdorf,[10] J. J. Berzelius, T. Scheerer, C. Bödecker, W. Odling, and D. A. Brauns. The idea was contested by V. Wartha. In illustration of the hypothesis that alumina may have acidic properties in the silicates, S. L. Penfield and H. W. Foote [11] suggested that the tourmalines and amphiboles are substitution products of tourmalinic and amphibolic acids where the hydrogen atoms of the hypothetical acids are replaced by different elements or radicles without change in crystalline form. W. Vernadsky and others have extended S. L. Penfield and H. W. Foote's idea that the **silicate minerals are salts of complex mineral acids** which are in many cases more complex than is indicated by the empirical formula. The aluminosilicate minerals are not regarded as salts of ortho-, meta-, or other silicic acids; nor as substitution products of normal aluminium silicate, but each group of minerals is regarded as comprising salts of particular aluminosilicic acids—*vide* heteropolyacids. Each group is characterized by a particular crystalline form, and considered to be capable of isomorphous substitutions. Just as it is convenient to refer the different silicates to more or less hypothetical silicic acids, so may it be convenient to refer compound silicates to hypothetical aluminosilicic acids:

| | Examples. |
|---|---|
| Alumino-monosilicic acid, $Al_2O_3.SiO_2.nH_2O$ . . . . | Augite. |
| Alumino-disilicic acid, $Al_2O_3.2SiO_2.nH_2O$ . . . . . | Kaolinite. |
| Alumino-trisilicic acid, $Al_2O_3.3SiO_2.nH_2O$ . . . . | Natrolite. |
| Alumino-tetrasilicic acid, $Al_2O_3.4SiO_2.nH_2O$ . . . . | Pyrophyllite. |
| Alumino-pentasilicic acid, $Al_2O_3.5SiO_2.nH_2O$ . . . . | Chabazite. |
| Alumino-hexasilicic acid, $Al_2O_3.6SiO_2.nH_2O$ . . . . | Felspar. |

The hypothetical acids are sometimes named after the leading minerals. The subject has been discussed by R. Scharizer, W. and D. Asch, K. Zulkowsky, R. Gans, T. Uffers, W. Pukall, W. Manchot, P. Erculisse, J. W. Mellor and A. D. Holdcroft, W. Stremme, etc. R. Schwarz and H. Bausch have prepared a cobaltic silicato-aluminosilicate in which part of the silicate forms part of the complex anion, and part is present as cation. This fact is taken to support the aluminosilicate hypothesis. In his interesting memoir: *The Constitution of the Natural Silicates* (Washington, 1914), F. W. Clarke argued that the natural silicates have probably a simple structure: (i) because of the small number—a few hundred at the most—of the known silicates. If complexity were the rule, a far greater number might have been expected because of the diverse conditions under which the silicates have been formed in thousands of different localities. (ii) As a general rule, also, complex structures are characterized by instability, whereas the silicates as a class are exceedingly stable. Again, in deciding between the rival formulæ, other things being equal, a symmetrical formula is preferable to an unsymmetrical formula because symmetry conduces to stability, and most of the silicates are very stable compounds.

This of course does not tell against the aluminosilicate hypothesis. The main difficulty in practice is to distinguish between aluminium as a base, and aluminium as part of the acid complex. Consequently, in the subsequent discussion of particular silicates it is generally assumed that the aluminium is a base until riper knowledge enables a distinction to be made. There is, however, no particular difficulty in building up a system of aluminosilicates as consistent as that obtained by regarding aluminium as a tervalent base. J. Jakob, and P. Erculisse have applied A. Werner's system:

I.—Silicates with simple silicic acid ions:

(1) *Hexoxysilicates.* *E.g. asperolite,* $\left[SiO_6\right]^{Cu}_{H_6}[SiO_6]^{Al}_{Mg}Fe$.

(2) *Pentoxysilicates.* *E.g. andalusite,* $[SiO_5]Al_2$; *titanite,* $\left[SiO_5\right]^{Ca}_{Ti}(Fe)$.

(3) *Tetroxysilicates.* *E.g. dioptase.* $\left[SiO_4\right]^{Cu}_{H_2}$.

II.—Silicates with complex silicic acid ions :

(1) *Monosilicohexoxysilicates.* *E.g. serpentine,* $\left[SiO_2.SiO_6\right]^{Mg}_{H_2}.H_2O$.

(2) *Disilicohexoxysilicates.* *E.g. meerschaum,* $\left[\begin{matrix}SiO_2\\SiO_2\end{matrix}SiO_6\right]^{Mg_2}_{H_4}+nH_2O$.

(3) *Trisilicohexoxysilicates.* *E.g. pyroxenes* and derivations like *talc,* $\left[Si(SiO_4)_3\right]^{Mg_3}_{H_2}$.

III.—Silicato-salts :

(1) *Tetroxysilicato-salts.* *E.g. nephelite,* $\left[Al(SiO_4)_3\right]^{Al_2}_{Na_2}$.

(2) *Pentoxysilicato-salts.* *E.g. sillimanite,* $[Al(SiO_5)_3]Al_5$.

(3) *Hexoxysilicato-salts.* *E.g. dumortierite,* $[SiO_6]_4Al_8$.

(4) *Trisilicotetroxysilicato-salts.* *E.g. leucite,* $\left[Al(SiO_4,SiO_2)_3\right]^{Al_2}_{K_2}(Na)$.

(5) *Hexasilicotetraoxysilicato-salts.* *E.g. orthoclase,* $\left[Al(SiO_4,SiO_2,SiO_2)_3\right]^{Al_2}_{K_3}$.

(6) *Trisilicopentoxysilicato-salts.* *E.g. rasonite,* $\left[Pb(SiO_3,SiO_2)_3\right]^{Pb_5}_{Ca_2.CaCl_2}$

(7) *Hexasilicopentoxysilicato-salts.* *E.g. pollux,* $\left[Al(SiO_6,SiO_2,SiO_2)_3\right]^{Al_3}_{Cs_2.H_2}$

(8) *Trisilicohexoxysilicato-salts.* *E.g. olivine,* $[Mg(SiO_6,SiO_2,SiO_2)_3]Mg,Fe_{11}$.

IV.—Compounds of a higher order in which not an atom, but an atomic grouping appears as the nucleus. *E.g. tourmaline.*

Many types of these silicate compounds are able to crystallize both with and without water of crystallization. The association with water mols. is fundamentally a partial regeneration of complex hydrated ions. This renders possible subsequent dissociation on hydrolysis.

W. and D. Asch, in their work *Die Silicate in chemischer und technischer Beziehung* (Berlin, 1911), have invented an extraordinarily comprehensive hypothesis ; they imagine that there are closed-ring polymers of silica, $SiO_2$, and alumina, $Al_2O_3$, arranged with five or six silicon or aluminium atoms alternating with oxygen atoms. Those rings with five atoms of silicon or aluminium are called *pentites*, and those with six, *hexites*. Using the hexites and pentites as bricks in the hands of a builder, the inventors of the hypothesis build up graphic formulæ in which the composition of any given silicate or alumino-silicate is finally represented as a multiple of the ordinary empirical formula. This mode of representing the constitution leads to many more types of complex silicates than nature has produced. If the imagination can proceed unrestrained by facts, an indefinite number of similar systems could be devised with an indefinite number of pairs of similar kinds of rings. For instance, in addition to the hexite-pentite hypothesis, it is open similarly to postulate an indefinite number of analogous hypotheses with pairs, 2–3, 3–4, 4–5 . . . of rings ; *e.g.* if a silicate has the empirical formula $MgO.Al_2O_3.SiO_2$, and the mol. weight is unknown, in the absence of proof to the contrary, it is open to postulate mol. wts., $(MgO.Al_2O_3.SiO_2)_n$, where $n$ has any desired integral value ranging upwards from unity. The inventors also represent by graphic formulæ glassy mixtures containing an indefinite number of fused silicates, and also impure silicates definitely known to be mechanical mixtures. F. W. Clarke rightly says of this system : "A generalization which does too much may be worse than no generalization at all."

These formulæ stand virtually on the same ground in illustrating our extreme ignorance of the mol. constitution of the silicates. Hypotheses are often multiplied with reckless abandon when the evidence is feeble and the facts are few. This has been the case with the formulæ of minerals. The hypotheses may serve a useful

purpose if they stimulate interest and work, but an inutile purpose if they hinder the exploration of other useful channels by a bigoted and intolerant attitude toward rival hypotheses. The insolubility and non-volatility of the silicates prevents a determination of their mol. wt.; and their general chemical stability offers a great obstacle to the study of their mol. constitution by the usual chemical methods. S. J. Thugutt,[12] J. Lemberg, F. W. Clarke and co-workers, G. Steiger, P. G. Silber, etc., have made a start on the substitution of radicles in the silicates; and on the fractional decomposition of these compounds—*vide* permutites and hydrated aluminium silicates. A. Damour, C. Boedeker, C. F. Rammelsberg, A. Laurent, A. Beutell and K. Blaschke, etc., have studied the nature of the water in some of the hydrates—*vide* zeolites. According to G. Tammann, the mol. sp. hts. of the silicates are additive, and therefore the molecules are independent, and at temp. far removed from their m.p., do not vibrate appreciably. Hence, only in the neighbourhood of the m.p. do isomorphous complex substances diffuse into one another visibly. In solution, silicates undergo hydrolysis, and their behaviour in a soln. therefore gives no definite information as to the molecules which exist in the solid. The complex silicates differ from the carbon compounds in that they are usually decomposed when dissolved or in the fused state, and the mol. theory of organic chemistry finds no application in the chemistry of silicates. As H. E. Boeke has shown, in a few cases determinations of surface tension, electrical conductivity, diffusion, and depression of f.p. have been employed to make an estimate of the mol. wt. The study of the space-lattice through the X-radiograms seems at the present time to hold alluring promises for the next advances of our knowledge of the constitution of the silicates. Although the existence of definite radicles are being recognized yet the condition of this branch of chemistry is very like that of the organic chemistry before Avogadro's hypothesis had been adopted as a guide. Such mol. formulæ as we have are at present of doubtful validity. After all has been said, the constitution of the silicates is not much in advance of A. Laurent's time, when he could say in his *Mémoir sur les silicates:*

> We have a silicate that contains $Si_{13}O_{31}Mg_{21}Al_4H_{30}$, and we discuss seriously whether the atoms have the arrangement $(11SiO_2.21MgO)+2(SiO_2.Al_2O_3)+15Aq.$; or $7(SiO_2 3MgO)+2(3SiO_2.Al_2O_3)+15Aq.$; or, $7(SiO_3.3MgO.2H_2O)+2(3SiO_2.Al_2O_3)+Aq.$; or a hundred other similar formulæ. What is there to prove that the silica is distributed into three principal groups; that the magnesia forms two distinct combinations; that the water occupies two different places? Does this salt by its reactions split into magnesian silicate on the one hand, and an alumino-magnesian silicate on the other? I have often read the discussions that have taken place on this subject, and I avow that I have never found anything but what was arbitrary or according to routine; what I saw most clearly, was that, in general, the greatest regard was paid to authority. . . . We should arrive at results quite as satisfactorily by putting the atomic letters of a formula into an urn, and then taking them out, haphazard, to form dualistic groups.

Graphic methods for representing the composition of the silicate minerals have been discussed by E. S. Fedoroff,[13] J. Stiny, J. F. Kemp, J. P. Iddings and co-workers, C. K. Leith and E. C. Harder, E. Steidtmann, W. J. Mead, W. Lindgren, F. L. Ransome, J. Stiny, W. Cross, L. V. Pirsson, H. S. Washington, W. H. Hobbs, L. C. Graton, A. Lacroix, W. C. Brögger, H. Rosenbusch, O. Mügge, A. Osann, F. Becke, A. Michel-Lévy, A. Harker, J. R. Dakyns and J. J. H. Teall, E. Reyer, W. S. von Waltershausen, V. A. Eyles and J. B. Simpson, E. T. Wherry, etc.

**The synthesis of minerals.**—The purest of minerals nearly always contain foreign matters which were originally present in the medium in which the crystals were formed. Analysis may then fail to reveal the true composition of the mineral, and an artificial preparation may not distinguish between the essential and accidental constituents. The experiments which have been made on the synthesis of minerals have shown that many of them are definite chemical compounds, and have established numerous points of contact between the two sciences—chemistry and mineralogy.

The experiments are no less useful in enabling geologists to appreciate the conditions which prevailed during the formation of the different mineral species, although, as was emphasized by E. Frémy,[14] nature sometimes works under conditions quite different from those which prevail in the laboratory. Still, as G. W. von Liebniz has said, *la nature n'est qu'un art plus en grand.* Indeed, H. B. de Saussure asked: *Ces lois générales du monde physique n'agissent-elles pas dans nos laboratoires de même que dans les souterrains des montagnes?* To-day, we realize that the answer must be: *Oui, certainement.* It has, however, not yet been found possible to synthesize some minerals; and it may be that it never will be possible to do so. This does not mean that the answer to the above question is in the negative. Take a simple case. A reaction may be so slow at ordinary temp. that an indefinitely large number of years is needed for the production of a particular compound. The reaction might be accelerated by raising the temp., but the products of the reaction might then be unstable and decompose. The synthesis of such a mineral could not be realized under practicable conditions.

The older researches of W. A. Lampadius,[15] N. G. Sefström, P. Berthier, J. Percy, F. Leblanc, and C. Bischof; and the more recent work by C. S. B. Richardson, A. L. Day and E. S. Shepherd, H. O. Hofman, W. Mostowitsch, R. Akerman, O. Boudouard, P. Gredt, H. Steffe, J. W. Cobb, and others show that the **temperature of formation** *of a silicate may be lower than the fusion temperature of the components*, provided they are finely ground, and intimately mixed. C. F. Plattner's observation to the contrary—*the fusion of a silicate occurs at a lower temp. than that at which its components originally fuse when they enter into combination*—is probably based on the use of mixtures neither finely ground nor intimately mixed; and without taking the time-factor into consideration.

Silicates have been formed by fusing a mixture of the basic oxide or salt with silica—*e.g.* the alkalies and alkaline earths, lead oxide, magnesium oxide, etc.; by the action of various bases on gaseous silicon halide, etc.; by the dissolution of silica gel in a salt soln., or by the treatment of a soln., of an alkali silicate with other salts whereby less soluble silicates are precipitated—$CuSO_4+Na_2SiO_3=Na_2SO_4+CuSiO_3$. Silicates imitating natural minerals have been synthesized in numerous ways, for example: (1) By heating a mixture of the required constituents with boric oxide in, say, a porcelain kiln; the boric oxide is volatilized, and the crystalline mineral is obtained.[16] (2) By heating a suitable mixture with alkali carbonate or by the fusion of the required base with a suitable borate or silicate. (3) By heating the oxide or a suitable salt with silicon halide—*e.g.* H. St. C. Deville's[17] synthesis of zinc orthosilicate by heating zinc oxide in a tube in a current of silicon fluoride: $SiF_4+4ZnO=Zn_2SiO_4+2ZnF_2$—the zinc fluoride volatilizes. (4) By heating the metal in a stream of water vap. and silicon halide—*e.g.* S. Meunier's synthesis of enstatite by heating magnesium in a current of water vap. and silicon chloride. (5) Silicates are often found well crystallized in furnace slags and similar products. (6) By heating soln. of alkali silicates, may be under press. with sodium aluminate, or some other metal salt. (7) A. C. Becquerel also obtained a number of crystalline silicates by electrocapillary action.[18] Crystals of the lime-soda felspars, baryta-soda felspars, and anorthite have been obtained by fusing the corresponding mixture of silica, alumina, lime, and soda. The alkali felspars are too viscid when fused to crystallize in this way. Crystals of both albite and orthoclase have been obtained by fusion along with tungstic acid, an alkali tungstate or phosphate, or an alkali fluoride. F. Fouqué and A. Michel-Lévy[19] obtained barium, strontium, and lead anorthites, oligoclases, and labradorites by fusing together mixtures containing 2–4·5 mols of silica; one, of alumina; 0–0·625, of sodium carbonate; and 0·375–1·0, of lead, barium, or strontium oxide.

One great difficulty attending the synthesis of silicates is their tendency to form glasses when the constituents are fused together. Some of these glasses readily crystallize if slowly cooled, but not if rapidly cooled. The presence of certain substances in the molten magma may promote rapid crystallization. For instance,

a tungstate or vanadate promotes the separation of crystals of felspar when mixtures of alkali, silica, and alumina are fused together. Certain gases, too, favour crystallization—*e.g.* nitrogen gas favours the conversion of amorphous into crystalline zinc sulphide. H. St. C. Deville,[20] following E. de Beaumont, employed the term *agents minéralisateurs* or mineralizers for the substances which favour crystallization.

> Je les characterise par cette perpétuité de leur action qui se continue indefiniment jusqu'a ce qu'elle soit fixée par les matières autres que celles sur lesquelles elles sont appelées á réagir pour ainsi dire par leur seule présence.

The *agents minéralisateurs* have also been called *cristallisateurs*, and *Krystallisationagentien*. The most common mineralizing agents are the chlorides and fluorides of calcium, magnesium, alkalies, and silicon; the borates, phosphates, and tungstates of the alkalies or alkaline earths. Although in some cases the action of the mineralizing agent may be catalytic—whatever that may mean—this does not appear to be usually the case, for the addition may act by diminishing the viscosity or solvent action of the magma, or by lowering the temp. limits of its stability. For example, calcium metasilicate separates above 1200° in hexagonal crystals, but, in the presence of calcium fluoride or sodium borate, monoclinic wollastonite separates at a temp. 200°–300° lower. Again, in P. Hautefeuille's [21] experiments on the formation of quartz by heating silica with lithium molybdate below 900°; without lithium molybdate a temp. exceeding 900° is necessary for the crystallization, and tridymite is formed. P. Hautefeuille also synthesized other silicates in presence of tungstates or vanadates, *e.g.* with a mixture of silica, alumina, and potassium tungstate, orthoclase was obtained; and leucite if the alumina be in excess; with lithium tungstate, petalite was formed; and with ferric-oxide, potassium hydroxide, and silica ferri-leucite was produced. Other substances may retard crystallization—alumina, for instance, as shown by J. Pelouze,[22] L. Appert, G. Bontemps, and J. H. L. Vogt, promotes the formation of glasses, and retards devitrification.

Other examples of the different syntheses are indicated in connection with specific minerals. The more important monographs on the subject are:

A. Daubrée, *Études synthétiques de géologie expérimentale*, Paris, 1879; F. Fouqué and A. Michel-Lévy, *Synthèse des minéraux et des roches*, Paris, 1882; S. Meunier, *Les méthodes de synthèse en minéralogie*, Paris, 1891; H. Michel, *Die künstlichen Edelstein*, Leipzig, 1914; A. Gurlt, *Uebersicht der pyrogenneten künstlichen Mineralien*, Freiberg, 1857; L. Bourgeois, *La synthèse minéralogique*, Paris, 1884; *Reproduction par voie ignée d'un certain nombre d'espèces minérales appartenant aux familles des silicates, des titanates et des carbonates*, Paris, 1883; E. Dittler, *Mineralsynthetisches Praktikum*, Dresden, 1915.

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## § 23. The Alkali and Ammonium Silicates—Water-glass

In the first century of our era, Pliny [1] described the preparation of a glass by fusing together a mixture of white sand with three parts of nitre. G. B. Porta likewise prepared a glass by fusing rock crystal and cream of tartar ; and G. Agricola, by fusing flint and cream of tartar. J. B. von Helmont said that this glass deliquesces when kept in a damp place. He added :

If stones, gems, sand, marble, flint, etc., be boiled in alkali-lye, they will dissolve, and the liquid when treated by acids, will yield a dust (precipitate) equal in weight to that of the original mineral used.

J. R. Glauber called the soln. of flint in alkali-lye *liquor silicum* or *oleum silicum* —*oil or liquor of flints*, sand, or crystal—and added :

Take one part of white quartz or sand, mix it with three or four parts of salt of tartar or any other alkali, and put the mixture into a crucible so as not to fill more than one-third of it ; since otherwise, in melting, the mixture would rise and flow out of the crucible. Let it stand in the fire half an hour that it may be well ignited and changed to a pellucid glass. Pour it out, and dissolve in water or better in lye ; and the sand or silica will be dissolved, and changed into a thick water. The transparent clear glass is nothing but the most fixed parts of the salt of tartar and of flint united by heat, and turned to a soluble glass wherein lies hidden a great heat and fire. So long as it is kept dry from the air,

it cannot be perceived in it; but if you pour water on it, then its secret heat will discover itself. If you make it into fine powder in a warm mortar, and lay it in a moist air, it will dissolve and melt into a thick fat oil, and leave some fæces behind.

J. N. von Fuchs, in 1818, made *soluble soda-glass* by fusing a mixture of 150 parts of white sand, 100 of soda ash, and 3 of charcoal in a reverberatory furnace, and extracting the cold glassy mass with water. The aq. soln. was evaporated to dryness and fused to form what he called *Natronwasserglas;* with potassium carbonate, in place of sodium carbonate, *Kaliwaserglas* results. Many other proportions have been recommended by P. Ebell,[2] A. Mitscherlich, J. M. Ordway, J. von Liebig, G. Forchhammer, D. A. Péniakoff, H. Propfe, B. von Ammon, H. V. Regnault, L. A. Buchner, H. Fleck, etc. Commercial **water-glass** is made by J. N. von Fuch's process, and the glassy mass is extracted with water in an autoclave. J. M. Ordway used sodium sulphate as the source of the alkali. If alumina, lime, or magnesia are present, the product will not be soluble. The attempt to make hydrogen chloride and sodium silicate by the action of steam on a mixture of sodium chloride and silica—discussed by R. A. Tilghman, W. Gossage, R. Lieber, H. Grüneberg and J. Vorster, H. H. Lake, C. F. Claus, and A. Ungerer —has not been successful (2. 20, 28). K. Schliephacke and H. Riemann fused felspar or a silicate rock—*e.g.* granite—with raw carnallite, and extracted the mass with water. Water-glass is also made by wet processes. For example, J. N. von Fuchs dissolved freshly precipitated silicic acid in an aq. soln. of the alkali hydroxide. Soln. of alkali silicate with a definite ratio of base to silica were made in this way by J. M. van Bemmelen, F. Mylius and F. Förster, R. Lüpke, L. Kahlenberg and A. T. Lincoln, etc. Commercially, water-glass is made in the wet way by dissolving powdered flint, quartz, or kieselguhr in a soln. of sodium hydroxide of sp. gr. 1·22–1·24 under 3–4 atm. press. in an autoclave for about 3 hrs. E. Kleinschmidt and F. Steinberg recommended calcined kieselguhr. The soln. is heated by blowing in steam; and the liquor is finally evaporated in iron pans to a sp. gr., say, 1·7. If the water-glass contains more silica than corresponds approximately with $Na_2O.3SiO_2$, the excess of silica for water-glass is particularly liable to separate from the soln. The use of kieselguhr as a source of silica has been discussed by J. von Liebig, J. M. Ordway, A. Scheurer-Kestner, and R. Meyer. J. W. Hinchley discussed the preparation of sodium silicate from the leucite residues left after the removal of potash and alumina. To convert the liquid into the solid form E. A. Paterson recommended warming it at 60° under reduced press. until the water-content is 30 per cent. The solid product is ground to a fine powder and dried until the water-content is 12 per cent. The resulting dry powder is readily soluble in water.

According to J. N. von Fuchs, and J. M. Ordway, water-glass in 10 per cent. soln. is purified by treating it with one-tenth its weight of alcohol whereby the earths and metal oxide impurities are precipitated; after standing a few hours, one part of the filtrate is treated with two parts of alcohol when most of the sodium silicate is precipitated. This can be dried on absorbent paper, dissolved in four times its weight of water, and the alcoholic treatment repeated—3 or 4 times if necessary. A. Lielegg had previously recommended the alcohol process for purifying water-glass. E. Jordis recommended digesting the soln. of water-glass at 50° for some time, when the flecks which separate contain most of the impurities.

The manufacture and properties of water-glass have been specially discussed by E. Kopp, A. A. Perazzo, O. Maetz, G. Deguide, W. H. Stanton, L. Schneider, J. M. Ordway, H. Zwick, J. W. Hinchley, L. Bernhard, H. Krätzer and L. E. Andés, M. Lenglen, F. Capitaine, F. C. Kuhlmann, F. Ransome, L. W. Codd, C. Bergeat, W. H. Dickerson, L. Schneider, W. H. Stanton, etc. According to F. J. Phillips, to obtain a soluble alkali silicate of high silica content, the product obtained by the fusion of alkali and silica is dissolved in water and an acid then added. Gelatinous silicic acid is precipitated. This precipitate by continued agitation is made to re-dissolve. The acid, preferably sulphuric acid, may be added in the form of spray, and after the subsequent agitation

or grinding, the soln. may be evaporated to dryness. To increase the fusibility of the alkali and silica, a little borax has been employed. I. P. Lihme evaporated the soln. by bringing a heated cylinder in contact with the soln. of water-glass in vacuo, and so obtained the dry product which could easily be broken up into fine flakes soluble in water; and W. Clayton and H. W. Richards sprayed the soln. into the top of a tower where hot air was introduced at 110°; the exit gases at the bottom passed through bag filters to collect the powdered silicate. A solid soluble glass is made by grinding the ordinary insoluble glass either dry (R. M. Caven) or wet (J. W. Spensley and co-workers), and heating the product mixed with a little water, until a vitreous solid is obtained which dissolves readily and completely even in cold water.

The composition of some commercial grades is shown in Table XI. Many other

TABLE XI.—COMPOSITION OF SOME COMMERCIAL GRADES OF WATER-GLASS.

| Sp. gr. | Molecular ratio: $\frac{SiO_2}{Na_2O}$ | Weight ratio: $\frac{SiO_2}{Na_2O}$ | Per cent. solid in soln. |
|---|---|---|---|
| 1·235 | 4·2 | 4·06 | 26·8 |
| 1·325 | 3·8 | 3·68 | 33·4 |
| 1·375 | 3·0 | 2·92 | 35·5 |
| 1·39 | 3·3 | 3·21 | 38·4 |
| 1·42 | 3·3 | 3·21 | 40·0 |
| 1·5 | 2·9 | 2·82 | 44·5 |
| 1·56 | 2·5 | 2·38 | 46·7 |
| 1·6 | 2·0 | 1·95 | 48·7 |
| 1·7 | 2·0 | 1·95 | 54·5 |

grades are available for special purposes. In addition to these soln., silicate of soda can also be obtained in the form of lump glass, which can be dissolved in press. dissolvers at high temp., and also in the form of white powders which can be easily dissolved in hot water. These powders usually contain 15 to 20 per cent. of water and 85 to 80 per cent. of solid sodium silicate. In order to prepare water-glasses with a high silica content, F. J. Phillips and E. J. Rose dissolved precipitated silica in a soln. of water-glass.

**The properties of water-glass.**—After a soln. of water-glass had been exposed to the atm. two days, H. Ditz detected nitrous acid in the soln., and the amount increased as time went on. No hydrogen dioxide could be detected by means of titanic acid. When a three months old soln. is acidified with hydrochloric acid, carbon dioxide is evolved, and there is an odour resembling chlorine, though none can be detected. The chlorine found by E. Jordis may have been due to the action of decomposition products of nitrous acid on hydrochloric acid in presence of ferric and manganese compounds. Fused water-glass is dissolved by cold *water* very slowly, and even with boiling water the process is slow, and it proceeds so uniformly that the bits retain to the last their original form, except for a rounding of the sharp angles. If the proportion of silica be greater than that of a disilicate, the process of dissolution is tardy, and this the more the greater the proportion of silica. F. Mylius and F. Förster said that water-glass is decomposed by water into free alkali and silicic acid, a certain proportion of the latter becoming hydrated and dissolved. The soda water-glasses dissolve rather more slowly than the potash water-glasses. The monosilicates are comparatively quickly dissolved. W. Pukall said that soda and potash glasses are about equally soluble in water, and the solubility of each falls with increasing silica content. The solubility is greatly impeded if earthy impurities be present, so that sands containing mica, felspar, lime, clay, iron oxides, etc., are not suited for making water-glasses. When a water-glass containing these impurities is treated with boiling water, earths and metal oxides may be left as

an insoluble sediment. Some foreign matters may be dissolved because a soln. of water-glass can dissolve traces of most oxides, and the solvent power increases with the conc. of the soln. Hence, a soln. which is slightly turbid when dil. becomes clear by conc.—and conversely. P. A. Bolley, indeed, found that even the oxides of calcium, barium, and magnesium are slightly soluble in water-glass liquor. Dry water-glass coloured with manganese oxide is pink or violet, and, as F. C. Kuhlmann showed, it furnishes a pink or brown soln. A conc. soln. of water-glass is syrupy; and, when boiled, or exposed to air, it becomes covered with a tough skin which disappears when thrust beneath the surface of the liquid. The general properties of water-glass were discussed by J. G. Vail. H. Steele and J. W. Mellor found a sample of soda water-glass with 16·1 per cent. of alkali, calculated as soda, 35·6 per cent. of silica, and 48·3 per cent. of water, or 51·7 per cent. of $Na_2O:2{\cdot}3SiO_2$, had a sp. gr. 1·71:

| Per cent. $Na_2O:2{\cdot}3SiO_2$ | 51·71 | 48·61 | 41·35 | 35·89 | 24·45 |
|---|---|---|---|---|---|
| Sp. gr. | 1·71 | 1·64 | 1·52 | 1·44 | 1·28 |

The liquor known in commerce as water-glass is a colloidal soln. of silica in a soln. of sodium silicate; the ratio $Na_2O:SiO_2$ varies molecularly from 1 : 1·5 to 1 : 4. The possible "dry contents" of a soln. increases greatly as the proportion of silica decreases, and at the same time, the viscosity of the liquid at a given sp. gr. decreases. Thus, according to R. Furness, with two soln. having the ratios 1 : 1·5 and 1 : 4, the former is a thin liquid easily poured, while the latter is jelly-like and stiff. He gave for the *viscosity* in C.G.S. units at 20°:

| Sp. gr. | 1·4250 | 1·4385 | 1·3580 | 1·3598 |
|---|---|---|---|---|
| Ratio $Na_2O:SiO_2$ | 1 : 3·26 | 1 : 3·16 | 1 : 3·53 | 1 : 3·48 |
| Viscosity | 21·9 | 10·8 | 3·1 | 1·7 |

J. D. Malcolmson found that the vol. of adhesive water-glass could be increased 25 per cent. without impairing the viscosity and other desirable qualities by the addition of urine. After the liquid has been evaporated at a high temp., the water-glass is malleable and very tenacious; and it may be drawn into threads like melted glass. It dries to a varnish of stony hardness when spread in a thin layer, but it does not part with its water except as the alkali is carbonated. J. F. Spencer and K. Proud obtained orthosilicic acid at the anode by the electrolysis of a 50 per cent. soln. of sodium silicate. The cathode was a platinum dish, and the anode a coil of platinum wire in a porous cell.

J. N. von Fuchs found that air-dried water-glass retained 12 per cent. of water; and J. M. Ordway found that a layer 0·25 in. thick retained 29 per cent. of water after being kept in a dry atm. for 2 years. The cake was then capable of bending under a steady press. The last portion of water was expelled only at a red heat. The affinity of water-glass for water is shown by the generation of heat observed by F. Mylius and F. Förster when the two substances are mixed. Fifty grammes of pulverized potash water-glass, $K_2O.3SiO_2$, were well mixed with enough water to form a thick pulp, which was left to itself at 18°. In a quarter of an hour the temp. had risen to 32°, and it remained at about this temp. for a long time. When the same glass, mixed with a little water, was warmed on a water-bath at 55°, the temp. of the mixture rose in a few minutes to 80°; and in about ten minutes the pulp had solidified into a homogeneous mass. This property accounts for water-glass setting like hydraulic cement, under water. The pulp formed by the swelling-up which occurs when it absorbs water, cements together the as yet unhydrated particles of the powder. In a day or two it becomes a glassy mass, of the hardness of stone, containing up to 50 per cent. of water. When heated, it gives out this water with violent tumescence; and at a red heat it acquires the character of pumice. Soda water-glass combines with cold water much more slowly. When reduced to powder, and kept under water, it takes two or three months to harden. *G. W. Morey* represented his observations on the effect of press.—*i.e.* the amount

of water added—on the solubility of water in water-glass by Fig. 55. According to W. Stericker, soln. of sodium silicate are shown by the ultra-microscope to be two-phase systems, and the disperse phase is negatively charged. He said that when, say, 2 grms. of anhydrous glass of the composition $K_2O : SiO_2$ is heated with 1–5 c.c. of water, the cooled product is a hard homogeneous **hydrated glass** containing 8–25 per cent. of water. The amount of water retained by the glass depends on the temp., and increases as the proportion of water initially employed is increased, in general accord with Henry's law. As the water-content of the glass increases above 25 per cent. the product passes gradually, and continuously, from a hard, brittle glass to a very stiff paste, and finally to a very viscous soln. resembling ordinary water-glass. This is a striking illustration of the fact that a glass is merely a supercooled liquid. Similar hydrated glasses were obtained by A. I. Walcker, J. N. von Fuchs, J. M. Ordway, etc., by evaporating aq. soln. of water-glass; for they noted that the last portions of water are expelled only at a temp. approaching redness. The hard glasses were liquid at the temp. of their formation so that liquid soln. containing water and alkali silicate, may exist in equilibrium with solid and vapour up to 500°. It should also be pointed out that these hydrated glasses, liquid at the temp. of the experiment, may be regarded as fused mixtures, for the m.p. of the alkali silicate is greatly lowered by the addition of water. For example, $K_2Si_2O_5$ melts at about 1015°, but addition of about 8 per cent. of $H_2O$ lowers its m.p. to about 500°. J. N. von Fuchs, A. I. Walcker, J. M. Ordway, C. Barus, etc., noted the swelling of hydrated glasses when heated; and G. W. Morey said that if a fragment of the clear, homogeneous, hydrated glass, the size of a pea, is contained in a 30 c.c. crucible, and heated over a flame, the substance swells enormously, often overflowing the crucible; the swelling continues until most of the water has been driven off. The spongy or pumiceous mass is composed of vesicles of the alkali silicate glass, often with walls thin enough to show interference colours.

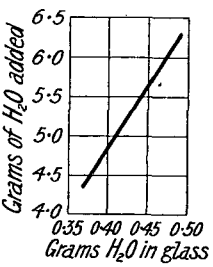



FIG. 55.—The Effect of Pressure (amount of added water) on the Solubility of Water in Water-glass at 420°.

In 1775, J. C. F. Meyer observed that *liquor silicum* diluted with a certain amount of water may be mixed with acids without precipitation; and he assumed that silica is either soluble in these acids or else is transformed into another earth. T. Bergman showed that the silica is precipitated if the soln. be not too dil.; and when the soln. is dil., he said that the particles of silica are so finely subdivided that they remain suspended in the liquid. When a dil. *acid* is added to a dil. soln. of sodium silicate, there is no immediate precipitation of silica, but after some time the whole liquid gelatinizes. The coagulation is faster with sulphuric acid than it is with hydrochloric acid; with the latter, the change may be delayed a long time, and the mixture may even be heated and partially evaporated without coagulation. According to T. Bergman, if acid be added sufficient just to neutralize the alkalinity of potash water-glass, the liquor remains clear, but it becomes turbid when boiled. According to J. Dalton, the addition of an acid, not sufficient for neutralization, precipitates a compound of alkali and silica, but with more acid, silica is precipitated as a gelatinous hydrate, some silica is left in soln., and this the more the greater the degree of dilution, and the less the acid employed. According to L. Doveri, an excess of acid added drop by drop to a soln. of potash water-glass of sp. gr. 1·200–1·332, precipitates 0·9 part of the silicic acid; with a soln. of sp. gr. 1·059, 0·4 part of the silicic acid is precipitated; and with a soln. of sp. gr. 1·029, the silica remains in soln.; but if the acid be added at once, and not in drops, or if the silicate liquor be added to the acid, no precipitation occurs even with conc. soln. The addition of potassium chloride to a silicate soln. of sp. gr. 1·043 renders it incapable of being precipitated by hydrochloric acid. He said: "The silica appears to combine with the acid at the moment of liberation, for on

neutralizing the acid with a soln. of potassium hydroxide added drop by drop, the whole of the silica is precipitated." According to C. J. B. Karsten, if a dil. silicate liquor be supersaturated with sulphuric, hydrochloric, nitric, or acetic acid, it remains clear even after long standing or exposure to heat, or when potassium nitrate or other salts are dissolved in it; and it is only by evaporation that the gelatinous silica is obtained. A. I. Walcker said that a soln. of soda water-glass diluted so as to contain 0·025–0·10 part of silica immediately gelatinizes when neutralized by an acid; with 0·01–0·02 part of silica, it does not form a jelly until after the elapse of 12 hrs.; and with 0·002 part of silica, no gelatinization occurs. J. von Liebig, O. Maschke, H. Rose, W. Lange, E. Ludwig, E. Jordis, C. Friedheim and A. Pinagel, etc., have made observations on this subject.

According to A. Hantzsch, F. Kohlrausch, and E. Jordis, an aq. soln. of alkali silicate has an alkaline reaction whatever be the proportion of acid to base. The hydrolysis of aq. soln. of alkali silicates is discussed below. According to E. Jordis, soln. of water-glass, freed from carbon dioxide, can be accurately titrated by acids with phenolphthalein as indicator, but with technical soln., the phenolphthalein fails more and more as the soln. is diluted, while the titration with methyl orange as indicator remains exact. F. Mylius and E. Groschuff found that the neutral point with hydrochloric acid using methyl orange as indicator varies with temp. and conc. W. Ludewig found that with increasing dilution, the amount of normal acid required for neutralization increases if methyl orange is used as indicator, and decreases if phenolphthalein is employed. Methyl orange gave the best results.

A dil. soln. of water-glass absorbs *carbon dioxide* from the atm.; but a conc. soln. scarcely absorbs any of that gas, and it is decomposed by a stream of carbon dioxide and gelatinized. Similar results are obtained when the soln. is treated with *hydrocarbonates*. According to F. C. Kuhlmann, when a soln. of water-glass is exposed to air, in about a fortnight it is converted into a transparent jelly which gradually shrinks, and in a few months is hard enough to scratch glass. C. J. B. Karsten found that if a dil. soln. of silica be supersaturated with hydrochloric acid, and then mixed in a closed vessel with enough *ammonium carbonate* to neutralize the hydrochloric acid, so that carbon dioxide is liberated in the liquid, the silica remains in soln., but separates on exposing the liquor to air, or on heating the liquor so as to drive the carbon dioxide from the soln. He therefore infers that the dissolved gas helps to keep the silicic acid in soln.; but this conclusion does not agree with other observations. The action of carbon dioxide and of alkali hydrocarbonates has been studied by L. Doveri, G. Lunge and W. Lohöfer, and E. Jordis. A conc. soln. of water-glass in the cold, or a boiling dil. soln., was found by L. Doveri to be coagulated by *boric acid*, *sulphurous acid*, *tartaric acid*, and by *citric acid*. F. A. Flückiger found that a soln. of water-glass is coagulated by *chlorine*, and *bromine*, but not by *iodine*.

When a few drops of dil. soln. of a *metallic salt* are added to water-glass, the precipitate first formed will generally disappear when the mixture is agitated. Consequently, *liquor silicum* may dissolve appreciable amounts of oxides of iron, zinc, manganese, tin, lead, copper, and mercury. Water-glass sat. with a zinc salt deposits a *zinc salt* when allowed to stand for a little while, and it may coagulate into a gelatinous mass; *sodium zincate* gives no change at first, but a precipitate soon forms. A highly alkaline *sodium stannate* may produce no change, but J. M. Ordway showed that with the normal alkali stannate, gelatinization may occur in a few hours or days. *Alkali aluminates or beryllates* also cause precipitation very quickly; while *alkali manganates or chromates* produce no alteration. Finely-divided *lead monoxide* coagulates the liquor, while the anhydrous *oxides of zinc, mercury, and copper*, or the *hydroxides of iron, aluminium, and chromium*, slowly change into silicates. Most metallic salts react with the liquor producing the colloidal metal silicate accompanied by a thickening of the whole mass. H. Ota and M. Noda obtained colloidal silicates by adding dil. soln. of water-glass to dil. soln. of salts of copper, silver, magnesium, zinc, aluminium, titanium, manganese,

iron (ous), and cobalt; and he studied the indophenol reaction with the products.

The formation of metallic silicates is well illustrated by a familiar experiment—*silica garden*: a litre beaker is filled with a soln. of sodium silicate (sp. gr. 1·1) and crystals of, say, cobalt nitrate, cadmium nitrate, copper sulphate, ferrous sulphate, nickel sulphate, manganese sulphate, zinc sulphate, etc., are allowed to fall into the beaker so as to rest on different parts of the bottom. The whole is allowed to stand overnight in a quiet place, when plant-like shoots are obtained which have a form and colour characteristic of each metal. R. Böttger, R. Dollfus, and G. J. Mulder discussed the nature of the silica trees.

B. von Ammon said that the precipitates obtained with metallic salts are usually metal silicates, and, in some cases, double silicates. L. Doveri found that *copper and ferrous sulphates, lead acetate, and silver nitrate* precipitate mixtures of the metal silicate and hydroxide, and silicic acid. The action of *ferric hydroxide* at 100° resulting in the formation of a silicate was studied by J. Lember, C. G. C. Bischof, and A. Daubrée. According to B. Bornträger, crystalline silicates can be produced by adding to a dil. soln. of water-glass, 10 per cent. soln. of the *salts of calcium, barium, aluminium, chromium, iron* (*ic*) *nickel, cobalt, manganese, zinc, uranium, copper, and tin*. W. Hennis studied the reaction with ferric chloride, and ferrous and cupric sulphates. F. Ulffers studied the reactions of water-glass with metal hydroxides and salts; and R. Eberhard, the effect of a little chromic acid on the precipitated silicates. A. H. Erdenbrecher found that the precipitates produced by zinc salts and sodium silicate soln. in the presence of hydrogen dioxide, contain amounts of oxygen varying with the conc. of the hydrogen dioxide. The products are not definite compounds, but rather mixtures of zinc dioxide, zinc silicate, and silicic acid.

According to J. M. Ordway, *barium carbonate and sulphate*, and *calcium fluoride*, have no appreciable action. L. B. G. de Morveau, C. F. Bucholz, and J. W. Döbereiner said that *baryta, strontia*, or *lime-water*, or a soln. of *potassium aluminate* or *calcium sulphate*, precipitate all the silica from a soln. of potash water-glass. The silica is combined with the alkaline earth and part of the potassium. Most calcium salts are particularly energetic in their action; *calcium carbonate* acts very slowly, but when boiled there is flocculation. *Magnesium, zinc, lead, and manganese carbonates* give an immediate coagulation; and *ammonium carbonate* or *alkali hydrocarbonates* cause an instantaneous thickening with conc. soln. *Ammonium salts* precipitate silica. F. A. Flückiger said that *aqua ammonia* of sp. gr. 0·921 gelatinizes a soln. of water-glass of sp. gr. 1·392, and that when warmed in a closed vessel, the precipitate dissolves. If the ammonia soln. is one-tenth of the vol. of the soda water-glass liquor, no precipitation occurs; if one-fifth the vol., the precipitate which is formed redissolves at 90°, and reappears on cooling; and if one-sixth to one-eighth the vol., the precipitate clears at 30°. W. Heintz said that the precipitate is unchanged sodium silicate. J. von Liebig said that if a soln. of water-glass is dil. enough to give no precipitation with acids, a drop of *ammonium carbonate or chloride* produces an opalescence. F. A. Flückiger found that a 0·5 per cent. soln. of water-glass is precipitated by *ammonium nitrate*, and scarcely affected by *ammonium chloride*. J. Persoz, F. A. Flückiger, J. M. Ordway, W. Heintz, F. Mylius, etc., found that a highly siliceous water-glass liquor gives precipitates with *alkali carbonates, acetates, tartrates, phosphates, borates, nitrates, sulphates, and chlorides*; but the bisilicate soln., and others still more alkaline, are not affected by alkali carbonates, tartrates, nitrates, or sulphates. J. N. von Fuchs said that "alkali salts, particularly the carbonates and chlorides, give pasty precipitates when added to a soln. of water-glass." J. M. Ordway said that the normal carbonates are not particularly active as precipitants, but the hydrocarbonates behave as described by J. N. von Fuchs. Sodium chloride, said F. C. Kuhlmann, combines directly with sodium silicate, forming an insoluble compound, and the adherent sodium chloride soln. can be

removed by press. The reaction was also studied by F. Mylius. J. M. Ordway found that the alkali salts precipitate from water-glass liquor an uncombined silicate. W. Hennis said that the precipitations are not chemical reactions, but rather indicate the flocculation of colloid sols. The alkali acetates were found to be rather more efficient flocculants than the chlorides in precipitating water-glass. *Sodium arsenate*, or *phosphate*, gelatinizes the liquor owing to the acidity of these salts, and in this respect they resemble the hydrosulphates or hydrocarbonates. J. N. von Fuchs found that when *aluminium phosphate*, or *lead phosphate, sulphate*, or *carbonate*, is rubbed up with a soln. of water-glass, a tenacious mass is formed which, when exposed to air, sets as hard as stone. J. H. Johnson observed no precipitation of silica from a soln. of water-glass, containing some potassium cyanide, when in contact with *quartz*, powdered *pyrites*, granulated *lead*, or *zinc* shavings; but alkali zincate was formed when in contact with lead-coated zinc, *i.e.*, a *zinc-lead couple*. J. Errera found the *copper* anode is attacked during the electrolysis of alkali silicate soln.

J. N. von Fuchs found that *ethyl alcohol* precipitates potash water-glass without change in composition from its aq. soln., and the supernatant liquor retains undecomposed alkali carbonate, sulphide, and chloride. He based a method of purifying water-glass on this observation. G. Forchhammer said that the alcohol-precipitation and washing removed from water-glass a part of the alkali, and that this separation continued until an octosilicate remained, $K_2O.8SiO_2$. J. M. Ordway added that water-glasses, containing less silica than $K_2O : 1{\cdot}7SiO_2$, furnish a precipitate which is liquid; and those with more silica yield solids of greater and greater "firmness" as the relative proportion of silica is increased; but all these hard products belong to the same class of viscous solids as pitch. The more any given soln. of water-glass is diluted before adding alcohol, the greater the relative amount of silica in the precipitate. By mere precipitation under varied conditions, an indefinite number of differently constituted silicates may be obtained. While the ratio of base to acid can be infinitely diversified, the quantity of water generally amounts to not far from 50 per cent. The action of alcohol was also studied by A. Lielegg, G. Forchhammer, E. Frémy, T. Scheerer, and F. Mylius. J. M. Ordway found *methyl alcohol* and *acetone* also give precipitates with soln. of water-glass. Several organic compounds were found by F. A. Flückiger to coagulate water-glass soln.—*e.g. phenol, creosote, chloral hydrate, egg-albumen, and glue.* No precipitation occurred with *arabic acid, sugar, dextrine, glycerol, alkali resinates*, etc. S. P. Kramer found that *animal or vegetable oils* added to a dil. soln. of water-glass (1 : 500) produce a fine and stable emulsion. The fatty acid of the oil forms with the sodium hydroxide, and the liberated colloidal silicic acid acts as a protective colloid.

**The uses of water-glass.**—The various applications of water-glass, said J. M. Ordway,[3] turn on its adhesiveness in the hydrated state; its vitrifying power in the dry state; its alkaline nature; its capability of yielding soluble silica; and its peculiar chemical relations as a whole. He discussed the use of water-glass soln. as an adhesive—a kind of *mineral glue*—as a colourless cement for glass, porcelain, and stone, and as a medium for fixing paper-labels on glass. The setting qualities can be controlled by the manufacturer, and R. Furness showed that a soln. of water-glass possesses all the essential qualities of an efficient adhesive: (i) the ease, suitability, flexibility, and general efficiency of application to the materials to be united, and (ii) its power of setting in a suitable manner and time with the formation of a bond of the desired strength. He concluded:

> Sodium silicate soln. are superior to animal and vegetable adhesives in that they are fire-resisting, do not become rancid, and are vermin-repellent. Silicate adhesives are quite odourless, and produce damp-proof articles; they have a relatively high bond strength, and their setting times can be varied over a wide range. They are ever-ready, requiring no heat before or during application, and they give consistent results.

According to J. D. Malcolmson, on adding an electrolyte to water-glass the

colloidal silica is coagulated, but if the soln. is stirred during the addition, and for some time afterwards, the gel particles cannot coalesce, but are redissolved, *i.e.* "peptized." By adding brine about two-thirds sat. in a thin stream to the water-glass whilst this is mechanically stirred it is possible to increase the vol. of the water-glass soln. up to about 25 per cent. without impairing the viscosity or adhesive properties of the liquid, which will contain from 3–4 per cent. of sodium chloride. The final viscosity of the soln. may be varied to a considerable extent by small changes in the conc. of the brine. The treated adhesive does not deteriorate when kept out of contact with the air.

Water-glass is used in preparing fireproof cements and lutings for jointing firebricks, etc. These can be made to set hard in the cold by admixture with lime, which causes the precipitation of gelatinous silica. The joint can be further strengthened by heat so as to form a fused silicate. Mixtures of conc. water-glass liquor and fibrous asbestos also make a good packing for joints exposed to hot acid vapours. J. N. von Fuchs used it for reducing the inflammability of wood. Walls plastered with lime-mortar are rendered hard and smooth, and capable of being washed, by applying a few coats of water-glass either alone or mixed with a colouring oxide. In the so-called *stereochrome process* of mural decoration, devised by J. N. von Fuchs in 1840, a plastered surface is decorated by pigments mixed with water, and the colours are then fixed by spraying with water-glass. The lime in the plaster fixes the silicate. The subject has been discussed by H. Creuzburg, F. C. Kuhlmann, etc. J. N. von Fuchs showed the possibility of making artificial stone by moulding a mixture of clay, sand, and a soln. of water-glass; F. Ransome patented an artificial stone made from sand water-glass, and powdered limestone or chalk; Brunner-Mond used it for hardening concrete roads; and L. Wagenmann made an artificial meerschaum by mixing water-glass, lime, magnesia, and magnesium carbonate. F. C. Kuhlmann said that lime-mortar can be made hydraulic by admixture with a small proportion of powdered water-glass. Water-glass is used as a hardening agent for the surface of concrete; in making soaps and washing fluids of various kinds; in paper-making; as egg-preservative; as a remedy for boiler-scaling; and in maintaining the fluidity of clay-slip with a large proportion of clay for the casting of fireclay goods, sanitary ware, earthenware, etc. It is also used as a detergent.[4]

**The alkali silicates.**—In his study of the mol. formula of silica, P. Yorke[5] tried the action of silica on the alkali carbonates at a high temp. He found that a mol of carbon dioxide is expelled from a mol of lithium carbonate by half a mol of silica, forming presumably the orthosilicate, $Li_4SiO_4$; and observations were also made with sodium and potassium carbonates. H. Rose, T. Scheerer, E. Mallard, and P. Ebell studied the expulsion of carbon dioxide from fused potassium and sodium carbonates by silica. In general, the proportions depend on the temp., the duration of the experiment, and on the relative proportions of silica and alkali carbonate. P. Yorke, and C. L. Bloxam also studied the expulsion of water from molten potassium and sodium hydroxides by silica. J. M. Ordway likewise studied the expulsion of sulphur trioxide from molten sodium sulphate, by silica.

E. J. Mills and D. Wilson investigated the distribution of potassium oxide between silica and carbon dioxide, and said that, owing to the evolution of carbon dioxide, the reaction is incapable of simultaneous inversion. N. M. von Wittorf obtained the results with various alkali oxides indicated in Table XII. There is evidence of the loss of rubidium and cæsium oxides by volatilization. P. Niggli has criticized these results, and made a more extended study of ternary systems containing one volatile and two non-volatile components; and of a portion of the system $R_2O$–$SiO_2$–$CO_2$ with a more accurate control of the press. and temp. than was the case in N. M. von Wittorf's experiments. P. Niggli found that in the case of potassium carbonate there is an equilibrium reaction: $K_2CO_3+K_2Si_2O_5 \rightleftharpoons CO_2+2K_2SiO_3$, and at 898°, $K_1=[K_2SiO_3][CO_2]/[K_2CO_3][K_2Si_2O_5]$ varies from 0·44–1·65; and at 956°, $K_2$ varies from 1·21–2·52; while $K_1/K_2$ is nearly

TABLE XII.—DISTRIBUTION OF THE ALKALI OXIDES, CARBON DIOXIDE, AND SILICA.

| Initial mixture (molar). | Molar proportions after fusion. | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | $CO_2$ 0·7 atm. | | | | $CO_2$ 1·0 atm. | | | |
| | Temp. | $CO_2$ | $SiO_2$ | $R_2O$ | Temp. | $CO_2$ | $SiO_2$ | $R_2O$ |
| $Li_2CO_3+SiO_2$ | — | 0 | 1 | 1 | — | 0 | 1 | 1 |
| $4Li_2CO_3+SiO_2$ | 900° | 1·74 | 1 | 4 | 900° | 1·94 | 1 | 4 |
| $Na_2CO_3+SiO_2$ | — | 0 | 1 | 1 | 825° | 0 | 1 | 1 |
| $2Na_2CO_3+SiO_2$ | 870° | 0·69 | 1 | 2 | 780° | 0·78 | 1 | 2 |
| $K_2CO_3+SiO_2$ | 870° | 0·18 | 1 | 1 | 780° | 0·24 | 1 | 1 |
| $Rb_2CO_3+SiO_2$ | 870° | 0·22 | 1 | 1 | 825° | 0·29 | 1 | 0·99 |
| $Cs_2CO_3+SiO_2$ | 870° | 0·27 | 1 | 0·94 | 825° | 0·38 | 1 | 0·95 |

constant, 2·2. With sodium carbonate, the equilibrium reaction is symbolized $Na_2CO_3+Na_2SiO_3 \rightleftharpoons CO_2+Na_4SiO_4$; and with lithium carbonate, probably $2Li_2CO_3+Li_4SiO_4 \rightleftharpoons Li_8SiO_6+2CO_2$. The effect of press. in the case of the potassium carbonate system is complex. He found that if the total press. acting on the melt is equal to the partial press. of carbon dioxide, the magnitude of the effect produced by change of press. will be somewhat different. Consider a very high press. of carbon dioxide. The progress of the reaction is accompanied by a considerable increase of vol. so long as the carbon dioxide is set free as a gas; consequently, if this condition obtains, increase of press. displaces the equilibrium towards the left, *i.e.* favours the substances $K_2CO_3$ and $K_2Si_2O_5$. If the carbon dioxide produced should be completely absorbed by the melt, the vol. change would be slight, and its direction could not be predicted; but there is a second effect produced in this case; for change of press. of carbon dioxide in the gas phase brings about, in accordance with Henry's law, a change of conc. of free carbon dioxide in the melt, and in this way displaces the equilibrium. Indeed, it is largely upon the increase, with increasing press. of the solubility of the gas in the melt that the resultant effect will depend.

In each system, the compound containing more silica is the poorest in silica which can be prepared pure, at the particular temp., merely by melting together carbonate and silica. Thus $K_2SiO_3$ or $Na_4SiO_4$ or $Li_8SiO_6$ cannot be prepared in the pure state from carbonate and silica at about 1000°; the compounds $K_2Si_2O_5$, $Na_2SiO_3$, and $Li_4SiO_4$, which have relatively more silica, can readily be obtained.

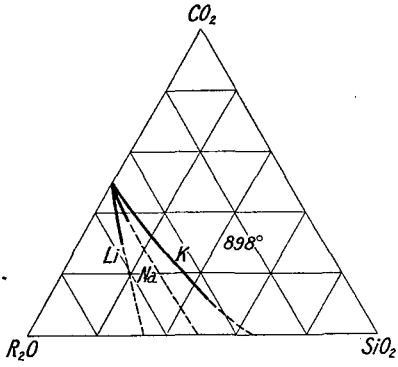



FIG. 56.—Relative Concentrations of $R_2O$, $SiO_2$, and $CO_2$ in Equilibrium in Melts at 898°.

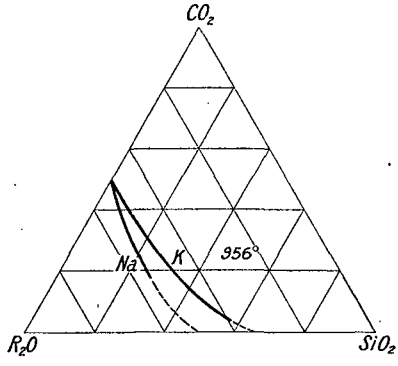



FIG. 57.—Relative Concentrations of $R_2O$, $SiO_2$, and $CO_2$ in Equilibrium in Melts at 956°.

Correspondingly, in Figs. 56 and 57, the equilibrium curves or their prolongations pass through these particular points on the side $R_2O$–$SiO_2$. When alkali carbonate

is melted up with silica, the amount of carbon dioxide displaced in the temp. region of the ternary equilibrium ranges from 0·5–1·0 eq. in the potash system, from 1–2 eq. in the soda system, and from 2–4 eq. in the lithia system. The extent of the displacement of carbon dioxide from the carbonate by silica is parallel with the amount of carbon dioxide which the pure carbonate when melted alone loses by dissociation, when the systems are taken in order as above; the relative compositions of the pairs of silicates in equilibrium in each system is such that the ratio of base to silica for the right-hand member of one system is the same as for the left-hand member of the following system. Rise of temp., the press. remaining constant, favours in each case the silicate poorer in silica; or, in other words, it increases the amount of carbon dioxide displaced.

G. W. Morey and C. N. Fenner studied the ternary systems, $K_2SiO_3$–$SiO_2$–$H_2O$, and determined the composition and properties of the solid phases which can coexist with soln. and vap. between 200° and 1000°—*vide* Fig. 58; the composition of the soln. in equilibrium with the solid phases; the change in the composition of the soln. with temp.; and of the corresponding three-phase pressure, Fig. 59, shows the isothermal polybasic saturation curves, and the polythermal curve at one atm. press.

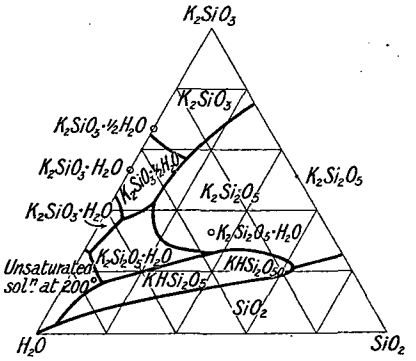



FIG. 58.—Stability Regions of the Solid Phases in the Ternary System, $K_2SiO_3$–$SiO_2$–$H_2O$.

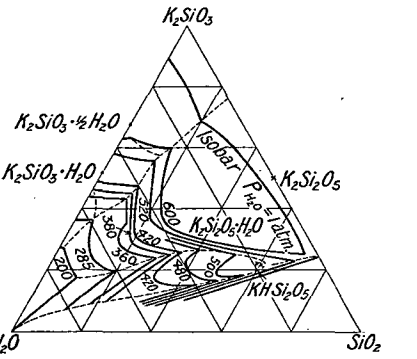
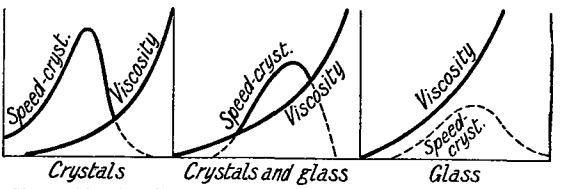



FIG. 59.—Isothermal Polybasic Saturation Curves; and an Isobasic Polythermal Curve in the Ternary System, $K_2SiO_3$–$SiO_2$–$H_2O$.

The fusibility of some mixtures of the alkali oxides and silica were observed by W. A. Lampadius, N. G. Sefström, and P. Berthier in their studies on slags. C. J. Peddle studied the glasses obtained from the binary and ternary systems with the components $SiO_2$–$Na_2O$–$K_2O$. The thermal diagrams of the alkali oxides and silica have not been obtained in a complete form because in some regions glasses only are produced and the cooling or heating curves of these exhibit no breaks. There is therefore a continuous gradation in the composition of these glasses, and no evidence of the formation of definite chemical individuals. E. Kittl found it impossible to measure the ratios of crystallization of the alkali silicate glasses. He inferred that there is a close relation between the viscosity of a molten silicate and its speed of crystallization. When the maximum speed of crystallization falls in the region of low viscosity, complete crystallization usually occurs, Fig. 61, while in the opposite case, a glass is formed, Fig. 62. In the intermediate case, both glass and crystals are formed, Fig. 61. P. Bary discussed the alkali silicate glasses.




FIGS. 60-62.—Relation between the Viscosity and the Speed of Crystallization.

Many of the alkali silicates described by the early workers are simply alkali silicate-glasses whose compositions corresponded with those which would be the case if the alleged silicates were chemical individuals; and this in spite of the fact that constitutional formulæ were sometimes assigned to them. W. Pukall, for instance, described a number of what he regarded as specific silicates but which he described as clear transparent glasses. Similar remarks apply to the alkali silicates obtained by saturating soln. of alkali hydroxide with silica; and to the precipitates obtained by adding alcohol to an alkali soln. of silica. Thus, G. Forchhammer [6] reported that he prepared $K_2O.2SiO_2$, $K_2O.8SiO_2$, and $Na_2O.3SiO_2$ by alcohol precipitation, but J. M. Ordway showed that actually the composition of the precipitate depends (i) on the conc. of the soln.; (ii) on the proportion of alkali present; and (iii) on the amount of alcohol added. The composition of the precipitate can be made to vary continuously by variations in these conditions so that the composition of G. Forchhammer's silicates represent arbitrarily selected points on a continuous curve.

The above remarks apply to T. Scheerer's $Na_2O.SiO_2$ and $4K_2O.3SiO_2$; to A. Lielegg's $Na_2O.2SiO_2$; to P. Ebell's $2Na_2O.5SiO_2$; to G. Forchhammer's $Na_2O.3SiO_2$, $K_2O.2SiO_2$, $K_2O.4SiO_2$, and $K_2O.8SiO_2$; to A. I. Walcker's $Na_2O.4SiO_2.10H_2O$; and to G. Forchhammer's $Na_2O.36SiO_2.4H_2O$, and $K_2O.24SiO_2.16H_2O$. The two last-named products are probably silica hydrates with absorbed potassium hydroxide. The product $K_2O.4SiO_2$ was also discussed by J. N. von Fuchs, B. von Ammon, J. von Liebig, H. V. Regnault, J. M. Ordway, and P. Ebell; $K_2O.8SiO_2$, by P. Ebell; $Na_2O.2SiO_2$, by A. Scheurer-Kestner, J. M. Ordway, T. Graham, A. Bornträger, and F. Kohlrausch; $2Na_2O.5SiO_2$, by W. Seleznеff, F. Kohlrausch, and F. Mylius. Trisilicate glasses, $2R_2O.3SiO_2$, were also described by E. Frémy, and E. Groschuff; $Na_2O.3SiO_2$, by T. Scheerer; $Na_2O.4SiO_2$, by J. M. Ordway, W. Heintz, A. Bornträger, R. Meyer, and J. W. Cobb. W. Pukall's *potassium trisilicate*, $K_2Si_3O_7$, and *sodium trisilicate* were glasses; likewise also his *potassium* or *sodium tetrasilicate*, $K_2Si_4O_9$ and $Na_2Si_4O_9$; *potassium* or *sodium pentasilicate*, $K_2Si_5O_{11}$, or $Na_2Si_5O_{11}$; and his *potassium* or *sodium hexasilicate*, $R_2Si_6O_{13}$. He obtained the hexasilicates in a devitrified state.

A solid **ammonium silicate** has not been isolated. The solubility of silica or silicic acid in aq. ammonia has been previously discussed. C. Struckmann [7] found that 100 parts of a 5 per cent. soln. of ammonium carbonate dissolved 0·02 part of silicic acid, and 100 parts of a 1 per cent. soln. dissolved 0·062 part of silicic acid. The soln. on standing in air became turbid owing to the separation of about half the dissolved silica. R. Schwarz showed that the solubility of silicic acid in aq. ammonium depends on the conc. of the ammonia, the temp., and the water content and physical form of the acid. R. Schwarz and O. Liede used quartz-glass vessels in order to eliminate the influence of alkalies derived from the glass containing vessels; the soln. were also filtered through an ultra-filter to retain colloidal silica. It was found that with silicic acid, equilibrium is attained after about 72 hrs. at 18°, and that the soln. contains 64 per cent. of the silica in true soln., 8 per cent. in colloidal soln., and 28 per cent. undissolved. The conductivity and solubility curves show that the amount of dissolved silica increases during the whole course of the experiment, whilst the colloidal silica gradually diminishes in quantity. The former therefore grows at the expense of the latter, and it appears justifiable to conclude that the formation of the colloidal soln. is the primary process which is followed by the production of the molecular soln.

According to C. Struckmann, the silicic acid, precipitated by ammonium carbonate from a soln. of an alkali silicate, and washed with water until the runnings give no turbidity with mercuric chloride, develops ammonia when treated with potassium hydroxide, and when dried in air, retains 0·78 per cent. of ammonia. The product obtained when ammonium chloride is the precipitant contains less ammonia. J. von Liebig, however, claimed that all the ammonia could be removed by washing. R. Schwarz showed that it is not always clear whether ammonia really neutralizes the silicic acid, or merely produces a colloidal soln. E. Jordis and E. H. Kanter showed that the electrical conductivity of a soln. of silicic acid

prepared by dialysis, and mixed with aq. ammonia, indicates that **ammonium hydrosilicate,** $H(NH_4)SiO_3$, and **ammonium metasilicate,** $(NH_4)_2SiO_3$, are probably present; there is, however, no definite proof that **ammonium orthosilicate,** $(NH_4)_4SiO_4$, is present. According to R. Schwarz, the solubility of the hydrate, $3SiO_2,H_2O$, in 3*N*-ammonia at 18° reaches a maximum in about two hundred hours, corresponding with about one-fiftieth of the amount of acid required to form a metasilicate; in 10*N*-ammonia at 100° the solubility after one hour reaches 84·3 per cent.; in 2*N*-ammonia at 100° the hydrate dissolves to the extent of 55·7 per cent., ignited precipitated silica to the extent of 24·4 per cent., both in one hour, whilst finely powdered quartz only loses 2·7 per cent. of its weight in a day. Soln. obtained in the hot way have the appearance of colloidal soln., but the cold preparations are clear. Inasmuch as the conductivity of the ammonia soln. rises with time (in the case of the hydrate, with negative acceleration: in the case of the anhydride, with positive acceleration during the first one hundred hours), the formation of a true ammonium silicate seems to be certain. Although the salt cannot well be isolated, the nearly related **tetraethylammonium metasilicate,** $(NEt_4)_2SiO_3$, can be obtained as a hygroscopic, amorphous powder by heating the silicic acid hydrate with 10 per cent. tetraethylammonium hydroxide in a sealed tube at 80°. R. Schwarz found that dioxodisiloxane, made by leading trichloromonosilane vap. into water, reacts with ammonia soln. just as it does with potassium or sodium hydroxide, that is, according to the equation $Si_2H_2O_3+4NH_4OH=2(NH_4)_2SiO_3+2H_2+H_2O$. The reaction is completed in about twenty minutes, and most of the silica, with which specimens of dioxodisiloxane are usually contaminated, remains as a precipitate. R. Schwarz and R. Souard studied the electrical conductivity of soln. of silicic acid and inferred from the increment of the conductivity that salt formation does take place just as the lowering of the conductivity of sodium hydroxide by the addition of silicic acid leads to a similar conclusion. The ratio $Q$ of the increment in conductivity to the dissolved silica decreases in three stages as the proportion of water in the silicic acid is diminished. The value of $Q$ is about 75 when the silicic acid has 4·5 per cent. of water, about 50 when about 2·0 per cent. of water is present, and about 25 when the silicic acid is almost dry. All the different preparations of silicic acid gave $Q=25$ when the specimen was nearly dry, and $Q=75$ when the specimen was rich in water. After ignition, however, silica causes no increment in the conductivity of ammonia soln. The different values of $Q$ suggest, therefore, that the dissolved silicic acid exists in three forms with mol. wts. in the ratio 1 : 2 : 3. The simplest forms of silicic acid are derived from dioxodisiloxane or monosilane, the direct hydrolysis of the latter in ammonia soln. being the most satisfactory way of preparing ammonium silicate soln.

K. A. Vesterberg [8] found that amorphous silica dried at 100° dissolves slowly in 2*N*-LiOH at ordinary temp., forming a soln. with 3·4 mols of silica to one mol of $Li_2O$. In warm soln. of lithium hydroxide, silica is almost insoluble, being transformed into an insoluble lithium silicate. P. Yorke prepared **lithium orthosilicate,** $Li_4SiO_4$, by heating lithium carbonate and silica in equimolar proportions; and N. M. von Wittorf found that **lithium metasilicate,** $Li_2SiO_3$, is also formed. K. A. Vesterberg prepared monohydrated lithium metasilicate in two forms, one insoluble, the other soluble. The former is produced as a white, granular precipitate by adding a fairly conc. soln. of sodium metasilicate to an eq. quantity of lithium hydroxide or chloride in *N*-soln. at 80°–90°; it is also obtained by dissolving freshly precipitated silicic acid in twice the theoretical amount of 2*N*-LiOH at ordinary temp., and heating the soln. a short time at 80°. According to P. Hautefeuille and J. Margottet, fused lithium chloride has no action on amorphous silica so long as no trace of lithium oxychloride is present; but if by the action of steam, or other agents, a little oxychloride is present, then the silica is converted into quartz or tridymite according to the temp. If much oxychloride is present, plates of **lithium pentasilicate,** $Li_2Si_5O_{11}$, or $Li_2O.5SiO_2$, are formed. They prepared the three

silicates just mentioned by melting together silica and lithia with or without lithium chloride ; in the one case measurable crystals are formed, and in the other case a crystalline mass is obtained. The three silicates were said to be as difficult to fuse as the magnesium silicates, and when melted, they form very fluid liquids and absorb much gas, which is rejected on cooling. Lithium chloride abstracts lithia from the lithium silicates, forming the oxychloride. According to H. S. van Klooster, the binary system $Li_2O$–$SiO_2$ forms *only two compounds, which are only slightly* miscible in the crystalline state. There is no evidence of the formation of the pentasilicate $Li_2Si_5O_{11}$ on the thermal diagram, Fig. 63. No crystalline products were obtained with over 82 per cent. silica. R. Rieke and K. Endell also explored the thermal diagram, and the results confirm those of H. S. van Klooster. The eutectic between the ortho- and meta-silicate, at about 1010° and 47·5 per cent. silica, corresponds in composition with $3Li_2O.2SiO_2$. They said that microscopically this mixture does not show any evidence of the eutectic structure, and suggest that there may be really a very small maximum corresponding with **lithium orthodisilicate,** $Li_6Si_2O_7$. F. M. Jäger and H. S. van Klooster obtained the orthodisilicate in large tabular biaxial crystals of sp. gr. 2·454 at 25° ; and indices of refraction with the *D*-ray, 1·545 and 1·525. At 1032°, there is an incongruent m.p., and a solid soln. of the orthodisilicate in an excess of the metasilicate is formed. A. Rosenheim and W. Reglin studied the adsorption of lithium hydroxide from soln. by lithium silicate.

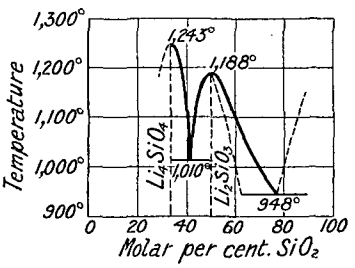



FIG. 63.—Freezing-point Curve of the Binary System : $Li_2O$–$SiO_2$.

P. Yorke, P. Hautefeuille and J. Margottet, R. Schwarz, and A. Haacke obtained lithium orthosilicate, as indicated above, by fusing together silica and a lithium salt. The conditions of formation, by W. Pukall, H. S. van Klooster, and R. Rieke and K. Endell, are indicated in Fig. 63. The last-named found that the fused glass is readily undercooled. E. Derome said that when the glass obtained by heating at 900° a mixture of lithium carbonate and silica in a current of hydrogen for a few hours, is heated in vacuo by an electric furnace, slow dissociation occurs, and lithia is volatilized until the composition of the residue approximates to that of the orthosilicate, when volatilization ceases. P. Niggli found that the orthosilicate is readily obtained from lithium carbonate and silica at about 1000°. P. Hautefeuille and J. Margottet said that the transparent, colourless, or slightly amber-coloured crystals are similar to peridote, and when crystallized from lithium chloride they form pseudohexagonal prisms derived from rhombic prisms. R. Rieke and K. Endell said that the crystals are greenish coloured if made in a platinum vessel. H. S. van Klooster found the sp. gr. to be 2·346 at 15°/15°, and F. M. Jäger and H. S. van Klooster, 2·392 at 25°/15°. The hardness is 3–4 on Mohs' scale. A. Haacke gave 2·280 for the sp. gr., and 1249° for the m.p. H. S. van Klooster found that the f.p. is 1188°, and the m.p. 1243°, and F. M. Jäger and H. S. van Klooster, 1256° ; according to R. Rieke and K. Endell, 1215°. R. Ballo and E. Dittler gave 1217° for the m.p. ; and R. Schwarz, 1249°. H. S. van Klooster found that in polarized light the crystals are feebly doubly refracting ; and they exhibit twinning. R. Ballo and E. Dittler obtained cellularly arranged crystals with refractive index, 1·616–1·624. F. M. Jäger and H. S. van Klooster gave 1·614 and 1·594 for the indices of refraction. The crystals appeared to be optically biaxial, with very small axial angle, or optically uniaxial, and always positive. F. M. Jäger and H. S. van Klooster suggest that 1256° is rather a transition temp. than a m.p. P. Niggli added the salt furnishes irregular equidimensional grains, without crystal outline and characterized by an albite-like twinning with large extinction angle ; a second set of twinning striations inclined to the first is less well developed. The crystals are optically biaxial with very small axial angle ; positive ; mean index of refraction is in the neighbourhood of

1·600; birefringence is fairly strong. P. Hautefeuille and J. Margottet, and H. S. van Klooster found that the crystals become flinty in appearance when in contact with water owing to a superficial decomposition; when boiled with water, some silica and lithia are dissolved; the decomposition by water, said R. Rieke and K. Endell, is complete. W. Pukall said that some *hydrate* of the orthosilicate, $Li_4SiO_4.2{\cdot}57H_2O$, remains as a residue when the anhydrous orthosilicate is decomposed by water. The salt is attacked by acids; and the resistance of the silicates to chemical agents increases as the silica increases.

P. Hautefeuille and J. Margottet prepared lithium metasilicate as indicated above; and G. Friedel, by heating a soln. of lithium hydroxide with an excess of precipitated silica to 500° in a steel tube. H. S. van Klooster, and R. Rieke and K. Endell showed that the conditions of formation are those represented in Fig. 63. According to P. Hautefeuille and J. Margottet, the silicate crystallizes from molten lithium chloride in long flat prisms sometimes terminating in symmetrical domes; they are six-sided, and are derived from rhombic prisms. According to G. Friedel, the colourless crystals resemble those of hypersthene, and the rhombic prisms have the axial ratio $a:c=1:0{\cdot}6681$, and $\alpha=107°\,48'$. F. M. Jäger and H. S. van Klooster state that the biaxial crystals are probably monoclinic, and that the trigonal form of G. Friedel was a twin formation. E. Kittl studied the velocity of crystallization of lithium ortho- and meta-silicates. The sp. gr. is 2·529 at 15°/15°; and R. C. Wallace gave 2·61 at 18°. F. M. Jäger and H. S. van Klooster gave 2·520 for the sp. gr. of the crystals, and 2·330 for the sp. gr. of the glass at 25°. H. S. van Klooster said that the metasilicate forms mixed crystals with up to 24·3 per cent. of silica; and that the m.p. is 1188°; while R. Rieke and K. Endell gave 1180°; R. C. Wallace, 1168°; F. M. Jäger and H. S. van Klooster, 1201°; and R. Ballo and E. Dittler, 1180°. F. M. Jäger found the surface tension at 1254° to be 374·6 dynes per sq. cm., and at 1601°, 346·6 dynes per sq. cm. According to E. Derome, when the metasilicate is heated in vacuo in an electric furnace, dissociation and volatilization of lithia occurs until there is an abrupt slackening of the speed when the composition approaches $Li_2Si_5O_{11}$. R. C. Wallace said that the mica-like crystals have a high refractive index, and a very high double refraction, with polarization colours of the third and fourth orders. The optical properties were also discussed by H. S. van Klooster, and R. Rieke and K. Endell. F. M. Jäger and H. S. van Klooster gave 1·609 and 1·584, with the *D*-ray, for the indices of refraction of the crystals parallel and vertical to the elongation of the needles; they also gave $\mu=1{\cdot}548$ for the glass. As P. Hautefeuille and J. Margottet, G. Friedel, and R. Rieke and K. Endell have shown, the crystals are decomposed by water and by acids; the latter say that the crystals are less decomposed by water than the other alkali metasilicates. L. Kahlenberg and A. T. Lincoln made aq. soln. up to a conc. of $\frac{1}{32}$ mol. per litre by gradually adding the alkali hydroxide to a colloidal soln. of silicic acid; they determined the lowering of the f.p. of soln. containing a mol of $Li_2SiO_3$ in $v$ litres of water and found:

| $v$ | 32 | 48 | 64 | 96 | 128 |
|---|---|---|---|---|---|
| Lowering f.p. | 0·228 | 0·166 | 0·120 | 0·090 | 0·070 |
| Calc. mol. wt. | 23·3 | 23·2 | 22·1 | 19·6 | 18·5 |

It was therefore inferred than when $v=32$, 95·5 per cent. of the salt is decomposed, and when $v=48$, the decomposition is practically complete. For the eq. conductivity, $\lambda$, at 25°, they found:

| $v$ | 32 | 64 | 128 | 256 | 512 | 1024 |
|---|---|---|---|---|---|---|
| $\lambda$ | 125·0 | 126·0 | 129·2 | 130·2 | 138·5 | 145·2 |

The increase beyond $v=64$ is said to be due to the decrease in the retarding influence of silicic acid on the movements of the ions. K. A. Vesterberg found that warm soln. of lithium hydroxide only slowly dissolve precipitated silica dried at 100°; and cold, moderately conc. soln. dissolve up to 3·4 mols. of $SiO_2$ per mol of $Li_2O$. He prepared **hydrated lithium metasilicate,** $Li_2SiO_3.H_2O$, by treating

sodium silicate with a lithium salt, or by dissolving silica in a solid soln. of lithium hydroxide. In both cases an excess of lithia should be present to prevent hydrolysis. The silicate is precipitated from the soln. at 80°–90°. There are two forms of this salt, one is readily soluble but the other dissolves with difficulty.

While H. S. van Klooster, and R. Rieke and K. Endell could find no evidence of the formation of lithium pentasilicate, $Li_2Si_5O_{11}$, P. Hautefeuille and J. Margottet obtained flexible rhombic lamellæ by crystallization from a soln. of the component in lithium chloride. There is a cleavage plane in the direction of greatest length, one perpendicular to that direction, one parallel to the plane of the lamellæ, and two others which furnish thin rhombic plates. E. Derome found that the speed of volatilization of lithia from lithium metasilicate suddenly slackens when the composition has reached $Li_2O.5SiO_2$, and that the latter is slightly dissociated in vacuo at 1300°. P. Hautefeuille said that this silicate is not decomposed by acids. L. Kahlenberg and A. T. Lincoln found that the lowering of the f.p. of soln. of lithium hydroxide in a colloidal soln. of silica corresponding with a mol of $Li_2Si_5O_{11}$ in $v$ litres, is :

| $v$ | 32 | 48 | 64 | 96 | 128 |
|---|---|---|---|---|---|
| Lowering f.p. | 0·172 | 0·139 | 0·112 | 0·077 | 0·062 |
| Mol. wt. | 113·2 | 93·3 | 86·9 | 84·3 | 78·5 |

This is taken to show that the salt $Li_2Si_5O_{11}$ is hydrolytically dissociated in aq. soln., and the dissociation is complete when $v=128$; eq. electrical conductivity, $\lambda$, is:

| $v$ | 32 | 64 | 128 | 256 | 512 | 1024 |
|---|---|---|---|---|---|---|
| $\lambda$ | 55·4 | 61·6 | 67·5 | 72·6 | 78·9 | 90·6 |

As indicated previously, P. Niggli obtained evidence of the formation of a basic orthosilicate or **lithium dioxyorthosilicate,** $Li_8SiO_6$, or $2Li_2O.Li_4SiO_4$.

According to E. Jordis,[9] crystal plates of what is probably **sodium orthosilicate,** $Na_4SiO_4$, is formed when a mol of silica is fused in a silver crucible with 8 mols of sodium hydroxide; while an aq. soln. of sodium hydroxide and silica with more than $14Na_2O : SiO_2$ furnishes crystals of the hydrated sodium metasilicate, $Na_2SiO_3.nH_2O$. W. G. Mixter calculated the heat of combination of silicon with an excess of sodium dioxide forming sodium orthosilicate. P. Niggli found evidence of the existence of sodium orthosilicate in his study of the ternary system $Na_2O$–$SiO$–$CO_2$, but did not isolate the compound—*vide supra.* The stable silicates in this system are the ortho- and meta-silicates. G. W. Morey failed to make *potassium orthosilicate,* $K_4SiO_4$, by melting potassium hydroxide in various proportions between $K_4SiO_4$ and $K_2SiO_3$ in an atm. of steam, and heating the mass finally over 1100°. The excess of alkali over that required for the metasilicate was present as potassium hydroxide. P. Niggli obtained no evidence of the formation of potassium orthosilicate in his study of the ternary system $K_2O$–$SiO_2$–$H_2O$; the metasilicate was always produced. The stable silicates here produced were the meta- and disilicates.

P. Niggli obtained crystals of anhydrous sodium metasilicate, $Na_2SiO_3$, from dry melts by heating an intimate mixture of eq. quantities (1 : 1) of quartz and sodium carbonate at 900°–1000° for some time. With less quartz, the system is heterogeneous. G. W. Morey also obtained evidence of the formation of this silicate when a glass of the composition $Na_2O : SiO_2$ is heated with water at temp. above 400°. The isolation of the crystals is not possible because they are rapidly decomposed by water. W. Pukall obtained a devitrified glass. G. W. Morey and C. N. Fenner found that the crystals are rarely well developed and fibrous and spherulitic forms are frequent; hexagonal prisms terminated by prisms were once obtained. The crystals prepared by G. W. Morey were usually acicular. In both cases, cleavage is well developed and parallel to the elongation. The crystals show parallel extinction. The compound is probably uniaxial and positive. The index of refraction $\gamma=1{\cdot}520$, and the $\alpha$-index is lower; the mean value is 1·510. R. C. Wallace also obtained ill-defined crystals by heating the hydrated meta-

silicate, and also by heating an eq. mixture of silica and sodium carbonate. The latter mixture crystallizes after the first fusion, the former needs to be repeatedly cooled and remelted before crystallization begins. It is assumed that in the latter case a small amount of water is retained even after fusion, and that this retards crystallization. R. C. Wallace gave 1018° for the m.p. of sodium metasilicate; W. Guertler, 1055°; and N. V. Kultacheff, 1007°. The latter found that the metasilicate can dissolve a little silica, and that this lowers the m.p. a little. According to G. Tammann, the heat of crystallization is 29 cals. per gram. G. W. Morey found the m.p. of sodium metasilicate appears 2° lower on the heating curve than on the cooling curve. The sp. hts. of crystals and glass were respectively 0·197 and 0·191. P. Niggli, and R. C. Wallace found that when the metasilicate is heated with quartz no combination occurs, although the latter found that the metasilicate can take up a little silica in solid soln. E. Greiner studied the viscosity of the molten silicate. The last-named also found the m.p. to be lowered by the addition of silica; thus:

| Silica (per cent.) | 0 | 2·5 | 3·7 | 5·0 | 6·5 |
|---|---|---|---|---|---|
| M.p. | 1007° | 942° | 920° | 862° | 820° |

G. Tammann found the sp. ht. of the amorphous salt to be 0·191 and of the crystalline salt 0·197 between 20° and 100°; while the heat of soln. of a gram of the amorphous salt in a mixture of 100 grms. of 10 per cent. hydrofluoric acid and 250 grms. of *N*-hydrochloric acid was found to be 486 cals., and 457 cals. for the crystalline salt. C. Matignon gave $Na_2SiO_{3solid}+2HCl_{soln.}=SiO_2.Aq._{solid}+2NaCl+H_2O+32·8$ cals.; consequently, from known reactions, $SiO_2Aq._{solid}+Na_2O=Na_2SiO_3+51·1$ cals.; $SiO_2.Aq._{solid}+Na_2CO_3=Na_2SiO_3+CO_2-24·7$ cals.; and $Si_{cryst.}+3O+2Na=Na_2SiO_3+331·4$ cals. When the result 51·10 cals. is compared with D. Tschernobaeff's value 45·2 cals. for anhydrous silica, and O. Mulert's 69·7 cals., it appears as if some erroneous deductions have been made somewhere. W. W. Coblentz found a maximum in the reflection of ultra-red rays at 9·95$\mu$. J. O. Perrine observed no sign of the excitation of fluorescence by the X-rays.

G. W. Morey found anhydrous **potassium metasilicate,** $K_2SiO_3$, to be the stable solid phase in the binary system $K_2SiO_3$–$H_2O$ from about 610° to its m.p., and it is obtained in a fairly pure condition by crystallizing the metasilicate glass at a high temp. The crystals usually appear in the form of rounded grains without crystal boundaries. There is evidence of cleavage parallel to the $\gamma$-axis. W. Pukall obtained only a metasilicate glass. G. W. Morey and C. N. Fenner found that the crystals are biaxial; the optical character is positive; the dispersion is strong and the birefringence high. The optic axial angle is 78·5°. The m.p. is 966°. The crystals are very hygroscopic and dissolve rapidly in water. The deliquescence of the hydrates makes their separation difficult; and they have not been isolated even in an approximately pure condition. M. A. Rakuzin measured the electrical conductivity of soln. of potassium metasilicate; and the reversible adsorption of the salt with animal charcoal, colloidal silica, and alumina.

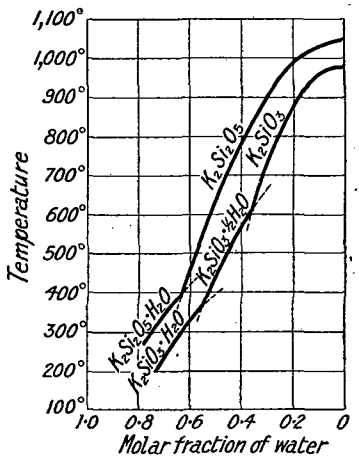



FIG. 64.—The Solubility or Melting-point Curves of the Binary Systems: $K_2Si_2O_5$–$H_2O$ and $K_2SiO_3$–$H_2O$.

In his study of the binary system $K_2SiO_3$–$H_2O$, G. W. Morey found that **hemihydrated potassium metasilicate,** $K_2SiO_3.\frac{1}{2}H_2O$, is the stable solid phase between 370°–610°—*vide* Figs. 58 and 64. The crystals occurred in elongated forms with good cleavage parallel to the elongation. The extinction was parallel to

the elongation in the $\gamma$-direction ; the birefringence is high ; the optic axial angle large ; and the optical character is probably positive. The crystals are completely soluble in water. He also found **monohydrated potassium metasilicate,** $K_2SiO_3.H_2O$, to be the stable phase between 200° and 370°—*vide* Figs. 58 and 64. Below 200°, the monohydrate is hydrolyzed by water, and above 370° it forms the hemihydrate. The crystals are biaxial, positive, with a small axial angle, and high birefringence. The crystals dissolve completely in water. W. Pukall obtained what he suggested to be *dihydrated potassium metasilicate,* $K_2SiO_3.2H_2O$, by the action of superheated steam on the metasilicate glass.

Crystals of hydrated sodium metasilicate have been reported by a number of investigators, but there is no agreement as to the degree of hydration. A. H. Erdenbrecher obtained hexagonal crystals of **tetrahydrated sodium metasilicate,** $Na_2SiO_3.4H_2O$, m.p. about 85°. T. Petersen obtained colourless, monoclinic crystals of what he regarded as the *pentahydrate,* $Na_2SiO_3.5H_2O$, with axial ratios $a:b:c=0{\cdot}6961:1:1{\cdot}2001$, and $\beta=95°\ 50'$. The crystals become turbid when exposed to air, they melt in their water of crystallization, leaving a voluminous residue which is soluble in water. E. Jordis prepared crystals with 43·42 per cent. of water, when the theoretical value for the pentahydrate is 42·37 per cent. A. H. Erdenbrecher obtained no signs of the pentahydrate on the vap. press. curves. J. Fritzsche obtained rhombohedral triclinic prisms which he regarded as the *hexahydrate,* $Na_2SiO_3.6H_2O$, by dissolving equimolar proportions of silica and sodium hydroxide in water ; when the soln. is conc. by evaporation, and allowed to stand for some days, it yields a crystalline mass which in more dil. soln. deposits hemispherical or fibrous masses, or yields a crystalline crust. E. Jordis obtained crystals with 45·81 per cent. of water when the theoretical value for the hexahydrate is 46·87 per cent. A. H. Erdenbrecher obtained monoclinic crystals of the hexahydrate and gave 62·5° for the m.p. P. Yorke fused 54 parts of sodium carbonate and 23 parts of silica ; dissolved the cold cake in water ; evaporated the aq. soln. in vacuo over sulphuric acid at ordinary temp., and in a few days obtained a crop of crystals which corresponded with the *heptahydrate,* $Na_2SiO_3.7H_2O$. A. H. Erdenbrecher found no signs of this hydrate on the vap. press. curve. R. Hermann obtained white rhombic crystals from the mother-liquor obtained in the purification of soda. Their composition corresponded with the *octohydrate,* $Na_2SiO_3.8H_2O$. L. Krafft reported crystals of the same composition to be present in a sand breccia from Sablenville. According to B. von Ammon, the crystals are monoclinic prisms with axial ratios $a:b:c=0{\cdot}6352:1:0{\cdot}6721$, and $\beta=109°\ 48'$. R. Hermann said the crystals are very soluble in water, and have a caustic taste. They melt in their water of crystallization leaving behind a swollen white mass. B. von Ammon, and J. M. Ordway gave 45° for the m.p. R. Hermann's crystals were said to be permanent in air, but B. von Ammon found that the crystals effloresce in moist air, and take up carbon dioxide, but they do not absorb carbon dioxide from a dry atm. At 100°, or confined over conc. sulphuric acid, the crystals lose 27·21 per cent. of water ; at 130°, 49·2 per cent. ; and at 150°, 53·75 per cent. A. H. Erdenbrecher obtained no signs of the octohydrate on the vap. press. curves. J. Fritzsche found that besides the hexahydrate, he sometimes obtained crystals of the *enneahydrate,* $Na_2SiO_3.9H_2O$, which A. E. Nordenskjöld found to be rhombic bipyramids with axial ratios $a:b:c=0{\cdot}6888:1:0{\cdot}3378$. The crystals effloresce over sulphuric acid and attract carbon dioxide from the atm. They melt at 40° to a syrupy liquid which solidifies when allowed to stand for some days. A. H. Erdenbrecher gave 47° for the m.p., and he measured the vap. press. A. Vesterberg also obtained the enneahydrate, and from the experiments on dehydration he inferred that a *trihydrate,* $Na_2SiO_3.3H_2O$, as well as a hexahydrate exists. E. Jordis obtained crystals of the *dodecahydrate,* $Na_2SiO_3.12H_2O$—or possibly of the *henahydrate,* $Na_2SiO_3.11H_2O$—in small prisms ; and R. Weber obtained the dodecahydrate by treating a soln. of water-glass with ether. It thus appears as if sodium metasilicate forms several hydrates, but the composition and range of stability of these hydrates are not known.

More knowledge will probably reduce the number very considerably. Thus A. H. Erdenbrecher's measurements of the vap. press. gave evidence of only the ennea-, hexa-, and tetra-hydrates, and the existence of a *tetradecahydrate*, $Na_2SiO_3.14H_2O$, was made probable but not certain.

Dil. aq. soln. of sodium metasilicate are strongly hydrolyzed; E. H. Loomis found that the hydrolysis is complete in a $\frac{1}{48}N$-soln., and 64·8 per cent. is hydrolyzed in a $\frac{1}{8}N$-soln. L. Kahlenberg and A. T. Lincoln found the lowering of the f.p. of soln. of silica in sodium hydroxide lye in the proportions $Na_2SiO_3$, $NaHSiO_3$, and $Na_2S_5O_{11}$ to be, for a mol of the salt in $v$ litres, at 25°:

| $v$ | 8 | 16 | 24 | 32 | 64 | 96 | 128 |
|---|---|---|---|---|---|---|---|
| $Na_2SiO_3$ | 0·695 | 0·385 | 0·280 | 0·210 | 0·110 | — | — |
| $Na_2SiO_3$ (by fusion) | — | — | — | 0·200 | 0·108 | 0·077 | — |
| $NaHSiO_3$ | 0·332 | 0·202 | 0·146 | 0·110 | — | — | — |
| $Na_2S_5O_{11}$ | — | — | — | 0·178 | 0·139 | 0·089 | 0·059 |
| $K_2SiO_3$ | 0·710 | 0·394 | 0·279 | 0·215 | 0·110 | 0·082 | — |
| $KHSiO_3$ | 0·316 | 0·196 | 0·153 | 0·110 | — | — | — |
| $Rb_2SiO_3$ | — | — | — | — | 0·139 | 0·098 | — |
| $Cs_2SiO_3$ | — | — | — | — | 0·102 | 0·068 | — |

The values for the two sodium metasilicates are virtually the same. The corresponding mol. wts. approach as their limit one-fourth the mol. wt. of $Na_2SiO_3$ with increasing dilution; with sodium hydrometasilicate, the limiting mol. wt. is one-half that of $NaHSiO_3$; and with the pentasilicate, the limiting mol. wt. is one-fourth that of $Na_2Si_5O_{11}$. With the potassium metasilicates under similar conditions the hydrolysis is practically complete when $v=48$, and with $v=8$, the normal salt is ionized 66·9 per cent., and the acid salt, 39 per cent. R. H. Bogue also found the hydrolysis of the $Na_2O : SiO_2$ products from 1 : 1 to 1 : 4 was greatest with the first, and decreased as the proportion of silica increased. The results with **rubidium metasilicate,** $Rb_2SiO_3$, and **cæsium metasilicate,** $Cs_2SiO_3$, are quite similar. The electrical conductivities, $\lambda$, of the soln. were determined by S. Arrhenius, F. Kohlrausch, E. H. Loomis, and L. Kahlenberg and A. T. Lincoln. The two last-named found at 25°:

| $v$ | 8 | 16 | 32 | 64 | 128 | 256 | 512 | 1024 |
|---|---|---|---|---|---|---|---|---|
| $Na_2SiO_3$ | 105·3 | 112·0 | 117·8 | 115·0 | 119·5 | 95·7 | 91·8 | 104·8 |
| $NaHSiO_3$ | 72·4 | 78·8 | 84·9 | 90·1 | 103·7 | 114·2 | 133·1 | 148·5 |
| $Na_2Si_5O_{11}$ | — | — | 73·0 | 79·9 | 87·3 | 93·1 | 101·1 | 113·3 |
| $K_2SiO_3$ | — | 130·9 | 176·4 | 182·6 | 185·5 | 187·1 | 191·8 | 182·5 |
| $KHSiO_3$ | 87·3 | 110·3 | 117·6 | 126·2 | 133·4 | 141·7 | 155·0 | 175 6 |

Similar results were obtained with rubidium and cæsium metasilicates. It is assumed that hydrolysis is complete when $v=64$, and that the increase in the conductivity with soln. of greater dilutions is produced by the retarding influence of silicic acid on the movements of the ions. F. Kohlrausch noted that equilibrium in the hydrolysis is attained very slowly; that the temp. coeff. of the conductivity is abnormal, and that the age of the soln. has a marked influence on the results. He also inferred that $Na_2Si_2O_5$ is the sodium silicate richest in silica which can exist in aq. soln., and that aq. soln. of the metasilicate contain NaOH and $Na_2Si_2O_5$. E. Jordis, F. Mylius, F. Kohlrausch, L. Kahlenberg and A. T. Lincoln, and R. H. Bogue showed that in the hydrolysis of the alkali silicates, the silica separates in the colloidal form, and, in consequence, conclusions about the relative strength of silicic acid, based on the apparent degree of hydrolysis of such soln., are not necessarily valid; indeed, there is ground for the belief that silicic acid is considerably stronger than has generally been supposed, just as W. Blum showed to be the case with aluminic acid. In any case, solubility experiments, such as those made by A. Vesterberg, are meaningless, because the phenomenon is one of decomposition. When, for instance, hydrated sodium metasilicate is treated with water, the first infinitesimal portion dissolved is immediately decomposed with the formation of colloidal silica, and the process will go on until some more or less definite end-point is attained; but this presumed equilibrium is in no way determined by

the real solubility of the sodium silicate itself. J. M. Ordway made some observations on rubidium silicate.

G. W. Morey found that when anhydrous potassium silicate glass, $K_2O.2SiO_2$, is heated to about 450° with an amount of water insufficient to give complete soln. crystals are obtained resembling **potassium disilicate,** $K_2Si_2O_5$, or $K_2O.2SiO_2$, prepared by P. Niggli by heating a mixture of $K_2CO_3+2SiO_2$. If less silica is used, a liquid phase appears, and with more silica, unattacked quartz remains. W. Pukall obtained only the disilicate glass. G. W. Morey showed the conditions of stability of the disilicate. The crystals are optically biaxial, and negative. They are rhombic. The habit is usually tabular, and the crystals appear as pearly scales. There is a strong cleavage parallel to the *c*-axis, and a weaker cleavage parallel to the *b*-axis. Perfectly rectilinear or irregular polysynthetic twinning, resembling albite twinning, often occurs. The birefringence is low. The $\beta$-index of refraction is near 1·500. The crystals were quite solid at 1005°, and were all melted at 1025°, so that the m.p. is 1015°±10°. G. W. Morey later gave 1041° for the m.p., and he obtained the m.p. curve shown in Fig. 65. The molten liquid

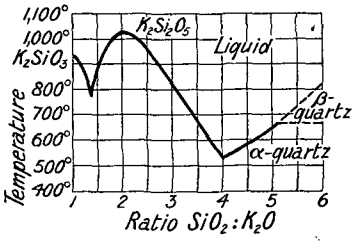



FIG. 65.—Melting-point Curve of the Binary System: $K_2SiO_3$–$SiO_2$.

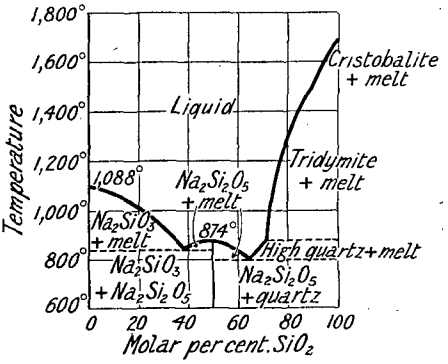



FIG. 66.—Melting-point Curve of the Binary System: $Na_2SiO_3$–$SiO_2$.

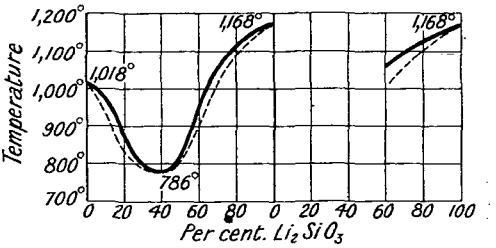
is very viscid, and solidifies to a glass. When a drop of water is placed on the crystals, on the stage of the microscope, they do not dissolve uniformly, but break up into thread-like forms. The solubility curves or m.p. of the binary system $K_2Si_2O_5$–$H_2O$ are shown in Fig. 64, and the range of stability in the ternary system $K_2SiO_3$–$SiO_2$–$H_2O$ is shown in Fig. 58. G. W. Morey found that if an anhydrous glass approximating $Na_2O : SiO_2$ is heated with much water above 400°, a homogeneous hydrated glass is formed; but if the amount of water is not sufficient to give complete soln., and the temp. is 300°, crystals of **sodium disilicate,** $Na_2Si_2O_5$, are formed. W. Pukall obtained a devitrified disilicate glass. G. W. Morey and N. L. Bowen's m.p. curves are shown in Fig. 66. The m.p. of the disilicate is 875°. According to G. W. Morey, the rhombic crystals usually appear in the form of scales with a pearly lustre; and micaceous cleavage. The extinction is parallel, and the optical character negative. The indices of refraction are $\alpha$=1·504; $\beta$=1·514; and $\gamma$=1·518.

G. W. Morey found that when an anhydrous alkali silicate glass is heated with water, the product obtained depends on the temp. and press., on the amount of water present, and on the ratio $R_2O : SiO_2$. If a glass, $K_2O : SiO_2$, is heated with an equal weight of water at 400°, the product is a clear, homogeneous, hydrated glass; but if half the proportion of water be used with glasses ranging from $K_2O : SiO_2$ to $K_2O : 5SiO_2$, at 200°–400°, the product is a mixture of the hydrated glass and crystals of **potassium hydrodisilicate,** $KHSi_2O_5$, or $K_2O.H_2O.4SiO_2$. The crystals can be freed from the adherent glass by leaching with hot water, without affecting the sharpness of the crystal angles. The crystals belong to the

rhombic system. The habit varies, exhibiting elongated forms parallel to the vertical axis, and tabular forms. These sometimes occur side by side. W. Pukall inferred that because plates and needles were present in one of his preparations, two different compounds were present. This by no means follows. The identification depends on measurements of the optical constants, etc. Cleavage is well developed, and parallel to the elongation; twinning is common; and the optic axial angle is 69·5°. The biaxial crystals are positive. The refractive indices are $\alpha$=1·480–1·495 and $\gamma$=1·530–1·535. The higher numbers are probably more correct. The crystallographic properties resemble those of a hydrated potassium silicate reported by C. Friedel and E. Sarasin in 1881. The sp. gr. is 2·417 ± 0·002 at 15°/4°. The crystals are not readily affected by water even when kept at 100° for several hours; they are decomposed when heated with dil. hydrochloric acid leaving a birefringent residue containing only silica and water—a similar residue has been described by F. Rinne. The vap. press. of the water is very slight since the crystals can be heated in air to 350° without loss, but at 450°, the loss is appreciable. G. W. Morey also obtained evidence of **monohydrated potassium disilicate,** $K_2Si_2O_5.H_2O$, on the solubility curves, Fig. 64, and in the ternary system, Fig. 65. This compound is decomposed by water below 280°, and at 405°, it passes into the anhydrous salt. The crystals occur in rounded forms, rarely showing crystal faces. The crystals are biaxial and positive, and have a small axial angle, and high birefringence. They dissolve completely in water.

W. Pukall obtained what he regarded as *dihydrated potassium disilicate*, $K_2Si_2O_5.2H_2O$, by crystallization from an aq. soln. of the metasilicate; he also reported *potassium dihydrotetrasilicate*, $K_2H_2Si_4O_{10}$, *potassium dihydrohexasilicate*, $K_2H_2Si_6O_{14}$, and *potassium dihydro-octosilicate*, $K_2H_2Si_8O_{18}$, to be formed as insoluble zeolites by the action of superheated steam on the glasses. G. W. Morey could not verify these observations. W. K. Sullivan obtained *tetradecahydrated potassium pentasilicate*, $K_2O.5SiO_2.14H_2O$, by leaving a soln. of potassium silicate in contact with carbon dioxide under press. for a few months. The white crust which adhered to the gummy silica was removed, and dried in contact with frequently renewed filter-paper. The excess of potassium carbonate was removed by allowing the crust to stand on filter-paper alongside a dish of water under a bell jar; the paper was frequently renewed. In a few months, the potassium carbonate was all removed, and the residue was dried at 60° in a current of air.

J. W. Döbereiner,[10] and C. L. Bloxam studied the action of silica on heated mixtures of sodium and potassium carbonates. J. Regnauld reported that the stickiness of potash water-glass is reduced when mixed with soda water-glass. B. von Ammon and J. M. Ordway said that the sodium and potassium silicates do not form a *potassium sodium silicate*. J. Lemberg studied the action of a soln. of sodium silicate on one of potassium salts, and conversely; C. G. C. Bischof, the effect of sodium chloride on a soln. of potassium silicate; and J. Lemberg, the action of potassium chloride or nitrate on a soln. of sodium silicate, and of sodium nitrate on a soln. of potassium silicate. O. Schott obtained glasses by fusing mixtures of sodium and lithium carbonates and silica. R. C. Wallace found that with mixtures of sodium and lithium silicates, no *sodium lithium silicate* is formed, but an unbroken series of mixed crystals is produced—Fig. 67; while with lithium and potassium silicates no evidence of the formation of a *potassium lithium silicate* was obtained—Fig. 68. No crystallization occurred with mixtures containing less than 50 per cent. of lithium silicate; and only when lithium silicate exceeded 60 per cent. were mixed crystals formed. For *potassium nitratosilicate, vide infra*, silver silicates.




FIGS. 67 and 68.—Binary Systems of Lithium Silicate with Sodium and Potassium Silicates.

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## § 24. Copper, Silver, and Gold Silicates

Copper oxide and silicic acid do not exhibit a marked affinity for one another, and stable compounds are not common. Copper silicates do not occur abundantly in nature. Copper oxide dissolves in fused silicates producing blue or green glasses. The alkali silicate glasses tinted by copper are blue.[1] The coloration of glass by copper has been discussed by P. Ebell, P. Hautefeuille, V. Auger, M. Pettenkofer, A. Lecrenier, F. Wöhler, E. Frémy and G. Clémandot, P. Zulkowsky, F. Knapp, H. S. Washington, H. Hecht, L. Jatschewsky, etc. The coloration of glass and glazes a ruby red, the so-called Chinese red, rouge flamme, rouge flambé, sang de bœuf, etc., has been discussed by C. Paal and W. Leuze, J. C. M. Garnett, F. Knapp, M. Pettenkofer, P. Zulkowsky, C. E. Guignet and L. Magne, R. Schwarz, H. A. Seger, C. Lauth and G. Dutailly, W. Spring, H. le Chatelier and G. Charpy, C. Otsuki, L. Franchet, W. H. Zimmer, etc. The general results indicate that the coloration is produced by colloidal copper in the same way that gold-ruby colours are produced by colloidal gold (*q.v.*). P. Zulkowsky considered that it is necessary to assume the existence of two modifications of copper to explain why strongly heated copper-ruby glass is colourless when rapidly cooled. The colourless variety is presumably dissolved copper, the red variety is copper which has had time to separate. P. Zulkowsky found that a blue soln. of an ammoniacal cupric salt is not decolorized by powdered copper-ruby glass, and hence inferred that the copper is not present in the metallic form. He assumed that sufficient copper would be exposed or accessible to the reagent under these conditions. It would not be surprising if he is wrong when it is remembered that copper-ruby glass has 0·1 per cent. of copper. For colloidal copper silicates, *vide supra*, water-glass.

According to M. Philips, when an alloy of copper and silicon is exposed to moist air for eight days, a black oxidized layer is formed ; and by using the alloy as anode in an alkaline soln. of potassium tartrate, a black deposit is formed which, when washed with alcohol and ether, and dried, has a composition corresponding with impure **cuprous orthosilicate,** $Cu_4SiO_4$. J. L. Jarman and J. F. MacCaleb investigated an acidic slag which was supposed to contain cuprous silicate. J. N. von Fuchs,[2] and A. I. Walcker obtained a bluish-green precipitate by adding a cupric salt soln. to one of water-glass, and the colour is retained when the soln. is boiled. Observations on the product were made by G. Barth, A. Keim, and R. Dollfus. O. Löw said that the precipitate is soluble in a conc. aq. soln. of potassium hydroxide, and J. Schröder, that it is insoluble in pyridine. According to E. Jordis and W. Hennis, the reaction between copper sulphate and sodium silicate in aq. soln. does not occur according to the equations which can be written for them. If the reagents are mixed in eq. proportions an acid liquid is obtained which contains silicic acid. The amount of metal in the filtrate varies independently of the reaction in the liquid. In the presence of much alkali, the metal dissolves together with the silicic acid. If an excess of either reagent is added, the proportion which passes into the filtrate increases from a minimum with the excess. The hydrated silicates are blue, the anhydrous silicates are green. M. Rüger obtained no *copper orthosilicate* by heating a mixture of the constituent oxides at 900°–1000°. C. N. Otin found that it is impracticable to make a thermal analysis of the binary system cuprous oxide-silica, on account of oxidation to cupric oxide, and a ternary system is thus formed. Basic mixtures were formed containing crystals of cuprous oxide, together with a eutectic. The thermal results, together with the determinations of density, indicate that several silicates are formed, the compositions of which are uncertain.

H. Schiff reported a green precipitate to be formed when an alkali silicate is added to a soln. of a cupric salt. Most of the copper oxide dissolves in aq. ammonia, and when the residue is dried, it furnishes an amorphous powder with a composition of **copper diammino-disilicate,** $CuO.2SiO_2.2NH_3$. C. Simmonds prepared by precipitation a product with the composition of a *sodium cupric silicate*, $3Na_2O.17CuO.27SiO_2.20H_2O$, and he examined its reduction when heated to redness in a stream of hydrogen.

According to A. Scacchi,[3] *neocyanite*, a sublimation product of Vesuvius, is probably **cupric metasilicate,** $CuSiO_3$. It was also described by F. Zambonini. By treating a soln. of water-glass with copper sulphate, W. Pukall obtained a hydrated mixture of cupric metasilicate and cupric hydroxide, $3CuSiO_3$, $Cu(OH)_2$, $4H_2O$. H. Schwarz and G. A. Mathis obtained a product agreeing with $CuSiO_3.H_2O$ by adding the proper proportion of a 0·25 per cent., soln. of sodium metasilicate to a 2 per cent. soln. of pentahydrated cupric sulphate ; and if the soln. contained a little *N*-NaOH, $CuSiO_3.2H_2O$ was obtained. They also made mono- and dihydrated **cupric amminometasilicates,** $CuSiO_3.H_2O.NH_3$ ; and $CuSiO_3.2H_2O.NH_3$, as well as dihydrated **cupric diamminometasilicate,** $CuSiO_3.2H_2O.2NH_3$, stable below −16°.

W. T. Schaller described crystals of what he called *shattuckite* from the Shattuck Arizona Copper Co.'s mine at Bisbee. According to F. Zambonini, the composition, $CuO.SiO_2.\frac{1}{2}H_2O$, **hemi-hydrated cupric metasilicate,** resembles that of the mineral *plancheite*. W. T. Schaller also found crystals of **monohydrated cupric metasilicate,** $CuSiO_3.H_2O$, in the same mine ; and the mineral was called *bisbeeite*. A. F. Rogers found it in a copper mine in the Grand Canyon, Arizona. The mineral belongs to the rhombic system. Both minerals are blue. E. S. Larsen gave for the refractive indices of bisbeeite, $\alpha=1{\cdot}615\pm0{\cdot}01$, $\beta=1{\cdot}625\pm0{\cdot}01$, and $\gamma=1{\cdot}71\pm0{\cdot}01$. A. F. Rogers considered this sample to be impure because he obtained for sodium light $\alpha=1{\cdot}589$, $\beta=1{\cdot}620$, and $\gamma=1{\cdot}649\pm0{\cdot}001$ ; W. T. Schaller's values are $\alpha$ or $\beta=1{\cdot}59$ and $\gamma=1{\cdot}65$. The birefringence, $\gamma-\alpha=0{\cdot}060\pm0{\cdot}002$ ; the extinction is parallel ; and the optical character is positive. The mineral is pleochroic, being

deep blue in the $\gamma$-direction; pale bluish-green in the $\beta$-direction; and neutral in the $\alpha$-direction. Fragments of the mineral are soluble in molten sodium metaphosphate. The colloidal mineral from Copper Mountain, Alaska, described by A. F. Rogers, was called *cornuite*, and a similar mineral described by H. Buttgenbach from Katanga, Belgian Congo, was called *katangite*.

In 1800, B. F. J. Hermann, before the St. Petersburg Academy, described a mineral which he had obtained indirectly from Achir or Aschir Mahméd, who found it near Semipalatna. The mineral was named *achirite* or *aschirite*. The account was published in 1802, but meanwhile, R. J. Haüy had published an account of the mineral and named it **dioptase**—from διά, through; ὁπτάζω, to see—because the cleavage directions could be seen by looking through the crystal.

The mineral was mentioned by J. J. Ferber, J. C. Delamétherie, and A. G. Werner, and they considered it to be a kind of emerald coloured with copper—*Kupfersmaragd*. F. Mohs called it *Smaragdochalcite*. Later descriptions were made by C. A. S. Hofmann, F. Sandberger, E. S. Dana, M. Bauer, N. von Kokscharoff, etc. The mineral occurs associated with limestone and quartz in the Kirghese Steppes, Malaja Urjumskaja (Russia), and was described by C. D. Schangin, N. von Kokscharoff, A. Breithaupt, M. Websky, A. Lévy, G. A. Kenngott, A. Lasaulx, R. Maack, P. W. Jeremejeff, A. des Cloizeaux, and H. Credner; at Rezbanya (Hungary), and was described by J. A. Krenner; near Comba in the French Congo, and was described by E. Jannetaz, and A. des Cloizeaux; (*Africa*); in Chili and Peru, and was described by G. vom Rath, M. Bauer, and C. A. Burghardt; at Clifton, Graham Co. (Arizona), and was described by E. R. Hills, and G. F. Kunz, and at Riverside, Pinal Co., when it was described by W. B. Smith.

The mineral was analyzed by L. N. Vauquelin, H. Hess, A. Damour, M. Henglein, F. Zambonini, G. Tschermak, etc. The data agree with the formula, $CuSiO_3.H_2O$. C. F. Rammelsberg regarded the mineral as *cupric dihydro-orthosilicate*, $CuH_2SiO_4$, because the combined water is not expelled below 400°. G. Tschermak first represented it as a metasilicate, $HO.Cu.SiO_3.H$, but later adopted the orthosilicate hypothesis. F. W. Clarke gave the graphic formula: $HCu\equiv SiO_4.Cu.H_2SiO_4.Cu.H_2SiO_4.Cu.SiO_4\equiv H_3$. F. Zambonini found that the water begins to be evolved at 95°, and the dehydration curve is continuous; at 478°, a little still remains. There is a slight change in colour at 398°. He represents the mineral as **hydrated cupric metasilicate,** $CuSiO_3.H_2O$. A. C. Becquerel synthesized the mineral by the action of soln. of cupric nitrate and potassium silicate separated by parchment paper: $K_2SiO_3+Cu(NO_3)_2+H_2O=CuSiO_3.H_2O+2KNO_3$.

A. Breithaupt found that the columnar emerald-green crystals belong to the rhombohedral system, and have the axial ratios $a:c=1:0{\cdot}53417$. The crystals were also measured by M. Websky, A. Lévy, G. A. Kenngott, N. von Kokscharoff, H. Credner, M. Bauer, E. Jannetaz, A. des Cloizeaux, J. A. Krenner, etc. The fracture is conchoidal. The sp. gr., according to A. Breithaupt, is 3·270–3·301; and, according to G. A. Kenngott, 3·314–3·348. The hardness on Mohs' scale is 5. R. Cusack gave 1171°, and A. L. Fletcher 1221° for the m.p. of dioptase. The pleochroism is feeble; and the double refraction strong and positive. W. H. Miller gave for the indices of refraction, $\omega=1{\cdot}667$, and $\epsilon=1{\cdot}723$; A. F. Rogers gave for cornuite, 1·549. A. Ehringhaus and H. Rose compared the dispersion and double refraction of the orthosilicates of copper, beryllium, and zinc with their mol. wts. W. Hankel found that the crystals are pyroelectric, and when cooled, both ends of the principal axis are negative, and the surfaces positive. J. Lemberg studied the microchemical reactions. When treated with hydrochloric or nitric acid, gelatinous silica is formed. According to A. Damour, a soln. of potassium hydroxide does not attack dioptase, but with a soln. of ammonia and ammonium carbonate, a blue soln. is formed. C. Matignon and G. Marchal examined the corrosive action of water on dioptase in the presence of carbon dioxide under 10 atm. press. during ten years. C. Simmonds examined the reduction of dioptase when heated to redness in a stream of hydrogen.

In the third century B.C., the term **chrysocolla**—from χρυσός, gold; κόλλα,

glue (solder)—was applied by Theophrastus in his Περὶ λίθων (**4.** 26) to a green stone containing copper, and it appears to have been used in soldering gold; the same name has been applied to borax, also used for a similar purpose. The mineral was also mentioned by Pliny, who, in his *Historia naturalis* (**33.** 86, 93), applied the term to a number of different minerals including a copper carbonate. Cyprus was named as a prominent locality. In his *De materia medica*, Dioscorides said that the best chrysocolla had a leek-green or prase colour.

G. Agricola,[4] J. G. Wallerius, and A. Cronstedt called it *Berggrün, cœruleum montanum, and viride montanum.* Hence the terms *mountain blue, mountain green,* etc. A. G. Werner called it *Kupfergrün.* Both chrysocolla and an earthy variety of copper carbonate were included in these terms from the sixteenth to the eighteenth centuries by A. Estner, A. G. Werner, and R. J. Haüy. The last-named, however, called it *cuivre hydrosiliceux* in 1820; and M. H. Klaproth argued that the silica in chrysocolla is not merely mixed with the copper oxide, because the two constituents form a chemical compound. J. F. John made a similar observation as a result of his analysis of a specimen of Siberian *Kieselkupfer.* J. F. L. Hausmann called the mineral *Kieselkupfer,* and C. C. Leonhard, *Kieselmalachit.* P. Berthier's specimen of chrysocolla from Somerville, New Jersey, was for a time called *somervillite.* The so-called *Kupferblau* of G. Rose contains some carbonate as impurity. *Kupferpecherz* or *melanochalcite,* analyzed by G. A. König and by W. Lindgren and W. F. Hillebrand, contains appreciable quantities, and have been called *cupric carbonato-silicates.* The *asperolite* of R. Hermann, named on account of its brittleness, was found at Taglisk, Russia, and it was considered to be trihydrated copper metasilicate, $CuSiO_3.3H_2O$, or dihydrated copper dihydro-orthosilicate, $H_2CuSiO_4.2H_2O$. He considered it a member of the series of hydrated cupric silicates dioptase, chrysocolla, asperolite. The Kupferpecherz of C. A. S. Hofmann is almost black in colour; it was described by A. Damour, C. F. Rammelsberg, and F. von Kobell, and is regarded as a mixture of limonite and chrysocolla; similar remarks apply to the *Hepatinerz* of A. Breithaupt.

The mineral has been reported from various localities. G. Rose, W. Haidinger, C. Baerwald, R. J. Haüy, P. W. Jeremejeff, J. R. Blum, and C. F. Rammelsberg mentioned its occurrence at Bogoslowsk, Niznij-Tagil, and Altai, in Russia; T. Scheerer, at Strömsheien in Norway; A. Breithaupt, in Baden; C. W. von Gümbel, at Kupferberg in Bavaria; E. S. Dana, and J. C. Ullmann, in Nassau; A. Frenzel, at Schneeberg in Saxony; M. Websky, and H. Traube, in Silesia; P. Herter, V. R. von Zepharovich, and K. F. Peters, at Rochlitz in Bohemia; G. Sillem, K. F. Peters, J. R. Blum, and V. R. von Zepharovich, at Libenthen in Hungary; L. von Köchel, and E. Fugger, in Salzberg; G. Tschermak, and L. Liebener and J. Vorhauser, at Falkenstein and Schwatz in Tyrol; G. A. Kenngott, in Switzerland; G. Roster, and A. E. Delesse, in Italy; D. F. Wiser, G. Freda, and J. R. Blum at Nicolosi, and Lipari, in Sicily; P. Berthier, at Canavailles, France; R. P. Greg and W. G. Lettsom, on the copper mines of Cornwall, England; A. Knop, P. Groth, and G. Gürich, at Namaqualand in Africa; G. T. Bowen, P. Berthier, and A. Dufrénoy, at Somerville in New Jersey; J. R. Santos, a specimen from Utah; G. F. Kunz, F. P. Dunnington, R. Robertson, and J. W. Mallet, in Gila Co., Arizona; G. A. König, in Denver, Colorado; L. C. Beck, at Franklin, New Jersey; E. Jannettaz, and W. M. Hutchings, in California; A. Breithaupt, at Zimapan, Mexico; C. A. Burghardt, in Peru; I. Domeyko, in Chile; and A. L. Sack, A. Liversidge, and J. R. Blum, in South Australia, and New South Wales. Analyses have been reported by J. R. Blum, T. Scheerer, F. von Kobell, C. F. Rammelsberg, R. Hermann, G. Freda, J. R. Santos, F. P. Dunnington, R. Robertson, J. W. Mallet, E. Jannettaz, W. M. Hutchings, I. Domeyko, N. Pellegrini, W. Lindgren and W. F. Hillebrand, H. F. Keller, E. Manasse, F. Field, P. Berthier, L. C. Beck, G. T. Bowen, P. Herter, E. S. Dana, A. Damour, T. Thomson, J. C. Ullmann, M. H. Klaproth, etc.

The analyses show that idealized chrysocolla is **dihydrated copper metasilicate,** $CuSiO_3.2H_2O$; and, excepting for the water content, it has the same ultimate composition as dioptase. As is usual with colloidal minerals, the composition varies much owing to impurities. The silica is probably derived from the decomposition of other minerals, and an excess appears in many analyses. Besides free silica, oxides of copper, iron, and manganese may be present, and this would change the colour to a brown or black. Some copper carbonate and sulphate may be present, as well as oxides of lead, antimony, arsenic, etc. C. G. C. Bischof suggested that copper silicates have been formed in nature by the action of silicates of the alkalies, alkaline earths, or magnesia from the weathering of silicate rocks on soln. of copper salts from the oxidation of copper pyrites. He also found that copper silicate is decomposed by carbonated waters, forming copper carbonate. E. S. Dana mentioned specimens of chrysocolla from Chili in which the interior was malachite.

T. Scheerer found chrysocolla associated with felspar, and assumed it to have been formed by the action of cupric sulphate on that mineral. The analyses of different samples, however, agree with the ratios $Cu : Si : H_2O = 1 : 2 : 2{\cdot}6$ (Lipari), $1 : 2 : 2{\cdot}3$ (Boleo), and $1 : 1 : 2$ (Nicolosi). H. F. Keller's analysis of a sample from Huiquintipa corresponds with $CuH_2(SiO_3)_2.H_2O$. P. Groth holds that chrysocolla may occur mixed with the *copper aluminosilicate*, $CuAl_2Si_2O_8$. Chrysocolla occurs both in the colloidal and crystalline states, and it is coloured blue or green. The colloidal nature is in agreement with the different views which have been reported as to the proportion of combined water. A. F. Rogers regarded the crystalline form as a metacolloid, *i.e.* a microcrystalline substance of colloidal origin. A. F. Rogers and F. H. Probert regard the variable composition as due to the adsorption of magnesia, lime, and other oxides. A. Breithaupt gave 2·560 for the sp. gr.; E. Jannetaz, 2·272; R. Hermann, 2·306; and T. Scheerer, 3·317. The sp. gr. of specimens with a low proportion of impurity ranges from 2·0–2·2. The hardness is between 2 and 4 on Mohs' scale. Chrysocolla is decomposed by acids with the separation of pulverulent silicic acid; and not gelatinous silicic acid as in the case of dioptase. C. Simmonds examined the reduction of chrysocolla in a stream of hydrogen at a red heat. E. Dittler said that chrysocolla readily adsorbs aniline dyes. E. Puxeddu and E. Manca found the mineral from Bena de Padru to be radioactive.

A. Lacroix [5] found a variety of chrysocolla at Mondouli in the French Congo, and he named it *plancheite*. Its composition approximated $15CuO.12SiO_2.5H_2O$. The formula has some analogies with that of ganomalite. It can be regarded as a basic copper metasilicate, $H_2Cu_7(CuOH)_8(SiO_3)_{12}$. The sp. gr. is 3·36. M. Henglein noted the occurrence of this mineral at Guchab, S.W. Africa. N. von Nordenskjöld described a blue mineral, *demidovite*, or *demidoffite*, found by A. von Demidoff in Niznij-Tagil (Ural). It appears to be a silicophosphate, a mixture of a silicate and phosphate, or a mixture of opal and phosphate. It was also examined by N. von Kokscharoff. The analysis indicates 31·55 per cent. $SiO_2$; 33·14, CuO; 0·53, $Al_2O_3$; 1·53, MgO; 23·03, $H_2O$; 10·22, $P_2O_5$. The sp. gr. is 2·25, and the hardness 2. R. P. Greg obtained a similar mineral in Cornwall. D. M. Kramberger described a mineral, *pilarite*, obtained at Pilar in Agram, having the composition $CaCu_5Al_6Si_{12}O_{39}.24H_2O$; sp. gr. 2·62; and hardness 3. It may be a mixture of copper aluminosilicate, etc. According to F. Cornu and M. Lazerevic, both demidovite and pilarite are colloidal chrysocolla with adsorbed matters. A. d'Ambrosio described a blue, compact, porcelain-like *nuova varieta di crisicolla* which he called *traversoite*, after G. B. Traverso. It was found at Arenas, Sardinia, and its composition corresponded with $2(Cu,Ca)O.Al_2O_3.2SiO_2.12H_2O$. The index of refraction of the isotropic mineral is 1·565. A. F. Rogers, and S. G. Gordon described samples from the Grand Canyon which are probably *cyanotrichite*, a blue mineral occurring in needle-like crystals described by E. S. Larsen with $\alpha = 1{\cdot}588$, $\beta = 1{\cdot}167$, and $\gamma = 1{\cdot}655$.

If a piece of silver be heated in contact with glass or glaze, below the softening temp. of either, the silicate acquires a yellow colour owing to the diffusion of the metal into the solid. The diffusion of silver in glass has been discussed by A. Heydweiller and F. Kopfermann,[6] E. Warburg, G. Schulze, etc. Glass coloured with colloidal silver, analogous to gold ruby glass, is blue. J. S. Stas also showed that finely divided silver combines with glass when heated in a current of air to near its softening temp., and that silicates and silica are attacked by the molten or vaporized metal. Porcelain is coloured yellow or yellowish-brown when heated with silver. J. J. Berzelius showed that silver introduced as oxide also dissolves in fused silicates, forming yellow glasses; and he said that when the precipitate obtained by adding aq. ammonia to a soln. of silver fluosilicate, is treated with an excess of ammonia, *silver silicate* is formed. For colloidal silver silicates, *vide supra*, water-glass. E. Jordis found that when sodium silicate is fused in a silver crucible, the metal is attacked, and when the product is extracted with water, a brown voluminous mass remains which becomes black when treated with an excess of water. It contains silver and soda in the ratio $Ag : NaOH = 0{\cdot}001296 : 1$. If silicic acid is added, a brown silver silicate is formed. J. D. Hawkins said that if a soln. of silver nitrate be treated with sodium silicate, a citron-yellow pre-

cipitate is formed, which becomes darker in colour when dried. Analyses show that it contains a little more silica (as impurity) than corresponds with **silver metasilicate,** $Ag_2SiO_3$. It is readily decomposed by acids, and is completely soluble in aq. ammonia. It can be heated without decomposition, but, at a red heat, it decomposes into silica, silver, and oxygen. W. Pukall claimed to have made a metasilicate by heating an intimate mixture of silicic acid and silver oxide in theoretical proportions. The dark yellow crystalline product is readily attacked by nitric acid. R. Schwarz and G. A. Mathis worked with dil. soln., and obtained a precipitate of dihydrated silver metasilicate, $Ag_2SiO_3.2H_2O$; and they converted this into dihydrated **silver diamminometasilicate,** $Ag_2SiO_3.2H_2O.2NH_3$.

According to G. Rousseau and G. Tite, when silver nitrate is heated with a small quantity of water and fragments of marble in sealed glass-tubes at 180°–300° for many hours, deep ruby crystals are obtained, adhering strongly to the sides of the tube. They correspond with **silver dinitratotriorthosilicate,** $2AgNO_3.3Ag_4SiO_4$, or $7Ag_2O.3SiO_2.N_2O_5$. A similar product is obtained if finely divided silica is added to the contents of the tube, and in this case the crystals do not adhere to the glass. Silver oxide may be used in place of calcium carbonate, but the excess is difficult to separate at the end of the operation. The same product is obtained in smaller crystals by heating silver nitrate with silica at 350°–440°. Silver nitratosilicate forms short, ruby prisms showing longitudinal extinction in parallel light. When heated to dull redness, the crystals intumesce with evolution of nitrogen oxides, leaving a residue of metallic silver and the silicate, $Ag_2SiO_3$. The nitratosilicate is easily soluble in dil. nitric acid, but after some time, and especially on heating, silica separates. Hydrochloric acid decomposes the compound immediately with the separation of silver chloride. Ammonium chloride also decomposes it, and the soln. smells of ammonia, but *nitratosilicic acid* could not be isolated. A soln. of potassium chloride soln. is without action even at 100°, but potassium iodide yields silver iodide and *potassium nitratosilicate,* the latter separating in long needles when the filtrate from the silver iodide is conc. in a vacuum.

For the coloration of glass with gold, *vide* **3.** 23, 11. According to P. P. von Weimarn,[2] if 0·1–1·0 per cent. soln. of sodium chloroaurate and sodium silicate are mixed, a clear soln. of, possibly, *auric silicate* is obtained. This gradually develops a reddish colour, and, changing slowly, finally becomes blue. Coagulation commences after several months, and the microscopic examination of the coagulum has shown a close similarity in structure with that presented by the gold in auriferous quartz. H. Rose assumed that the colourless glass which becomes ruby-red when reheated contains gold silicate, and that the red colour occurs when the silicate changes to red oxide. Had he said that the red colour is due to the separation of ultra-microscopic particles of gold, many would have agreed with him to-day.


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## § 25. The Silicates of the Alkaline Earths

P. Berthier [1] tried to make a definite silicate by fusing a mixture of lime and silica, and separating the free lime by washing. This method led him to the formula $2CaO.3SiO_2$ for the product; L. E. Rivot, to $2CaO.SiO_2$; and E. Landrin, to $4CaO.3SiO_2$. Assuming that the mixture was completely fused, the anhydrous basic silicates are partially decomposed by water, and the hydrated silicates are progressively decomposed by the washing with water. N. G. Sefström heated various mixtures of quartz and marble in carbon crucibles in a blast furnace, and obtained products which were represented by the older chemists as definite calcium silicates — *e.g. calcium orthosilicate*, $2CaO.SiO_2$; *calcium metasilicate*, $CaO.SiO_2$; *calcium sesquisilicate*, $2CaO.3SiO_2$; *calcium mesodisilicate*, $CaO.2SiO_2$; and *calcium paratrisilicate*, $CaO.3SiO_2$—although there was little or no evidence that the products were chemical individuals. Similar remarks apply to the silicates reported by E. Martin—*viz.* $2CaO.5SiO_2$; $8CaO.5SiO_2$; $10CaO.5SiO_2$; $10CaO.5SiO_2.2H_2O$; $13CaO.5SiO_2$; and $2CaO.5SiO_2.3H_2O$. W. S. Patterson and P. F. Summers discussed the effect of additions of alumina, and oxides of copper, zinc, iron, and magnesium on the fusibility of lime silicate slags.

Observations on the fusibility of mixtures of silica and calcium oxide were made by A. Petzholdt, H. Philippi, W. A. Lampadius, P. Berthier, N. G. Sefström, P. Gredt, W. Heldt, G. Oddo, E. Jordis, O. Schott, R. Rieke, and A. J. Rossi.

J. W. Cobb noted that the reaction begins below the m.p. of either component. O. Boudouard observed three maxima and four eutectics on the fusion curve. The maxima corresponded with calcium orthosilicate, calcium metasilicate, and tricalcium silicate. A. L. Day and E. S. Shepherd showed that under normal conditions, combinations are formed at temp. below the m.p. provided the constituents are finely powdered and adequately mixed. They found that silica and calcium carbonate (1 : 1) begin to react at 800°, and the reaction is nearly complete at 1400°; and mixtures of silica and calcium sulphate (between 1 : 3 and 3 : 1) react between 1005° and 1010°. J. A. Hedvall detected signs of a reaction between precipitated silica with calcium oxide at 1000°, and silicate formation at 1400°; and with barium oxide at 900°. E. Tischler found that at a press. of 25 atm. in steam it is not possible to effect the union of eq. proportions of lime and silica, but at 200 atm. very little escapes combination; and the compound formed is $CaSiO_3.2{\cdot}34H_2O$, but the proportion of water varies a little. H. O. Hofman made observations on the temp. of formation; and R. Akerman measured the heats of solidification, $Q$, of some calcium silicate mixtures. If $\theta°$ be the m.p.; $C$ cals., the sp. ht. between 0° and $\theta°$; $L$, the latent heat of fusion, $Q=C\theta+L$. D. Balareff found that the presence of water, and of traces of hydrogen chloride or sulphide vap. favours the reaction between silica and calcium oxide; while air, hydrogen, and carbon dioxide also favour the reaction. It is assumed in some cases that the gas forms a surface skin of, say, sulphide or chloride, which fuses easily and brings the two materials in better contact. In other cases, the surface mols. are loosened by the adsorption of the gas, and the effect is comparable with softening or melting.

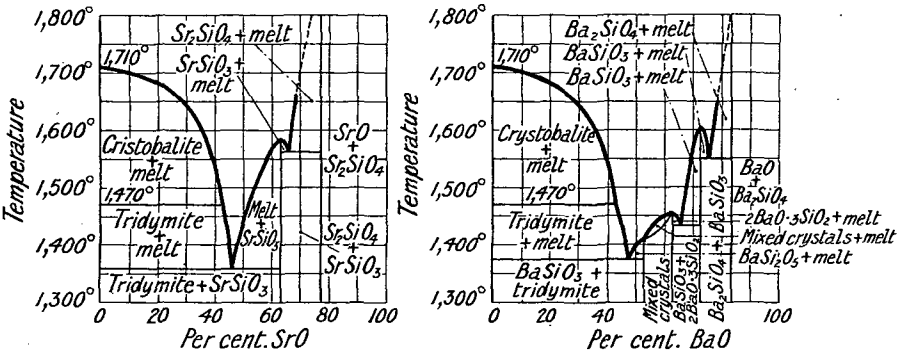
The thermal diagram of mixtures of calcium oxide and silica has been developed by A. L. Day and co-workers, C. Doelter, G. A. Rankin and co-workers, P. Niggli, and J. B. Ferguson and H. E. Merwin. This work is summarized in Fig. 70. Calcium forms at least four definite silicates: the orthosilicate, $Ca_2SiO_4$; the metasilicate, $CaSiO_3$; the orthodisilicate, $Ca_3Si_2O_7$; and the basic silicate, $Ca_3SiO_5$. In addition, the ortho- and meta-silicates exhibit crystalline modifications. The mutual relations of these different compounds are illustrated in the equilibrium diagram, Fig. 70. S. G. Gordon reported the occurrence of the $\alpha CaSiO_3$–$Ca_3Si_2O_7$ eutectic at Spartanburg, S.C. The compositions and temp. of critical points are summarized in Table XIII, where the temp. marked with an asterisk are incongruent m.p., the others are congruent.

TABLE XIII.—COMPOSITIONS AND TEMPERATURES IN THE SYSTEM, $CaO$–$SiO_2$.

| — | — | Per cent. by weight. | | — |
|---|---|---|---|---|
| | | CaO | $SiO_2$ | |
| Eutectic: cristobalite—$\beta CaSiO_3$ | *B* | 37·0 | 63·0 | 1436° |
| Eutectic: $\beta.CaSiO_3$–$Ca_3Si_2O_7$ | *D* | 54·5 | 45·5 | 1455° |
| Invar.: $Cu_3Si_2O_7$–$Ca_2SiO_4$ | *H* | 55·5 | 44·5 | 1475° |
| Eutectic: $Ca_2SiO_4$–CaO | *F* | 67·5 | 32·5 | 2065° |
| $\beta$-$CaSiO_3$ | *C* | 48·2 | 51·8 | 1540° |
| $Ca_3Si_2O_7$ | *H* | 58·2 | 41·8 | 1475° |
| $Ca_2SiO_4$ | *E* | 65·0 | 35·0 | 2130° |
| $Ca_3SiO_5$ | — | 73·6 | 26·4 | 1900° |
| CaO | *G* | 100 | 0 | 2570° |

P. Berthier tested the fusibility of various mixtures of silica with baryta and with strontia. P. Eskola's equilibrium diagrams for strontium and barium oxides with silica are shown in Figs. 69 and 70. The results are summarized in Table XIV. The m.p. in the table are all congruent. Strontium furnishes the orthosilicate, $Sr_2Si_5O_4$, and the metasilicate, $SrSiO_3$, but not in polymorphic forms. Barium also furnishes one form each of the orthosilicate, $Ba_2SiO_4$; the metasilicate, $BaSiO_3$;

the mesodisilicate, $BaSi_2O_3$; and the mesotrisilicate, $Ba_2Si_3O_8$. P. Bary discussed the glassy silicates of the alkaline earths.




FIGS. 69 and 70.—Temperature-Concentration Diagrams of the Binary Systems: SrO–$SiO_2$ and BaO–$SiO_2$.

A number of hydrated calcium silicates have been reported in nature, and some have been prepared artificially. The products obtained by the wet processes are usually variable in composition and have the character of colloids. Near the

TABLE XIV.—COMPOSITIONS AND TEMPERATURES IN THE BINARY SYSTEMS: SrO–$SiO_2$ AND BaO–$SiO_2$.

| | Per cent. by weight. | | m.p. | Per cent. by weight. | | m.p. |
|---|---|---|---|---|---|---|
| | SrO | $SiO_2$ | | BaO | $SiO_2$ | |
| Eutectic: tridymite—RO | 46·5 | 53·5 | 1358° | 47 | 53 | 1374° |
| $RSiO_3$ | 63·2 | 36·8 | 1578° | 71·8 | 28·2 | 1604° |
| $R_2SiO_4$ | 77·5 | 22·5 | — | 83·6 | 16·4 | — |
| $R_2Si_3O_8$ | — | — | — | 62·9 | 37·1 | 1450° |
| Eutectic: $R_2Si_3O_8$—RO | — | — | — | 65 | 35 | 1437° |
| Eutectic: $RSiO_3$—$R_2SiO_4$ | 65·5 | 34·5 | 1545° | 74·5 | 25·5 | 1551° |
| Eutectic: $R_2SiO_4$—RO | — | — | — | — | — | — |

end of the eighteenth century, J. Gadolin,[2] and L. B. G. de Morveau precipitated alkali silicates by a calcium salt, and by treating hydrated silica with calcium hydroxide. J. N. von Fuchs stated that hydrated silica added to lime-water precipitated a white, pulverulent calcium silicate. W. Heldt observed that silicic acid mixed with milk of lime forms a hard mass. E. Landrin stated that gelatinous and dialyzed silicic acid acts on lime-water forming various hydrated calcium silicates which play a rôle in the setting of hydraulic cement. He represented the composition of the precipitate by $4CaO.3SiO_2$; L. E. Rivot, by $2CaO.SiO_2$; and P. Berthier, by $2CaO.3SiO_2$. This subject was studied by H. le Chatelier, who demonstrated that products with a composition between $CaO.10SiO_2$ and $2CaO.SiO_2$ can be obtained by varying the proportions of lime and silica used in their preparation, and by using a sufficient vol. of water in washing, a residue of nearly pure silica can be obtained. E. Jordis found that the action of hydrated silica on a boiling soln. of lime-water gives products of variable composition the mean of which is $0{\cdot}65CaO.SiO_2$. E. Jordis and E. H. Kanter did not obtain homogeneous products by heating silicic acid and calcium hydroxide in the presence of a molar soln. of calcium chloride; and when a soln. of calcium hydroxide, either alone, or in the presence of a calcium salt, and suspended silicic acid, is boiled, the calcium from the hydroxide combines with the silica, and is afterwards removed from the

compound formed, and then again combines with it to a greater extent than before. The anion of the calcium salt plays a part in the reaction. A mixture of calcium oxide or hydroxide and quartz or amorphous silica—kieselguhr—was heated under press.—20–200 atm.—in an autoclave. The tenacity of the product with calcium hydroxide was less than if the mixture with calcium oxide was afterwards hydrated. The tenacity was greater the greater the density of the silica. Quartz reacts most slowly. The maximum tenacity was obtained with $CaO : SiO_2 = 1 : 3$, combination was not complete. With a mixture $CaO : SiO_2 = 1 : 1$, combination was complete at 200 atm. press., and the resulting silicate had the composition $CaO.SiO_2.2{\cdot}34H_2O$ — *vide infra*, hydrated calcium metasilicate. E. Tischer obtained a similar product, and H. le Chatelier said that in the hydration of hydraulic cement, elongated crystals of $CaO.SiO_2.2{\cdot}5H_2O$ are formed by the decomposition of the basic tricalcium silicate: $3CaO.SiO_2+4\frac{1}{2}H_2O=2Ca(OH)_2+CaO.SiO_2.2\frac{1}{2}H_2O$, Fig. 71. When a mixture of milk of lime and a conc. soln. of water-glass is stirred, speedy coagulation occurs, and the mixture "sets," and it becomes crumbly if the stirring is continued. If the soln. be sufficiently dil. a voluminous precipitate of calcium silicate is formed. These phenomena were observed by J. N. von Fuchs, J. M. Ordway, etc.

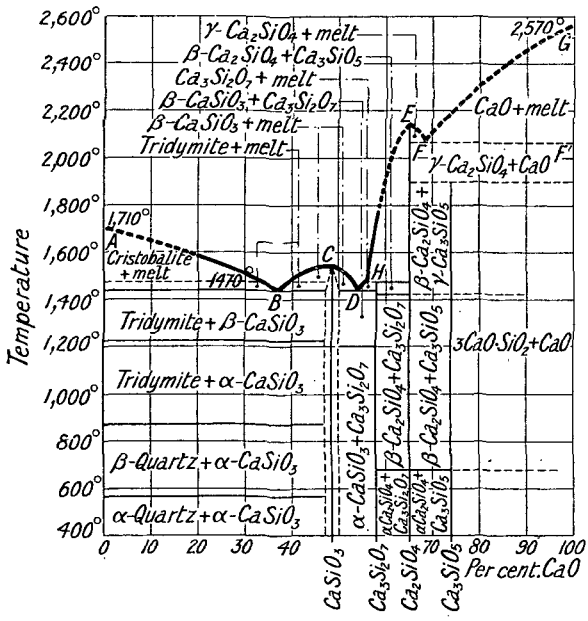



FIG. 71.—Equilibrium Diagram of Binary Mixtures of Calcium Oxide and Silica.

F. Kuhlmann also noted that an aq. soln. of an alkali silicate is decomposed by calcium carbonate, sulphate, or phosphate, forming calcium silicate and an alkali salt. C. G. C. Bischof said that calcium carbonate does not react with hot or cold soln. of alkali silicate; J. von Liebig said that washed chalk adsorbs but a little alkali silicate from a dil. aq. soln. of water-glass; J. M. Ordway, and F. von Kobell noted that calcium carbonate decomposes a hot soln. of water-glass. A. C. Becquerel obtained stalactitic formations of calcium silicate by introducing chalk impregnated with lead or cupric nitrate into a soln. of water-glass of sp. gr. 1·074; and by separating soln. of calcium acetate and potassium silicate by means of a porous membrane, he obtained a deposit of doubly refracting crystals of calcium silicate on the membrane. C. F. Rammelsberg reported the presence of needle-like crystals of hydrated *calcium orthodisilicate*, $3CaO.2SiO_2.H_2O$, or $CaSiO_3.Ca_2SiO_4.H_2O$, from the hearth of a Leblanc soda-ash furnace. W. Heldt reported the formation of the hydrated salts: pentahydrated *calcium tripentitasilicate*, $5CaO.3SiO_2.5H_2O$, by triturating a mixture of calcium hydroxide and a soln. of water-glass; and of trihydrated *calcium paratrisilicate*, $CaO.3SiO_2.3H_2O$, by the action of calcium chloride on a soln. of water-glass. T. J. Pélouze, and J. Weisberg precipitated the silica as calcium silicate from a soln. of an alkali silicate by the addition of calcium chloride; W. Heldt used calcium saccharate as precipitant. E. Jordis and E. H. Kanter could not obtain evidence of the formation

of definite chemical individuals by the action of calcium chloride on aq. soln. of sodium silicate, or by the action of gelatinous silica on lime-water in the presence of calcium chloride. According to A. L. Herrera, when a soln. of potassium silicate, with a sp. gr. of 1·5 or more, and containing potassium carbonate not in excess of a normal soln., is placed inside an unglazed porcelain cup, and the latter placed in calcium chloride soln. of sp. gr. 1·007, after 24 hrs., numerous very fine tubes of calcium silicate are formed on the outside of the porous cup. The surfaces of the films have a number of microscopic cells, and in some cases are formed entirely of cells.

According to H. le Chatelier,[3] crystals of **calcium oxyorthosilicate,** $CaO.Ca_2SiO_4$, or $3CaO.SiO_2$, occurs in hydraulic cement, and the product obtained by calcining the limestone of Teil has very nearly this composition, and it is an excellent hydraulic cement. L. E. Rivot, G. Oddo, and E. Jordis mention this compound; while A. L. Day and E. S. Shepherd say that no one has isolated a definite homogeneous compound of the composition, $3CaO.SiO_2$; and attempts to make it by fusing the constituents together furnish mixtures with ill-defined optical qualities. G. A. Rankin and F. E. Wright found that the compound is unstable at its m.p., and it does not occur in contact with the melt in the binary system, Fig. 71, so that it does not occur as a primary base at any point of the liquidus curve. It does, however, occur as a primary base within the ternary system, $CaO–Al_2O_3–SiO_2$. In the formation of the compound from the mixed oxides at 1400°–1500°, the orthosilicate is first produced, and this, on longer heating, unites with free lime to produce the basic orthosilicate. It dissociates at 1900° ± 20°, forming CaO and the orthosilicate; this temp. is below that of the eutectic, 2065°, between calcium oxide and calcium orthosilicate. The basic silicate occurs in small, colourless grains about 0·3 mm. long which are apparently without cleavage; the refractive index approximates 1·715, and the birefringence is weak, not over 0·005. The grains appear to be uniaxial or biaxial with a small optic axial angle. The optical character is negative. Fine twinning lamellæ, with low extinction angles, occur on some of the grains, indicating that the crystal system is possibly monoclinic. H. le Chatelier suggested that the oxyorthosilicate and the orthosilicate are isomorphous.

**The anhydrous orthosilicates.**—N. G. Sefström could not fuse a mixture of two molar proportions of calcium carbonate with one molar proportion of silica in the furnaces available in his day; but G. Oddo fused the mixture in an electric furnace, and obtained a porcelain-like mass. G. Stein, H. Hanemann, W. Pukall, and V. Pöschl made observations on this subject. E. Kittl noticed that during crystallization there are 190,000 centres of crystallization per sq. cm. H. le Chatelier, C. Zulkowsky, E. Jordis, etc., noted the occurrence of crystals of **calcium orthosilicate,** $2CaO.SiO_2$, or $Ca_2SiO_4$, in the clinker of portland cement. A. Meyer, C. Zulkowsky, and P. Rohland suggest that two isomeric forms occur in portland cement; and the latter symbolized these hypothetical isomers:



A. Gorgeu found the orthosilicate among the products of the action of steam on a mixture of silica and calcium chloride at a high temp. F. de Lalande and M. Prud'homme, and W. Löwenstein obtained this compound by the action of heat on various mixtures of silica, lime, and calcium chloride. J. H. L. Vogt also found crystals of the orthosilicate in blast furnace slags. To emphasize its relation to the orthosilicates of the magnesium family, calcium orthosilicate is sometimes called *limeolivine*. D. A. Tschernobajeff and S. P. Wologdine estimated the heat of formation of $2CaO.SiO_2$ to be 28·7 Cals.

According to A. L. Day and co-workers, the individuality of calcium orthosilicate is established by its appearance as a maximum, corresponding with a m.p. of 2080° on the equilibrium diagram, Fig. 71, and by the optical properties of the product. It crystallizes in three, possibly four, distinct forms. The α-form

here described is that designated the $\gamma$-form by A. L. Day and co-workers, while the $\gamma$-form here described is A. L. Day's $\alpha$-form. The alteration is made in accord with general usage, where the form stable at the low temp. is called the $\alpha$-variety. The $\gamma$-calcium orthosilicate is stable between 1410° and the m.p.; $\beta$-calcium orthosilicate is stable between 675° and 1410°; and $\alpha$-calcium orthosilicate is stable below 675°. $\beta'$-calcium orthosilicate is a monotropic, unstable form. G. A. Rankin and co-workers give $1420° \pm 2°$ for the higher transition temp. of the $\gamma$- to the $\beta$-form. The changes are reversible so that they also give $2130° \pm 20°$ for the

$$\alpha\text{-}Ca_2SiO_4 \overset{675°}{\rightleftharpoons} \beta\text{-}Ca_2SiO_4 \overset{1420°}{\rightleftharpoons} \gamma\text{-}Ca_2SiO_4$$

m.p. of the $\gamma$-form; while A. L. Day and co-workers gave 2080°. O. Boudouard gave 1420° for the m.p. of the orthosilicate; R. Rieke, 1435°; and H. Philippi, 1450°. The different forms can be obtained in a metastable state at ordinary temp. by rapid cooling. As a result of the quenching, the transformations are checked for considerable intervals of time. R. Lorenz and W. Herz studied the relation between the m.p. and the transition temp.

The transformation of the $\beta$- to the $\alpha$-form, in cooling, is attended by an expansion of about 10 per cent. This shatters the product to fine dust. The phenomenon is sometimes observed in the manufacture of portland cement, and is known as *dusting*. The phenomenon occurs with calcareous blast furnace slags. For this reason the form stable at ordinary temp., **$\alpha$-calcium orthosilicate,** appears as a fine, colourless, transparent dust, prismatic in habit, with reflect cleavage along the prism axis. It usually extinguishes parallel to the direction of elongation, but occasionally there are indications of twinned forms with a small extinction angle, 3°. The sp. gr. is 2·97. The refractive indices are $\alpha = 1·640 \pm 0·003$, $\beta = 1·645 \pm 0·003$, and $\gamma = 1·654 \pm 0·003$. The birefringence is medium, being about 0·014. The optic axial angle is 52°. The plane of the optic axes in contradistinction to the $\beta$- and $\gamma$-forms, is perpendicular to the prism axis or the direction of cleavage.

The colourless, transparent crystallites of **$\beta$-calcium orthosilicate** are prismatic; they have a cleavage parallel to the prism axis, and probably belong to the rhombic system. The sp. gr. is near 3·27. The least ellipsoidal axis is parallel to the prism axis, and the optic axial angle is very large. Twinning is absent, and the extinction is parallel. The refractive indices are large $\alpha = 1·722 \pm 0·003$, and $\gamma = 1·733 \pm 0·003$. The birefringence is medium, being about 0·01. The progressive paramorphic change of the $\beta$- to the $\alpha$-form can be followed under the microscope. Soon after cooling, irregular interference colours appear as though induced by internal strains, and soon the mass resembles a crystalline aggregate of minute fibres. Towards the end of the process and, for the reason stated above, the larger masses usually disintegrate as fine powder. An unstable form, called **$\beta'$-calcium orthosilicate,** was once obtained by quenching an old hydrated sample from 1415°; it could not be obtained from fresh samples. It appears as fine colourless equant grains without visible cleavage. The average refractive index is very nearly the same as that of calcium oxyorthosilicate, being about 1·715, and the birefringence is very weak. Interference figures were difficult to obtain because of the fine granularity, and the weak birefringence; but the optic axial angle appears to be small or zero, and the optical character positive. The last characteristic distinguishes the $\beta'$-form from calcium oxyorthosilicate. This form appears to be monotropic, but the evidence of its existence cannot be regarded as conclusive.

Like $\beta$-$Ca_2SiO_4$, **$\gamma$-calcium orthosilicate** shows prismatic development with a good cleavage parallel with the prism axis. The crystals occur in irregular grains so intricately interwoven and twinned that a satisfactory measurement of the optical constants is difficult. Twinning is a characteristic feature and is often extremely complex. Different sets of the twinning lamellæ occur intersecting at various angles, and together form an interpenetrating mass not unlike microcline or leucite. Occasionally, in a thin plate, only one set of polysynthetic twinning

lamellæ is present, and resembles a section of plagioclase twinned after the albite law. Extinction angles were noted as high as 18°, though smaller angles appear more frequently. The crystals are either monoclinic or triclinic—probably the former. The sp. gr. is near 3·27; and the hardness between 5 and 6. The refractive indices are approximately $\alpha=1{\cdot}714\pm0{\cdot}003$, $\beta=1{\cdot}720\pm0{\cdot}004$, and $\gamma=1{\cdot}737\pm0{\cdot}003$; the birefringence is about 0·02; and the optical character is positive. The optic angle is about 180°, and the plane of the optic axes is nearly parallel with the direction of elongation of the crystals.

The $\alpha$-form is readily distinguished from $\beta$- and $\gamma$-forms by its low refractive index, its optical character, optic axial angle, and the position of the plane of the optic axis to the prism axis; while the $\beta$-form is distinguished from the $\gamma$-form by the absence of twinning and the parallel extinction. H. le Chatelier found that calcium orthosilicate is readily decomposed by hot or cold, dil. or conc. soln. of ammonium salts. The action of acids is still more rapid. The decomposition by carbonic acid is much faster than is the case with the metasilicate. Hot or cold water has no appreciable action; and only a small proportion was dissolved after a month's action.

R. Kirwan,[4] L. N. Vauquelin, and O. Bourgeois obtained glasses by fusing together mixtures of strontia and silica. G. Stein melted two mols of strontia and one mol of silica in a carbon tube and obtained only the metasilicate and carbide, but when a porcelain tube was employed, large, doubly-refracting, biaxial crystals of **strontium orthosilicate,** $Sr_2SiO_4$, were obtained. The sp. gr. is 3·84, and he gave for the m.p. 1593°. If cooled rapidly, a glass is produced. The diagram, Fig. 69, indicates the region of stability of strontium orthosilicate; its m.p. was found by P. Eskola to be above the range of the platinum resistance furnace. G. Stein gave 1593° for the m.p. No evidence of polymorphic forms was obtained by heating the crystals between 990° and 1634°; by slow cooling; or by melting with strontium chloride. The salt did not show the phenomenon of dusting exhibited by the calcium salt. The indices of refraction with the *F*-ray, Tl-ray, *D*-ray, and the *C*-ray were respectively $\alpha=1{\cdot}740$, 1·7325, 1·7275, and 1·722; $\beta=1{\cdot}744$, 1·737, 1·732, and 1·727; and $\gamma=1{\cdot}766$, 1·760, 1·756, and 1·752. The optic axial angle $2E=58°$, and $2V=32°\ 30'$. The optical character is positive. The twinning of many crystals on the (100)-plane was observed. The crystals are thought to be monoclinic—or possibly rhombic. W. Pukall made some observations on strontium orthosilicate.

R. Kirwan, B. Kerl, and G. Wagener obtained glasses by fusing together mixtures of baryta and silica. C. L. Bloxam studied the expulsion of water from barium hydroxide by heating it with silica. A. Mitscherlich noted that much heat is evolved when silica is dissolved in baryta at a white heat. The crystalline product is readily soluble in hydrochloric acid. G. Stein, by the above-named process, obtained only the metasilicate. H. le Chatelier did not make **barium orthosilicate,** $Ba_2SiO_4$, but obtained a sintered mass with a crystalline structure by heating the necessary components in a wind-furnace. The product when treated with water decomposed into barium hydroxide and the hydrated metasilicate. E. Jordis said that it is doubtful if the barium orthosilicate so produced is a homogeneous individual. W. Pukall made some observations on barium orthosilicate. The diagram, Fig. 70, indicates the region of stability of barium orthosilicate; and its m.p. was found by P. Eskola to be higher than that of platinum. F. M. Jäger and H. S. van Klooster said the m.p. exceeds 1750°. The crystals were found by P. Eskola to be in the form of rounded grains, and they did not show any cleavages or twinning. The indices of refraction for the *D*-ray were $\alpha=1{\cdot}810\pm0{\cdot}005$, and $\gamma=1{\cdot}830\pm0{\cdot}005$. Both H. le Chatelier and E. Jordis failed to prepare the orthosilicate by wet processes. F. Pisani reported $3BaO.2SiO_2.2H_2O$, but he made a mistake in the calculation of his results; his product was probably the hexahydrated *metasilicate* (*q.v.*).

**The anhydrous metasilicates.**—The most important of the calcium silicates occurring in nature is **calcium metasilicate,** $CaSiO_3$, known as the mineral **wollas-**

**tonite.** This name was applied in honour of W. H. Wollaston, and, according to C. C. von Leonhard,[5] it was catalogued by S. Léman as a specimen found at Capo di Bove, near Rome, and it was supposed to be different from the ordinary tabular spar. In 1793, A. Stütz first described the mineral as *tabular spar*, and A. Estner used the same term in 1797. M. H. Klaproth analyzed it in 1802. D. L. G. Karsten called it *grammite*, and A. G. Werner, *Schalstein*. R. J. Haüy first called it *spath en tables*, but later he called it **wollastonite**, a term used at the present day.

Wollastonite is rarely found in eruptive rocks, but is commonly found as a product of contact metamorphism, more particularly in granular limestones. It occurs in felspathic schists, basalts, etc.; and A. Lacroix found wollastonite associated with aplite. F. A. Walchner, F. Koch, and J. H. L. Vogt described the occurrence of the crystals in blast furnace slags, and in volcanic lavas. A. Gurlt, F. Koch, F. Fouqué, J. Morozewicz, etc., L. Appert and J. Henrivaux found wollastonite crystals in devitrifying glass. R. Brenosa showed that the devitrification product is possibly a tetragonal modification, and he found it in the obsidian glass in a tunnel at Pisona. He proposed to call the natural tetragonal form *bourgeoisite*. C. Vélain reported wollastonite in the slag formed during the burning of some corn-stacks. G. vom Rath described its occurrence at Kaiserstuhl, and P. Platz, at Bellenwald in Baden; C. W. C. Fuchs, P. Platz, P. Groth, and A. Streng, at Auerbach in Hessen; P. Platz, at Pfaffenruth, and F. Sandberger, at Schweinheim and Gailbach in Bavaria; A. Frenzel, at Lengefeld and Berggieshübel in Saxony; E. Leisner, and E. Schuhmacher, at Geppersdorf, and H. Traube, at Neudeck in Silesia; F. Katzer, at Humpoletz in Bohemia; V. R. von Zepharovich, at Blunda in Mähren; K. F. Peters, F. Hessenberg, F. Sandberger, L. S. Szathmary, and V. R. von Zepharovich, at Rezbanya and Cziklova in Hungary; G. vom Rath, A. d'Achiardi, L. Busatti, G. Strüver, A. des Cloizeaux, F. von Kobell, T. Monticelli and N. Covelli, A. Scacchi, B. Mierisch, and P. Grosser, in Elba, Sardinia, Bracciano, Capo di Bovo, and Vesuvius in Italy; F. Fouqué, K. von Seebach, F. Hessenberg, and A. Michel-Lévy and A. Lacroix, in Santorin, Greece; A. Piquet, and G. A. Kenngott, at Merida in Spain; A. Lacroix, and C. W. Cross, at Argentières and Roguedas in France; R. P. Greg and W. G. Lettsom, at Dunmore Head in Ireland, and near Aberdeen in Scotland; A. Erdmann, P. Groth, A. E. Törnebohm, F. von Kobell, W. Hisinger, G. A. Kenngott, and G. Forchhammer, at Gökum, Wetternsee, Ålnö, etc., in Sweden; A. E. Nordenskjöld, and F. J. Wiik, in Finland; A. des Cloizeaux, A. Lagorio, and N. von Kokscharoff, at Wilna, Kasbek, etc., in Russia; H. Wulf, O. Mügge, and G. Gürich, in Damaraland, Namaqualand, and Massaland, Africa; L. Hundeshagen, in Sumatra; A. K. Coomaraswamy, in Ceylon; T. Wada, in Japan; G. C. Hoffmann, at Grenville, North Burgess, etc., in Canada; and L. Vanuxem, H. Seybert, J. D. Whitney, J. D. Dana, E. A. Schneider, J. F. Williams, etc., in Bucks County, Willsborough Diana, Bonaparte Lake, etc., in the United States. The mineral *wilnite* (or vilnite) from Wilna (or Vilna) was shown by A. des Cloizeaux to be wollastonite. The calcium trisilicate, $2CaO.3SiO_2$, found at Ædelfors, and Gjellebäk (Norway), by W. Hisinger, and named *ædelforsite*, was shown by G. Forchhammer to be wollastonite contaminated with quartz, felspar, garnet, and sometimes with calcium carbonate. Analyses have been made by C. F. Rammelsberg, R. Brandes, F. S. Beudant, M. H. Klaproth, H. Traube, J. Loczka, F. Stromeyer, H. St. C. Deville, J. Lemberg, F. von Kobell, A. Funaro, G. vom Rath, A. von Reis, F. Fouqué, A. Piquet, M. F. Heddle, C. E. Weidling, W. Hisinger, H. Rose, O. Widman, L. C. Beck, P. A. von Bonsdorff, N. von Kokscharoff, H. Wulf, L. Vanuxem, H. Seybert, J. D. Whitney, J. H. L. Vogt, W. Hampe, G. Tschermak, E. Manasse, A. d'Achiardi, F. Zambonini, C. Doelter, P. P. Sustchinsky, T. Wada, L. Hundeshagen, A. K. Coomaraswamy, E. A. Schneider, J. F. Williams, L. S. Szathmary, etc. *Vide* laumontite.

F. Zambonini [6] described a pale blue mineral from Vesuvius, found in loose nodules, which he called *rivaite*—after C. Riva. Its composition approximated $(Ca,Na_2)Si_2O_5$. The sp. gr. was 2·55–2·56; and the hardness 5. The birefringence was weak. N. L. Bowen showed, however, that rivaite is heterogeneous, being wollastonite embedded in a blue glass. The same remark applies to the so-called *reaumurite*.

Calcium metasilicate exists in at least two forms—natural wollastonite, which is monoclinic, and artificial **pseudowollastonite**, which is pseudohexagonal. Both forms can be prepared artificially. The two forms are sometimes mistaken for one another, and although wollastonite has been frequently reported in slags and glasses—*vide supra*—J. H. L. Vogt,[7] and P. Heberdey said that it is rarely found in slags, while pseudowollastonite is common. According to J. H. L. Vogt, the synthetic wollastonite prepared by B. Mauritz, and L. S. Szathmary was really pseudowollastonite. According to E. T. Allen and W. P. White, wollastonite is

stable only below 1190°, and above that temp. it passes into pseudowollastonite. By heating a glass of the composition $CaSiO_3$ between 800° and 1000°, crystals of wollastonite were formed. The conversion of pseudowollastonite to wollastonite was effected by dissolving the former in molten calcium vanadate and crystallizing between 800° and 900°. The fact that pseudowollastonite does not occur in nature is taken to show that rocks containing free calcium metasilicate must have crystallized at temp. below the inversion point of wollastonite. Pseudowollastonite has also been called α-wollastonite, and the ordinary form β-wollastonite; but since in other cases of allotropism, the α-form is the variety stable at a low temp., pseudowollastonite is designated β-$CaSiO_3$, *i.e.* β-**wollastonite,** in Fig. 72, and wollastonite, α-$CaSiO_3$, *i.e.* α-**wollastonite.**

N. G. Sefström obtained a vitreous mass mixed with acicular crystals by melting a mixture of equimolar proportions of quartz and marble. H. Lechartier melted a mixture of silica, lime, and calcium chloride and obtained what he regarded as crystals of wollastonite; and A. Gorgeu obtained similar crystals by heating a mixture of silica, and calcium oxide and chloride in a current of steam. J. H. L. Vogt, however, showed that the alleged wollastonite was probably the pseudo-variety. L. Bourgeois melted equimolar parts of lime and silica in a platinum crucible; the cooled mass was then slowly heated nearly to the m.p., and needle-like crystals appeared near the walls of the crucible. By heating the mass for two days, needle-like crystals 2–3 mm. long and 0·1 mm. thick were obtained. E. Hussak obtained wollastonite by fusing and slowly cooling a glass containing silica, lime, soda, and boric oxide—say, a mixture of sodium metasilicate and calcium borate. The crystals appear to be formed best in the presence of an *agent minéralizateur—e.g.* boric oxide (E. Hussak), sodium or calcium fluoride (C. Doelter, B. Karndéeff, and F. Tursky), calcium chloride (H. Lechartier, and A. Gorgeu), and calcium vanadate (E. T. Allen and W. P. White). G. Oddo, H. le Chatelier, G. Tschermak, and G. Stein made crystals of pseudowollastonite from a molten mixture of lime and silica. The formation of pseudowollastonite in slags has also been discussed by F. Koch, C. Schnabel, J. F. L. Hausmann, L. Bourgeois, P. Heberdey, C. Doelter, J. H. L. Vogt, etc. G. V. Wilson observed the formation of crystals of wollastonite, but not pseudowollastonite, in glasses. W. Löwenstein noted the formation of calcium metasilicate when silica is dissolved in molten calcium chloride—*vide* silica. A. Daubrée claimed to have made wollastonite in microscopic needles by the action of superheated steam on a glass tube, but J. H. L. Vogt contested this statement. C. Doelter, however, heated a mixture of calcium carbonate and silicic acid in a sealed iron tube at 400°–425°. It was not possible to isolate the product from the excess of silica, but the monoclinic crystals closely resembled those of wollastonite. The genesis of wollastonite in nature has been discussed by U. Grubenmann, G. Spezia, V. M. Goldschmidt, C. Doelter, etc.

Wollastonite occurs in white, grey, yellow, or brown tabular crystals which are monoclinic prisms. P. Groth [8] gives for the axial ratios $a : b : c = 1·0523 : 1 : 0·9694$, and $\beta = 95° 24\frac{1}{2}'$. Measurements of the crystals of native wollastonite were made by R. J. Haüy, W. Phillips, F. Mohs, H. J. Brooke, F. von Kobell, J. F. L. Hausmann, A. des Cloizeaux, H. Rose, A. Michel-Lévy and A. Lacroix, G. vom Rath, C. F. Rammelsberg, A. Funaro and L. Buzatti, N. von Kokscharoff, F. Hessenberg, etc. Fig. 72 represents the crystals from Diana, measured by J. D. Dana, with *c* (001), *a* (100), *v* (101), *t* (101), and *h* (540). According to E. T. Allen and W. P. White, the lath-shaped crystals of artificial wollastonite often present the same arrangement of divergent fibres as is given by natural wollastonite, and the two kinds are similar in every respect. The crystals often show perfect cleavage cracks parallel to the long direction. The crystals of pseudowollastonite appear in the form of small irregular grains often tabular in shape; in short prisms; or else as fibres arranged in parallel or divergent groups. C. Doelter, and J. H. L. Vogt

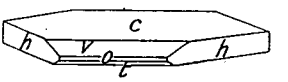


FIG. 72.—Wollastonite from Diana.

consider the crystals of pseudowollastonite to be hexagonal. L. Bourgeois, A. L. Day and co-workers, and E. T. Allen and W. P. White have shown that the crystals are pseudohexagonal, and are probably monoclinic. The crystals often show distinct and repeated twinning lamellæ parallel to the basal pinacoid and with an extinction angle of 2°. E. Kittl measured the rate of crystallization of wollastonite and found a curve, Fig. 73, with a sharp maximum at the most favourable temp. The maximum is about 20° below the temp. at which crystallization begins. He estimated that during crystallization there are 330 crystallization centres per sq. cm.

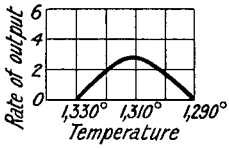



FIG. 73.—Effect of Temperature on the Speed of Crystallization.

H. Traube gave 2·81 for the sp. gr. of wollastonite; C. F. Peters, 2·919; A. Funaro and L. Buzatti, 2·7–2·8; and A. Piquet, 2·80. E. T. Allen and W. P. White found the sp. gr. of fibrous wollastonite made by the devitrification of glass to be 2·915 at 25°/25°, and the sp. gr. of the glass, 2·904, at 25°/25°; and the sp. gr. of the crystals from calcium vanadate, 2·913 at 25°/25°; the sp. gr. of pseudowollastonite under similar conditions was 2·912, so that the differences observed might be attributed to experimental error. R. C. Wallace found the sp. gr. of pseudowollastonite to be 2·91 at 18°, and the mol. vol., 40. J. H. L. Vogt gave 2:86 for the sp. gr. of pseudowollastonite, and C. Doelter, 2·88–2·90. P. Lebedew found the sp. gr. of pseudowollastonite to be 2·88, and the hardness 3·5. The hardness of wollastonite is 4–5. The coeff. of thermal expansion of the glass calculated by A. Winklemann and O. Schott's rule [9] is 0·000028. A. Brun gave 1366° for the m.p. of wollastonite crystals from Auerbach. O. Boudouard gave 1440° for the m.p. of the metasilicate, and O. Schott, 1300° (1450°); A. S. Ginsberg, and S. Smolensky, 1512°; E. Rieke, 1525°; H. Philippi, 1515°; and N. V. Kultascheff, >1400°. A. L. Fletcher, 1253°–1258°; and C. Doelter, 1240°–1265° for the m.p. of the crystals, from Auerbach; 1245°–1265° for those from Cziklowa; 1250°–1300° for those from Diana; 1235°–1275° for those from Elba; and 1260°–1325° for those from Kimito—the first number represents the temp. at which fusion begins, the last number the temp. at which the silicate is fluid. E. T. Allen and W. P. White, A. L. Day and E. S. Shepherd, and J. P. Lebedew gave 1512° for the m.p. of pseudowollastonite; G. A. Rankin and F. E. Wright gave 1540° ± 2°. R. C. Wallace found the crystallization of the molten mass begins at 1502°. R. Lorenz and W. Herz studied the relation between the m.p. and the transition temp. H. Kopp gave 0·178 for the sp. ht. of wollastonite between 19° and 51°; and W. P. White gave:

| | 100° | 500° | 700° | 900° | 1100° | 1300° |
|---|---|---|---|---|---|---|
| Pseudowollastonite . . | — | 0·2164 | — | — | 0·2377 | 0·2419 |
| Wollastonite . . . | 0·1833 | 0·2174 | 0·2287 | 0·2354 | 0·2403 | — |

D. A. Tschernobajeff and S. P. Wologdine gave for the heat of formation, $(CaO,SiO_2)$ =17·4 Cals; and H. le Chatelier gave $CaO+SiO_2=CaSiO_3+33·1$ Cals. The transition temp. of the enantiomorphic forms is given as 1180° by E. T. Allen and W. P. White, while G. A. Rankin and F. E. Wright gave 1200°, which is lowered to 1190° by the dissolution of 2 per cent. of calcium oxide, and raised to 1210° by the dissolution of 2 per cent. of silica.

E. Mallard [10] found the indices of refraction of a sample of wollastonite from Pargas (Finland), to be $\alpha=1·619$, $\beta=1·632$, and $\gamma=1·634$; and A. Michel-Lévy and A. Lacroix, one from Cziklova (Hungary), $\alpha=1·621$, $\beta=1·633$, and $\gamma=1·635$. For artificial or $\alpha$-wollastonite, E. T. Allen and W. P. White, and G. A. Rankin and F. E. Wright found with sodium light $\alpha=1·616\pm0·002$, $\beta=1·629\pm0·002$, and $\gamma=1·631\pm0·002$; likewise for pseudowollastonite or $\beta$-wollastonite, $\alpha=1·610\pm0·002$, and $\gamma=1·654\pm0·002$. The birefringence of $\alpha$-wollastonite is medium, $\gamma-\alpha=0·015$; that of $\beta$-wollastonite is strong, $\gamma-\alpha=0·041$; the extinction of $\alpha$-wollastonite is parallel to the elongation. The optical character of $\alpha$-wollastonite is negative, that of $\beta$-wollastonite positive. The optical axial angle of

α-wollastonite is about 70° ; and that of β-wollastonite is small being nearly uniaxial. A. des Cloizeaux found 70° 40′ for the optic axial angle of wollastonite with red light, 69° with green light, and 68° 24′ with violet light. He also found that an optic axial angle 73° 32′ at 17° became 73° 4′ at 126°. W. F. Hillebrand found some samples give a greenish-yellow thermoluminescence. K. Przibram studied the colour changes and the luminescence produced by radium rays. F. Farup and co-workers investigated the electrical conductivity of fused calcium silicates.

Wollastonite is soluble in hydrochloric acid, and gelatinous silica separates from the soln. The reaction was studied by G. Rose, and G. Tschermak. A. Gorgeu said that boiling hydrochloric acid completely decomposes the mineral ; and with the dil. acid a part of the silica remains pulverulent and soluble in a soln. of sodium carbonate —the more conc. the acid the less residual silica. Cold dil. acetic acid does not appreciably affect the mineral. According to W. Flight,[11] a conc. soln. of sodium hydroxide attacks wollastonite, and lime and silica pass into soln. in the same proportions as they are present in the mineral. J. Lemberg found that when wollastonite is treated with a soln. of magnesium sulphate or chloride, wollastonite is transformed into a hydrated magnesium silicate. He also studied the exchange of bases with soln. of sodium and potassium silicates, and potassium aluminate. A. Gorgeu said that 0·01 grm. of wollastonite dissolves in about a litre of water. G. A. Kenngott observed that powdered wollastonite before and after calcination, reacts strongly alkaline to red litmus. A. Gorgeu found water sat. with carbon dioxide acts slowly on wollastonite ; and C. Matignon and G. Marchal examined the corrosive action of water on wollastonite in the presence of carbon dioxide under ten atm. press. during 3 years. A. Gorgeu noted the solubility of wollastonite in fused calcium chloride from which it separates in fine crystals—*vide supra* in connection with the synthesis of wollastonite. According to G. E. Rankin and F. E. Wright, pseudowollastonite can take up 2 per cent. of lime or silica in solid soln. C. Doelter found that calcium metasilicate can dissolve 13 per cent. of silica. P. Lebedeff measured the f.p. of mixtures of calcium metasilicate and calcium sulphide. The corrosive action of the latter prevented experiments with mixtures containing over 50 per cent. of calcium sulphide. The curves are shown in Fig. 74. The solid soln. undergo a transformation at temp. below their f.p., the transformation curve having a maximum at about 1300° and 20 mol. per cent. of calcium sulphide. Rapidly cooled mixtures disintegrate completely when cold, whilst slowly cooled mixtures show, when examined microscopically, separate crystals of the pseudowollastonite and of calcium sulphide identical with the *oldhamite*, CaS, found by N. S. Maskelyne, W. Flight, C. Friedheim, E. Cohen, G. Hinrichs, and J. van Laar in meteorites. W. S. Patterson and P. F. Summers found that alumina and magnesia decreased, while ferric oxide increased, the fluidity of fused calcium monosilicate ; while zinc oxide at first increased and then decreased the fluidity. O. Schott, and C. Zulkowsky discussed the hydration of calcium metasilicate contained in portland cement. H. le Chatelier found that when mixed with water charged with carbon dioxide, and left in an atm. of carbon dioxide, calcium metasilicate sets to a hard mass ; E. Landrin based on this fact an hypothesis on the setting of cements. On the other hand, when finely powdered and left for several days in water, in soln. of ammonium salts, or in lime-water, the silicate does not change, and this is taken to show that it cannot take part in the normal hardening of cements. W. Suida noted that wollastonite is feebly stained by basic aniline dyes. H. Hanemann said that molten cast iron reduces calcium metasilicate to silicon. N. G. Chatterji and N. R. Dhar found that calcium silicate is not peptized by a conc. soln. of cane sugar.

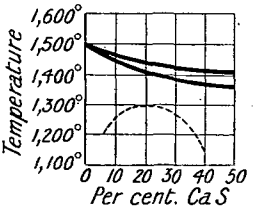



FIG. 74.—Freezing Curves of Mixtures of Calcium Metasilicate and Sulphide.

G. Stein[12] prepared **strontium metasilicate,** $SrSiO_3$, by melting equimolar

parts of strontia and silica in a carbon tube. When quickly cooled, doubly refracting granules are obtained; and with slow cooling prismatic crystals are formed. The glass was not produced—*vide* the orthosilicate. P. Eskola found the zone of stability of strontium metasilicate indicated in Fig. 69. Attempts were made to prepare polymorphic forms analogous with those of the calcium salt by holding the glass at 1020°; by melting with strontium chloride, and with strontium vanadate, but without success. F. M. Jäger and H. S. van Klooster also obtained only one form with sodium tungstate as a flux. Strontium metasilicate furnishes one form which closely resembles pseudowollastonite, or $\beta$-$CaSiO_3$. The crystals are pseudohexagonal, uniaxial and positive, and the characteristic habit is tabular parallel to (0001)-face. On account of the resemblance to an isomorphism with $\beta$-$CaSiO_3$, the crystals might be supposed monoclinic, but decisive evidence was not obtained by P. Eskola, who found the axial ratio for the presumably pseudohexagonal crystals to be $a:c=1:0{\cdot}98$. There is a fairly good basal cleavage. The pyramidal faces of the crystals are striated parallel to the edge with the basal plane; and most of the crystals are twinned on the base. G. Stein found the sp. gr. of the slowly cooled salt to be 3·90, and if rapidly cooled, 3·89; F. M. Jäger and H. S. van Klooster gave 3·652 at 25·1°/4°; and P. Eskola, 3·650 at 30°/4°, and 3·653 at 25°/4°. G. Stein gave 1287° for the m.p.; R. C. Wallace, 1529°; F. M. Jäger and H. S. van Klooster, 1578°±1°; and P. Eskola, 1580°±4°. The indices of refraction of granular crystals for the *F*-, Tl-, *D*-, and *C*-rays are respectively $\alpha$=1·606, 1·602, 1·599, and 1·596; and $\beta$=1·646, 1·641, 1·637, and 1·634. F. M. Jäger and H. S. van Klooster gave $\alpha$=1·590 and $\beta$=1·620. W. Pukall made some observations on this silicate.

O. Bourgeois made a crystalline mass of **barium metasilicate,** $BaSiO_3$, by reheating the product obtained by melting the two constituents. G. Stein made crystals of the compound by a process similar to that which he employed for strontium metasilicate—*vide* barium orthosilicate. P. Eskola found the zone of stability of barium metasilicate indicated in Fig. 70. Crystals were obtained in the form of rounded globules or short rods with rounded ends having a negative elongation and parallel extinction. The crystals were monoclinic, and no evidence of polymorphic forms was obtained by heating at 1100°, or by fusion with barium vanadate, and F. M. Jäger and H. S. van Klooster obtained only one form by fusion with sodium tungstate. There is a well-developed cleavage parallel to $\alpha\beta$, and sometimes blue interference colours are obtained. The optic axial angles are $2E$=50°, and $2V$=29°. G. Stein found the sp. gr. of the crystals is 3·77, and of the glass 3·74; F. M. Jäger and H. S. van Klooster gave 4·435 at 25°/4°; R. C. Wallace gave 4·44 for the sp. gr. at 18°; and P. Eskola, 4·399 at 4°. R. C. Wallace gave 1490° for the m.p.; G. Stein gave 1368·5°; P. Lebedeff, 1438°; S. Smolensky, 1470°; F. M. Jäger and H. S. van Klooster, 1604°±0·5°; and P. Eskola, 1604°. The m.p. of the metasilicates of the three alkaline earths increases regularly with increasing at. wt. of the metal. P. Eskola found the indices of refraction for the *F*-, Tl-, *D*-, and *C*-rays were respectively $\alpha$=1·682, 1·677, 1·673, and 1·669; $\beta$=1·684, 1·678, 1·674, and 1·670; and $\gamma$=1·688, 1·682, 1·678, and 1·673. The birefringence is very weak. F. M. Jäger and H. S. van Klooster gave $\alpha$=1·670 and $\gamma$=1·667. E. Jordis, and W. Pukall made some observations on this silicate.

**The hydrated calcium silicates.**—F. E. Wright[13] found rhombic, white, or pale green crystals of a radiating fibrous mineral in the Velardena district, Mexico, which he named **hillebrandite**—after W. F. Hillebrand. According to E. T. Allen's analysis, the composition corresponds with **monohydrated calcium orthosilicate,** $Ca_2SiO_4.H_2O$. The mineral occurs in radial fibres possibly rhombic. The sp. gr. is 2·692 at 25°; the hardness 5–6; the indices of refraction $\alpha$=1·605, $\beta$=1·612, and $\gamma$=1·612. The optic axial angle is 60°–80°; and the crystals are optically negative. Water decomposes the mineral; it is attacked by hydrochloric acid; and fuses to a white enamel before the blowpipe. F. W. Clarke suggested that this mineral may really be *calcium dihydroxymetasilicate,* $(CaOH)_2SiO_3$. B. von

Ammon treated a dil. aq. soln. of calcium chloride with an excess of crystallized sodium silicate, and obtained a gelatinous precipitate which was partially decomposed by atm. carbon dioxide. The composition corresponded with a *hydrated calcium metasilicate*. W. Pukall similarly obtained a product with the composition, $CaSiO_3.2{\cdot}39H_2O$. As previously indicated, the calcium silicates prepared in the wet way can be regarded only as arbitrarily selected stages in the progressive hydrolysis of the hydrated silicate, and almost pure silica can be obtained if the washing be prolonged. The washing of the alkali from B. von Ammon's product must therefore be a serious disadvantage. E. Jordis and E. H. Kanter claim to have made **monohydrated calcium metasilicate,** $CaSiO_3.H_2O$, by boiling hydrated silica containing at least 23 per cent. of water, or a 1·8 per cent. sol of silicic acid, and lime-water. The product is indistinctly crystalline. A. Gages said that the monohydrate remains as a residue when the dihydrated disilicate, $CaSi_2O_5.2H_2O$, is treated with a soln. of potassium hydroxide. A. S. Eakle reported a snow-white earthy mineral, the **hemitrihydrated calcium metasilicate**, $CaSiO_3.\frac{3}{2}H_2O$, in the limestone of Crestmore, Cal., and he called the mineral **crestmoreite**. It may be an orthosilicate, $H_2CaSiO_4.\frac{1}{2}H_2O$. The extinction is straight; the elongation, positive; the birefringence, low; the index of refraction, 1·590, or $\alpha=1{\cdot}593$, $\beta=1{\cdot}603$, and $\gamma=1{\cdot}607$. The sp. gr. is 2·22, and the hardness, 3. Crestmoreite is readily decomposed by acids with the separation of some of the silica as hydrogel; and boiling water extracts some calcium. At 200°, 3·27 per cent. of water is evolved, and at 300°, 10·27 per cent. A. S. Eakle found a white fibrous **hemihydrated calcium metasilicate,** $CaSiO_3.\frac{1}{2}H_2O$, in the massive idocrase, at Crestmore, Cal., and he called it **riversideite**. The extinction is straight; the elongation, positive; the refractive indices, $\alpha=1{\cdot}595$, $\beta=1{\cdot}60$, and $\gamma=1{\cdot}603$; the sp. gr. 2·64, and the hardness, 3. It is soluble in hydrochloric acid.

J. Parry and F. E. Wright assigned to a colourless mineral from the Dutoitspan Mine, Kimberley, the name **afwillite**—after A. F. Williams, who discovered it in the mine. The analyses agree closely with $3CaO.2SiO_2.3H_2O$, and since only a small proportion of the water is evolved below 300°, and all is expelled at about 900°, the water is considered to be an integral part of the mineral, and not zeolitic. They consider it to be a basic orthosilicate, $2H_2CaSiO_4.Ca(OH)_2$; but it may also be represented as **trihydrated calcium orthodisilicate,** $Ca_3Si_2O_7.3H_2O$. The monoclinic prismatic crystals have the axial ratios $a:b:c=2{\cdot}097:1:{\cdot}2381$, and $\beta=98°\ 26'$. The corrosion figures with hydrochloric acid on the (001)-face agree with the monoclinic symmetry; the cleavage parallel to the (001)-face is perfect, and that parallel to the (100)-face is noticeable. The sp. gr. is 2·630 at 18°; and the hardness, 4. The optic axial angle $2E=94°\ 08'$ for the Li-line, 96° 05′ for the Na-line; and 96° 18′, 97° 13′, and 100° 28′ for the mercury lines of the respective wave-lengths 578$\mu\mu$, 546$\mu\mu$, and 536$\mu\mu$; while $2V=54°\ 40'$ for the Na-line, and 55° 00′ for the line of wave-length 546$\mu\mu$. The optical character is positive. The refractive indices $\alpha$, $\beta$, and $\gamma$ are respectively 1·6148, 1·6179, and 1·6312 for the helium red line (668$\mu\mu$); 1·6169, 1·6204, and 1·6336 for the Na-line (589$\mu\mu$); and 1·6201, 1·236, and 1·6366 for the mercury green line (546$\mu\mu$). Water has a slow action on the mineral, and the liquid colours red-litmus blue; and phenolphthalein, red. Both sulphuric and hydrochloric acids attack the mineral freely.

E. Jordis obtained **dihydrated calcium metasilicate,** $CaSiO_3.2H_2O$, contaminated with 3 per cent. of acetic acid, by adding hydrated silica to a soln. of calcium acetate sat. with calcium hydroxide; when repeatedly washed with a soln. of potassium hydroxide, the acetic acid is removed, and the monohydrate remains. Some observations on this hydrate were made by W. Heldt, E. Tischler, and others—*vide supra*. H. le Chatelier prepared a hydrated silicate by adding an excess of lime-water to a colloidal soln. of silicic acid. The precipitate is very voluminous, for after complete deposition a gram occupies 2 litres. A certain amount of this was suspended in almost sat. lime-water, and after settling, half the liquor was removed, analyzed, and replaced by water. The operation was repeated a number of times,

and if $a$ grms. represents the total amount of lime removed; and $b$ grms. the quantity of lime in soln. per litre of liquor:

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| $a$ | 0·000 | 0·500 | 0·755 | 0·890 | 0·955 | 0·990 | 1·030 | 1·070 |
| $b$ | 1·000 | 0·510 | 0·270 | 0·140 | 0·085 | 0·065 | 0·053 | 0·052 |

Hence, the conc. of the soln. at first decreased very nearly proportionally with the vol. of water added, showing that the quantity of lime given to the liquid by the precipitate is nearly zero; but when the quantity of lime in the liquor has fallen to 0·052 grm. per litre, the addition of fresh water no longer changes the lime content of the liquor. This shows that in accord with the law of mass action, the hydrolysis of the silicate introduces lime to the liquid. After standing 6 months, in contact with a sat. soln. of lime-water, the composition of the precipitate approximates $1{\cdot}7CaO.SiO_2.Aq.$, although at the moment of precipitation the composition was $1{\cdot}3CaO.SiO_2.Aq.$ By washing the precipitate until the filtrate contains a little more than 0·052 grm. of lime per litre, at which conc. the decomposition of the silicate begins, the product contains $1{\cdot}1CaO.SiO_2.Aq.$ The excess of lime is taken to be adsorbed calcium hydroxide; and, allowing for this, the analysis corresponds with **hemipentahydrated calcium metasilicate,** $CaSiO_3.2\frac{1}{2}H_2O$.

A. Daubrée reported the occurrence of dihydrated calcium metasilicate, $CaSiO_3.2H_2O$, which he called *plombièrite*, as a gelatinous suspension in the waters of the thermal springs at Plombières. It dries to a hard mass on exposure to air. There is some doubt if this is an accurate interpretation of the facts. F. W. Clarke, regarding $Si_2O_7$ as a sexivalent radicle, represents plombièrite by the formula $Ca(Si_2O_7) : (Ca.Si_2O_7.CaH_3)_2+9H_2O$. F. Cornu considers it to be a hydrogel, possibly of wollastonite.

C. Doelter said that wollastonite is formed when the hydrated metasilicate is calcined between 300° and 1100°. B. von Ammon found that the fresh precipitate dissolves in water—perhaps as a peptized colloid. It is decomposed by hydrochloric acid before or after calcination; and if it has been strongly calcined, the separated silica is granular. The precipitate is also decomposed by carbon dioxide.

In 1866, C. F. Rammelsberg [14] described a mineral which he named **xonotlite** because it was obtained from Tetela de Xonotla (Mexico). A similar mineral was obtained by M. F. Heddle from Loch Screden, Isle of Mull (Scotland). C. F. Rammelsberg's analyses agree with **pentitahydrated calcium metasilicate,** $CaSiO_3.\frac{1}{5}H_2O$, and he regards the mineral as a transformation product of wollastonite. A. Lacroix, and P. Groth emphasized the optical and structural resemblance of xonotlite to okenite (*vide infra*). The sp. gr. is 2·710–2·718; that of M. F. Heddle's sample was 2·05; and the hardness, $6\frac{1}{2}$. E. V. Shannon found the mineral at Leesburg, Virginia, is biaxial and positive, with the indices of refraction $\alpha=1{\cdot}583$, $\beta=1{\cdot}583$, and $\gamma=1{\cdot}595$. Hydrochloric acid decomposes the mineral with the separation of gelatinous silica. The *eakleite* described by E. S. Larsen was later shown to be identical with xonotlite. G. M. Schwartz found xonotlite nodules surrounded by a border of diopside. The so-called *natroxonotlite* found by J. F. Williams in the sulphur springs at Magnet Cove, Arkansas, is considered to be a transformation product of wollastonite. The analysis approximates to $RSiO_3.\frac{1}{4}H_2O$, where R represents 0·9Ca and 0·1Na.

J. Dalton,[15] F. Kuhlmann, and B. von Ammon obtained hydrated silicates by the action of strontia or strontium salts on a soln. of water-glass. E. Jordis and E. H. Kanter made **monohydrated strontium metasilicate,** $SrSiO_3.H_2O$, by boiling dialyzed silicic acid with strontium hydroxide, or by the action of silica hydrogel, with at least 23 per cent. of water, on a soln. of strontium hydroxide. It is more stable than the calcium salt and less stable than the barium salt. The white crystalline powder is decomposed by boiling with water, forming an acid silicate; and an acid silicate is produced by mixing strontium hydroxide with silica hydrogel containing less water than has just been indicated. E. W. Prevost, W. Wahl, E. Jordis, and B. von Ammon obtained hydrated products by the action of baryta or of barium salts on a soln. of water-glass. The alkali requires a prolonged washing for its removal. E. Jordis and E. H. Kanter prepared **monohydrated barium metasilicate,**

$BaSiO_3H_2O$, as a white crystalline powder, by a process similar to that employed for the strontium salt.

According to H. le Chatelier, when a soln. of sodium silicate or colloidal silicic acid is treated with baryta-water, a voluminous precipitate is formed. It appears to be amorphous, but is probably crystalline when the crystals are too small to be visible under high magnification. If allowed to stand 24 hrs., the precipitate collects as a thin layer of tabular crystals visible to the naked eye. Comparatively large crystals can be obtained by allowing superposed soln. of sodium silicate and barium hydroxide to mix slowly by diffusion. A prolonged washing decomposes the crystals. At 15°, the decomposition stops when the washing liquor has 0·91 grm. of baryta per litre. The analysis agrees with **hexahydrated barium metasilicate,** $BaSiO_3.6H_2O$. Rather more water was found in some analyses, probably owing to the presence of water occluded by the crystals. H. Bäckström's analyses corresponded with $5H_2O$; W. Wahl's and J. M. van Bemmelen's with $6H_2O$. According to F. Pisani, and H. le Chatelier, the same crystals are produced spontaneously in laboratory bottles of baryta-water at the expense of the silica of the glass. The crystals collect on the sides of the bottle. F. Pisani's formula is wrong owing to an error in his calculation. J. M. van Bemmelen found that a small quantity of baryta converts the hydrosol into the hydrogel, by which baryta is also absorbed. When mol. proportions of silicon dioxide and barium hydroxide are taken, the crystalline hexahydrate separates. E. Jordis found that a homogeneous product is not formed by the action of quartz or silica hydrate on baryta-water. A. Cossa and G. la Valle found that one mol. of the water of crystallization is retained more tenaciously than the remaining five, and, according to W. Wahl, the formula may be $BaH_2SiO_4.5H_2O$, analogous with dioptase, $CuH_2SiO_4$. The dehydrated product can reabsorb some water. The crystals were found by J. M. van Bemmelen to be rhombic bipyramids with axial ratios, according to H. le Chatelier, of $a:b:c=1{\cdot}1723:1:0{\cdot}6628$. The double refraction is weak. The heat of formation from dissolved baryta and gelatinous silica is 4 cals. The salt is decomposed by water; J. M. van Bemmelen said that 100 parts of water at 15° dissolve 0·17 part of the hexahydrate. Washing with hot water removes virtually all the barium. The salt is decomposed by carbon dioxide.

The mineral **okenite,** discovered by A. Breithaupt,[16] was considered by C. F. Rammelsberg to be **dihydrated calcium mesodisilicate,** $CaSi_2O_5.2H_2O$. It may be **monohydrated calcium metasilicate,** $CaSi_2O_6.H_2O$. C. Doelter regarded it as a solid soln. of calcium metasilicate and silicic acid, $CaSiO_3.SiO(OH)_2.nH_2O$. Analyses of okenite were reported by F. von Kobell, J. Lemberg, A. Connell, P. A. Dufrénoy, E. E. Schmid, S. Meunier, T. L. Walker, J. T. Würth, C. von Hauer, O. B. Böggild; S. Haughton, L. Darapsky, etc. It occurs on the island of Disko in Greenland; at Poonah in India; near Rio Putagan in Chili, etc. A sample from Faröe Islands was called *dysclasite*—δύς, difficult; κλάν, to break—by A. Connell; and one from Bordöe, Faröe Islands, was called *bordite* by P. A. Dufrénoy. C. Doelter obtained it by heating in a sealed tube to about 200°, a mixture of calcium oxide or silicate, silicic acid, and carbonic acid. A. de Schulten obtained a product, which he likened to okenite, by heating the precipitate obtained by adding lime-water to a conc. soln. of potassium silicate in a glass tube at 180°–220° for 24 hrs. The analysis, however, showed too little calcium oxide, too much silica, and 5·5 per cent. of alkalies derived in part from the glass containing vessel. E. Jordis also described the synthesis of amorphous okenite. W. Pukall obtained a similar product, $CaSi_2O_5.2\frac{1}{2}H_2O$, by the action of calcium chloride on a soln. of potassium disilicate. A. S. Eakle and A. F. Rogers described the alteration of wiikeite to okenite. F. W. Clarke represented the formula of okenite:

$$\left.\begin{matrix}H_5(Si_2O_7)Ca\\H_5(Si_2O_7)Ca\end{matrix}\right\rangle(Si_2O_7)CaH_2$$

The mineral occurs as a white fibrous or compact aggregate of needle-like crystals belonging, said A. Breithaupt, to the rhombic system. O. B. Böggild assigned the mineral to the triclinic system, and gave for the axial angles $\alpha=122°\ 54'$, $\beta=67°\ 46'$, and $\gamma=50°\ 10'$; and 2·326–2·332 for sp. gr. of the crystals, and 2·325–2·323 for the sp. gr. of the aggregates. A. Breithaupt gave 2·5 for the sp. gr.; A. Connell, 2·362; P. A. Dufrénoy, 2·33; and E. E. Schmid, 2·324. S. Meunier found the sp. gr. to be 1·75 when the mineral was dried at 110°. A. Breithaupt gave 4–5 for the degree of hardness. C. Doelter said that when melted and slowly cooled pseudowollastonite is obtained, hence his hypothesis for the constitution of okenite; E. E. Schmid that okenite lost 2 per cent. of water when confined over conc. sulphuric acid; and on heating the mineral, 2·55 per cent. was lost at 100°; 12·95 per cent. was lost when the mineral sintered; and 13·97 per cent. when the mineral fused. G. Tammann measured the vap. press. of okenite in equilibrium with atm. containing water vap. at the vap. press. $p$ mm.; the vap. press. of the mineral changes continuously. Thus, at 19°:

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| Water | 0·06 | 0·84 | 1·02 | 1·29 | 1·67 | 2·10 | 2·66 | 3·21 | 3·56 per cent. |
| $p$ | 15·72 | 14·55 | 12·48 | 9·11 | 6·05 | 1·23 | 0·39 | 0·11 | — |

As a rule, if definite hydrates are formed there are abrupt changes in the continuity of the curve; usually also hydration and dehydration are reversible; here, if the vap. press. falls below 1 mm., the rehydration does not reach its original value. O. B. Böggild classed okenite as a fibrous zeolite. A. Michel Lévy and A. Lacroix gave for the index of refraction, 1·556; and for the positive birefringence, $\gamma-\alpha=0·0091$. O. B. Böggild gave $\alpha=1·530$, and $\gamma=1·541$, for the indices of refraction, and he found the extinction with single crystals is parallel, and with aggregates, it is oblique up to 34°. The values $\alpha=1·512$, $\beta=1·514$, and $\gamma=1·515$ have been reported. The optic axial angle is large; and the optical character negative. When okenite is heated, water is given off, and the mineral becomes opaque; it finally melts with frothing to an opaque enamel. Hydrochloric acid decomposes the mineral with the separation of gelatinous silica. J. Lemberg studied the replacement of the calcium oxide in okenite by the action of a 10 per cent. soln. of potassium or sodium hydroxide, and by a soln. of sodium silicate at 100°. Between 9 and 10 per cent. of sodium oxide was introduced, and a little potassium oxide. Most of the calcium was replaced by magnesium when the okenite was digested for 15 days at 100° with a soln. of magnesium chloride.

There are a number of other ill-defined hydrated calcium silicates which occur as minerals. The mean of the number of analyses indicated in brackets is given in Table XV. They contain alkalies, magnesia, alumina, and iron oxides in quantities small enough to represent impurities. H. How [17] reported the occurrence of thin white plates of what he called *centrallassite* in the trap-rock of Bay of Fundy, Nova Scotia. W. F. Foshag represented it by the formula $4CaO.7SiO_2.5H_2O$; and H. How, $2CaO.3SiO_2.2H_2O$. The sp. gr. is 2·45–2·46; W. F. Foshag gave 2·51; hardness $2\frac{1}{2}$–4; and indices of refraction, $\alpha=1·535$, $\beta=1·548$, and $\gamma=1·549$. With hydrochloric acid no gelatinous silica is formed. The mineral called *cyanolite* was found in the same locality. The amygdaloid nodules contained an inner bluish mass of cyanolite, a thin outer layer which H. How named *cerinite*, and an intermediate layer of centrallassite. Cyanolite forms a bluish-white amorphous mass of sp. gr. 2·495, which J. D. Dana suggested is a mixture of chalcedony and centrallassite. M. F. Heddle reported a compact, fine-grained, reddish-white mineral which he found near Tobermory, Isle of Mull, and which he called *tobermorite*. Its sp. gr. is 2·423. M. F. Heddle represented its composition by $3(4CaO.H_2O).5SiO_2.10H_2O$; and P. Groth, by $H_2Ca_4(SiO_3)_5.3H_2O$. G. vom Rath found white hexagonal crystals of a mineral which he called *chalcomorphite* in the lava of Nieder-Mendig. The axial ratio was $a:c=1:1·90914$; the sp. gr. 2·51–2·57; and the hardness 5. When treated with hydrochloric acid, it forms gelatinous silica.

T. Anderson found concretions of a radiating lamellar structure near Portree, Isle of Skye, and he called the mineral *gurolite*—*γυρός*, round; and *λίθος*, a stone—W. H. Miller called it **gyrolite**. H. How also reported specimens from Port George, Nova Scotia; F. W. Clarke, and W. T. Schaller, from New Almaden and Fort Point, California; E. Hussak, from Mogy Guassa, Brazil; F. Cornu from Poonah, India; F. N. A. Fleischmann, from Legoniel, Collinard, and Ballyhenry in County Antrim; etc. Other observations were made by R. P. Greg and W. G. Lettsom, M. F. Heddle, A. Lacroix, G. A. Kenngott, and

L. Saemann. Analyses were also made by these observers. They are summarized by the formula $2CaO.3SiO_2.3H_2O$, or $2CaO.3SiO_2.2H_2O$, corresponding with **dihydrated calcium mesotrisilicate,** $Ca_2Si_3O_8.2H_2O$; or **calcium tetrahydrometatrisilicate,** $Ca_2H_4Si_3O_{10}$. F. Cornu gave the formula $4CaO.5(H,K,Na)_2O.6SiO_2$; E. S. Dana, **calcium dihydrotrimetasilicate,** $H_2Ca_2(SiO_3)_3.H_2O$; and F. W. Clarke, $H_4(Si_2O_7)\{Ca(Si_2O_7)CaH_3\}_2$. E. Baur obtained a silicate analogous to gyrolite by heating in an autoclave at 450°, mixtures of water-glass, potassium or sodium aluminate, calcium carbonate, potassium hydrocarbonate, and silica. F. Cornu's experiments in this direction were not successful. According to O. B. Böggild, the crystals of the gyrolite belong to the trigonal system, and have the axial ratio $a:b=1:1{\cdot}9360$. F. Cornu found the sp. gr. of samples from Bohemia to range from 2·343–2·368; from Greenland, from 2·388–2·422; and one from Brazil, 2·420. O. B. Böggild found the sp. gr. of samples from Greenland ranged from 2·383–2·446. The hardness is between 3 and 4. The mineral is colourless or white. *It is optically uniaxial or feebly biaxial. The cleavage is well marked.* When heated, it fuses with swelling and forms a white glass. F. Cornu found the index of refraction of a number of samples, the ordinary ray to be between 1·445 and 1·548, and E. Baur gave $\omega=1{\cdot}529$, $\epsilon=1{\cdot}523$; so that the double refraction is $\omega-\epsilon=0{\cdot}006$. J. Königsberger and W. J. Müller also measured the indices of refraction; and they found that the mineral has a higher refractive index and a feebler birefringence after it has been dehydrated. F. Cornu said gyrolite is readily soluble in dil. hydrochloric, nitric, or sulphuric acid; and that it gives a well-marked alkaline reaction when moistened with water. F. Cornu separated from gyrolite from Niakornat, Greenland, another mineral which was called *reyerite.* The composition is indicated in Table XV. The crystal form, hardness, solu-

TABLE XV.—ANALYSES OF SOME NATURAL HYDRATED CALCIUM SILICATES.

| — | $K_2O$ | $Na_2O$ | CaO | MgO | $Al_2O_3$ | FeO | $Fe_2O_3$ | $SiO_2$ | $H_2O$ |
|---|---|---|---|---|---|---|---|---|---|
| Centrallassite (3) . | 0·67 | — | 29·12 | 0·16 | 1·49 | — | — | 57·48 | 11·47 |
| Cyanolite (2) . . | 0·57 | — | 17·85 | — | 1·04 | — | — | 73·33 | 7·15 |
| Tobermorite (2) . | 1·01 | 0·62 | 33·69 | 0·47 | 3·15 | 1·46 | 0·90 | 46·56 | 12·36 |
| Chalcomorphite (1) . | — | — | 44·70 | — | 4·00 | — | — | 25·4 | 16·40 (some $CO_2$) |
| Gyrolite (11) . . | 1·19 | 0·62 | 31·69 | 0·13 | 1·34 | — | — | 32·19 | 13·42 |
| Reyerite (2) . . | — | 1·74 | 31·17 | — | 4·15 | — | — | 54·07 | 7·43 |
| Afwillite . . | — | — | 49·00 | 0·02 | 0·05 | — | — | 35·10 | 15·82 |
| Hillebrandite . . | 0·05 | 0·03 | 57·76 | 0·04 | 0·23 | — | 0·15 | 32·59 | 9·36 |
| Crestmoreite . . | — | — | 42·71 | — | — | — | — | 36·12 | 14·98 |
| Riversideite . . | — | — | 44·58 | — | — | — | — | 41·26 | 8·11 |
| Okenite . . . | — | 1·04 | 25·14 | — | 0·67 | — | — | 56·92 | 14·19 |
| Xenotlite . . | — | — | 43·65 | 0·74 | — | 2·42 | — | 47·91 | 3·76 |

bility, and behaviour when heated resemble those of gyrolite. The sp. gr. was found by F. Cornu to be 2·499–2·578, and by O. B. Böggild, 2·578—values rather higher than those for gyrolite. F. Cornu's value for the index of refraction is $\omega=1{\cdot}564$; and O. B. Böggild gave $\omega=1{\cdot}5645$, $\epsilon=1{\cdot}5590$—which are rather higher than for gyrolite. Reyerite is uniaxial, and optically positive. A. Pelikan [18] referred to a mineral occurring at Gross-Priessen, Bohemia, etc., which he called *zeophyllite.* It furnishes white or colourless crystals with the composition $SiO_2$, 37·67 per cent.; CaO, 46·82; $H_2O$, 7·52; and F, 7·99. The crystals are rhombohedral with the basal cleavage perfect. F. Cornu studied the corrosion figures. A. Himmelbauer give $\omega=1{\cdot}565$ for the refractive index; and F. Cornu, 1·545. The optic axial angle is $2\epsilon=27\frac{1}{2}°$. The sp. gr. is 2·764, and the hardness 3. A. S. Eakle described a mineral from Crestmore, California, which he called *foshagite*—after W. F. Foshag. Its composition corresponds with **calcium dihydrotriorthosilicate,** $H_2Ca_5(SiO_4)_3$; its sp. gr. is 2·36; its indices of refraction $\alpha=\beta=1{\cdot}594$, and $\gamma=1{\cdot}598$; and it is optically positive.

P. Eskola [19] found the **barium mesodisilicate,** $BaO.2SiO_2$, or $BaSi_2O_5$, is formed within the zone indicated in Fig. 69. The crystals were reported by N. L. Bowen to occur in baryta crown glass. The glass, $BaO–2SiO_2$, kept at 1385°, gave rhombic crystals of tabular habit parallel to $\alpha\beta$. The cleavages are well marked in all the pinacoidal directions. The optic axial angle $2V=74°\ 45'$; the sp. gr. was 3·73; the m.p. $1420°\pm4°$; and the indices of refraction for the *D*-line are $\alpha=1{\cdot}597$, $\beta=1{\cdot}612$, and $\gamma=1{\cdot}621$. The small differences in the properties of the mesodisilicate prepared from its constituents from that formed in baryta-crown-glass are possibly due to the latter holding a little alkali disilicate in solid soln. There was

no evidence of barium mesodisilicate holding alkali silicate in solid soln.; but it forms a well-defined series of solid soln., with the **barium mesotrisilicate,** $Ba_2Si_3O_8$, which was formed in granular rounded masses. The rhombic crystals are perfectly isomorphous with those of the mesodisilicate with which it forms a complete series of solid soln. It is unusual to find two compounds of the same element, so different in constitution, furnishing so complete and perfect an isomorphous series. The twinning is well marked. The cleavage is perfect along $\beta\gamma$, and poor along $\alpha\beta$, and $\alpha\gamma$. The optic axial angle $2V=53°\ 30'$ to 58°. The sp. gr. is 3·93; the m.p. 1450°; the indices of refraction for the *D*-line are $\alpha=1{\cdot}620$, $\beta=1{\cdot}625$, and $\gamma=1{\cdot}645$. The optical character is positive. P. Eskola found no evidence of the corresponding strontium compounds. G. A. Rankin and co-workers prepared **calcium orthodisilicate,** $Ca_3Si_2O_7$, in colourless crystals belonging to the rhombic system—*vide* Figs. 71, and 60. The crystals are best obtained by holding the glass with 54·5–55·5 per cent. of lime at a temp. slightly lower than 1475°. G. V. Wilson obtained these crystals in the actions of glass on limestone. Calcium orthodisilicate exhibits an incongruent m.p. at $1475°\pm5°$. The refractive indices are $\alpha=1{\cdot}641$, and $\gamma=1{\cdot}650\pm0{\cdot}002$ for Na-light. The birefringence is weak, $\gamma$-$\alpha$ being about 0·01; the optic axial angle is large, and the optical character positive.

According to E. Martin,[20] when the silicic acid, $5SiO_2.2H_2O$, derived from silicic acetate is treated with lime-water, *tetrahydrated calcium tetreropentasilicate,* $Ca_2Si_5O_{12}.4H_2O$, is formed; and if the silicic acid, $5SiO_2.H_2O$, derived from calcium silicate is similarly treated, *trihydrated calcium tetreropentasilicate,* $Ca_2Si_5O_{12}.3H_2O$, is formed. When this silicate is ignited, **calcium tetreropentasilicate,** $Ca_2Si_5O_{12}$, is produced. For E. Martin's pentasilicates $10CaO.5SiO_2$, *i.e.* $(Ca_2SiO_4)_5$; $(Ca_2SiO_4)_5.2H_2O$; and $13CaO.5SiO_2$, *vide* cements.

H. le Chatelier [21] melted a molar mixture of one of silica, two of calcium oxide, and four of calcium chloride at a dark red heat, and extracted the excess of calcium chloride by dried alcohol. Analyses correspond with **calcium chlororthosilicate,** $Ca_2SiO_4.CaCl_2$. A. Gorgeu obtained the same substance by fusing a mixture of silica and calcium chloride in the presence of water vap. E. Jordis and E. H. Kanter studied the reaction between calcium chloride lime-water and silica. The microscopic crystals of calcium chlororthosilicate belong to the rhombic system; they have the axial ratios $a:b:c=0{\cdot}726:10{\cdot}287$. They exhibit a strong double refraction; the cleavage is well defined; and the optic axial angle is 25°. The sp. gr. is 2·77; the m.p. near 800°; and the mol. ht. of soln. in hydrochloric acid is 36 cals. The salt is decomposed by a soln. of carbon dioxide, and dissolved by dil. acids. It is also decomposed superficially by water: $Ca_2SiO_4.CaCl_2+H_2O=3CaO.SiO_2+2HCl$, followed by the hydration of $3CaO.SiO_2$ as indicated above. A. Gorgeu obtained crystals of **calcium chlorometasilicate,** $CaSiO_3.CaCl_2$, along with those of the chlororthosilicate by the reaction just indicated. It forms regular hexagonal plates; the two optic axes approach very closely to one another. The chemical characters of the chlorometasilicate are like those of the chlororthosilicate, but the former is insoluble in a 5 per cent. soln. of acetic acid.

According to B. Karandéeff, the eutectic point in mixtures of calcium metasilicate and calcium chloride lies close to the m.p. of calcium chloride, and 8° below it. Solid soln. may be formed up to 10 mols. per cent. $CaCl_2$. There is no evidence of the formation of additive compounds. A. Woloskoff found that the system $BaSiO_3$–$BaCl_2$ forms a eutectic with the m.p. 902° when the m.p. of barium chloride is 968°. The eutectic has 8 molar per cent. of barium metasilicate. In the system $BaSiO_3$–BaS, there is a eutectic with 25 molar per cent. of barium sulphide at 1325°. Barium sulphide alone does not melt, and with the mixture $BaSiO_3$–FeS, there is a liquation of ferrous sulphide, until 10 molar per cent. of ferrous sulphide remains in the barium metasilicate.

The *calcium phosphatosilicates* have been treated in connection with calcium phosphate. F. E. Wright [22] obtained a mineral from Velardena, Mexico, which

was named *spurrite*—after J. E. Spurr; the analyses correspond with **calcium carbonatodiorthosilicate,** $2Ca_2SiO_4.CaCO_3$. F. W. Clarke represents it constitutionally:

$$CO_3<\begin{matrix}Ca\\Ca\end{matrix}>SiO_4<\begin{matrix}Ca\\Ca\end{matrix}>SiO_4=Ca$$

The sp. gr. is 3·014 at 25°; the hardness 7; the refractive indices $\alpha=1{\cdot}640$, $\beta=1{\cdot}674$, $\gamma=1{\cdot}679$ with sodium light; the double refraction $\gamma-\alpha=0{\cdot}039$, and $\beta-\alpha=0{\cdot}034$. It is decomposed by hydrochloric acid with the separation of gelatinous silica. For the synthesis of spurrite, *vide infra*, W. Eitel on the action of calcite on nephelite.

The analyses by A. E. Nordenskjöld, and G. Lindström, of a fibrous chalk-white mineral found in the Bjelke mine near Aareskuta, Sweden, correspond with tetradecahydrated *calcium sulphatocarbonatometasilicate,* $CaSiO_3.CaSO_4.CaCO_3.13$–$15H_2O$; and it was named *thaumasite*—from θαυμάζω, to be surprised—in allusion to its remarkable composition. It has also been found in New Jersey, and in Utah. Analyses were also reported by O. Widman, F. Pisani, R. P. D. Graham, S. L. Penfield and J. H. Pratt, H. Bäckström, and B. S. Butler and W. T. Schaller. The mineral is either hexagonal or tetragonal. The sp. gr. is between 1·870 and 1·877, and the hardness 1·5–3·5. The soft mineral hardens on exposure to air. F. Zambonini found that 13 mols of water are lost at 112°; another mol at 158°–160°; and the last mol is driven off at 200°. S. L. Penfield found that at

| | 112° | | | 205° | | |
|---|---|---|---|---|---|---|
| Hours' heating . . . | 17 | 71 | 478 | 5 | 280 | 1000 |
| Percentage loss of water . . | 11·59 | 13·41 | 14·96 | 11·22 | 19·18 | 21·55 |

H. E. Merwin emphasized how 14 of the 15 mols of water are expelled more readily than the remaining mol. There is a distinct prismatic cleavage. The indices of refraction determined by E. Bertrand, A. Michel-Lévy and A. Lacroix, H. Bäckström, etc., range from B. S. Butler and W. T. Schaller's $\omega=1{\cdot}500$, $\epsilon=1{\cdot}461$, to S. L. Penfield and J. H. Pratt's $\omega=1{\cdot}519$, $\epsilon=1{\cdot}476$. The double refraction is high. The mineral is optically uniaxial and negative. G. Lindström said that the material analyzed was homogeneous under the microscope; this was confirmed by E. Cohen. E. Bertrand said he identified calcite, gypsum, and a third mineral, probably wollastonite, in thaumasite, hence he regards it as a mixture. A. E. Nordenskjöld said that E. Bertrand's sample was very impure. C. F. Rammelsberg represented thaumasite as a double salt, $(CaCO_3.CaSiO_3)+CaSO_4+15H_2O$. P. Groth represented the composition graphically:

$$\begin{matrix}HO.CaO\\HO\end{matrix}>Si<\begin{matrix}O.CO.O.CaOH\\O.SO_2.O.CaOH\end{matrix}+13H_2O$$

E. F. Holden's measurement of the refractivity fits the assumption that it contains two hydroxyl groups. A hydrogel form is known, and C. Doelter and F. Cornu consider that thaumasite is an adsorption product in which a hydrogel like plombière, $CaSiO_3.nH_2O$, has adsorbed calcium carbonate and sulphate.

**Complex alkaline earth silicates.**—A. Haacke,[23] and R. Schwarz studied the binary system $Li_4SiO_4$–$Ca_2SiO_4$, and the f.p. curves are shown in Fig. 75. It appears as if two **lithium calcium orthosilicates** were formed, $2Li_4SiO_4.3Ca_2SiO_4$, and $3Li_4SiO_4.2Ca_2SiO_4$, with the respective m.p. 1104° and 1092°. He added that it is probable that the compound $Li_4Ca_2(SiO_4)_2$, or $Li_2CaSiO_4$, is formed, but decomposed at the higher temp. into the 2 : 3 and 3 : 2 silicates. This assumption agrees with the breaks in the cooling curves, with the microscopic appearance of sections of the cooled products, and with the sp. gr. which are:

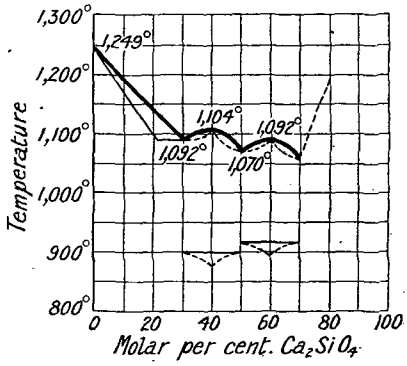



FIG. 75.—Binary System: $Li_4SiO_4$–$Ca_2SiO_4$.

| $Ca_2SiO_4$ . . | 0 | 10 | 20 | 30 | 40 | 50 | 60 | 100 per cent. |
|---|---|---|---|---|---|---|---|---|
| Sp. gr. . . | 2·280 | 2·400 | 2·423 | 2·424 | 2·591 | 2·847 | 2·566 | 2·970 |

R. C. Wallace studied the thermal diagram of mixtures of calcium and lithium metasilicates; and the results are summarized in Fig. 75. There is a gap in the miscibility roughly from 27–83 per cent. calcium metasilicate; and with from 40–80 per cent. calcium metasilicate there is a eutectic crystallization effect at 979°. The eutectic contains 50 per cent. calcium metasilicate. The sp. gr., mol. vol., and the f.p. represented by the temp. at which crystallization begins, are, for different percentages by weight of calcium metasilicate:

| $CaSiO_3$ | 0 | 10 | 30 | 50 | 60 | 70 | 80 | 90 | 100 |
|---|---|---|---|---|---|---|---|---|---|
| Sp. gr. | 2·61 | 2·64 | 2·72 | 2·80 | 2·80 | 2·84 | 2·85 | 2·88 | 2·91 |
| Mol. vol. | 34·64 | 34·87 | 35·62 | 36·36 | 37·30 | 37·74 | 38·62 | 39·30 | 40·00 |
| F.p. | 1168° | 1147° | 1083° | 979° | 1056° | 1214° | 1252° | 1315° | 1502° |

C. J. Peddle studied the glasses with $SiO_2$–$CaO$–$Na_2O$; with $SiO_2$–$CaO$–$K_2O$; with $SiO_2$–$CaO$–$K_2O$–$Na_2O$; and with $SiO_2$–$BaO$–$K_2O$ or $Na_2O$. R. C. Wallace's f.p. diagram for mixtures of sodium and calcium metasilicates, Fig. 76, has a

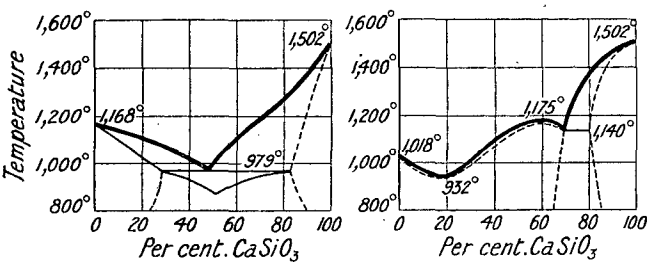



FIG. 76.—Freezing-point Curves of Binary Mixtures of Calcium Metasilicate with Lithium and Sodium Metasilicates.

maximum at 1175° corresponding with **sodium tricalcium pentametasilicate,** $2Na_2SiO_3.3CaSiO_3$. N. V. Kultascheff gave 1160° for the m.p. The f.p. are:

| $CaSiO_3$ | 0 | 20 | 30 | 50 | 58·8 | 65 | 75 | 85 | 100 |
|---|---|---|---|---|---|---|---|---|---|
| F.p. | 1018° | 932° | 1024° | 1143° | 1175° | 1165° | 1140° | 1449° | 1502° |

N. V. Kultascheff also investigated the f.p. curves of sodium and potassium metasilicates, and he isolated the compound $2Na_2SiO_3.3CaSiO_3$ in monoclinic twin crystals. He obtained mixed crystals of **sodium dicalcium pentametasilicate,** $3Na_2SiO_3.2CaSiO_3$, with another silicate. The latter was removed by boiling with water.

F. von Kobell found a fibrous mineral at Mount Baldo in Tyrol and named it **pectolite**—*πηκτός*, composed of pieces firmly joined together, *λίθος*, a stone—in reference to its structure. A. Breithaupt called a similar mineral *photolite*—*φῶς*, light, in reference to its phosphorescent qualities; and another mineral from Wolfstein, Bavaria, he called *osmelite*—*ὀσμή*, smell—in reference to its odour when breathed upon. J. Adam showed that osmelite and pectolite are the same minerals, although E. Riegel maintained that they are different. F. von Kobell, however, said that E. Riegel must have had some other mineral in hand. T. Thomson described a mineral *stellite* which occurs in radiant aggregates at Kilsyth, Stirlingshire, and R. P. Greg and W. G. Lettsom considered it to be natrolite, but J. D. Dana showed that the stillite from Bergen Hill, New Jersey, is pectolite. T. Thomson's *soda table-spar* is probably pectolite. The *walkerite* of M. F. Heddle, from Costorphine Hills, is probably pectolite. The *ratholite* of R. P. Greg and W. G. Lettsom from Ratho Quarry and Castle Rock, near Edinburgh, is probably pectolite. J. F. Williams reported a *manganopectolite* from Arkansas with 4 per cent. MnO.

The occurrence of the mineral in Tyrol has been discussed by G. A. Kenngott, L. Liebener and J. Vorhauser, J. R. Blum, V. von Zepharovich, A. Cathrein, J. Lemberg, and F. von Kobell; in Silesia, by M. Websky, B. Schubert, and A. von Lasaulx; in Scotland, by

M. F. Heddle, R. Jameson, A. J. Scott, T. Thomson, etc.; in Sweden, by J. L. Igelström; in Canada, by G. C. Hoffmann; in Greenland, by O. B. Böggild, and A. H. Chester; in the United States, by V. M. Goldschmidt, J. D. Dana, A. des Cloizeaux, J. F. Williams, E. F. Smith and E. B. Knorr, F. W. Clarke, J. D. Whitney, A. Leeds, etc. Analyses have been made by F. von Kobell, J. Lemberg, A. Breithaupt, M. F. Heddle, R. S. Houghton, J. Young, A. L. Parsons, J. L. Igelström, J. D. Whitney, F. W. Clarke and G. Steiger, F. W. Clarke, A. S. Eakle, E. F. Smith and E. B. Knorr, L. C. Beck, A. B. Meyer, O. B. Böggild, E. Reuning, J. F. Williams, etc. According to J. J. Berzelius, some specimens contain fluorine.

The older analyses were found by C. F. Rammelsberg to give a ratio Na : Ca =1 : 1·9 to 1 : 2·4; and $Na_2O : SiO_2$=1 : 3 to 1 : 5·7. More recent analyses by G. Tschermak gave Na : Ca : Si=1 : 1·9 : 3·1, and by F. W. Clarke, 1 : 2·1 : 3·1. This is in agreement with the formula $NaCa_2HSi_3O_9$—**sodium calcium hydro-trimetasilicate.** G. A. Kenngott, and P. Groth assumed that the contained water is constitutional. C. Doelter found a sample lost 4·09 per cent. of water when strongly heated; while the fresh powder for 14 days over sulphuric acid lost 0·405 per cent.; at 100°, 0·09 per cent.; at 200°, 0·128 per cent.; and at 300°, 0·959 per cent. P. A. Bolley, and A. von Schulten obtained substances resembling pectolite in composition by adding lime-water to a soln. of sodium silicate. J. N. von Fuchs, and C. G. C. Bischof treated calcium carbonate with sodium silicate and obtained a pectolitic substance. J. Lemberg obtained similar results by the action of octohydrated sodium metasilicate on datolite, or wollastonite, or gypsum, or calcium carbonate for 78–100 hrs. at 190°–200°. J. Lemberg also obtained an analogous product by the action of a soln. of calcium chloride on sodium silicate. C. Doelter also obtained a pectolite product by heating a mixture of silica, sodium carbonate, and lime in the proportions required for $Na_2CaSi_2O_6$. C. Doelter's product does not appear on the thermal diagram, Fig. 75. E. Baur succeeded in the synthesis of substances with the optical properties of pectolite in needle-like crystals, by heating to 400°–450°, mixtures of silica, alumina, soda, lime, and water. He also obtained *potash-pectolite* by substituting potash for soda. J. Lemberg converted okenite (*q.v.*) into pectolite by the action of sodium silicate. H. Rosenbuch and E. Wülfing, J. Lemberg, F. Cornu, and E. Baur have discussed the formation of pectolite in nature.

Observations on the crystals of pectolite were made by A. Arzruri, R. P. Greg and W. G. Lettsom, A. des Cloizeaux, P. Groth, C. F. Rammelsberg, A. L. Parsons, G. A. Kenngott, J. F. Williams, A. Michel-Lévy and A. Lacroix, M. F. Heddle, etc. J. D. Dana showed that pectolite is a monoclinic mineral with axial ratios $a : b : c$=1·1141 : 1 : 0·9864 and $\beta$=84° 40′. A. Breithaupt gave 2·799–2·833 for the sp. gr.; M. F. Heddle gave 2·712–2·881; V. M. Goldschmidt, 2·880; J. F. Williams, 2·845; F. W. Clarke, 2·873; and A. B. Meyer, 2·85–2·86. The hardness is about 5. A. Michel-Lévy and A. Lacroix gave 1·61 for the mean refractive index; 0·038 for the dispersion; and 15° for the optic axial angle. W. W. Coblentz observed no bands near to those of water in the ultra-red transmission spectrum of pectolite; the reflection spectrum has maxima at 9·4$\mu$, 10·3$\mu$, and 10·8$\mu$. The mineral is triboluminescent and it phosphoresces when exposed to radium. F. W. Clarke found that water in contact with pectolite acquires an alkaline reaction. G. Steiger found that after a month's contact with the mineral from Bergen Hill, water contained 0·57 per cent. of $Na_2O$. Uncalcined powdered pectolite was found by F. W. Clarke and G. Steiger to give to water 2·98 per cent. of silica, 0·30 per cent. of CaO, and 0·81 per cent. of $Na_2O$, after 14 hrs.' boiling; whereas with calcined powdered pectolite, after 4 hours' action, 3·03 per cent. silica, 0·10 per cent. CaO, and 1·50 per cent. $Na_2O$ were dissolved. Hence they concluded that the action of water is not one of simple dissolution. F. W. Clarke and G. Steiger found that in contact with ammonium chloride, pectolite gives a product $R'_2Ca_2Si_3O_9.6H_2O$, where R′ is approximately two-thirds $NH_4$, and one-third sodium. This makes it appear as if an *ammonia-pectolite* was formed. They also found that a soln. of 250 grms. of sodium carbonate in a litre of water extracts

8·68 per cent. of silica, or one-sixth the total amount from pectolite dehydrated by calcination. This is taken to indicate that the mineral is an acid metasilicate, $HNaCa_2Si_3O_9$. Before ignition, sodium carbonate soln., or even distilled water, has a slow decomposing action, both silica and bases being withdrawn. J. Roth discussed the transformation of pectolite into talc; and J. Lemberg effected the transformation of wollastonite into a substance resembling *spadaite*, $H_8Mg_5Si_6O_{21}$, by the prolonged action of soln. of magnesium chloride or sulphate. G. Steiger heated a mixture of powdered pectolite and silver nitrate in a sealed tube for 22 hrs. at 240°–280°, and obtained a kind of *silver-pectolite*.

In 1784, C. Rinman[24] described the occurrence of a zeolite at Hällesta, Sweden, and C. C. von Leonhard referred to it as the *zeolithus lamellaris* of J. Müller. M. F. R. d'Andrada designated a specimen from Utö, Sweden, as *ichthyophthalmite*—from *ἰχθύς*, fish; *ὀφθαλμός*, eye—in reference to the mother-of-pearl lustre. A. G. Werner called it *Fischaugenstein*. In 1801, R. J. Haüy referred to a sample from Iceland as *mesotype épointée*. J. N. von Fuchs and C. Gehlen showed the identity of the mineral with apophyllite. In 1805, R. J. Haüy called it **apophyllite**—*ἀπὸ*, away from; *φύλλον*, a leaf — in allusion to its tendency to exfoliate before the blowpipe flame. A. G. Werner investigated samples from Orawieza, Aussig, and the Faröe Islands, and he called the mineral *albin*—*albus*, white. D. Brewster called a white specimen from the Faröe Islands *tesselite*, because it had a tesselated structure in polarized light. D. Brewster called a pale green specimen found in petrified wood at the Oxhaver Springs, Husavisk, Iceland, *oxhaverite*. It was also investigated by E. Turner, and A. des Cloizeaux. G. S. von Waltershausen called an olive-green sample from Sicily, *xylochlore*—from *ξύλον*, wood; *χλωρός*, green. Both minerals were shown by G. A. Kenngott to be apophyllites. Specimens from Skye, Andreasberg, etc., showing alternate white and violet-black rings in polarized light were called by J. F. W. Herschel *leucocyclite*—*λευκός*, white; *κύκλος*, circle—and *chromocyclite*—*χρῶμα*, colour—by W. Klein. The mineral *louisite*, $CaSi_3O_7.2H_2O$, reported by D. Honeymann, was named after H. Louis. It was shown by T. L. Walker and A. L. Parsons to be a mixture of radiating quartz and cleavable apophyllite.

The apophyllite in various German provinces has been described by K. Busz, G. Cesaro, A. des Cloizeaux, C. Doelter, A. Frenzel, J. Fromme, G. Greim, C. W. von Gümbel, J. F. L. Hausmann, G. A. Kenngott, A. Knop, A. Koch, A. von Lasaulx, J. E. Hibsch, G. Leonhard, O. Luedecke, C. F. Peters, H. Pohlig, C. F. Rammelsberg, F. A. Roemer, J. Rumpf, F. Sandberger, J. Schill, A. Schrauf, H. Stölting, A. Streng, H. Traube, M. Websky, E. Weinschenk, A. Weisbach, A. von Zepharovich, G. Zimmermann, etc. In the Tyrols, by E. Baschieri, C. G. C. Bischof, J. R. Blum, A. des Cloizeaux, J. D. Dana, H. Dauber, C. Doelter and E. Mattersdorf, C. Gehlen, G. A. Kenngott, J. Lemberg, L. Liebener and J. Vorhauser, O. Luedecke, A. Pichler, F. von Richthofen, J. Rumpf, A. Schrauf, G. Tschermak, etc. In Switzerland, by P. Groth, and G. A. Kenngott. In Russia, by P. P. Pilipenko. In Italy, by E. Artini, L. Colomba, G. Leonhard, E. Manasse, L. Meschinelli and A. Balestra, J. Rumpf, L. Sipocz, S. J. Thugutt, D. F. Wiser, etc. In France, by A. Daubrée, A. Dufrénoy, F. Gonnard, etc. In Great Britain, by R. P. Greg and W. G. Lettsom. In Norway and Sweden, by J. J. Berzelius, W. C. Brögger, C. Gmelin, G. Hallberg, A. Hennig, L. J. Igelström, G. Leonhard, C. C. von Leonhard, C. F. Rammelsberg, C. Rinman, G. Seligmann, P. C. Weibye, etc. In the Faröe Islands, by J. J. Berzelius, D. Brewster, G. Leonhard, J. Rumpf, etc. In Iceland, by D. Brewster, P. Groth, G. A. Kenngott, G. Leonhard, E. Turner, G. S. von Waltershausen, etc. In Greenland, by C. Gmelin, G. Leonhard, J. Rumpf, A. Schrauf, F. Stromeyer, etc. In Finland, by W. Beck. In Canada, by G. C. Hoffmann, and A. L. Parsons. In the United States, by H. Credner, W. Cross and W. F. Hillebrand, J. D. Dana, J. Eyerman, F. A. Genth, C. Hersch, C. Klein, E. B. Kneer and J. Schönfeld, J. Rumpf, B. Sadtler, A. Schrauf, J. L. Smith, F. Tamnau, etc. In Mexico, by C. Klein, C. F. de Landero, S. J. Thugutt, etc. In Brazil, by P. A. von Sachsen-Coburg. In Africa, by L. Gentil (Algiers), and J. A. L. Henderson (S. Africa). In India, by J. R. Blum, P. Groth, S. Haughton, F. R. Mallet, J. Rumpf, etc. In Siberia, by G. Leonhard. In Japan, by K. Jimbo, and T. Wada. Analyses are also reported by most of these observers.

A. B. de Fourcroy and L. N. Vauquelin, and V. Rose made the earliest analyses of apophyllite. J. J. Berzelius reported the presence of fluorine. C. Friedel

reported ammonia, but no fluorine, in samples from Utö, and Andreasberg. He, however, did find fluorine in some samples. Observations on the fluorine in apophyllite were made by A. E. Nordenskjöld, C. F. Rammelsberg, and S. J. Thugutt. The last-named showed that the water-content of the powdered mineral is smaller than when in lumps—presumably water is lost in the process of comminution. C. F. Rammelsberg found that water is not lost over sulphuric acid, or at 100°; but at 200°, the evolution of water begins, and about 4 per cent. was lost at 260°. C. Doelter found that about 45 per cent. of the water is lost at 240°, and 55 per cent. at 260°. C. Hersch found apophyllite from Bergen Hill lost

| | 100° | 160° | 200° | 240° | 275° | 300° | Red heat. |
|---|---|---|---|---|---|---|---|
| Loss . . . | 0·11 | 0·38 | 0·77 | 2·03 | 9·08 | 9·91 | 16·61 per cent. |

L. Colomba found with another specimen

| | 100° | 160° | 200° | 250° | 270° | 285° | 325° | 360° | 400° |
|---|---|---|---|---|---|---|---|---|---|
| Loss . . | 0·17 | 0·51 | 0·86 | 6·51 | 8·49 | 9·89 | 11·60 | 13·35 | 15·85 per cent. |

The dehydration curve shows two well-defined breaks—one at about 200° and one at 285°. Observations were also made by A. Hennig, by F. Zambonini, and by C. Doelter. A certain proportion of the water loss by dehydration is reabsorbed from a moist atm. This is therefore regarded as water of crystallization. G. Stoklossa inferred that the 2 mols of water in apophyllite are chemically combined, and the dehydrated mineral does not reabsorb the water as do the zeolites.

The composition of idealized apophyllite was represented by C. F. Rammelsberg by the formula $H_7KCa_4Si_8O_{24}.4\frac{1}{2}H_2O$, *i.e.* as P. Groth puts it, $H_7KCa_4(SiO_3)_8.4\frac{1}{2}H_2O$; C. F. Rammelsberg also used $R_2Ca(SiO_3)_2Aq.$; and C. Doelter regarded apophyllite as hydrated **potassium calcium hydrodimetasilicate,** $H_2(Ca,K_2)Si_2O_6+Aq.$, or $(Ca,K_2)SiO_3+H_2SiO_3+Aq.$, or $Ca(H,K)_2(SiO_3)_2.H_2O$. E. Baschieri gave:

$$O<\begin{matrix}SiO.O\\SiO.O\end{matrix}>R+2H_2O$$

where R denotes $Ca,K_2$, and possibly $Na_2$ and $(CaOH)_2$. G. Tschermak used $4(H_6Ca_2Si_3O_{11})H_3K_2Si_3O_{11}$; and F. W. Clarke regarded apophyllite, gyrolite, and okenite as salts of the acid, $H_6Si_2O_7$, and apophyllite becomes $H_4(Si_2O_7)\{Ca(Si_2O_7)H_2CaOH\}_2$, where some of the univalent CaOH-group may be replaced by potassium. J. Dalton obtained a precipitate which he seemed to regard as a double silicate of calcium and potassium by adding lime-water to a soln. of alkali silicate.

F. Wöhler, and C. Doelter obtained crystals of apophyllite by heating to 150°–160° the powdered mineral and water in a gun-barrel after treatment with carbon dioxide. If okenite be heated with potassium silicate and carbonated water to 200°, new crystals of okenite and apophyllite are formed. Similarly, if okenite, sodium carbonate, and aluminium chloride be heated to 220°, apophyllite is formed. A. Daubrée observed the formation of apophyllite in the masonry of the baths at Plombières. A. C. Becquerel covered a gypsum plate with a soln. of potassium silicate and, after the mixture had stood for some time, found that crystals of potassium calcium silicate were formed. The product was insoluble in water, and decomposed by hydrochloric acid. J. Lemberg obtained the double silicate by the action of calcium chloride on potassium silicate for 57 hrs. at 185°; also by digesting calcium carbonate and an aq. soln. of potassium silicate for 20 days at 100°. A. Duboin melted calcium oxide with potassium fluoride and silica, and obtained mixtures of crystalline products containing fluorine, or chlorine, if potassium chloride be used in place of the fluoride. He obtained **potassium pentacalcium tetrafluohexametasilicate,** $K_2O.5CaO.6SiO_2.4KF$. With baryta, the products were free from halogens. A. Streng studied the formation of apophyllite in nature by the action of carbonated waters on wollastonite: $2CaSiO_3+CO_2+2H_2O=CaCO_3+H_2CaSi_2O_6.H_2O$; and S. J. Thugutt gave $8CaSiO_3+8H_2O+4CO_2+KF=4CaCO_3+4(CaSi_2O_5.2H_2O).KF$.

Apophyllite is colourless, white, pale yellow, red, or green. G. Suckow said that the red apophyllite of Andreasberg is coloured with cobalt fluoride. Measurements of the crystals have been made by J. F. L. Hausmann, J. Rumpf, H. Dauber, O. Luedecke, C. F. Rammelsberg, A. Streng, P. Groth, K. Busz, J. Schill, H. Traube, G. Flink, B. Jezek, A. Schrauf, A. Pichler, A. des Cloizeaux, P. I. Ploner, E. Artini, J. Königsberger, L. Meschinelli and E. Balestra, A. Dufrénoy, F. Klocke, W. C. Brögger, G. Seligmann, F. Tamnau, L. Gentil, etc. According to W. H. Miller, the crystals belong to the tetragonal system, and have the axial ratio $a:c = 1:1{\cdot}2515$. E. Mallard's view is that the mineral is pseudo-tetragonal, but it is really a complex of lamellar twinned, monoclinic individuals. This was supported by H. Haga and F. M. Jäger's observations on the X-radiograms. J. Rumpf gave 40° for the optic axial angle. The cleavage is well marked. O. Mügge studied the percussion figures; F. Rinne, the corrosion figures; and J. Lehmann, the contraction crazing, and the hissing of the mineral with water. O. Luedecke gave 1·961 for the sp. gr.; C. Rinman, 2·377; O. B. Böggild, 2·379; G. d'Achiardi, 2·2; A. Russell, 2·31; J. Rumpf, 2·339; H. Credner, 2·37; and B. Sadtler, 2·5. Most of the material analyzed—*vide supra*—had also its sp. gr. determined. The best representative value is 2·3–2·4; the hardness is 4–5. The indices of refraction have been determined by A. des Cloizeaux, L. Gentil, K. Zimanyi, O. Luedecke, etc. For Na-light, the values range from $\omega=1{\cdot}5331$–$1{\cdot}5379$, and $\epsilon=1{\cdot}5356$–$1{\cdot}5414$; for Li-light, $\omega=1{\cdot}5309$–$1{\cdot}5240$, and $\epsilon=1{\cdot}5332$–$1{\cdot}5404$; for Tl-light, $\omega=1{\cdot}5405$; and $\epsilon=1{\cdot}5429$; and for Cs-light, $\omega=1{\cdot}5311$, and $\epsilon=1{\cdot}5335$. The birefringence $\epsilon$-$\omega=0{\cdot}002$ is weak and positive. A. Ehringhaus gave for light of wave-length $\lambda$, between 17·5° and 18°:

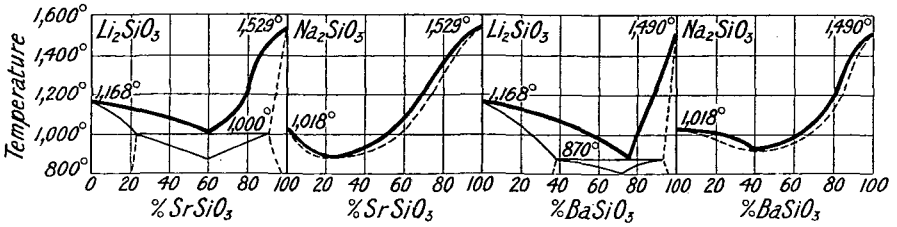
| | | | | | | | |
|---|---|---|---|---|---|---|---|
| $\lambda$ . | 690·7 | 623·9 | 589·3 | 513·2 | 491·6 | 435·7 | 404·7 |
| $\omega$ . | 1·53108 | 1·53294 | 1·53437 | 1·53876 | 1·54032 | 1·54559 | 1·54959 |
| $\epsilon$ . | 1·53257 | 1·53418 | 1·53555 | 1·53964 | 1·54101 | 1·54591 | 1·54962 |

The interference figures of the apophyllites are peculiar. Instead of showing the sequence of colours of Newton's rings characteristic of crystals in which the birefringence does not alter with wave-length, D. Brewster noted that in white light some varieties of apophyllite give rings with a different sequence—*e.g.* violet, greenish-yellow, and white circles alternating without any tint of red—*vide supra, chromocyclites*—or, as reported by J. F. W. Herschel, the rings may be black and white. These samples were called *leucocyclite* (*vide supra*). In some apophyllites, the birefringence is the same for red and yellow light, but other specimens may be positive, isotropic, or negative for differently coloured light. C. Klein showed that the apophyllite rings may be imitated by a combination of uniaxial positive and negative crystals. This supports the hypothesis that apophyllite is an isomorphous mixture of a positive and negative substance. The leucocyclite variety is positive; and C. Doelter showed that heating to 275° changes the rings of ordinary apophyllite to those of the leucocyclite variety—it is assumed that leucocyclite is a less hydrated variety. Many apophyllites exhibit in basal section a partition into sectors, some of which are biaxial and negative for blue and positive for red, with the axial planes crossed. Hence, argued H. A. Miers, apophyllite is an intergrowth of two or more silicates with different optical qualities. The subject has also been discussed by R. Brauns, C. Skoetsch, A. Ehringhaus, A. Wenzel, H. Michel, E. Mallard, F. Pfaff, F. Klocke, B. Trolle, etc. W. W. Coblentz found that the ultra-red transmission spectrum of apophyllite has water bands at $1{\cdot}5\mu$ and $2\mu$; and the mineral is almost opaque between $3\mu$ and $8\mu$. The reflection spectrum has the usual region common to silicates, and maxima at $9{\cdot}15\mu$ and $9{\cdot}7\mu$. According to W. G. Hankel, the pyroelectrical properties of apophyllite are shown by cooling a crystal, when the ends and vicinities of the principal axes are positively electrified; and the intermediate region, negatively electrified. O. Weigel studied the electrical conductivity.

Powdered apophyllite was found by G. A. Kenngott, F. Cornu, and F. W. Clarke to have an alkaline reaction both before and after calcination. F. Wöhler observed

that apophyllite dissolves in water at 180°–190°, and a press. of 10–12 atm. On cooling, the solute separates as crystalline apophyllite. Temp., said R. Bunsen, is the most important factor. C. G. C. Bischof found one part of apophyllite dissolves in 28,802 parts of water. C. Doelter found that after 14 days' action at 90°, distilled water dissolves only a trace of silica and lime; and after 21 days at 120°, 2·98 per cent. of matter was dissolved by the water, and of this, 64·2 per cent. was silica, and the remainder lime with an unweighable trace of potash. G. Spezia found that water at 25° and 1750 atm. press. dissolved no apophyllite (Poonah) after 6 months' action; some action occurred at 193°–211° and at a press. of 14 atm. in 13 days; but not at 93°–107° and 500–1056 atm. press. J. Lemberg treated apophyllite with soln. of magnesium sulphate or chloride in sealed tubes for periods extending from 4½ hrs. at 180° to 3 mons. at ordinary temp. The lime was partially replaced by magnesia; and if soln. of alkali aluminate be used, then lime is also replaced by alumina; and with soln. of sodium silicate apophyllite passes into pectolite. F. W. Clarke studied the action of soln. of ammonium chloride and found that lime and alkali are removed. Apophyllite dissolves in acids with the separation of flocculent silica which E. Baschieri claimed to have the composition $H_2Si_2O_9$. F. Cornu found that hydrochloric, nitric, or sulphuric acid attacks the (111) and the (001) crystal faces strongly, but the (100) face was scarcely attacked. J. Samoiloff found that the alkali was extracted by plants from apophyllite about as easily as from leucite and orthoclase, but not so easily as from phillipsite. Natural transformations of apophyllite have been studied by F. Cornu, J. Roth, A. Himmelbauer, G. Tschermak, W. T. Schaller, A. Scheit, R. Görgey, J. R. Blum, H. Michel, M. Websky, A. Streng, J. Königsberger, F. von Richthofen, E. S. Dana, C. F. Peters, etc.

J. Dalton obtained a precipitate which appeared to be a *potassium barium silicate* by mixing baryta-water with a soln. of the alkali silicate. J. M. Ordway made some observations on the subject, and A. Duboin melted baryta with potassium fluoride and silica, and obtained **potassium dibarium trimetasilicate,** $K_2O.2BaO.3SiO_2$, of sp. gr. 3·78; and if this compound be fused with potassium chloride, the main product is **potassium heptabarium octometasilicate,** $K_2O.7BaO.8SiO_2$. J. M. Ordway heated mixtures of barium and sodium sulphates with silica and carbon and obtained products which he regarded as *sodium barium silicates*. The results of R. C. Wallace's observations on *lithium strontium silicates, lithium barium silicates, sodium strontium silicates,* and *sodium barium silicates* are summarized in Figs. 77–80. Lithium and strontium metasilicates




FIGS. 77–80.—Freezing-point Curves of Binary Mixtures of Strontium and Barium Metasilicates with Lithium and Sodium Metasilicates.

form mixed crystals with a lacuna between 22 and 92 per cent. of strontium silicate, and with lithium and barium metasilicates there is a lacuna with between 35 and 92 per cent. of barium silicate. Sodium metasilicate forms a continuous series of mixed crystals with both barium and strontium metasilicates.

According to A. de Schulten,[25] when lime-water is added to a conc. soln. of potassium silicate until a slight precipitate is formed, and the mixture is then heated in sealed tubes at 180°–200° for 24 hrs., the gelatinous mass which forms on cooling encloses a small quantity of some substance crystallized in prismatic needles. If the tube is heated for several days with occasional agitation, the

gelatinous matter gradually disappears, and the quantity of the crystals increases. By repeated levigation, the plates of silica can be removed, and the prismatic crystals are then obtained, mixed with only a small quantity of hexagonal plates: the quantity of hexagonal plates increases, and that of the needles diminishes if the lime-water is added in too small a quantity; if, however, too much lime-water is added, no crystals are formed at all. The prismatic crystals are white, they have a nacreous lustre, melt before the blowpipe, and are decomposed by hydrochloric acid with separation of gelatinous silica which retains the form of the original crystals. Analyses correspond with the triple salt dihydrated **sodium potassium calcium trimetasilicate,** $(K_2,Na_2,Ca)O.3SiO_2.2H_2O$. The soda is derived from the alkalies in the glass. P. Eskola found that calcium and strontium metasilicates form a complete series of mixed crystals with a minimum in the curve, Fig. 81, at 1474° ± 3° and 56 per cent. $SrSiO_3$. The mixed crystals are crystallographically like $\beta$-$CaSiO_3$.

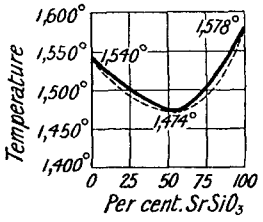



FIG. 81.—Freezing-point Curve of the Binary System: $CaSiO_3$–$SrSiO_3$.

Mixtures of silica, baryta, and lime were fused into glasses by H. Benrath, G. Wagener, and C. F. Plattner. According to P. Lebedeff, *calcium and barium metasilicates* give an isomorphous series with a continuous f.p. curve, having a minimum at about 1000° with nearly 35 per cent. of barium metasilicate. A glass is obtained on cooling rapidly, while slowly cooled mixtures solidify to a homogeneous series of monoclinic solid soln., which do not disintegrate or undergo further change. P. Eskola, however, obtained the curves shown in Fig. 82. This diagram shows that a compound **barium dicalcium metasilicate,** $BaCa_2Si_3O_9$, is formed which has an incongruent m.p. at 1320° ± 4°, forming $\beta$-calcium metasilicate and liquid. The crystals of the compound are usually in the form of elongated fibres; they are uniaxial and negative; and probably hexagonal. The crystals have good cleavages in their prismatic zone. The indices of refraction for the *F*-, Tl-, *D*-, and *C*-rays are respectively $\epsilon$=1·690, 1·685, 1·681, and 1·677; and $\omega$=1·678, 1·672, 1·668, and 1·664.

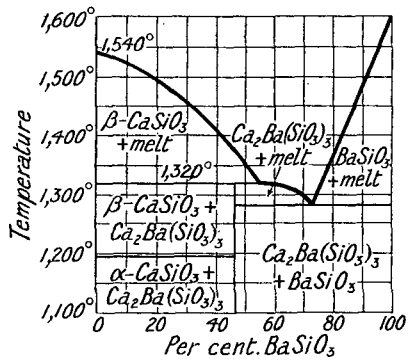



FIG. 82.—Freezing-point Curve of the Binary System: $CaSiO_3$–$BaSiO_3$.

An artificial blue pigment was used by the Egyptians from the time of the 4th dynasty, and was also used at the time of the Roman Empire. M. P. Vitruvius[26] said that the colour was made by heating a mixture of copper filings, soda, and sand. Observations on the colour were made by H. Davy, L. N. Vauquelin, J. P. J. d'Arcet and co-workers, W. J. Russell, F. C. J. Spurrell, W. Burton, H. le Chatelier, etc. H. de Fontenay found the percentage composition of an *Egyptian blue* body to be 70·25 per cent. $SiO_2$; 2·36, $Al_2O_3+Fe_2O_3$; 8·35, CaO; 16·44, CuO; and 2·83, $Na_2O$, with no trace of cobalt oxide. It can be made by heating a mixture of sand, 70; copper oxide, 15; whiting, 25; and soda ash, 6, below 1000°. F. Fouqué made a particular study of the colour, and considered it to be due to the formation of a **calcium cupric metadisilicate,** $CaO.CuO.4SiO_2$, or $CaCu(Si_2O_5)_2$. He prepared this quite free from alkali, and called it *Vestorian blue*. The calcium cupric silicate was obtained in azure-blue crystals. These results were confirmed by A. P. Laurie and co-workers. The crystals belong to the tetragonal system. The sp. gr. is 3·04 (F. Fouqué), 2·948 (A. P. Laurie). In convergent polarized light, said F. Fouqué, the crystals exhibit the characteristics of uniaxial minerals. The crystals are optically negative. They are remarkably pleochroic, being of a pale rose colour with rays vibrating parallel to the axis, and intensely blue with rays

vibrating perpendicular to that axis. The double refraction is 0·031. A. P. Laurie and co-workers found the refractive index of the ordinary ray is $\omega=1{\cdot}6354$, and that of the extraordinary ray, $\epsilon=1{\cdot}6053$, so that the double refraction is in agreement with F. Fouqué's value. H. le Chatelier, and G. Barth obtained a blue colour by heating a mixture of copper oxide or silicate, silica, and barium carbonate or silicate—with or without sodium carbonate. G. Barth also used strontium silicate in place of barium silicate. There is nothing here to show that the products are chemical individuals, *barium cupric silicate*, or *strontium cupric silicate*. The double silicates were also obtained by precipitation.

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## § 26. Beryllium or Glucinum Silicates

Beryllium forms an anhydrous orthosilicate—*phenacite*—and a hemihydrated orthosilicate—*bertrandite*; the orthosilicate also forms a series of solid soln., with manganese, zinc, and ferrous silicates, known as *trimerite*. There is a dimorphous hydrated beryllium alkali silicate furnishing *eudidymite*, and *epidymite*; and a series of fluoriferous metasilicates—*leucophane* and *melinophane*. There are also the aluminosilicates exemplified by *beryl*. According to W. C. Brögger,[1] the minerals phenacite, trimerite, willemite, and dioptase form a morphotropic family.

The mineral **phenacite** was discovered by N. von Nordenskjöld in the emerald mines near Tokowaja, Urals. The crystals had previously been mistaken for quartz—hence the name from φέναξ, a deceiver. It has also been found near Miask, Ilmen Mts.; Framont, Vosges Mts.; Reckingen, Switzerland; Darango, Mexico; Topaz Butte, Colorado; in New Hampshire, Virginia, etc. Analyses have been reported by N. von Nordenskjöld, C. G. C. Bischof, L. A. Aars, C. F. Rammelsberg, S. L. Penfield, E. S. Sperry, K. Vrba, K. Chroustchoff, G. Seligmann, etc. The results show that phenacite is **beryllium orthosilicate,** $Be_2SiO_4$.

A. Daubrée synthesized phenacite by passing a current of silicon chloride over beryllia at a red heat; C. J. St. C. Deville, however, thought that the analysis of the product of this operation agreed more nearly with **beryllium metasilicate,** $BeSiO_3$. G. Stein made the orthosilicate by fusing 2 mols of beryllia with a mol of silica in carbon or porcelain crucibles, and he obtained the metasilicate by heating a mixture of equimolar proportions at 1600°. J. J. Ebelmen fused silica and beryllia with borax, and obtained hexagonal crystals which E. Mallard found to have optical properties like phenacite. P. Hautefeuille and A. Perrey heated a mixture of silica, beryllia, and lithium vanadate and carbonate, or lithium molybdate for a long time at 600°–700°, and obtained well-defined crystals. C. Doelter made crystals of phenacite by melting beryllium nitrate and silica with ammonium fluoride as *agent minéralisateur*. W. Pukall made the meta- and ortho-silicates by heating intimate mixtures of beryllium hydroxide and silicic acid in theoretical proportions. F. M. Jäger and H. S. van Klooster made the metasilicate in a somewhat similar way.

Phenacite occurs in colourless, yellow, pale rose-red, or brown crystals. The crystals were examined by N. von Nordenskjöld, G. Rose, R. Hermann, G. Seligmann, E. Beyrich, A. des Cloizeaux, A. Russell, M. Websky, W. H. Miller, W. Phillips, M. Henglein, J. C. G. de Marignac, S. L. Penfield, W. E. Hidden, W. Cross and W. F. Hillebrand, H. J. Burkart, L. Weber, etc. According to N. von Kokscharoff, the crystals belong to the trigonal system, and the axial ratio $a:c$ is 1 : 0·661, and M. Websky gave 1 : 0·661958. C. Doelter's crystals were short prisms. Penetration twinning occurs about the vertical axis; the cleavage is well marked. H. Haga and F. M. Jäger studied the X-radiograms of phenacite. A. von Lasaulx noted in the crystals liquid inclusions which still remain at 100°, and cannot therefore be liquid carbon dioxide. N. von Nordenskjöld gave 2·969 for the sp. gr.; A. Breithaupt gave 3·001; K. Chroustchoff, 2·945–2·986; and

W. Cross and W. F. Hillebrand, 2·967. According to G. Stein, the sp. gr. of the crystals of the orthosilicate is 2·46, and of the metasilicate 2·35. K. Chroustchoff gave 7–8 for the hardness. According to F. M. Jäger and H. S. van Klooster, the m.p. of the metasilicate is over 1750°; and, according to G. Stein, the m.p. of both silicates is over 2000°. G. Spezia melted the mineral in the oxyhydrogen blowpipe. A. des Cloizeaux, W. Haidinger, and A. Offret measured the indices of refraction. A. Offret obtained 0°:

| Li-line. | Na-line. | Green Cd-line. | Blue Cd-line. |
|---|---|---|---|
| 1·6509 | 1·6542 | 1·6570 | 1·6610 |
| 1·6666 | 1·6700 | 1·6729 | 1·6770 |

A. des Cloizeaux observed that at 100°, the refractive index was increased by 0·00108. The birefringence is higher than that of quartz, the crystals are optically positive. A. Ehringhaus and H. Rose compared the dispersion and double refraction of the orthosilicates of zinc, beryllium, and copper with their mol. wts. W. Haidinger noted that the crystals are pleochroic, being colourless for the ordinary ray, and pale yellowish-brown for the extraordinary ray. T. Liebisch found the crystals phosphoresce feebly. W. G. Hankel, and C. Friedel and A. de Gramont studied the pyroelectricity of the crystals. Acids do not attack the mineral. F. Cornu said that phenacite moistened with water reacts feebly alkaline to litmus. W. Pukall found the meta- and ortho-silicates to be but slightly attacked by acids and alkalies.

According to G. Flink,[2] *trimerite* is a Swedish mineral whose analysis corresponds with *beryllium manganese orthosilicate*, $BeMnSiO_4$; or with a solid soln. of the orthosilicates of beryllium, calcium, and manganese. The triclinic crystals have the axial ratios $a:b:c = 0·5774:1:0·5425$; or, pseudohexagonal $a:c=1:0·9424$. W. C. Brögger gave 3·474 for the sp. gr. The hardness is 6–7. The indices of refraction for Li-, Na-, and Tl-light are respectively $\alpha=1·7119$, 1·7148, and 1·7196; $\beta=1·7173$, 1·7202, and 1·7254; and $\gamma=1·7220$, 1·7253, and 1·7290. The birefringence $\gamma-\alpha$ is 0·0105; and $\gamma-\beta$ is 0·0051. The optic axial angles $2H=120°\ 1'$, and $2V=83°\ 29'$.

The mineral **bertrandite** was found by E. Bertrand[3] *des environs de Nantes*; and it was named by A. Damour. Occurrences have been described by A. Russell, H. L. Bowman, C. Baret, A. Lacroix, S. L. Penfield, O. C. Farrington and E. W. Tillotson, etc. Analyses reported by A. Damour, S. L. Penfield, P. P. Pilipenko, K. Vrba, and T. Vogt correspond with the idealized formula $H_2Be_4Si_2O_9$, or with **hemihydrated beryllium orthosilicate,** $Be_2SiO_4.\frac{1}{2}H_2O$, or, as P. Groth expresses it, with **beryllium dihydroxydisilicate,** $(BeOH)_2Be_2Si_2O_7$, since water is evolved only at a red heat, and it is therefore probably present in hydroxylic form and not as water of hydration. Bertrandite is colourless or pale yellow, with a vitreous lustre. The crystals have been measured by E. Bertrand, S. L. Penfield, etc. K. Vrba showed that the rhombic crystals have the axial ratios $a:b:c = 0·56988:1:0·59442$. Twinning occurs with axes crossed at about 60° and 120°. The cleavage is perfect. The optic axial angles $2H=118°$; and $2V=74°\ 51'\ 34''$. E. Bertrand gave 2·593 for the sp. gr.; K. Vrba gave 2·5963–2·6008; R. Scharizer, 2·55; and S. L. Penfield, 2·598. The hardness is 6·0–6·5. The optical properties of the crystals have been examined by E. Bertrand, A. des Cloizeaux, R. Scharizer, K. Vrba, T. Vogt, S. L. Penfield, etc. The indices of refraction for Na-light are $\alpha=1·5914$, $\beta=1·6053$, and $\gamma=1·6145$. The birefringence $\gamma-\alpha=0·0231$. The optical character is negative. S. L. Penfield found the crystals are pyroelectric. According to F. Grünling, the *hessenbergite* of G. A. Kenngott, and the *sideroxene* of F. Hessenberg are varieties of bertrandite.

A colourless and water-clear mineral found on the Island of Oevre-arö, Norway, was analyzed by W. C. Brögger,[4] and A. E. Nordenskjöld. It appears to be **beryllium sodium hydromesotrisilicate,** $NaBeHSi_3O_8$. It was named *eudidymite*, from εὖ, easily; δίδυμος, twin. The crystals are always twinned and of tabular habit. According to W. C. Brögger, it forms monoclinic crystals with the axial

ratios $a:b:c=1{\cdot}7108:1:1{\cdot}1071$, and $\beta=93°\ 45\frac{1}{2}'$. The sp. gr. is 2·548, and the hardness under 6. The optic axial angle $2V=31°\ 4'$, and $2H=29°\ 43'$. The indices of refraction for red light, sodium light, and thallium light are respectively $\alpha=1{\cdot}54444$, 1·54533, and 1·54763; $\beta=1{\cdot}54479$, 1·54568, and 1·54799; and $\gamma=1{\cdot}54971$, 1·55085, and 1·55336. The water is but incompletely expelled even at a red heat; a blast flame is needed for its complete expulsion. It is rapidly and easily decomposed by hydrofluoric acid, but, calcined or uncalcined, it is incompletely decomposed by hydrochloric acid, and then only with difficulty. G. Flink, and H. Sjögren analyzed a white mineral from Narsasik, Greenland, and found it to have the same composition as eudidymite, but it furnishes rhombic crystals with the axial ratios $a:b:c=1{\cdot}7367:1:0{\cdot}9274$. It was named *epididymite*. Beryllium sodium hydrotrisilicate is therefore dimorphous, but whether isomeric or polymeric is not known. The optic axial angle $2V=31°\ 4'$. The sp. gr. is 2·553; and the hardness 6. The indices of refraction for Na-light are $\alpha=1{\cdot}5645$, $\beta=1{\cdot}5685$, and $\gamma=1{\cdot}5688$. The behaviour of the mineral on heating, and towards acids resembles that of eudidymite.

According to P. Hautefeuille and A. Perrey, when the constituents of the alkali beryllium silicates are fused at 600°–700°, with an excess of potassium vanadate, mineralization occurs. The product after washing with water and dil. potassium hydroxide, can be separated into crystalline constituents by a soln. of cadmium borotungstate of varying sp. gr. A series of *potassium beryllium silicates*, having $K_2O:BeO:SiO_2$ as 1 : 1 : 4, 1 : 2 : 4, 1 : 1 : 5, and 1 : 2 : 5, has been reported; similarly with *sodium beryllium silicates*, having $Na:BeO:SiO_2$ as 1 : 2 : 6, 1 : 2 : 3, 3 : 4 : 15, 3 : 4 : 14, and 3 : 4 : 18. A. Duboin dissolved beryllia and silica in fused potassium fluoride, and submitted the product to a prolonged fusion with potassium chloride. He obtained products varying between $2K_2O:3BeO:7SiO_2$ and $2K_2O.3BeO.5SiO_2$.

C. W. Blomstrand [5] described a mineral he found in the crystalline limestone of Langban, Sweden, which he called **barylite**—from *βαρύς*, heavy; *λίθος*, a stone. The composition corresponds with $Ba_4Al_4Si_7O_{24}$; and F. W. Clarke symbolized its composition $Al(Si_2O_7.AlBa)_3$. G. Aminoff, however, gave the formula $Be_2BaSi_2O_7$, and said that C. W. Blomstrand had mistaken beryllia for alumina in his analysis. This makes the mineral **barium diberyllium orthosilicate.** The mineral occurs in groups of white or colourless, prismatic crystals, more or less of tabular habit, and, according to M. Weibull, probably rhombic. G. Aminoff gave for the axial ratios of the rhombic crystals $a:b:c=0{\cdot}8025:1:0{\cdot}8376$. There are two distinct cleavages, forming an angle of 84°. The optical axial angle $2V=80°\ 54'$. The sp. gr. is 4·027, and the hardness 7. The indices of refraction are $\alpha=1{\cdot}6911$, $\beta=1{\cdot}6957$, and $\gamma=1{\cdot}7028$; and the birefringence, according to E. Dittler, is $\gamma-\alpha=0{\cdot}014$. The optical character is positive. The mineral is not attacked by the ordinary mineral acids.

The mineral *helvite* or *helvine* was first described by F. Mohs,[6] and named by A. G. Werner, from *ἥλιος*, the sun, in allusion to its yellow colour. Analyses were made by H. A. von Vogel, C. G. Gmelin, C. F. Rammelsberg, N. Teich, N. von Kokscharoff, R. Haines, B. E. Sloan, W. C. Brögger, H. A. Miers and G. T. Prior, H. Bäckström, etc. The results have been discussed by C. F. Rammelsberg, who gave $(Mn,Fe)S.3(Be,Mn,Fe)_2,SiO_4$; G. A. Kenngott gave $MnS.3R_2SiO_3$; V. M. Goldschmidt gave $3RBeSiO_4.RS$; and P. Groth, $(Be,Mn,Fe)_7S(SiO_4)_3$. W. C. Brögger and H. Bäckström made some observations on this subject. The idealized mineral is **beryllium sulphosilicate,** the actual mineral is a solid soln. with various other silicates. The mineral is usually yellow, brownish-red, or green. The crystals belong to the cubic system. The sp. gr., determined in many cases by those who analyzed the mineral, range from 3·165–3·383. The hardness is over 6. A. Michel-Lévy and A. Lacroix gave 1·739 for the refractive index. The pyroelectric properties were studied by W. G. Hankel, and J. and P. Curie. When treated with hydrochloric acid, hydrogen sulphide is evolved, and gelatinous silica is formed.

J. P. Cooke found a beryllium sulphosilicate in the granite of Rockport, Mass., which was called *danalite* after J. D. Dana. According to C. F. Rammelsberg, analyses by J. P. Cooke, F. A. Genth, and H. A. Miers and G. T. Prior correspond with $RS.3R_2SiO_4$; according to G. A. Kenngott, with $ZnS.3(Be,Fe,Mn)_2SiO_4$; and, according to P. Groth,

$(Fe,Zn,Be,Mn)_7S(SiO_4)_3$. The sp. gr. is 3·427, and the hardness 5–6. With hydrochloric acid, hydrogen sulphide is evolved and gelatinous silica remains.


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## § 27. Magnesium Orthosilicates

The mineral **forsterite** was first described by A. Lévy[1] in 1824. It was named after L. Forster. The mineral was found as crystals and crystal aggregates in Vesuvian lava. G. Strüver found it in the Baccano crater. Observations on Italian forsterite were also made by B. Mierisch, G. vom Rath, M. Bauer, F. Hessenberg and A. Scacchi, A. A. Lösch; N. von Kokscharoff reported it in a mine at Slataust, Urals; A. Knop, at Schelingen, Kaiserstuhl, Baden; A. Helland, at Snarum, Norway; and A. K. Coomaraswamy, at Kakgala, Ceylon. C. U. Shepard called a variety he found at Bolton, Mass., *boltonite*. Analyses were made by those just mentioned and by C. F. Rammelsberg, E. Weinschenk, K. Thaddéeff, F. Zambonini, H. Arsandaux, J. L. Smith, G. J. Brush, etc. E. Cohen found the mineral in a meteorite from Los Muchachos. The results correspond with **magnesium orthosilicate**, $Mg_2SiO_4$. J. J. Ebelmen reported that he synthesized crystals of forsterite, *qui présentent exactement les mêmes faces que les cristaux du péridot du Vésuve*, by fusing a mixture of boric oxide, silica, and magnesia. The boric oxide simply served as a solvent of relatively low m.p., and it was evaporated by a protracted heating at a high temp. G. Lechartier fused silica and magnesia along with calcium chloride; and P. Hautefeuille operated with the same oxides and magnesium chloride. S. Meunier heated magnesium vapour to redness in a mixture of steam and silicon chloride.

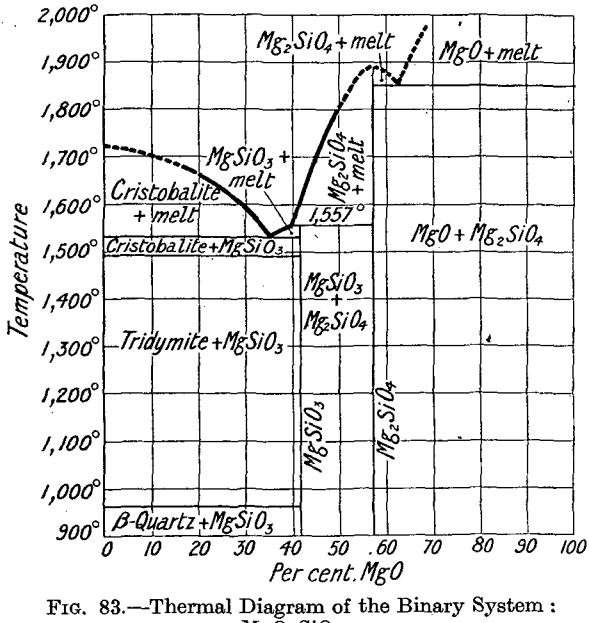



FIG. 83.—Thermal Diagram of the Binary System: $MgO$–$SiO_2$.

N. G. Sefström, W. A. Lampadius, J. A. Hedvall, and P. Berthier heated various mixtures of magnesia and silica, and obtained more or less devitrified enamels. J. W. Cobb noted that the reaction begins below the m.p. of either component. W. Pukall also obtained the orthosilicate by heating an intimate mixture of magnesia and silicic acid. G. Stein fused a mixture of the constituents at a temp. exceeding 2000° in an electrically heated carbon tube furnace, and obtained crystals which *mit dem des Minerals Fosterit übereinstimmt*. The f.p. curves of mixtures of silica and magnesia have been studied by N. L. Bowen and O. Andersen. The results are indicated in Fig. 83. Both the ortho- and the meta-silicates can exist

in contact with the liquid. The maximum corresponding with the orthosilicate is at 1890° ± 20°; and the eutectic with magnesium oxide and the orthosilicate is at 1850° ± 20°, at which the mixture has 14 per cent. of magnesia, and 86 per cent. of the orthosilicate. The eutectic with silica and magnesium metasilicate as solid phases has 12·5 per cent. of the former, and 87·5 per cent. of the latter, and the temp. is 1543° ± 20°. For the colloidal magnesium silicates, *vide supra*, water-glass.

The crystals of forsterite belong to the rhombic system. They have been studied by W. H. Miller, G. vom Rath, F. Fouqué and A. Michel-Lévy, V. Goldschmidt, E. T. Allen and co-workers, A. Scacchi, F. Hessenberg, G. Strüver, N. von Kokscharoff, etc. M. Bauer gave for the axial ratios $a:b:c=0{\cdot}46476:1:0{\cdot}58569$. The cleavage after the (001 and the (010) faces is perfect. The optic axial angle is large, being 86°. G. vom Rath gave 3·191 for the sp. gr. of forsterite; C. F. Rammelsberg, 3·243; K. Thaddéeff, 3·223; N. von Kokscharoff, 3·191; A. Helland, 3·22; J. L. Smith, 3·208–3·328; H. Arsandaux, 3·248; and E. Cohen, 3·199. The natural crystals usually contain a little iron; H. Backlund's sample from Slataust was very low in iron, and its sp. gr. was 3·191. J. J. Ebelmen's synthetic forsterite had a sp. gr. 3·237; N. L. Bowen and O. Andersen's, 3·216 ± 0·002; G. Stein's, 3·21; and G. Lechartier's, 3·22. The hardness of forsterite is between 4 and 5. N. L. Bowen and O. Andersen gave 1890° ± 20° for the m.p.; G. Stein said the m.p. is below 1900°. A. S. Deleano gave 1600° for the m.p.; C. Doelter, 1700° for the m.p., 1655° for the f.p., and 1785° for the temp. of formation. The indices of refraction have been determined by A. des Cloizeaux. H. Backlund found for Na-light with a sample from Slataust, $\alpha=1{\cdot}6361$, $\beta=1{\cdot}65185$, and $\gamma=1{\cdot}66975$. N. L. Bowen and O. Andersen gave $\alpha=1{\cdot}635$, $\beta=1{\cdot}661$, and $\gamma=1{\cdot}670$; and birefringence 0·035 for Na-light; and E. T. Allen and co-workers gave $\alpha=1{\cdot}645$, $\beta=1{\cdot}656$, and $\gamma=1{\cdot}668$ all ± 0·003; and birefringence 0·023. The crystals extinguish parallel to the cleavage directions. The crystals are decomposed by hydrochloric acid with the separation of gelatinous silica—*vide* olivine. W. Pukall said that his product gained only 2·58 per cent. after lying in water for 70 days.

It is really difficult to obtain minerals quite free from iron. The colours, ranging from pale cream, yellow, red, and brown to black, are usually produced by iron oxide as the predominant tinctorial agent, for, as R. J. Haüy remarked: "When Nature takes up her brush, iron is almost always on her palette." Forsterite may be white, yellowish-white, greyish-white, or greenish-white, and it sometimes becomes yellow on exposure to air, owing to the oxidation of the "ferrous" iron. The white and colourless crystals—*e.g.* those from Vesuvius—have been also called *white olivine*, or *white peridote*. The ferrous oxide in the published analyses of forsterite ranges from 0·22 up to 4·56 per cent.; with higher proportions, the mineral passes into chrysolite or olivine. There is, however, no sharp line of demarcation, It would appear as if fayalite, $Fe_2SiO_4$, and forsterite, $Mg_2SiO_4$, are the terminal members of a continuous series of solid soln.

Near the beginning of the present era, *chrysolite*—χρυσός, gold: λίθος, a stone—was referred to by Pliny in his *Historia naturalis* (**37.** 42), and it is thought to refer to what is now called topaz, and his topaz refers to the present-day chrysolite. Some varieties of both are used as gem-stones. Chrysolite was referred to by the older writers: J. G. Wallerius,[2] A. J. d'Argenville, A. Cronstedt, J. B. L. Romé de l'Isle, and F. de St. Fond. A. G. Werner applied the name **olivine**, in reference to the olive-green colour of many specimens. According to R. J. Haüy, the term *peridot* is of unknown derivation, but it had been used for a long time by the French jewellers for chrysolite. He showed that the three names referred to the one mineral. G. Romanovsky's *glinkite* was shown by W. Beck to be nothing but chrysolite or olivine. V. Iskyul studied the action of hydrochloric acid on glinkite. The term olivine is used not only for a specific mineral, but also for a group of ferro-magnesian orthosilicates of the general formula $R''_2SiO_4$. The family includes *forsterite*, $Mg_2SiO_4$; *monticellite*, $CaMgSiO_4$; *olivine peridote*, or *chrysolite*,

$(Mg,Fe)_2SiO_4$; *hortonolite*, $(Fe,Mg,Mn)_2SiO_4$; *fayalite*, $Fe_2SiO_4$; *tephroite*, $Mn_2SiO_4$; and *roepperite*, $(Fe,MnZn)_2SiO_4$. Calcium orthosilicate is sometimes called *lime-olivine*.

Olivine is an essential constituent and characteristic mineral of many basic rocks. It is commonly developed in the less siliceous magmas and lavas. It is rarely found crystallized on a large scale, but well-defined, small crystals are common in basic eruptive rocks like basalt, limburgites, peridotites, and gabbros. It is less common in trachytes, andesites, and dacites. Olivine is the predominant mineral in some ultra-basic rocks, and, associated with diallage or bronzite, may form an olivine-rock. At the Dun Mt. in New Zealand, it is associated with chromite, forming a mass of rock called *dunite*. Olivine is a common constituent of meteorites. Numerous analyses have been reported.[3] The silica in the analyses ranges from 36·72–42·81 per cent.; the magnesia, from 28·48–51·64 per cent.; and the ferrous oxide, from 5·01–29·96 per cent. If the formula be $(Mg,Fe)_2SiO_4$, the ratio Mg : Fe ranges from 9 : 1 to about 2 : 1. G. Cesaro agreed with G. Tschermak in considering olivine to be an oxymetasilicate :

$$O<\begin{matrix}Mg\\Mg\end{matrix}>SiO_3$$

A. Damour [4] described a *péridot titanifère*, or *titanolivine*, of a deep yellow or red colour containing 5–6 per cent. $TiO_2$. It was discussed by A. Lacroix, and L. Brugnatelli; its composition is represented $(Mg,Fe)_2(Si,Ti)O_4$.

P. Berthier [5] first synthesized olivine by simply fusing a mixture of the constituent oxides. F. Fouqué and A. Michel-Lévy obtained it by fusing a mixture of magnesia, silica, and ferrous ammonium sulphate; A. Daubrée, by recrystallization from fused meteorites, magnesian eruptive rocks, and serpentine; and also by the partial oxidation of an iron silicide and subsequent fusion of the product; V. Pöschl, fused mixtures of silica, iron carbonate, and magnesium carbonate. He also made a partial study of the binary system, $Mg_2SiO_4$–$Fe_2SiO_4$ (*vide infra*), and of the ternary system, $Mg_2SiO_4$–$Fe_2SiO_4$–$Ca_2SiO_4$. C. Doelter made olivine by fusing hornblende with calcium and magnesium chlorides; G. Lechartier, by fusing silica, magnesia, and calcium chloride and some iron compound; P. Hautefeuille, by fusing silica, magnesia, and magnesium chloride in a similar way; and likewise also J. J. Ebelmen, by fusing together silica, magnesia, iron oxide, boric acid, and potassium tartrate. H. H. Reiter fused mixtures of albite, nephalite, augite, olivine, and magnetite in different proportions, and observed that olivine separates along with several other minerals when the mass cools. C. Doelter obtained olivine among the products of the fusion of biotite, vesuvianite, tourmaline, clinichlore, and garnet. G. vom Rath found some crystals of olivine formed in the mantle of a blast furnace; P. W. Jeremeéff, in some cast-iron; and J. H. L. Vogt, and F. W. Rüsberg, in some blast furnace slags.

The **colour** of olivine is commonly olive-green, but it is sometimes brownish or greyish-red, or greyish-green; and its colour may change on exposure to air owing to oxidation of the ferrous iron. The lustre is usually vitreous. The **crystals** have been measured by G. vom Rath,[6] V. von Zepharovich, A. Scacchi, H. Traube, G. Rose, F. A. Quenstedt, W. Haidinger, M. F. Heddle, etc. The crystals belong to the rhombic system, with axial ratios $a : b : c = 0·4658 : 1 : 0·5865$. A. des Cloizeaux found the optic axial angle to be 87° 46′. F. Rinne and co-workers, N. Alsen and G. Aminoff, and C. Berndt have obtained the **X-radiogram** of olivine; but the space-lattice has not been established. According to C. Berndt, the elementary parallelopiped has the dimensions $a = 4·84 \times 10^{-8}$ cm., $b = 10·40 \times 10^{-8}$ cm., and $c = 6·10 \times 10^{-8}$ cm. The lattice is occupied only at the corners, and there are 4 molecules $Mg_2SiO_4$ in each unit; it does not appear to be either an ortho- or a meta-silicate, but rather $4(MgO.MgO.SiO_2)$. The speed of crystallization at different temp. has been measured by E. Kittl. He found that the **speed of**

**crystallization** shows a sharp maximum at about 1370°, 20° above the temp. at which the crystallization of the glass begins; and he estimated that in the crystallization of the glass $MgFeSiO_4$, there are 130,000 centres of crystallization per sq. cm.; with the glass $5Mg_2SiO_4.Fe_2SiO_4$, 430,000 centres; and with $9Mg_2SiO_4.Fe_2SiO_4$, 250 centres. The **cleavage** of olivine is distinct. Fig. 85 shows diagrammatically a transverse section of a prismatic crystal of olivine with obtuse angles 94° and acute angles 86°. The outer dotted line is the primary form. The broken lines are the rectangular cleavage. Most of those who have analyzed olivine also measured the **specific gravity.** In general, the sp. gr. rises with increasing iron content; thus:

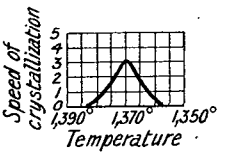



FIG. 84.—Effect of Temperature on the Speed of Crystallization of Olivine.

| Per cent. FeO | 5·01 | 9·90 | 14·06 | 174·5 | 29·96 | 44·37 |
|---|---|---|---|---|---|---|
| Sp. gr. | 3·261 | 3·360 | 3·336 | 3·479 | 3·566 | 3·910 |

There are a few discrepancies dependent, in part, on the nature of the impurities associated with the olivine. The hardness is about 7. The m.p. varies markedly with the proportion of iron. The more ferruginous olivines are decomposed at a high temp., and the ferrous oxide is transformed into ferrosic oxide. Hence, the m.p. determination loses its significance. V. Pöschl found for mixtures of forsterite and fayalite, *i.e.* of magnesium and ferrous orthosilicates,

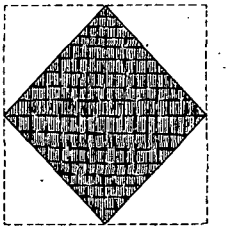


FIG. 85.—Transverse Section of Olivine.

| $Mg_2SO_4$ | 100 | 90 | 80 | 70 | 60 per cent. |
|---|---|---|---|---|---|
| Sp. gr. | 3·11 | 3·16 | 3·30 | 3·36 | 3·46 |
| M.p. mean | 1600° | 1350° | 1332° | 1322° | 1350° |

K. Thaddéeff, and A. Moitessier have studied the behaviour of olivine when heated in an oxidizing atm. The former found only three-fifths of the ferrous oxide was converted to ferric oxide. A. Brun's value for the m.p., *viz.* 1750°, is too high; C. Doelter found 1360°–1410°, for a specimen from Kapfenstein; 1395°–1430° for one from Söndmöre; 1310°–1315°, for one from Somma; and 1395°–1445°, for one from Egypt. A. des Cloizeaux gave for the **indices of refraction** $\alpha$=1·661, $\beta$=1·678, and $\gamma$=1·697. H. Backlund, M. Stark, N. H. Magnusson, and S. L. Penfield and E. H. Forbes investigated the relation between the proportion of contained iron and the optical properties. H. Backlund gave the results indicated in Table XVI. M. Stark found the **axial angle** decreases with increasing proportions of iron. S. C. Lind and D. C. Bardwell found no change of colour or thermoluminescence when peridote is exposed to **radium radiations.**

TABLE XVI.—EFFECT OF THE PROPORTIONS OF IRON ON THE REFRACTIVE INDICES OF OLIVINE.

| Occurrence. | Molar per cent. $Fe_2SiO_4$ | $\alpha$ | $\beta$ | $\gamma$ | $\gamma-\alpha$ |
|---|---|---|---|---|---|
| Ural | 0·12 | 1·6361 | 1·6519 | 1·6698 | 0·0337 |
| Somma | 2·20 | 1·6386 | 1·6544 | 1·6719 | 0·0323 |
| Wind Matrey | 7·36 | 1·6507 | 1·6669 | 1·6856 | 0·0349 |
| Kosakoff | 9·48 | 1·6526 | 1·6691 | 1·6884 | 0·0358 |
| Kapfenstein | 9·57 | 1·6533 | 1·6705 | 1·6887 | 0·0354 |
| Vesuvius | 9·88 | 1·6548 | 1·6719 | 1·6919 | 0·0371 |
| Pallaseisen | 12·48 | 1·6562 | 1·6726 | 1·6921 | 0·0359 |
| Kammerbühl | 15·42 | 1·6649 | 1·6830 | 1·7015 | 0·0366 |
| Vesuvius | 17·25 | 1·6674 | 1·6862 | 1·7053 | 0·0379 |
| Itkal (glinkite) | 19·85 | 1·6694 | 1·6878 | 1·7067 | 0·0373 |
| Skurruvasely | 22·53 | 1·6775 | 1·6974 | 1·7163 | 0·0388 |
| Limberg (hyalosiderite) | 33·92 | — | 1·7276 | 1·7426 | — |
| Hortonolite | 67·45 | 1·7684 | 1·7915 | 1·8031 | 0·0347 |
| Fayalite | 98·40 | 1·8236 | 1·8642 | 1·8736 | 0·0500 |

F. von Kobell found that olivine is gelatinized when treated with sulphuric acid. Olivine is quite soluble in conc. hydrochloric acid, and the most ferruginous varieties dissolve fastest. The silicic acid which separates is granular. G. Tschermak said that it is meta- not ortho-silicic acid. V. Iskyul studied this subject. G. Lewinstein found that there is a 22·6 per cent. undissolved residue when olivine from Ihringen is treated with hydrochloric acid; and he analyzed the part which passed into soln. C. F. Rammelsberg made some observations on this subject. F. W. Clarke and E. A. Schneider treated olivine at 383°–412° with dry hydrogen chloride, and observed but a small proportion to be decomposed. G. A. Kenngott, and F. Cornu observed that powdered olivine has an alkaline reaction. R. Müller, E. W. Hoffmann, and A. Johnstone found that olivine is decomposed by carbonated water. H. Lotz studied the effect of air charged with sulphur dioxide on olivine. E. C. Sullivan studied the basic exchange which occurs with olivine in contact with soln. of cupric sulphate. V. Iskyul studied the solubility of silica in forsterite, olivine, and glinkite. Olivine readily weathers on exposure; serpentine and talc appear to be formed. The subject has been discussed by S. Hillebrand,[7] G. Tschermak, P. V. von Jeremeéff, B. Kolenko, W. Lindgren, J. F. Gmelin, K. A. Redlich, F. L. Hess, J. Roth, K. Busz, F. Becke, C. G. C. Bischof, A. E. Törnebohm, C. R. van Hise, A. M. Finlayson, etc. C. Madelung,[8] J. R. Blum, and C. Doelter described the partial conversion of olivine into carbonate.

The mineral *villarsite* found by A. Dufrénoy [9] at Traversella and named after M. Villars is a serpentinized olivine. It has also been described by L. R. Fellenberg, L. Heffter, L. Duparc and F. Pearce, A. Lacroix, A. des Cloizeaux, and W. T. Schaller. The so-called *iddingsite* is possibly a similar product.[10] M. F. Heddle [11] described a mineral which he called *ferrite*. It was considered to be an olivine largely transformed into ferric oxide, etc. Similar products were described by A. Moitessier, F. Gonnard, K. Thaddéeff, and A. Liebrich, The *matricite* of N. O. Holst [12] found at Krangrufva, Sweden, is a variety of olivine which has been weathered.

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## § 28. Magnesium Metasilicates

Magnesium metasilicate introduces two classes of minerals—the pyroxenes and the amphiboles. The name **pyroxene** was originally applied by R. J. Haüy [1] to some greenish crystals which had been found in the lavas of Vesuvius, Etna, and Auvergne. He intended to indicate that the crystals were only accidentally caught up in the lavas which contained them—πῦρ, fire; ξένος, a stranger—but in reality the pyroxenes come next to the felspars in their abundant distribution in igneous rocks. Many different minerals have been called pyroxene, and the term is now used for a whole group of minerals which have a cleavage of about 88°, and which, excepting where they contain alumina, have the general metasilicate formula $M''SiO_3$. These minerals also pass into one another by a continuous series of solid soln. They include minerals belonging to three different systems.

The **rhombic pyroxenes** include *enstatite*, $MgSiO_3$; *bronzite* and *hypersthène*, $(Mg,Fe)SiO_3$. The **monoclinic pyroxenes** include *wollastonite*, $CaSiO_3$; *diopside*, $MgCa(SiO_3)_2$; *sahlite*, $(Mg,Fe)Ca(SiO_3)_2$; *hedenbergite*, $FeCa(SiO_3)_2$; *schefferite*, $(Mg,Fe)(Ca,Mn)(SiO_3)_2$; *jefferonite*, $(Mg,Fe,Zn)(Ca,Mn)(SiO_3)_2$; *augite*, $(Mg,Fe)Ca(SiO_3)_2$; *fassaite*, $(Mg,Fe)(Al,Fe)_2SiO_6$; *spodumene*, $(Li,Na)Al(SiO_3)_2$; *acmite*, $NaFe(SiO_3)_2$; and

*pectolite*, $Na_2Ca_2(SiO_3)_3$. The **triclinic pyroxenes** include *rhodonite*, $MnSiO_3$; *bustamite*, $(Mn,Ca)SiO_3$; *fowlerite*, $(Mn,Fe,Ca,Zn)SiO_3$; *babingtonite*, $(Ca_3Fe''_3,Mn_3Fe'''_2)(SiO_3)_3$.

The term **amphibole**—from ἀμφίβολος, doubtful—was applied by R. J. Haüy to replace schorl, an old mining term previously applied to black tourmaline, hornblende, etc. The word is now used for a whole group of minerals related to the pyroxenes in being represented, except where alumina is present, by the general metasilicate formula $M''SiO_3$, and they likewise pass one into the other by a series of solid soln. The cleavage angle of the amphiboles is about 57° instead of 87° as with the pyroxenes. Like the pyroxenes, the amphiboles include minerals belonging to three different systems.

The **rhombic amphiboles** are rare. They include *anthophyllite*, $(Mg,Fe)SiO_3$; and *gedrite*, $2(Mg,Fe)SiO_3.MgAl_2SiO_3$. The **monoclinic amphiboles** are common. They include *cummingtonite*, $(Fe,Mg)SiO_3$; *dannemorite*, $(Fe,Mg,Mn)SiO_3$; *richterite*, $(K_2,Na_2,Mg,Ca,Mn)SiO_3$; *tremolite*, $Mg_3Ca(SiO_3)_4$; *actinolite*, $(Mg,Fe)_3Ca(SiO_3)_4$; *hornblende*, $(Mg,Fe)_3Ca(SiO_3)_4$; *edenite*, $Na_2Al_2(SiO_3)_4$; *pargasite*, $(Mg,Fe)_2(Al,Fe)_4(SiO_6)_2$; *arfvedsonite*, $(Na_2,Ca,Fe)_4(SiO_3)_4$, and $(Ca,Mg)_2(Al,Fe)_4(SiO_6)_2$, and the related *barkevikite*; *glaucophane*, $NaAlSi_2O_6$, or $(Fe,Mg)SiO_3$; *riebeckite*, $NaFeSi_2O_6$; *jadeite*, $NaAl(SiO_3)_2$. **Triclinic amphibole** is rare, and is represented by *œnigmatite*, $Na_4Fe_9(Al,Fe)_2(SiTi)_{12}O_{38}$.

According to E. T. Allen and co-workers,[2] **magnesium metasilicate,** $MgSiO_3$, is tetramorphous. The different forms represent the end-members of four series of solid soln. represented by natural minerals. Two belong to the pyroxene family, and two to the amphibole family. Each of these families is represented by magnesium metasilicates which crystallize in the rhombic and monoclinic systems. They can be classed:

| | | | |
|---|---|---|---|
| Magnesium metasilicates | Pyroxenic | rhombic | **Enstatite** |
| | | monoclinic | **Clinoenstatite** |
| | Amphibolic | rhombic | **Anthophyllite** |
| | | monoclinic | **Clinoanthophyllite** |

A fifth rhombic form, called *α-magnesium metasilicate*, was reported by E. T. Allen and co-workers to be an enantiomorphic variety of ordinary clinoenstatite, which they called *β-magnesium metasilicate*. The transition temp. was given as 1365°. N. L. Bowen and O. Andersen, however, showed that the alleged α-$MgSiO_3$ is really a product of the dissociation of clinoenstatite at 1557°, being therefore magnesium orthosilicate, *i.e.* forsterite, and not a form of the metasilicate: $2MgSiO_3 \rightleftharpoons Mg_2SiO_4 + SiO_2$. On account of the breaking up of clinoenstatite into forsterite and liquid, there is no eutectic between these two compounds, Fig. 100; but, on cooling the liquids, there is a complete or partial re-solution of forsterite at 1557°, and clinoenstatite is formed.

Native magnesium metasilicate free from iron is scarce. The name **enstatite** was applied by G. A. Kenngott to a white, yellowish, greyish, or greenish white mineral which he found in the Zdjar Mt., Moravia, and which had been previously regarded as seapolite. The term enstatite—ἐνστάτης, an opponent—was intended to refer to its refractoriness. He noted the close chemical relationship between it and the rhombic pyroxenes: bronzite, and hypersthene. The dark brown, or greyish, or greenish-black mineral designated *labradorische Hornblende* by A. G. Werner, and L. A. Emmerling, was recognized by R. J. Haüy, in 1803, to be different from hornblende, and he accordingly renamed it **hypersthene,** from ὑπέρ, very; σθένος, strong, in reference to its exceeding hornblende in hardness or toughness. He had previously called the mineral *diallage métalloïde*. A. G. Werner named the hypersthene from Paul Island, Labrador, *paulite*. The term **bronzite** was used by D. L. G. Karsten and M. H. Klaproth for a mineral with a bronze metallic lustre obtained from Styria. R. J. Haüy referred to it as being *une variété fibro-laminaire métalloïde à reflets bronzés*. A. Breithaupt, F. Mohs, E. F. Glocker, W. Haidinger, J. F. Hausmann, C. Hartmann, etc., referred paulite and bronzite to the same mineral species.

About 1869, G. vom Rath described crystals of a rhombic pyroxene which he obtained from the volcanic ejecta at Lake Laach, and which he called *amblystegite*—ἀμβλύς, blunt; στέγη, dome, in reference to the form of the crystals. He later identified this with hypersthene. S. Meunier called the enstatite from a meteorite at Deesa, Chile, *victorite*, in honour of Victor Meunier. C. U. Shepard described crystals of what he regarded as magnesium trisilicate, and named *chladnite*, which he found in a meteorite at Bishopville, South Carolina. The observations of G. S. von Waltershausen, J. L. Smith, C. F. Rammelsberg, and G. A. Kenngott showed that chladnite is essentially enstatite. G. Rose called the mineral *shepardite*, but this term had been previously applied to another mineral by W. Haidinger in 1847. G. Tschermak separated from the same mineral a ferruginous pyroxene, like bronzite, which he named *diogenite*, after Diogenes of Apollonia. The *szaboïte* of A. Koch, and A. von Lasaulx was shown by J. A. Krenner, and F. Koch to be hypersthene. The *schiller-spar* of Baste in the Harz, etc., was described by M. F. Heddle, F. W. H. von Trebra, C. Heyer, F. Köhler, J. F. Gmelin, J. C. Freiesleben, W. Hetzer, F. Pisani, D. L. G. Karsten, L. A. Emmerling, R. J. Haüy, A. J. M. Brochant, J. F. Hausmann, G. A. Kenngott, K. Johannson, A. Breithaupt, A. G. Werner, F. Mohs, etc. W. Haidinger called it *bastite*. G. Rose showed that schiller-spar is probably an alteration product of a mineral of the pyroxene group. This was confirmed by F. Köhler, J. A. Drappier, H. Girard, A. Baentsch, and A. Streng. The fresh mineral was called *protobastite* and regarded as being allied to bronzite. M. Websky, G. Tschermak, and H. Rosenbusch showed that there are no real reasons for regarding protobastite and enstatite as distinct mineral species. A. Breithaupt applied the term *phästine* to an alteration product of bronzite or a bronze-like pyroxene. A similar view was taken by A. des Cloizeaux, G. Tschermak, and R. von Drasche. A yellow pyroxene with a mother-of-pearl lustre, obtained by A. Breithaupt from the serpentine at Matrey, Tyrol, etc., was called diaclase—or, according to J. F. Hausmann, *diaclasite*—διά, through; κλαστός, broken. A. G. Werner called it *schillerstein*; J. C. Freiesleben, yellow schiller-spar; R. J. Haüy, *diallage verte*; and J. F. Hausmann, talc-like hornblende. F. Köhler, A. Streng, C. F. Rammelsberg, A. des Cloizeaux, M. Websky, etc., made some observations on the mineral and co-ordinated it with enstatite or hypersthene. The *germarite* of A. Breithaupt is a slightly altered hypersthene. J. L. Smith applied the term *peckhamite*, after S. F. Peckham, to some rounded nodules he found in the meteorite of Estherville, Iowa. It is not clear if this is a mixture of enstatite and, say, olivine. G. Tschermak gave the name *grahamite* to the mixture, presumably, of plagioclase, enstatite, and olivine, which occurred in a meteorite from Sierra de Chaco; and S. Meunier, *logronite* to that in a meteorite at Barea, Logrono, Spain. C. U. Shepard found what appeared to be a hydrated bronzite which he called *antillite*. Its composition approached that of serpentine.

C. Hintze has given a list of the many places where enstatite, bronzite, and hypersthene have been reported, and they include nearly all countries on earth—in England and Scotland,[3] Germany,[4] Hungary,[5] Austria,[6] Italy,[7] Portugal,[8] Spain,[9] France,[10] Santorin,[11] Norway,[12] Sweden,[13] Finland,[14] Urals,[15] Siberia,[16] Russia,[17] Cracow,[18] Persia,[19] Sumatra and Borneo,[20] Japan,[21] South America,[22] United States,[23] Canada,[24] Labrador,[25] Greenland,[26] Africa,[27] and New Zealand.[28] The occurrence of enstatite, bronzite, or hypersthene in meteorites has been investigated by C. U. Shepard,[29] N. S. Maskelyne, G. Tschermak, etc.

Analyses are given by most of the authorities quoted in connection with the occurrence of the mineral. The magnesia content of enstatite varies from 29·7–41·8 per cent.; the silica from 54·0–62·1 per cent.; the ferrous oxide from 0·21–4·5 per cent.; the alumina from mere traces up to about 3 per cent. A little alkali, manganese oxide, nickel oxide, chromic oxide, sulphate, phosphate, carbonate, and water may also be present. In bronzites and hypersthenes, the magnesia ranges from about 15–36 per cent.; the silica from about 50–58 per cent.; the ferrous oxide from 5–25 per cent.; the alumina from mere traces to about 5 per cent., although there are a few with alumina ranging up to that of the aluminous pyroxenes, say, 10 per cent. Eliminating what are thought to be accidental contaminations, there appears to be a continuous series of solid soln., with magnesium metasilicate and ferrous metasilicate as terminal members. The term enstatite is applied to the forms near the magnesium silicate end of the series. There is no sharp line of demarcation between enstatite and hypersthene. Bronzite is usually considered to be intermediate between enstatite and hypersthene; but, the affixing of a lower limit for the proportion of ferrous oxide for bronzite and hypersthene is quite an arbitrary convention. The general formula may therefore be written $(Mg,Fe)SiO_3$; and in the tables of analyses, the ratio Mg : Fe in enstatite, and bronzite ranges from 8 : 1 to about 3 : 1; while in hypersthene, this ratio falls from 3 : 1 to nearly 1 : 1. Some-

what similar suggestions were made by A. des Cloizeaux,[30] G. A. Kenngott, G. Tschermak, etc. C. Hintze considers the two minerals enstatite and hypersthene, and applies the term bronzite only to those varieties showing schillerization.

E. T. Allen, F. E. Wright, and J. K. Clement [31] prepared rhombic enstatite, or magnesium metasilicate free from iron oxide, by suddenly quenching the thoroughly molten metasilicate glass in water; and afterwards annealing the glass in fragments of about 10 grms. between 1000° and 1100°. The crystallization begins at the surface and proceeds inwards with a rise of temp. The outer portion contracts, and squeezes out the liquid interior, forming hollow, rounded projections which crystallize last. If the temp. be 1125° or higher, the rhombic enstatite is accompanied by the monoclinic form, and this the more the higher the temp.; over 1300°, nearly all the product is monoclinic. M. Schmidt claimed that when the glass is rapidly cooled the monoclinic form predominates, and if slowly cooled a smaller proportion is formed. E. T. Allen and co-workers also point out that the alleged syntheses of enstatite by J. J. Ebelmen, P. Hautefeuille, and S. Meunier were afterwards shown by F. Fouqué and A. Michel-Lévy, and J. H. L. Vogt, to be really clinoenstatite. A. Daubrée melted portions of meteorites, but obtained crystals too opaque to determine their optical properties—monoclinic or rhombic. He also melted a mixture of olivine and 15 per cent. of silica, and obtained a fibrous mass with the properties of enstatite. E. T. Allen and co-workers, however, found that clinoenstatite is formed under these conditions. F. Fouqué and A. Michel-Lévy prepared rhombic enstatite, mixed with but a small amount of the monoclinic form, by melting and rapidly cooling a mixture of 12 grms. of silica, 3 grms. of magnesia, and 5 grms. of ferric oxide. The cold cake contained arborescent crystals which developed into needles with parallel extinction when reheated at a temp. just over the m.p. of copper. J. Morozewicz obtained rhombic enstatite in his experiments on the synthesis of basalt. J. H. L. Vogt, and W. Wahl suggested that the production of the monoclinic form is favoured by the presence of ferrous oxide, and calcium oxide.

The **colour** of the crystals is largely determined by the contained iron and varies from a brownish-green, olive-green, greenish-brown, or black, or greenish, greyish, or yellowish white. The lustre may be glassy, mother-of-pearl, or metallic. The enstatite prepared by E. T. Allen and co-workers was obtained only in fibrous aggregates and radial spherulites which did not admit of the measurement of the morphologic constants. The direction of elongation of the fibres in the spherules was not that of the prism axis, but parallel to that of the greater ellipsoidal axis. The crystals of the minerals enstatite, bronzite, and hypersthene have been measured by C. F. Rammelsberg, B. Weigand, F. Becke, H. Bücking, H. Sommerlad, A. des Cloizeaux, A. Schmidt, J. A. Krenner, G. H. Williams, W. C. Brögger and H. H. Reusch, H. Rosenbusch, Y. Kikuchi, N. V. Ussing, V. von Lang, etc. According to G. vom Rath, the rhombic **crystals** have the axial ratios $a:b:c = 0{\cdot}97133 : 1 : 0{\cdot}57000$. E. T. Allen and co-workers found the cleavage of artificial enstatite to be well marked, making an angle approximately 90°. The **optic axial angle** ranged from 44°–70°. G. Tschermak found the axial angle depends on the proportion of contained iron. Thus, for yellow light (and for red light in the case of those marked *):

| Per cent. FeO | 2·76 | 5·77 | 9·86 | 15·14 | 19·70 | 27·70 | 33·60 |
|---|---|---|---|---|---|---|---|
| Axial angle | *133° 8′ | *123° 38′ | 106° 51′ | 98° 0′ | 84° 18′ | 79° 48′ | 59° 20′ |

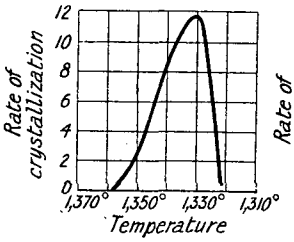
According to A. des Cloizeaux, raising the temp. to about 75° produced no perceptible change in the angles of the optic axes. C. Berndt studied the **X-radiogram** of olivine. E. Kittl found sharp maxima in the variation of the **speed of crystallization** of bronzite and hypersthene with temp. as illustrated in Figs. 86 and 87. He estimated that during crystallization with magnesium metasilicate there are 930 centres of crystallization per sq. cm.; with bronzite, 14 per sq. cm.

The **specific gravity** of artificial enstatite, free from the monoclinic variety, was

found by E. T. Allen and co-workers to be 3·175 at 25°. The sp. gr. of many of the specimens of enstatite and bronzite, indicated above, were determined, and, as a rule, the sp. gr. has a tendency to rise as the proportion of the contained iron increases :

| | | | | | |
|---|---|---|---|---|---|
| Per cent. FeO . . . | 0·90 | 6·44 | 13·6 | 19·84 | 26·93 |
| Sp. gr. . . . . | 3·217 | 3·308 | 3·333 | 3·487 | 3·531 |

There are, however, many apparent exceptions due to the presence of impurities, differences in the method of determination, etc. The **hardness** ranges from 5–6. L. H. Adams and E. D. Williamson found the **compressibility** of enstatite, $(MgSiO_4)_{88}(FeSiO_3)_{12}$, to be $\beta=1{\cdot}03\times10^{-6}$ between 0 and 10,000 megabars press. ; and for hypersthene, $(MgSiO_3)_{70}(FeSiO_3)_{30}$, $\beta=1{\cdot}01\times10^{-6}$ between 0 and 10,000 megabars press. J. Joly gave 0·179 for the **specific heat** of hypersthene between 13·3° and 100° ; and R. Ullrich, 0·1914 between 19° and 98°. W. P. White gave for the mean **atomic heat** of magnesium metasilicate, $MgSiO_3$, 4·42 at 100° ; 5·26 at 300° ; 5·62 at 500° ; 5·87 at 700° ; and 6·04 at 900°. E. T. Allen and co-workers gave 1521° for the **melting point** of artificial enstatite. C. Doelter gave 1380°–1400° for the m.p. of enstatite ; and 1330°–1380° for bronzite ; J. Joly gave for bronzite, 1300° ; R. Cusack, 1295° ; and A. L. Fletcher, 1345°. V. S. Deleano gave 1500° for the m.p. of enstatite ; and Y. Yamashita and M. Majima gave 1459° for the m.p. of bronzite. According to N. L. Bowen and O. Andersen, magnesium metasilicate has no true m.p. where solid $MgSiO_3$ is in equilibrium with a liquid of its own composition. There is a strong absorption of heat at 1557°, but this is not the m.p., for at that temp. the metasilicate dissociates into the orthosilicate and liquid ; and the dissolution of the forsterite is completed only by raising the temp. to about 1577°—*vide* Fig. 98. R. Lorenz and W. Herz studied the relation between the m.p. and the transition temp. ; and V. S. Deleano, the softening temp. of mixtures of magnesium ortho- and meta-silicates, and found :




FIGS. 86 and 87.—Effect of Temperature on the Speed of Crystallization of Bronzite and Hypersthene.

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Per cent. $Mg_2SiO_4$ . | 80 | 60 | 40 | 30 | 20 | 10 | 0 |
| Softening temp. . . | 1640° | 1605° | 1520° | 1480° | 1500° | 1505° | 1500° |

E. T. Allen and co-workers found the **indices of refraction** of artificial enstatite to be $\alpha=1{\cdot}640$, $\beta=1{\cdot}646$, and $\gamma=1{\cdot}652$, each $\pm0{\cdot}004$. The birefringence is not strong, about 0·01. The optical character of enstatite is positive, that of hypersthene, negative. The **extinction** of enstatite is parallel, while that of the monoclinic variety is oblique. E. Mallard gave for the mineral from Zdjar Mt., Moravia, with 2·76 per cent. FeO, $\alpha=1{\cdot}656$, $\beta=1{\cdot}659$, and $\gamma=1{\cdot}665$ ; and A. Michel-Lévy and A. Lacroix, for a sample from Paul Island, Labrador, with about 22·6 per cent. of iron, $\alpha=1{\cdot}692$, $\beta=1{\cdot}702$, and $\gamma=1{\cdot}705$. W. W. Coblentz found the ultra-red transmission spectrum gave a large absorption band at $1{\cdot}85\mu$, and smaller depressions at $2{\cdot}9\mu$ and $5{\cdot}2\mu$. The reflection spectrum shows a small maximum at $9{\cdot}1\mu$. The **pleochroism** is dependent upon the proportion of contained iron ; it is scarcely perceptible in samples free from iron. G. Tschermak found that with a sample from Paul Island, with about 22·6 per cent. of FeO, $\alpha$ is hyacinth-red ; $\beta$, reddish-yellow ; and $\gamma$, greyish-green ; F. Becke gave for a sample from Bodenmais, Bavaria, with 18·6 per cent. FeO, $\alpha$, dark reddish-brown ; $\beta$, yellowish-brown ; and $\gamma$, dark green ; while G. Tschermak gave for a sample from Kraubat, Styria, $\alpha$, greenish-yellow ; $\beta$, grass-green ; and $\gamma$, bluish-green. H. Rosenbusch also dis-

cussed this subject. The **schillerization** of the surface has been described by B. Kosmann, P. Trippke, H. Rosenbusch, and J. W. Judd. The *schiller* is an interference effect generally attributed to the presence of very thin films or scales of oxides or hydroxides of iron in the cleavage cracks—*vide* felspar.

Hydrochloric acid has but little action on enstatite, but the effect becomes more and more marked as the proportion of iron increases. N. S. Maskelyne found that after an hour's digestion of a sample of enstatite from Bustee with $HCl+H_2O$, the liquid had 7·78 per cent. of matter in soln.; 20 hrs.' digestion of two other varieties gave 9·41 and 12·68 per cent.—in the latter case, the sample was more ferruginous than in the former case. E. Cohen found that by 48 hrs.' digestion with fuming hydrochloric acid, 13 per cent. passed into soln. C. Doelter passed hydrogen chloride over red-hot enstatite and anthophyllite, and only in the latter case was matter produced which was soluble in water. C. Doelter digested enstatite and a 10 per cent. soln. of sodium hydroxide in a sealed tube at 180° for 9 weeks, but no appreciable solvent action was observed; with 12 hrs.' digestion in a 12 per cent. soln. of potassium hydroxide, 4·84 per cent. was dissolved. The silica content of the residue decreased, while the manganese content remained unchanged, and the water content was raised about 4 per cent. By digesting artificial enstatite in 2 5*N*-NaOH, about 4 per cent. passed into soln. in 4 hrs. E. C. Sullivan studied the basic exchange which occurs with olivine in contact with a soln. of cupric sulphate. C. R. van Hise discussed the transformation of bronzite and hypersthene into talc by the action of water, or carbonic acid. C. Simmonds found hypersthene to be only partially reduced by hydrogen at a red heat.

As indicated above, the early syntheses of enstatite really produced monoclinic, not rhombic, crystals. J. J. Ebelmen fused a mixture of silica, magnesia, and boric oxide. A. Daubrée fused meteorites; magnesian eruptive rocks; mixtures of olivine and silica; and serpentine. W. Pukall obtained what was probably clinoenstatite by heating the right proportions of magnesia and silicic acid in a silver crucible. P. Hautefeuille dissolved amorphous silica in molten magnesium chloride. S. Meunier acted on magnesium vap. with silicon chloride and steam. F. Fouqué and A. Michel-Lévy, J. H. L. Vogt, and E. T. Allen and co-workers found that in all these cases the main product is monoclinic pyroxenic enstatite; or, using the term suggested by W. Wahl, **clinoenstatite.** H. Michel detected clinoenstatite in meteorites. G. Zinke made it by fusing mixtures of magnesium and ferrous metasilicates. He found that bismuth oxide, magnesium fluoride or chloride, or calcium fluoride had no effect as *agent minéralizateur*. E. T. Allen and co-workers found that clinoenstatite is the most stable form of magnesium metasilicate. It is formed when the metasilicate glass is allowed to crystallize at a little below 1521°; and that it can be crystallized at lower temp. from soln. in molten sodium vanadate, magnesium vanadate, or magnesium tellurite. The three other forms of magnesium metasilicate pass into this variety when they are heated in molten magnesium chloride to about 1000°, and in a stream of dry hydrogen chloride. N. L. Bowen and O. Andersen studied the synthesis of clinoenstatite.

The **crystals** of clinoenstatite obtained by these different processes are usually small; those obtained from the glass appear as large spherulitic masses of radiating fibres. E. T. Allen and co-workers found that monoclinic crystals have the axial ratios $a:b:c=1{\cdot}033:1:0{\cdot}77$ when those of rhombic crystals are $1{\cdot}0308:1:0{\cdot}5885$. F. Zambonini said that the crystals of clinoenstatite are identical with those of enstatite having the axial ratios $a:b:c=1{\cdot}0331:1:0{\cdot}591$ and $\beta=90°\ 49'$; but F. E. Wright does not agree. There is almost always polysynthetic **twinning** after the orthopinacoid; and it is very characteristic. Between crossed nicols, the sections frequently very closely resemble those of plagioclase. The **cleavage** is prismatic like that of the pyroxenes. The plane of the **optic axes** is normal to the (010)-face, and in the plane of the clinopinacoid. The **optic axial angle** is large; F. E. Wright and E. S. Larsen found 53·5°. The **specific gravity** at 25°/25° is 3·192. The m.p. is indicated in connection with enstatite. E. T. Allen and

co-workers give 6 for the **hardness**; and for the **indices of refraction**, $\alpha=1{\cdot}647$, $\beta=1{\cdot}652$, and $\gamma=1{\cdot}658$, each $\pm 0{\cdot}003$; N. L. Bowen and O. Andersen gave $\alpha=1{\cdot}651$ and $\beta=1{\cdot}660$, each $\pm 0{\cdot}001$. The **birefringence** is about 0·01. The **extinction angle** on the clinopinacoid is very low for a pyroxene, and for crystals with polysynthetic twinning—as is the case with felspars—the extinction angle 19·5°–24·5° was obtained by using the symmetrical extinction angles of adjacent lamellæ. The crystals are only slightly attacked by acids. W. Pukall observed that no hydrate is formed when the metasilicate lies under water for some time. V. Iskyul studied the action of hydrochloric acid on enstatite, and bronzite.

J. A. Michaelson [32] obtained a yellowish or reddish-brown, augite-like mineral from Längban and Pajsberg, Sweden. It was called *schefferite*—after H. T. Scheffer—and described by A. Breithaupt as *wallerian*. It contained 50·88–52·28 per cent. $SiO_2$; 3·83–17·48 per cent. FeO; 9·08–15·17 per cent. MgO; 12·72–19·62 per cent. CaO; and 6·67–8·32 per cent. MnO. It is a monoclinic pyroxene, and probably a complex solid soln., not a chemical individual. A dark variety rich in iron was called *eisenschefferite* by G. Flink, who represented his analyses by the formula $6CaMg(SiO_3)_2.MgFe(SiO_3)_2.2MnSiO_3$. C. Doelter synthesized schefferite by crystallization from the molten constituents. Schefferite is then regarded as a mixed monoclinic pyroxene. The optic axial angles were measured by G. Flink, and by J. Sioma. The latter gave for the sp. gr. 3·457–3·546. C. Doelter gave 1200°–1250° for the m.p.; $\alpha=1{\cdot}660$, and $\gamma=1{\cdot}698$ for the indices of refraction; and for the birefringence, $\gamma-\alpha=0{\cdot}035$.

V. Schumacher [33] discovered a mineral which occurred near Kongsberg, Norway, in thin long plates, and fibres, and which he named **anthophyllite**—from *anthophyllum*, clove—in allusion to its clove-brown colour. The name was abbreviated to *antophyllite* by D. L. G. Karsten. A. G. Werner referred to a *strahligen* anthophyllite and a *blätterigen* anthophyllite, the latter was bronzite, and A. Breithaupt called the former *antholite*, and later *anthogrammite*. J. F. John made analyses of the mineral, and J. F. Gmelin showed by analysis that anthophyllite is a ferruginous magnesium silicate; and A. des Cloizeaux, that its optical properties belong to a member of the rhombic system. E. C. Sullivan studied the basic exchange with anthophyllite in contact with soln. of cupric sulphate.

N. von Kokscharoff described a magnesian silicate from the Senarka River, Ural; and it was also obtained from the Tunkinsk Mt. near Lake Baikal. R. Hermann reported a specimen from Miask in the Ilmen Mts. It was named *kupfferite* after A. T. Kupffer. N. von Kokscharoff said the kupfferite occurs in rhombic prisms, and, according to C. Hintze, this, through a misunderstanding, was taken to mean that it belonged to the rhombic system. Thus, G. A. Kenngott, and E. S. Dana regarded it as the amphibole analogue of enstatite. It was examined by J. Lorenzen. E. T. Allen and J. K. Clement found that water is always present, not combined, but dissolved as in tremolite. A. des Cloizeaux referred to an amphibole of the same chemical composition as anthophyllite as *amphibolic-anthophyllite*. A. Dufrénoy obtained a dark-coloured mineral analogous to anthophyllite from the valley of Héas near Gèdres, France, and he called it *gedrite*. A. des Cloizeaux showed that the optical properties of gedrite and anthophyllite are analogous. A. Breithaupt's *thalackerite* is an anthophyllite from Greenland with a metallic lustre; and A. Breithaupt, and F. Pisani's *snarumite* is an altered anthophyllite. Several hydrated and altered anthophyllites have been described by T. Thomson, J. L. Smith and G. J. Brush, A. Lacroix, and M. F. Heddle. The *piddingtonite* of W. Haidinger was found in the meteorite first described by H. Piddington, and is very close to anthophyllite in composition.

Anthophyllite occurring in England and Scotland has been described by J. J. H. Teall, M. F. Heddle, and A. Lacroix; in Germany, by W. Beck, G. A. Kenngott, C. W. von Gümbel, C. F. Rammelsberg, A. Frenzel, and F. Becke; in France, by A. P. Dufrénoy, A. Lacroix, W. Cross, C. Friedel, F. Gonnard, and F. Pisani; in Norway, by T. Scheerer, J. F. Gmelin, F. Pisani, L. Vopelius, C. C. von Leonhard, A. des Cloizeaux, H. Sjögren, and A. Breithaupt; in Finland, by F. J. Wiik; in Austria, by J. Ippen, F. Becke, and H. Commenda; in Moravia, by G. Tschermak, A. Brezina, W. C. Blasdale, and V. von Zepharovich; in North America, by S. L. Penfield, J. R. Blum, J. Pratt, B. K. Emerson, T. Thomsen, N. N. Evans and J. A. Bancroft, and A. des Cloizeaux; in Greenland, by O. Böggild, A. des Cloizeaux, H. Rose, M. Lappe, and N. V. Ussing; and in the Urals, by G. Rose.

Analyses have been made by many of the observers mentioned in connection with the occurrence of the mineral. E. T. Allen and J. K. Clement found kupferrite

(rhombic) containing nearly 4 per cent. of water which is slowly and continuously lost by heating the mineral to about 900°. The water is assumed not to be chemically combined, but adsorbed or in solid soln. Eliminating what are considered to be accidental impurities, the idealized mineral appears to be rhombic magnesium metasilicate of the amphibole type ; and the actual mineral, solid soln. of magnesium and ferrous metasilicates. The formula thus reduces to $(Mg,Fe)SiO_3$, where the ratio Mg : Fe ranges from 2 : 1 to 8 : 1. The relation between gedrite and anthophyllite may be likened to that between hypersthene and enstatite. In some cases, the gedrites carry up to about 16 per cent. of alumina, and the mineral becomes an aluminous amphibole, or it is present as an aluminosilicate, $MgAl_2SiO_6$. B. Gossner represented anthophyllite by $[2SiO_2.Mg(OH)_2].6MgSiO_3$ ; and gedrite, by $[SiO_2.2AlO(OH)].6MgSiO_3$. E. T. Allen and co-workers made rhombic amphibolic magnesium metasilicate, *i.e.* the end-term of the series of solid soln. or idealized anthophyllite, by rapidly cooling the molten magnesium silicate glass from a temp. over 1500° ; and then annealing the product between say 1177° and 1180°. The crystallization usually begins on the upper surface of the melt near the walls of the crucible, forming a fringe of converging fibres which grow towards the centre of the mass. The amphibolic form readily passes into monoclinic pyroxene with the evolution of heat.

The **colour** of anthophyllite ranges through brownish-grey, yellowish-brown, brownish-green, emerald-green, and almost black. The artificial form is white and porcelainic. Anthophyllite sometimes shows a pearly lustre on the cleavage faces. It often occurs in lamellar or fibrous masses. **Crystals** are rare ; but they have the prismatic habit, and may occur in aggregates of prisms. The crystals belong to the rhombic system, and, according to S. L. Penfield, they have the axial ratios $a : b : c = 0{\cdot}5137 : 1 : ?$ with the prism angle 125° 27′, while for an aluminous gedrite, N. V. Ussing gave for the axial ratios $a : b : c = 0{\cdot}5229 : 1 : ?$ with a prism angle of 124° 48′. E. T. Allen and co-workers obtained for the magnesium metasilicate analogue, radical spherulites and fibrous aggregates, but crystals suitable for the measurement of the morphologic constants were not obtained. The **cleavage** of anthophyllite is prismatic and perfect ; and E. T. Allen and co-workers observed an indistinct cleavage at an angle of 120°. The plane of the optic axes lies parallel to the long direction ; the **optic axial angle** is large. A. des Cloizeaux, and A. Michel-Lévy and A. Lacroix measured the axial angles of anthophyllite, and found for 2H, for red light, 110° 49′ to 112° 13½′, and, for blue light, 109° 5′ to 111° 5½′ ; for red light $2V$ is 95° 8′ to 96° 12′, and, for blue light, 94° 14′ to 95° 46′. S. L. Penfield gave 90° 4′ for $2V$ for Li-light, 88° 46′ for Na-light, and 87° 28′ for Tl-light. N. V. Ussing gave for a sample of gedrite $2V = 78°\ 33'$, and $2H$, 89° 24′ for red light, 89° 6′ for yellow light, and 88° 45′ for green light ; N. L. Bowen gave $2V = 88°\ 46'$. The axial angle decreases with increasing iron and alumina content. A. des Cloizeaux observed no perceptible change in the axial angles by raising the temp. to 146·5°. H. Mark discussed the structure of the crystals.

The **specific gravity** of the preparation of E. T. Allen and co-workers was 2·857 at 25°. S. L. Penfield gave 3·093 for the sp. gr. of anthophyllite with 10·39 per cent. FeO. F. Pisani, 2·98 (12·40 per cent. FeO) ; M. F. Heddle, 3·068 (8·13 per cent. FeO) ; A. Dufrénoy, 3·260 (45·83 per cent. FeO) ; F. Gonnard, 2·9–3·0 ; A. des Cloizeaux, 3·225 (28·9 per cent. FeO), etc. The **hardness** is 5·5–6·0. A. Brun gave 1150°–1230° for the **melting point** of anthophyllite ; and C. Doelter, 1325°–1340°. E. T. Allen and co-workers observed that the rhombic amphibolic type changes into clinoenstatite when heated to a sufficiently high temp. A similar result was obtained with enstatite. The change is sluggish. There were indications of the change in a sample heated for 2 days between 1055° and 1077° ; but no change was observed in 20 hrs. at 1100° ; the change was observed after 18 hrs.' heating between 1120°–1140° ; and all was changed after 3 days' heating between 1127°–1153°.

The **indices of refraction** of anthophyllite were measured by A. des Cloizeaux. A. Michel-Lévy and A. Lacroix found $\alpha=1{\cdot}633$, $\beta=1{\cdot}642$, $\gamma=1{\cdot}657$; and N. V. Ussing found for red light with gedrite, $\alpha=1{\cdot}623$, $\beta=1{\cdot}6358$, and $\gamma=1{\cdot}6439$. S. L. Penfield gave for anthophyllite $\beta=1{\cdot}6276$ with Li-light; $\beta=1{\cdot}6353$ with Na-light; and $\beta=1{\cdot}6495$ with Tl-light. N. L. Bowen gave $\alpha=1{\cdot}6195$, $\beta=1{\cdot}6301$, and $\gamma=1{\cdot}6404$. E. T. Allen and co-workers found for their amphibolic magnesium metasilicate, $\alpha=1{\cdot}591$, and $\beta=1{\cdot}578$, each $\pm 0{\cdot}004$. The **birefringence** is approximately 0·013, and the **interference colours** are confined to the bright tints of the first and second orders. The **extinction** is usually parallel to the direction of elongation, though in a few cases a small angle of 3°–6° was observed, indicating intergrowths of rhombic and monoclinic amphiboles. The optical character is positive—anthophyllite was found by A. des Cloizeaux to be optically positive for red, negative for yellow and green light; while gedrite was found by N. V. Ussing to be optically negative. H. Rosenbusch found the **pleochroism** depends on the depth of colour. In the $\gamma$-direction the colour is pale yellowish-brown, greenish, or colourless, and in the $\alpha$ and $\beta$ directions clove-brown.

Anthophyllite is not decomposed by acids. C. Doelter found that when powdered anthophyllite is exposed for 3 hrs. at a red heat to dry hydrogen chloride, about 3 per cent. becomes soluble. When treated with 2 per cent. hydrofluoric acid, about 46·23 per cent. passed into soln. V. Iskyul studied the action of hydrochloric acid, and the solubility of silica in enstatite, bronzite, and anthophyllite; he found the silica solubility of the amphiboles is twice as great as that of the pyroxenes. C. R. van Hise discussed the transformation of anthophyllite into talc by the action of water.

E. T. Allen and co-workers frequently found small quantities of the monoclinic amphibolic form of magnesium metasilicate, **clinoanthophyllite**, when the glass is more or less rapidly cooled; and when water is allowed to act on the rhombic form at 375°–475°, the monoclinic form appears more abundantly. Well-formed crystals were not obtained. K. Chrustschoff reported the synthesis of an amphibole by heating a mixture of silicic acid, alumina, lime, magnesia, alkalies, ferrous and ferric oxides, and water in a glass vessel for 3 mons. at 550°. The kind of glass is not stated. As indicated above, N. von Kokscharoff described the crystals of kupfferite as being monoclinic. E. T. Allen found that the maximum extinction angle is 11°, though more usually the angle is smaller, 4°–8°. The average refractive index is nearly the same as that of rhombic anthophyllite, and the birefringences are the same order of magnitude.

There are cases of allotropy in which two or more solids yield identical liquids, soln., and vap. When one form passes without melting into another form at a definite temp.—called the *inversion point*, or the *transition temperature*—and the change is reversible, the substances are said to be enantiotropic allotropes—*ἐναντίος*, opposite; *τροπός*, habit. For example, the $\alpha$- and $\beta$-forms of sulphur; wollastonite and pseudowollastonite, etc. In this case, J. H. van't Hoff showed that the inversion of the form stable at the lower temp. to the second form is attended by an absorption of heat, and the reverse change occurs with an evolution of heat. The vap. press. relations are illustrated diagrammatically in Fig. 88, where $T_2$ represents the inversion temp., and $T_1$ the m.p.; $aT_1b$ represents the vap. press. of the liquid; $dT_2$, the vap. press. of the solid stable below $T_2$; and $T_2T_1$, the vap. press. of the solid stable above $T_2$. The dotted lines represent metastable states. Under ordinary conditions, the line $aT_2$ does not intersect $aT_1b$, the solid stable at the lower temp. has no m.p. In another case of allotropy, when there is no such inversion temp., the change is irreversible, and one form is metastable at all temp. below the m.p., the substances are said to be monotropic allotropes, *e.g.* diamond and graphite, explosive antimony, etc. The vap. press. relations are illustrated diagramatically by Fig. 89, where $T_1$ represents the m.p. of the stable form; $T_2$, the m.p. of the unstable form; $aT_2T_1b$ is the vap. press. curve of the liquid; $cT_2$, the vap. press. curve of the unstable solid; and $dT_1$, the vap. press.

curve of the stable solid. For a given temp., the vap. press. of the unstable form is always greater than that of the stable form; the two curves do not intersect below the m.p. of either form, and the two solids are not therefore in equilibrium at any temp. The solid with the lower vap. press. is the more stable form at all temp. The m.p. of the unstable form is therefore lower than that of the stable form. In practice the unstable form changes into the stable form before its own m.p. is reached. The tetramorphic forms of magnesium metasilicates are examples of monotropism. The case is illustrated diagrammatically by Fig. 90, where clinoenstatite is the stable form. In view of Figs. 88 and 89, Fig. 90 explains itself.

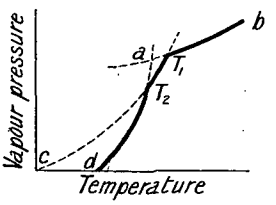



FIG. 88.—Vapour Pressure Curves of Enantiotropic Allotropes.

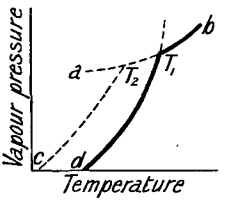



FIG. 89.—Vapour Pressure Curves of Monotropic Allotropes.

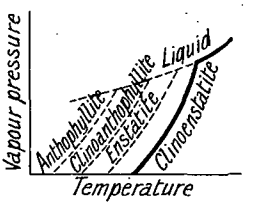



FIG. 90.—Vapour Pressure Curves of the Monotropic Magnesium Metasilicates.

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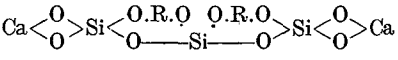
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## § 29. The Higher Silicates of Magnesium

The *melilite group of minerals* (*q.v.*) belonging to the tetragonal system includes a series of aluminosilicates—melilite, a complex aluminosilicate; gehlenite, $3CaO.Al_2O_3.2SiO_2$; sarcolite, $3CaO.Al_2O_3.3SiO_2$; and velardenite, $2CaO.Al_2O_3.SiO_2$. J. H. L. Vogt[1] assumed that the idealized type is *akermanite*—named after R. Akerman—which he represented by $4CaO.3SiO_2$. The calcium oxide is in part replaced by magnesia or the oxides of manganese and iron. The mineral is formed during the rapid cooling of certain slags. A. L. Day and E. S. Shepherd were unable to obtain any evidence of the formation of J. H. L. Vogt's akermanite on the f.p. curves of fused mixtures of lime and silica—Fig. 70. There is, therefore, no evidence of the existence of this compound other than J. H. L. Vogt's analysis of the crystals in the slags which ran: $SiO_2$, 43·17 per cent.; $Al_2O_3$, 3·43; MnO, 5·85; CaO, 37·89; MgO, 9·0. G. A. Rankin and F. E. Wright noted the similarity between some of the properties ascribed to akermanite, and those of the rhombic calcium orthodisilicate, $3CaO.2SiO_2$, which they prepared. W. T. Schaller emphasized the ternary nature of the minerals of the melilite group, and he interpreted two analyses by F. Zambonini of a tetragonal Vesuvian mineral to mean that the formula of akermanite is $8CaO.4MgO.9SiO_2$. The graphic formula can be written:



J. B. Ferguson and H. E. Merwin did not succeed in preparing a compound of this composition, but they did obtain **magnesium dicalcium orthodisilicate,** $2CaO.MgO.2SiO_2$, or $Ca_2MgSi_2O_7$, and they suggest that this is the true formula of akermanite. The interpretation of F. Zambonini's analyses require very little modification to fit them to this compound. The range of stability of this compound is indicated in Fig. 95, of the ternary system, MgO–CaO–$SiO_2$. The compound $2CaO.MgO.2SiO_2$ forms no appreciable solid soln. The binary system $CaO.MgO.2SiO_2$ and $2CaO.MgO.2SiO_2$ has a eutectic at about 1360°, and 42 per cent. of the latter component; the binary system $2CaO.SiO_2$ and $2CaO.MgO.2SiO_2$ has a eutectic at about 1470°, and 91 per cent. of the latter component; while the system $CaO.SiO_2$ and $2CaO.MgO.2SiO_2$ has a eutectic and a broken liquidus curve as illustrated in Fig. 91. V. Schumoff-Deleano and E. Dittler measured the speed of crystallization of fused melilite.

The thin tabular crystals were found by J. H. L. Vogt to belong to the tetragonal system; and to be isomorphous with melilite and gehlenite. W. T. Schaller gave 3·12 for the sp. gr. of the mineral; and J. B. Ferguson and A. F. Buddington

found for the artificial crystals, 2·944 at 25°, and 2·955 for the glass. It is unusual for a glass to have a greater sp. gr. than the corresponding crystals. They are optically positive. C. Hlawatsch studied the double refraction of akermanite. The indices of refraction are $\omega=1{\cdot}6332$ and $\epsilon=1{\cdot}639$. J. B. Ferguson and H. E. Merwin found that with the synthetic material, the stubby, prismatic crystals occasionally have a definite octagonal cross-section; and their index of refraction is $\omega=1{\cdot}631$, and $\epsilon=1{\cdot}638$, each $\pm 0{\cdot}002$. J. B. Ferguson and A. F. Buddington gave for Na-light $\omega=1{\cdot}632$, and $\epsilon=1{\cdot}639$; and the birefringence 0·007. The refractive index of the glass is $1{\cdot}641 \pm 0{\cdot}002$. J. H. L. Vogt gave 0·187 for the sp. ht. between 0° and 100°, and 1200° for the m.p.; R. Akerman gave 1310°; J. H. L. Vogt, 1175°; and J. B. Ferguson and H. E. Merwin gave $1458° \pm 5°$—*vide* Fig. 90. R. Akermann gave 404 cals. per gram for the total heat of fusion; and C. Doelter, and J. H. L. Vogt gave 90 cals. for the latent heat of fusion. J. B. Ferguson and A. F. Buddington studied the binary system $Ca_2MgSi_2O_7$ and gehlenite, $Ca_2Al_2SiO_7$—*vide* yelardenite.

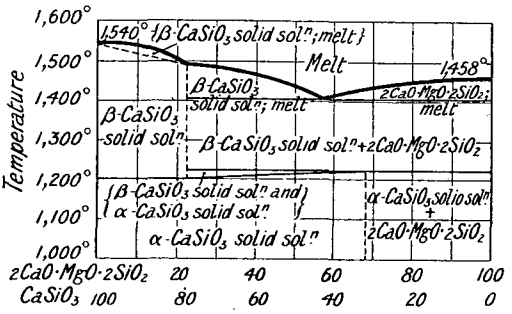



FIG. 91.—Equilibrium in the Binary System: $CaSiO_3$–$2CaO.MgO.2SiO_2$.

J. B. Ferguson and H. E. Merwin[2] obtained evidence of the formation of **dimagnesium pentacalcium hexasilicate,** $5CaO.2MgO.6SiO_2$, in their study of the ternary system, $CaO$–$MgO$–$SiO_2$. The field in the diagram belongs to a series of solid soln. which are not stable at their m.p., and which lie on or near the composition $5CaO.2MgO.6SiO_2$. The decomposition temp. of these solid soln. rise sharply as this composition is attained. The decomposition temp. is $1365° \pm 5°$. The compound appears in irregular elongated grains with the optic axial angle, $2V$, about 80°; and the indices of refraction, $\alpha=1{\cdot}621$, $\beta=1{\cdot}627$, $\gamma=1{\cdot}635$.

The mineral *tremolite* was mentioned by H. B. de Saussure,[3] in 1796, as being obtained from Val Tremola, south of St. Gotthard. It is an amphibole. R. J. Haüy called the mineral *grammatite, c'est-à-dire, marquée d'une ligne*—from γραμμή, a line—in reference to a line in the direction of the longer diagonal which can be seen on transverse sections of some crystals. R. H. Haüy's term is rarely used.

A. G. Werner called a green mineral from Nordmarken, Sweden, *calamite*—from κάλαμος, a reed—was shown by E. F. Glocker, and A. Breithaupt to be tremolite. T. Thomson's *raphilite* from Lanark, Canada; E. Goldsmith's *hexagonite* from Edwards, St. Lawrence; and G. A. Kenngott's *nordenskjöldite* from Ruscola, Lake Onega, are all considered to be varieties of tremolite. G. A. König discussed the relation of hexagonite to tremolite.

Many analyses have been reported.[4] These agree with the assumption that the idealized mineral is a **calcium trimagnesium tetrametasilicate,** $CaMg_3(SiO_3)_4$. Tremolite does not appear among the phases formed in the ternary system, $MgO$–$CaO$–$SiO_2$, Fig. 94, under the conditions studied by J. B. Ferguson and H. E. Merwin. This, of course, does not mean that tremolite is not a chemical individual, for it may be a stable compound under another set of conditions. Ferrous oxide replaces up to about 3 per cent. of the magnesia. E. T. Allen, and J. K. Clement showed that up to about 2·5 per cent. of water may be present. This water is gradually lost on a rising temp. without any loss of homogeneity and with but a slight change in the optical properties. The dehydration is not complete until the powdered mineral has been heated to 900°. The water is not chemically combined, and is assumed to be adsorbed in solid soln. Tremolite varies in colour from white to dark grey, and is sometimes water-clear and colourless.

It may occur in compact granular masses, in fibrous aggregates; in long-bladed, short and stout, or thin-bladed crystals. L. H. Adams and E. D. Williamson found the compressibility, $\beta$, of actinolite to be $\beta=1{\cdot}32\times10^{-6}$ between 0 and 10,000 megabars press. A. des Cloizeaux, G. Flink, K. Zimanyi, A. Michel-Lévy and A. Lacroix, and H. Rosenbusch have measured the optical properties of the crystals. The sp. gr. is 2·9–3·1. A. L. Fletcher gave 1269°–1273° for the m.p. R. Cusack obtained a lower value. The optic axial angle, $2V$, is 87°–88°; and $2H=99°$–$101°$. The extinction angle is 16°; and the indices of refraction $\alpha=1{\cdot}6065$, $\beta=1{\cdot}6233$, and $\gamma=1{\cdot}6340$. The optical character is negative. W. W. Coblentz found the ultra-red transmission spectrum has bands at 2·8, 4·8, 6, 7·4, and 8·2$\mu$; and the reflection spectrum has maxima at 8·7, 9·45, 10·03, and 11$\mu$. G. A. Kenngott found that in contact with water the calcined or uncalcined mineral has an alkaline reaction.

When the ferrous oxide in tremolite approaches 3 per cent., it passes into the mineral *actinolite*, but there is no sharp line of demarcation. The ferrous oxide is supposed to be present as **ferrous tricalcium tetrametasilicate**, $Ca_3Fe(SiO_3)_4$, and to form a series of solid soln. with tremolite proper. A. Cronstedt [5] called the mineral Strälskörl; and *A. G. Werner, Strahlstein, which R. Kirwan translated to actinolite, from* ἀκτίν, *a ray*; and λίθος, stone. R. J. Haüy used the term *actinote*; and J. C. Delamétherie, *schorl verte du Zillerthal*, or *zillerthite*. Many analyses have been reported.[6] E. T. Allen and J. K. Clement found that actinolite contains up to about 3 per cent. of water, which is retained over 100°. The mineral is green, and it occurs in crystals as in tremolite, or fibrous, columnar, or massive. The sp. gr. is 3·0–3·2. The optical constants were investigated by A. des Cloizeaux, A. Michel-Lévy and A. Lacroix, and K. Zimany; and the pleochroism, by A. Michel-Lévy and A. Lacroix, and G. Tschermak. R. Cusack gave 1272°–1288° for the m.p. of green actinolite; and A. L. Fletcher, 1322°–1338°. E. Reymond studied the action of chlorine and of hydrogen chloride on actinolite; and V. Iskyul, the action of hydrochloric acid, and the solubility of the silica in actinolite.

A tough, compact, fine-grained tremolite or actinolite, varying in colour from a cream to a dark green, is called *nephrite*—from νεφρός, a kidney—because it was formerly supposed to have a medicinal value in diseases of the kidney. The term *jade* is applied generally to various mineral substances which have the appearance of nephrite, and *jadeite*. The latter is a kind of soda-spodumene (*q.v.*). Jade was used by early man for utensils and ornaments of great beauty and variety. Jade has been found among the relics of early man—*e.g.* in the remains of the lake-dwellers of Switzerland, at various places in France, in Mexico, Greece, Egypt, Asia Minor, etc. The quarries in Central Asia in the Kuen Hun Mts. have been worked by the Chinese for 2000 years. The *greenstone* ornaments of the Maoris of New Zealand are made from nephrite. The subject has been much discussed.[7] Numerous analyses have been reported.[8] The analyses have been discussed by S. L. Penfield, A. Damour, and L. Colomba. The crystals have been investigated by G. vom Rath, J. D. Dana, W. C. Brögger, A. W. G. Bleeck, M. Bauer, A. des Cloizeaux, F. Berworth, etc. S. L. Penfield gave for the axial ratios of the monoclinic crystals $a:b:c=1{\cdot}103:1:0{\cdot}613$, and $\beta=72°\ 44\frac{1}{2}'$. The microstructure has been studied by F. W. Clarke and G. P. Merrill, A. Arzruni, A. des Cloizeaux, E. Cohen, J. A. Krenner, etc. H. R. Bishop gave a collection of about 500 samples of nephrite, and 100 of jadeite. The average for nephrite is 2·9505, and for jadeite, 3·3202. The hardness of nephrite is nearly 6, and of jadeite, nearly 6·5. The results of the impact test have been reported by H. R. Bishop, H. von Schlagintweit, and A. Rosival; the crushing strength, by H. R. Bishop, and L. Jaczewsky; the elastic constants, by H. R. Bishop, and W. Voigt; the acoustic qualities, by H. R. Bishop. The optical properties have been investigated by A. des Cloizeaux, J. A. Krenner, E. Cohen, M. Bauer, A. Arzruni, A. Michel-Lévy and A. Lacroix, H. R. Bishop, L. Mrazec, S. Franchi and L. Colomba, etc. The fusibility has been studied by C. Doelter, V. S. Deleano, etc., and the actions of acids and salt soln., by J. Lemberg. C. Doelter has compiled data pertaining to nephrite and jadeite.


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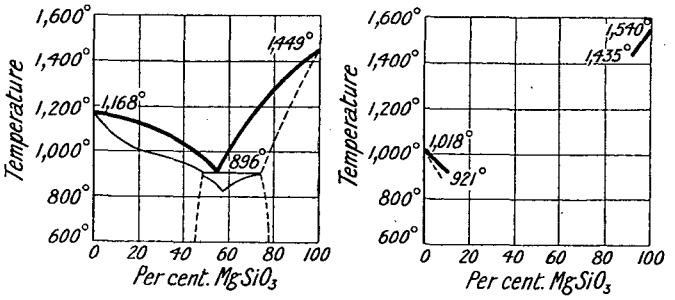
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## § 30. The Complex Silicates of Magnesium

R. C. Wallace [1] found that in the binary system, $MgSiO_3$–$Li_2SiO_3$, two series of mixed crystals were formed, with a break from 50 to about 75 per cent. of magnesium metasilicate, Fig. 92. The eutectic temp. was 876°. No *lithium magnesium metasilicate* appeared. In the system $MgSiO_3$–$Na_2SiO_3$, all the mixtures between 20 and 80 per cent. magnesium metasilicate solidified to a glass, Fig. 93. No *sodium magnesium metasilicate* was produced. F. Focke obtained a




FIGS. 92 and 93.—Freezing Curves of Binary Mixtures of Magnesium Metasilicate with Lithium and Sodium Metasilicates.

green mineral resembling serpentine from Wildkreuzjoch, Tyrol, and he called it *nemaphyllite*, It contained 42·49 per cent. $SiO_2$; 0·40, $Al_2O_3$; 4·63, $Fe_2O_3$; 37·60, MgO; 0·72, CaO; 2·11, $Na_2O$; and 13·11, $H_2O$. The sp. gr. was 2·6; hardness, 3; cleavage, perfect; and the birefringence, negative and weak.

The colourless, transparent mineral *tainiolite*, obtained by G. Flink from Narsarsuk, Greenland, has a composition corresponding with $H_2(Li,Na,K)_2$-$(Mg,Fe)_2(SiO_3)_3$, and in the ideal case is a *potassium magnesium metasilicate*. The

name is derived from ταινία, a band or strip; λίθος, a stone—in allusion to the form of the crystals. The monoclinic crystals resemble mica; the axial ratios are $a:b:c=0{\cdot}5773:1:3{\cdot}2743$. The birefringe is negative and weak; the optic axial angle $2E=50°$; the sp. gr. 2·86; and the hardness 2·5–3·0. The mineral is slowly but completely decomposed by hydrochloric acid. According to A. Duboin, no silicate is obtained when silica is added to a fused mixture of magnesia and potassium fluoride, but if one part of magnesia and 4 parts of silica are dissolved in fused potassium fluoride and the product is afterwards fused with potassium chloride and kept at a red heat for about three days, **potassium magnesium trisilicate,** $MgO.K_2O.3SiO_2$, is obtained in hexagonal crystals, with a negative axis, and flattened parallel with the base. Its sp. gr. at 0° is 2·55, and it is readily attacked by acids.

P. Berthier,[2] F. C. Achard, W. A. Lampadius, and N. G. Sefström made a number of glasses by heating various mixtures of lime, magnesia, and silica. Thus, $CaO:MgO:SiO_2=1:1:2$; $1:2:3$; $2:1:3$; $1:1:3$ were formed. Some of these crystallized. There is, however, nothing to show what chemical individuals were formed. C. Mutschler and E. C. F. von Gorup-Besanez obtained from the ash of the *calamus rotang* what they regarded as a compound $CaO.MgO.4SiO_2$. Here again the individuality of the product was not established.

The very rare mineral **monticellite** was named after T. Monticelli; it was found in yellowish crystals at Mount Vesuvius. The mineral belongs to the olivine family which includes forsterite, fayalite, and tephroite. The crystals were first described by H. J. Brooke[3] in 1831. N. Nordenskjöld called it *scacchite* (misprinted *sacchite*), after A. Scacchi. A. Breithaupt, and L. Liebener and J. Vorhauser called a greenish-grey product *batrachite*—from βάτραχος, a frog—in reference to the colour. The analyses by C. F. Rammelsberg, G. vom Rath, F. A. Genth, G. Tschermak, S. L. Penfield and E. H. Forbes, P. von Jeremejeff, J. Lemberg, etc., correspond with **magnesium calcium orthosilicate,** $CaMgSiO_4$. N. G. Sefström obtained a glass of this composition by fusing the constituents together. V. Pöschl, and V. S. Deleano studied the fusion curves of mixtures of magnesium and calcium orthosilicates. The latter found that a eutectic is produced at 1400° with about 80 per cent. of magnesium orthosilicate. No monticellite was formed, and it was assumed that the occurrence of this mineral in volcanic products shows that an *agent minéralizateur* was present. Mixtures rich in calcium orthosilicate disintegrate on cooling. Enstatite is formed, and the disintegration of calcium orthosilicate occurs in the presence of up to 50 per cent. of enstatite. A. F. Hallimond obtained crystals of monticellite from a steel-works mixer slag, and of the composition $Ca(Mg,Fe,Mn)SiO_2$. J. B. Ferguson and H. S. Merwin have shown the field of stability of monticellite in the ternary system, $MgO–CaO–SiO_2$, Fig. 95. P. Hermann showed that solid soln. are formed between forsterite and monticellite; and J. B. Ferguson and H. E. Merwin place the limit at about 10 per cent. of forsterite. J. H. L. Vogt found crystals of monticellite in slags; and H. le Chatelier, in portland cements. V. Pöschl, and J. Morozewicz prepared products containing monticellite by fusing the component silicates, and the former gave for mixtures of forsterite and lime-olivine, *i.e.* of magnesium and calcium orthosilicate:

| $Mg_2SiO_4$ | 100 | 90 | 80 | 70 | 50 | 30 | 20 | 0 |
|---|---|---|---|---|---|---|---|---|
| Sp. gr. | 3·11 | 3·04 | 3·01 | 2·96 | 2·90 | 2·88 | 3·04 | 3·1 |
| M.p. (mean) | 1600° | 1340° | 1327° | 1315° | 1310° | 1302° | 1335° | 1600° |

V. Pöschl also studied the ternary system, $Mg_2SiO_4–Ca_2SiO_4–Fe_2SiO_4$. J. B. Ferguson and H. E. Merwin's attempts to isolate monticellite were not successful; a mixture of crystals of calcium orthosilicate and the forsterite-monticellite solid soln. was always obtained.

The crystals of monticellite, according to G. vom Rath, belong to the rhombic system, and they have the axial ratios $a:b:c=0{\cdot}43369:1:0{\cdot}57569$. H. J. Brooke,

and A. Scacchi made some observations on this subject. J. B. Ferguson and H. E. Merwin's products contained crystals of monticellite in equant grains, without facets. As emphasized by N. L. Bowen, the optic axial angle is large, $2V=85°–90°$. F. A. Genth gave for the sp. gr., 3·108; S. L. Penfield and E. H. Forbes, 3·022–3·047; G. Tschermak, 3·098; and G. vom Rath, 3·054 (batrachite). The hardness is 5–6. C. Doelter gave 1180°–1200° for the m.p. J. Joly gave 0·1963–0·2113 for the sp. ht. S. L. Penfield and E. H. Forbes gave for the indices of refraction $\beta=1·6584$ for Li-light, or for Na-light, $\alpha=1·6505$, $\beta=1·6616$, and $\gamma=1·6679$; and for the birefringence, $\gamma-\alpha=0·0174$. J. B. Ferguson and H. E. Merwin found for artificial crystals $\alpha=1·638–1·640$; $\beta=1·646$; and $\gamma=1·651–1·655$. A. des Cloizeaux investigated the optical properties of monticellite. V. Pöschl obtained 1460°, and J. B. Ferguson and H. E. Merwin, 1502° for the m.p. E. Kittl found that in the crystallization of the glass, 1600 nuclei are present per sq. cm. According to G. Tschermak, when monticellite is treated with acids, orthosilicic acid separates out. F. Cornu found the moistened powder reacts alkaline towards litmus. F. Sestini, and J. Lemberg examined the effect of water on the mineral; C. Doelter, the effect of dry hydrogen chloride on the heated mineral; and also the effect of a soln. of sodium carbonate. W. Suida found that the mineral is feebly stained by basic aniline dyes. The monticellite changes on weathering into serpentine, fassaite, etc. The metamorphoses have been investigated by P. von Sustschinsky, G. vom Rath, J. Lemberg, K. Oebbeke, R. Brauns, etc. E. S. Larsen and W. F. Foshag [4] obtained a colourless or pale green mineral resembling monticellite from the limestone of Crestmore, California. The composition corresponded with $Ca_3Mg(SiO_4)_2$, **magnesium tricalcium di-orthosilicate,** and they called the mineral *merwinite*—after H. E. Merwin. The mineral is monoclinic; the cleavage (010) is perfect; lamellar twinning occurs on the prism faces, forming an angle of 42·5°; the optical axial angles, $2V=66·5°$; the axial angle $a:c=36°$; the sp. gr. is 3·150; the hardness, 6; and the indices of refraction are $\alpha=1·708$, $\beta=1·711$, and $\gamma=1·718$. It readily dissolves in hydrochloric acid.

P. C. Abilgaard,[5] and J. C. Delamétherie applied the term *malaconite* to a bluish-grey, or greyish-green mineral from Sala, Sweden, which was softer than the associated felspar, hence the name was adapted from μαλακός, soft. It is related with the mineral *salite* or *sahlite* which has a similar colour. Salite was found in Sala, Sweden, by M. F. R. d'Andrada, and it was analyzed by L. N. Vauquelin. The granular variety, with more or less indistinct crystals, from Arendal was described by P. C. Abilgaard, and M. F. R. d'Andrada, and called *coccolite*, from κόκκος, a grain. It, too, was analyzed by L. N. Vauquelin. B. Bonvoisin described greenish prismatic crystals of a mineral from the Mussa Alp, Ala Valley, Piedmont; and a white, greyish-white, or apple-green, crystalline aggregate from the same locality. The former was called *alalite*, after the Ala Valley, and the latter *mussite*, from the Mussa Alp. R. J. Haüy showed that both these minerals belong to one mineral species, which he designated **diopside,** from δύς, double; and ὄψις, appearance. He also showed that salite, coccolite, and malaconite are varieties of diopside.

T. Scheerer's [6] *traversellite*, from Traversella, Piedmont, is a fibrous aggregate of the same mineral. The mineral named baikalite by H. M. Renovanz [7] is from the Lake Baikal district, Siberia. It was also described by R. J. Haüy, and D. L. G. Karsten. The bluish-white mineral *canaanite* of F. Alger from Canaan, Connecticut, was described by C. H. Hitchcock, and J. D. Dana. The *funkite* of A. P. Dufrénoy is a dark olive-green cococlite from Boksäter, Göthland. N. von Kokscharoff's *lawroffite, lavrovite*, or *lawrowite* is a diopside coloured green by vanadium, and came from Lake Baikal, Siberia. The *proteite* of E. F. Glocker, and A. Breithaupt from Zillerthal, Tyrol, is a form of alalite and mussite. H. von Eckermann called a fluoriferous diopside, $Ca(Mg.Fe)(SiO_3)_2.nMg(OH,F)_2$, from Mansjö Mountains, *mansjoeite*.

The reported occurrences of diopside as a rock-forming mineral are very

numerous; and hundreds of analyses have been made. The composition of colourless or white diopside approximates very closely to that required for **magnesium calcium dimetasilicate,** $CaMg(SiO_3)_2$. E. T. Allen and J. K. Clement found that diopsides may have up to about one per cent. of water which is only lost completely and continuously by heating the mineral up to 900°. The water is adsorbed or in solid soln. E. A. Wülfing regarded the ferruginous diopsides as being members of a series of isomorphous mixtures with varying proportions of the metasilicates: diopside proper, $CaMg(SiO_3)_2$; hedenbergite, $CaFe(SiO_3)_2$; and $MgFe(SiO_3)_2$. The structure has been discussed by P. Groth, L. Duparc and T. Hornung, G. Becker, J. H. L. Vogt, R. Scharizer, and W. Vernadsky. J. Jakob applied the co-ordination theory and represented diopside:

$$O{=}Si{<}\begin{matrix}O.Mg.O\\O.Ca.O\end{matrix}{>}Si{=}O \qquad \text{P. Groth.}$$

$$\left[Si\begin{pmatrix}O\\O\end{pmatrix}_2Si\begin{pmatrix}O\\O\end{pmatrix}_3\right]^{Mg_2(Fe)}_{Ca_2} \qquad \text{J. Jakob.}$$

Assuming that the ferrous oxide is present as $CaFe(SiO_3)_2$, the ratio of $CaMg(SiO_3)_2$ to $CaFe(SiO_3)_2$, ranges upwards, passing through 8 : 1, 7 : 1, 4 : 1, 3 : 1, 2 : 1, to nearly 1 : 1; then appear the varieties of hedenbergite and schefferite in which the ratio passes through 2 : 3, 1 : 2, and 1 : 9. In 1858, C. F. Rammelsberg emphasized the importance of distinguishing between ferrous and ferric oxides in the analyses of these minerals. The proportions of alumina and ferric oxide rise from zero until the diopside pyroxenes pass into augites. These monoclinic pyroxenes can then be approximately arranged in two classes according as the sesquioxides are or are not present as essential constituents:

| | | |
|---|---|---|
| Monoclinic pyroxenes | without sesquioxides . . . | DIOPSIDES |
| | with sesquioxides . . . . | AUGITES |

A greenish variety, coloured with chromic oxide, is called *chrome-diopside*, and it was described by A. Knop, E. Jannetaz, R. Scharizer, etc. The occurrence of diopside in meteorites was discussed by N. S. Maskelyne, and S. Meunier; and in slags by F. von Kobell, G. vom Rath, L. Gruner, P. S. Gilchrist, T. Scheerer, C. F. Rammelsberg, J. E. L. Hausmann, C. C. von Leonhard, J. Nöggerath, F. Sandberger, G. J. Brush, N. S. Maskelyne, C. Vélain, E. Mallard, P. W. von Jeremejeff, A. Knop, J. H. L. Vogt, etc.

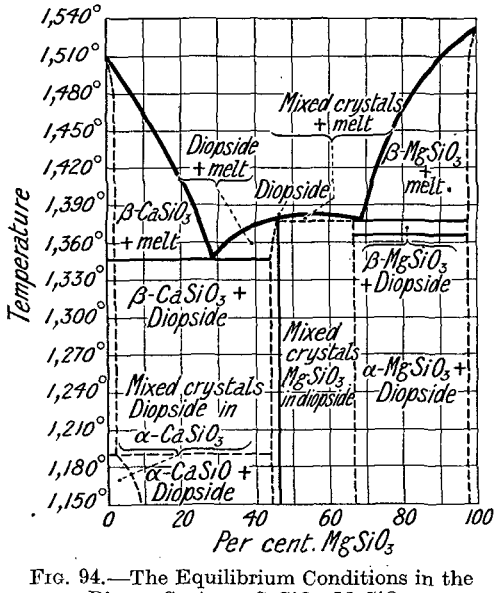



FIG. 94.—The Equilibrium Conditions in the Binary System: $CaSiO_3$–$MgSiO_3$.

P. Berthier [8] made diopside by fusing a mixture of the constituents. G. Lechartier used calcium chloride as a flux; J. J. Ebelmen, boric oxide; C. J. St. C. Deville, F. Fouqué and A. Michel-Lévy, A. Lacroix, E. Hussak, A. Becker, P. Hautefeuille, A. Gorgeu, and C. Doelter made observations with respect to diopside analogous to those indicated in connection with the other magnesium silicates. L. Bourgeois made diopside by suspending a block of marble in fused basalt. G. Rose observed crystals of diopside in some augite which had been fused and cooled. The formation of diopside and augite in the crystallization of fused silicates has been observed

by J. Morozewicz, G. Medanich, K. Petrasch, H. H. Reiter, C. Doelter, etc. H. J. Johnston-Lavis observed crystals of pyroxene on fossil bones in the volcanic tufa of Faiano, Nocera, and assumed that the mineral was formed under little press., and at a temp. insufficient to carbonize or even discolour the organic matter of the bones. L. Appert and J. Henrivaux found crystals of diopside were formed when ordinary window-glass was kept for some time just below the softening temp. A. Daubrée made diopside by the action of the water of Plombières on a hot glass tube. V. Pöschl prepared diopside by the union of magnesium and calcium metasilicates. V. S. Deleano found that the binary system, $Mg_2SiO_4$–$CaSiO_3$, has a eutectic at about 1300° with 90 molar per cent. of calcium metasilicate. The system is really a quaternary one because periclase and enstatite are formed. In the system of $Ca_2SiO_4$–$MgSiO_3$ there is a eutectic with about 80 molar per cent. of magnesium metasilicate at about 1300°. E. T. Allen and W. P. White studied the conditions of formation of diopside in the binary system, $CaSiO_3$–$MgSiO_3$. The range of stability of diopside is indicated in Fig. 94. The best crystals were obtained by heating a glass of the composition $MgCa(SiO_3)_2$ in a flux of calcium chloride, in an atm. of dry hydrogen chloride at 1000° for a week. J. B. Ferguson and H. E. Merwin found the limits of stability of diopside in the ternary system, CaO–MgO–$SiO_2$, Fig. 95; P. Niggli described this system; and N. L. Bowen, the relations in the ternary system, diopside–forsterite–silica.

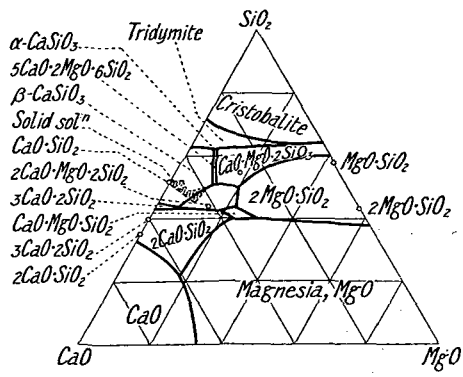



FIG. 95.—The Limits of the Different Phases on the Concentration Diagram of the Ternary System: CaO–MgO–$SiO_2$ (wt. per cent.).

J. B. Ferguson and H. E. Merwin's conc. diagram, showing the limits of the fields of stability of the various phases in wt. per cent., is shown in Fig. 95. The range for

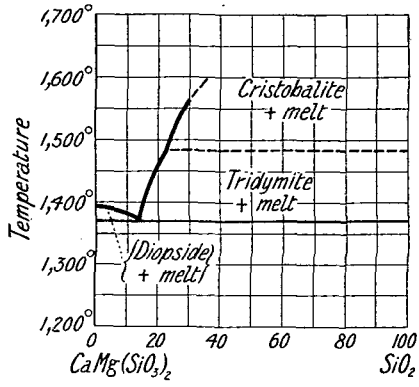



FIG. 96.—Freezing-point Curves of the Binary System: Diopside–Silica.

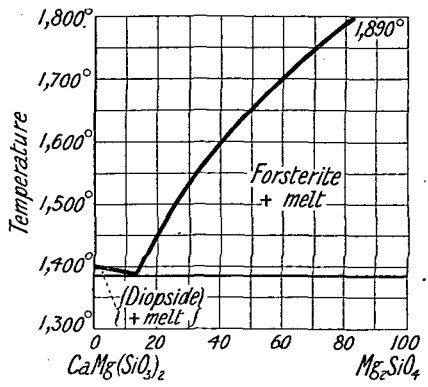



FIG. 97.—Freezing-point Curves of the Binary System: Diopside–Forsterite.

β-wollastonite is too small to appear in the diagram. There are four complex calcium magnesium silicates, namely: (i) $5CaO.2MgO.6SiO_2$; (ii) akermanite, $2CaO.MgO.2SiO_2$; (iii) monticellite, $MgO.CaO.SiO_2$, or $MgCaSiO_4$; and (iv) diopside, $MgO.CaO.2SiO_2$ or $MgCa(SiO_3)_2$. Diopside does not form a solid soln. with

silica, forsterite, or pseudowollastonite ; nor does it form a solid soln. to any marked degree with $2CaO.MgO.2SiO_2$ ; but it does form a continuous series of solid soln. with clino-enstatite, which crystallizes in forms corresponding with the monoclinic pyroxenes. N. L. Bowen has made a special study of the binary and ternary systems with diopside, forsterite, and silica as components. Fig. 97 shows that no higher silicate is formed with diopside. The topography of the ternary system is shown in Fig. 98, and the isothermal f.p. curves in Fig. 99. N. L. Bowen found that

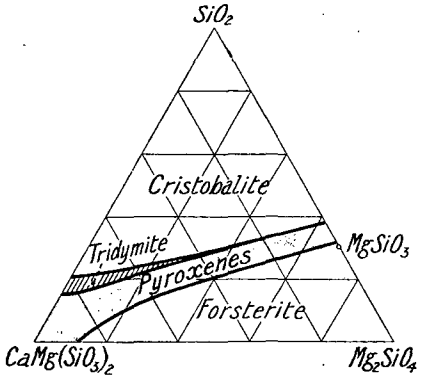



FIG. 98.—Ternary System : Diopside–Forsterite–Silica.

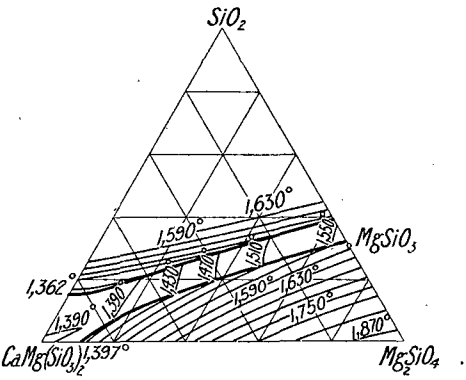



FIG. 99.—Isothermal Freezing Curves in the Ternary System: Diopside–Forsterite–Silica.

there is a eutectic with 88 per cent. of diopside and 12 per cent. of forsterite at a temp. about 4°–5° lower than the m.p. of diopside, Fig. 99. The compositions of the phases worked out by J. B. Ferguson and H. E. Merwin are illustrated by the triangular diagram, Fig. 98. V. Pöschl measured the sp. gr., m.p., and angle of extinction of mixtures of enstatite and diopside, and found :

| Diopside | 0 | 25 | 40 | 50 | 60 | 75 | 100 per cent. |
|---|---|---|---|---|---|---|---|
| Sp. gr. | 3·2 | 3·12 | 3·05 | 2·98 | 3·25 | 3·04 | 3·08 |
| M.p. | 1375° | 1320° | 1300° | 1300° | 1295° | 1300° | 1300° |
| | 1400° | 1350° | 1325° | 1320° | 1315° | 1320° | 1325° |
| Extinction | — | — | — | — | 39° | 37° | 32° |

G. Zinke examined the products obtained by cooling molten mixtures of the two compounds, and he likewise obtained a series of pyroxenes of varying composition. The nature, but not the composition, of the phases at any temp. during the cooling is illustrated by N. L. Bowen's diagram, Fig. 100. With a molten mixture containing, say, $19MgCa(SiO_3)_2+81MgSiO_3$, forsterite begins to crystallize out at 1552°, and continues crystallizing down to 1523°, when pyroxene also appears. The three phases coexist down to 1420°, when both forsterite and liquid disappear, and all consists of pyroxene. N. L. Bowen discussed the effect of the sp. gr. and viscosity of the molten magma on the crystallization.

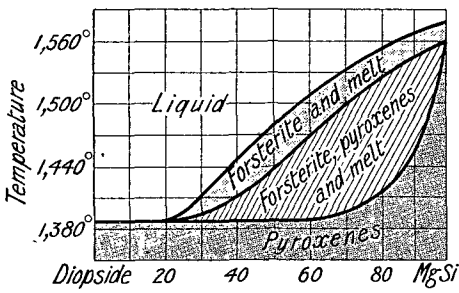



FIG. 100.—Nature of the Solid Phases in Cooling Molten Mixtures of Diopside and Magnesium Metasilicate.

P. Eskola said that his attempts to make *strontia-diopside* and *baryta-diopside* were not successful. There is no evidence that the metasilicates of barium or strontium and magnesium form a double compound. This is remarkable, especially in the case of strontium, which in other ways showed such a close similarity with

calcium. P. Eskola pointed out that in compounds in which the lime may possibly be replaced by magnesia and ferrous iron, it cannot be replaced by strontia or baryta. Accordingly, barium and strontium compounds form mixed crystals with lime and alkali minerals, but not with ferromagnesian minerals.

The **colour** of diopside, or calcium magnesium dimetasilicate in the limiting case, is water-clear, or white; the mineral is variously tinted green, and various shades of yellow, red, and brown, according to the proportion of ferrous oxide and other impurities which may be present. The compound was found by E. T. Allen and W. P. White to crystallize readily, usually in the form of radiating prismatic individuals intricately intergrown and overlapping. There are often fine bubble-like inclusions or cavities in the crystalline mass; these are either tabular in shape and parallel with the prismatic elongations of the crystallites, or else they are irregular. The cavities are probably due to the shrinkage accompanying the crystallization of the glass; they are rarely observed in the crystals from the molten calcium chloride flux. Both the natural and artificial **crystals** belong to the monoclinic system, and the artificial crystals have the axial ratios $a : b : c = 1{\cdot}096 : 1 : 0{\cdot}591$, and the natural crystals $a : b : c = 1{\cdot}0934 : 1 : 0{\cdot}5894$. The differences are within the limits of experimental error. F. Zambonini gave $a : b : c = 1{\cdot}0503 : 1 : 0{\cdot}5894$, and $\beta = 90° 9'$ for the natural crystals. Observations on the native diopside crystals have been made by E. Artini, R. B. Hare, A. Schmidt, H. Baumhauer, J. Götz, K. Busz, G. vom Rath, G. Flink, J. Lehmann, A. Streng, F. Hessenberg, N. von Kokscharoff, A. des Cloizeaux, G. la Valle, A. Michel-Lévy, G. Nordenskjöld, G. Rose, J. D. Dana, etc. F. Rinne, and R. Grossmann measured the change in the angles on heating the crystals. F. Rinne obtained **X-radiograms** of the mineral; and the shape and size of the unit cells of diopside, and diopside-like pyroxenes have been studied by R. W. C. Wyckoff and co-workers. The **twinning** of the artificial crystals after (100) was found by E. T. Allen and W. P. White to be common, while polysynthetic twinning after (100) was rare. The twinning has been studied by F. Becke. In the natural crystals twinning by the (100)-face is common; the crystal may be traversed by twin lamellæ parallel to that face, and sometimes also parallel to the (001)-face. The crystals of the mineral generally appear to be holosymmetric; but the two ends of the prism are sometimes different, indicating that the mineral probably possesses only a plane of symmetry, and not a digonal axis perpendicular to it. This is confirmed by the observations of E. A. Wülfing, H. Baumhauer, and G Greim on the **corrosion figures** produced on the prism faces by hydrofluoric acid. F. Mohs showed that the diopsides from Sala and the Ala Valley possess a kind of **cleavage** parallel to the (100)- and the (001)-faces. These are not true cleavages, but rather partings due to these faces being glide-planes and planes of secondary twinning. The partings occur only at intervals, and are not uniformly distributed through the crystals as would be the case with true cleavages. The partings are supposed to be produced by press. They have been studied by A. H. Phillips, J. H. Teall, G. W. Hawes, G. vom Rath, L. van Werveke, A. Osann, O. Mügge, J. W. Judd, T. Scheerer, G. Rose, F. Zirkel, F. Becke, etc. E. Kittl's measurement of the **speeds of crystallization** of three samples of diopside at different temp. are shown in Fig. 101. There is a well-defined maximum about 1270°; and he found that in the crystallization of the glass, 1·3–9·3 nuclei are present per sq. cm. Measurements were also made by V. Schumoff-Deleano and E. Dittler. The plane of the optic axes is the plane of symmetry (010). The **optic axial angles** $2V = 59' 3° \pm 1{\cdot}0°$, and $2E = 114°$. E. A. Wülfing found $2V = 58° 40'$ for the natural crystals; and with Li-light, 59° 28'; with Na-light, 59° 15'; and with

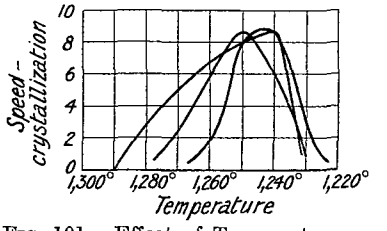



FIG. 101.—Effect of Temperature on the Speed of Crystallization of Diopside.

Tl-light, 58° 58′; the numbers for a ferruginous diopside are respectively 59° 48′, 59° 52′, and 59° 38′. E. T. Allen and W. P. White measured the optical axial angles of solid soln. with mixtures containing 28–95 per cent. of magnesium metasilicate. N. L. Bowen's values for the optical axial angles, $2V$, of solid soln. of diopside and clinoenstatite were :

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Diopside . | 100 | 75 | 65 | 56 | 37 | 19 | 0 per cent. |
| $2V$ . . | 59° | 56° | 47° | 40° | smell | 20° | 53° |

G. Zinke made some measurements of this constant. G. Tschermak, F. Herwig, C. Doelter, F. J. Wiik, G. Flink, and A. Schmidt have made observations on this subject, and in general, the angle increases as the proportion of iron is raised. A. des Cloizeaux measured the effect of temp. on the optic axis.

E. T. Allen and W. P. White measured the **specific gravity** of various combinations of calcium and magnesium metasilicates, and found

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| $MgSiO_3$ . | 0 | 20 | 46·3 | 50 | 60 | 70 | 72 | 72 | 100 per cent. |
| Sp. gr. . | 2·912 | 3·046 | 3·236 | 3·245 | 3·229 | 3·205 | 3·196 | 3·194 | 3·193 |
| Sp. vol . | 0·3434 | 0·3283 | 0·3090 | 0·3082 | 0·3096 | 0·3120 | 0·3129 | 0·3130 | 0·3132 |

The **specific volume** curve is shown in Fig. 102. There are three distinct curves : *AB* represents mechanical mixtures of pseudowollastonite and diopside ; *BC*, solid soln. of diopside with magnesium silicate ; and *CD*, solid soln. of magnesium silicate with diopside. The sp. gr. of artificial diopside is 3·245. J. W. Retgers inferred that diopside is a chemical compound because its sp. vol. cannot be calculated additively from the sp. vol. of its constituents. E. T. Allen and W. P. White gave 3·270–3·275 for the crystals at 25°/25°, and 2·830 for the glass at 30°/25°. This gives an idea of the expansion which occurs in the process of melting. The sp. gr. of crystals from Alaska was 3·268 at 25°/25°. The sp. gr. of many of the specimens which have been analyzed have been determined—*vide supra*—and the results show that the sp. gr. increases with the proportion of ferrous oxide up to about 3·53. V. Pöschl found the sp. gr. of the artificial mixtures or solid soln. is almost always smaller than with the natural crystals, presumably because the former have more pores and cavities. He found the physical characters of solid soln. of diopside and hedenbergite varied continuously, but not linearly, with the composition. Thus :

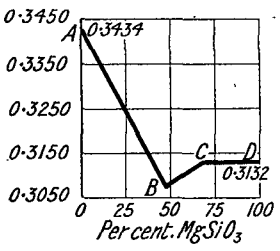



FIG. 102.—Specific Volume Curves in the Binary System : $MgSiO_3$–$CaSiO_3$.

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| Diopside . | 100 | 90 | 80 | 70 | 60 | 50 | 40 | 30 | 0 |
| Hedenbergite . | 0 | 10 | 20 | 30 | 40 | 50 | 60 | 70 | 100 |
| Per cent. FeO | 0 | 2·40 | 5·00 | 7·03 | 9·98 | 12·57 | 14·87 | 17·07 | 25·00 |
| Sp. gr. . . | 3·08 | 2·87 | 2·90 | 2·96 | 2·98 | 3·01 | 3·16 | 3·26 | 3·53 |
| M.p. . . | 1325° | 1265° | 1250° | 1240° | 1230° | 1225° | 1210° | 1200° | 1140° |
| Axial angle . | 32° | 36° | 38° | 43° 40′ | 45° 50′ | 47° | 49° 20′ | 50° | 50° 30′ |

The **hardness** of diopside is about 5. L. H. Adams and E. D. Williamson found the **compressibility** of diopside to be $\beta=1{\cdot}09\times10^{-6}$ between 0 and 10,000 megabars press.

F. Pfaff found the coeff. of **thermal expansion** between 0° and 100° in the *a*-direction to be 0·0008125 ; in the *b*-direction, 0·0016963 ; and in the *c*-direction, 0·0001707 ; thus making the coeff. of cubical expansion 0·002330. P. E. W. Oeberg gave 0·1871, 0·192, and 0·2036 for the **specific heat** of diopside between 0° and 100° ; F. E. Neumann gave 0·1906 ; and H. Kopp, 0·184 between 19° and 50°. W. P. White gave for the mean sp. ht. of artificial diopside between ordinary temp. and

| | 100° | 500° | 700° | 900° | 1100° | 1300° |
|---|---|---|---|---|---|---|
| Mean sp. ht. . . . | 0·1912 | 0·2309 | 0·241 | 0·2483 | 0·2563 | 0·2603 |
| True sp. ht. . . . | — | 0·262 | 0·272 | 0·281 | 0·286 | — |

E. T. Allen and W. P. White gave 1381° for the **melting point** of artificial diopside; A. L. Day and R. B. Sosman, 1395°; E. Kittl, 1280°–1310°; J. H. L. Vogt, 1225°; V. Pöschl, 1325°; and A. L. Fletcher, 1237°–1245°—R. Cusack obtained a lower value. C. Doelter found diopside begins to melt at 1305°, and is quite fluid at 1345°. V. S. Deleano gave 1280°–1310°, and E. Dittler 1300°–1320° for the m.p., and H. Leitmeier, by very slowly raising the temp. during 24 hrs., obtained 1305°–1315°. C. Doelter found for diopside from Ala Valley 1250°–1270°; from Zermatk, 1270°–1300°; and from Zillertal, 1300°–1340°. The results with native diopside depend also on the nature of the impurities, and the m.p. is reduced when ferrous oxide is present; with mixtures of $CaFe(SiO_3)_2$ and $CaMg(SiO_3)_2$, V. Pöschl found the m.p. ranged from 1140°–1325° respectively, and he gave for mixtures of enstatite and diopside:

| Diopside | 100 | 75 | 60 | 50 | 40 | 25 | 0 per cent. |
|---|---|---|---|---|---|---|---|
| Sp. gr. | 3·08 | 30·4 | 3·25 | 2·98 | 3·05 | 3·12 | 3·2 |
| M.p. (mean) | 1312° | 1310° | 1305° | 1310° | 1312° | 1325° | 1387° |
| Axial angle | 32° | 37° | 39° | — | — | — | — |

H. Leitmeier observed that the m.p. is reduced when the mineral is very finely powdered. R. Akermann gave 444 cals. per gram for the total **heat of fusion**; while C. Doelter, 94 cals., and J. H. L. Vogt, 100 cals., for the latent heat of fusion. G. Tammann gave for the **heat of solution** of diopside crystals in 100 grms. of 30 per cent. hydrofluoric acid mixed with 250 c.c. of 1·1*N*-hydrochloric acid 472 cals. per gram; and for diopside glass, 565 cals. Hence the **heat of crystallization** is 93 cals. per gram. O. Mulert obtained a similar result.

E. T. Allen and W. P. White gave for the **indices of refraction** of artificial diopside in Na-light, $\alpha=1{\cdot}664$, $\beta=1{\cdot}671$, and $\gamma=1{\cdot}694$, each $\pm 0{\cdot}002$. This gives for the **birefringence** $\gamma-\alpha=0{\cdot}030$, $\gamma-\beta=0{\cdot}023$, and $\beta-\alpha=0{\cdot}007$. They also measured the indices of refraction, and extinction angles of solid soln. of combinations with 28–95 per cent. of magnesium metasilicate. Observations on the mineral were made by A. des Cloizeaux, E. Dufet, E. A. Wülfing, A. Schmidt, A. Michel-Lévy and A. Lacroix, G. Nordenskjöld, etc. G. Flink and E. A. Wülfing found:

| | α | | | β | | | γ | | |
|---|---|---|---|---|---|---|---|---|---|
| Colour | Li | Na | Tl | Li | Na | Tl | Li | Na | Tl |
| White | 1·6675 | 1·6710 | 1·6749 | 1·6744 | 1·6780 | 1·6818 | 1·6962 | 1·7000 | 1·7045 |
| Yellowish-green | 1·6697 | 1·6734 | 1·6770 | 1·6767 | 1·6804 | 1·6838 | 1·6990 | 1·7029 | 1·7057 |
| Grass green | — | — | — | 1·6889 | 1·6959 | 1·7003 | — | — | — |
| Dark green | — | — | — | 1·7005 | 1·7047 | 1·7106 | — | — | — |
| Black | 1·6956 | 1·6986 | 1·7030 | 1·7028 | 1·7057 | 1·7103 | 1·7244 | 1·7271 | 1·7326 |

N. L. Bowen's values for the maximum indices of refraction of the solid soln. of diopside and clinoenstatite were:

| Diopside | 100 | 92 | 84 | 75 | 65 | 56 | 37 | 19 | 0 per cent. |
|---|---|---|---|---|---|---|---|---|---|
| Max. | 1·694 | 1·692 | 1·684 | 1·684 | 1·678 | 1·675 | 1·671 | 1·665 | 1·660 |
| Min. | 1·664 | 1·664 | 1·662 | 1·660 | 1·655 | 1·655 | 1·653 | 1·651 | 1·651 |

E. T. Allen and W. P. White found the **extinction angles** on the clinopinacoid or (010)-face to be $-38{\cdot}5° \pm 1°$; and on the prism or (110)-face $-39{\cdot}9° \pm 10$. Measurements were made by G. Tschermak, F. J. Wiik, C. Doelter, F. Herwig, P. Mann, W. C. Brögger, H. Rosenbusch, G. Flink, etc. The effect of ferrous oxide on the extinction angle on the (010)-face is:

| FeO per cent. | 2·91 | 3·09 | 3·49 | 4·50 | 17·34 | 26·29 |
|---|---|---|---|---|---|---|
| Extinction | 36° 5′ | 36° 50′ | 37° 10′ | 39° 10′ | 46° 45′ | 47° 50′ |

G. Flink found for a white dioptase, the extinction angle 38° 11½′ with red light, 38° 3½′ with yellow light, and 37° 54½′ with green light. F. J. Wiik represented the relation between the extinction angle and the per cent. $x$ of ferrous oxide by:

Extinction angle=$35{\cdot}5+0{\cdot}8719x-0{\cdot}0167x^2$; other formulæ have been given for other types of mineral. E. T. Allen and W. P. White, and A. Michel-Lévy and A. Lacroix measured the effect of the angle of the prism face with the orthopinacoid or (100)-face, on the extinction, and found a rapid rise for the first 40°; and for faces near the clinopinacoid, the changes are slight. Diopside is optically positive. N. L. Bowen's values for extinction angles, $\phi$, of solid soln. of diopside and clino-enstatite were:

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Diopside . . . | 100 | 93 | 74·5 | 56 | 46·5 | 37 | 19 | 0 per cent. |
| $\phi$ . . . . | 38·5° | 37·5° | 36° | 34° | 31·5½ | 30° | 26° | 22° |

The interference figures have been studied by H. de Sénarmont, and A. Bertin and co-workers. The **pleochroism** of the pyroxenes is so slight that it has been recommended as a test for distinguishing amphiboles from pyroxenes. There is, however, a distinct pleochroism when the coloured diopsides are rotated on the microscope. This subject has been investigated by G. Tschermak.

The **electrical conductivity** of diopside at ordinary temp. is too small to detect. C. Doelter found that at 1478° K., the conductivity is perceptible, and it increases with rising temp. He found the specific conductivity to be 0·009 mhos at 1340°, and 0·039 mhos at 1366°. There is a marked increase when the mineral melts. The sp. **electrical resistance** curve, with a 1000 ohms as unit, is shown in Fig. 103.

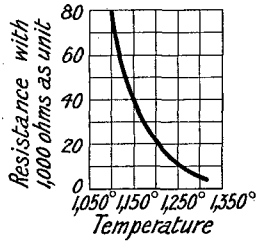



FIG. 103.—The Electrical Resistance of Diopside.

G. A. Kenngott found that diopside, and the green and black augites react strongly alkaline when moistened with water. W. B. and R. E. Rogers discussed the behaviour of diopside with water sat. with carbon dioxide. F. Sestini investigated the action of water at a high temp. A. Daubrée found that steam at 400° decomposes diopside and small crystals of quartz are formed. W. Suida showed that diopside is not coloured by basic aniline dyes, while more or less weathered varieties are stained. Hydrofluoric acid readily decomposes diopside, but other acids have but a slight action on the mineral, while the aluminous varieties are scarcely unaffected by acids. A. Becker studied the action of hydrochloric acid; C. Doelter, the action of dry hydrogen chloride; W. B. Schmidt, the action of sulphurous acid on diopside; J. Lemberg, the action of soln. of potassium carbonate; and C. Doelter, the action of soln. of sodium carbonate. The weathering of diopside in metamorphic or igneous rocks may produce talc or serpentine, and sometimes epidote; it may furnish amphibole, tremolite, or actinolite. L. Milch showed that carbonates may also be formed. The aluminous diopsides may form chlorite, asbestos, etc. H. Rose described the passage of salite into the *picrophyll* of L. Svanberg—πικρός, bitter; φύλλον, leaf, in allusion to the odour when moistened. L. Jaczewsky described the transformation of diopside into chrysolite serpentine. The *pitcärantite* of T. Scheerer is a green product from Pitkäranta, Sweden, and is supposed to be derived from diopside or augite. *Traversellite*—*vide supra*—is also derived from diopside; so also is *uralite*. R. van Hise has discussed some of these changes. A. S. Eakle[9] described a hydrated silicate from the limestone of Crestmore, Cal., with a composition approximating $2(Ca,Mg)O.2SiO_2.H_2O$; it may be $H_2(Ca,Mg)_2Si_2O_7$, or hydrated calcium magnesium dimetasilicate, $2(Ca,Mg)(SiO_3)_2.H_2O$. The mineral was called *zurupaite*. It forms compact spheres of soft, silky radiating fibres. The oblique extinction corresponds with monoclinic symmetry. The mineral is easily decomposed by hydrochloric acid, and when moistened it gives no coloration with phenolphthalein. Less than one per cent. of water is given off at 120°, and all is not expelled over Bunsen's flame.

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## § 31. Hydrated Magnesium Silicates

A number of ill-defined hydrated magnesium silicates have been reported. J. N. von Fuchs [1] noted that magnesium hydroxide hardens rapidly in contact with a soln. of water-glass, although W. Heldt said that neither the hydroxide nor the calcined oxide suffers any change in contact with water-glass; J. Lemberg, however, said that under these conditions brucite is very slowly converted into a silicate which is gelatinized by hydrochloric acid, and that magnesite in contact with water-glass at 100° for 10 days is partially converted into a silicate.

By adding water-glass to a soln. of magnesium sulphate, W. Heldt obtained a gelatinous mass which, when dried at 100°, had the composition $MgO.3SiO_2.2H_2O$; and K. Haushofer similarly obtained a product $2MgO.7SiO_2.6H_2O$. J. Lemberg added to a sat. soln. of magnesium hydrocarbonate an eq. quantity of alkali disilicate soln. and obtained a precipitate approximating, when dried, to $2MgO.5SiO_2.nH_2O$. E. Tischler believed the hydrate $MgSiO_3.2{\cdot}31H_2O$ to be a constituent of sand-lime bricks; and he found that this product is obtained by heating a mixture of eq. proportions of silica and magnesia at 8–10 atm. press. in steam. B. von Ammon obtained **hydrated magnesium metasilicate,** a voluminous mass, by adding an excess of crystallized sodium silicate to a soln. of magnesium sulphate. The washed precipitate forms a white opaline mass, which, when dried at 100°, has the composition $3MgSiO_3.5H_2O$. The moist precipitate dissolves in hydrochloric acid. Further observations on this subject by A. Gages, J. Lemberg, etc., are indicated below. N. O. Holst claimed to have found white or grey, radiating, crystalline masses with mother-of-pearl lustre, and with a composition corresponding with **dihydrated magnesium orthosilicate,** $Mg_2SiO_4.2H_2O$. He named the mineral *natricite*. Its sp. gr. is 2·53; and hardness, 3–4. It is attacked by acids. A. S. Eakle found a white radiating fibrous mineral at Crestmore, Jurupa Mts., California, and he called it *jurupaite*. The composition approximated **calcium magnesium dihydro-orthodisilicate,** $H_2(Ca,Mg)_2Si_2O_7$. The crystals are probably monoclinic; the sp. gr. is 2·75; the hardness, 4; the index of refraction parallel with the fibres, 1·576, and perpendicular thereto, 1·568; and the birefringence, 0·007. The water is expelled only at a high temp. The mineral is decomposed by dil. hydrochloric acid without gelatinization.

There is some evidence in favour of the belief that three hydrated magnesium silicates can exist as chemical individuals: namely, *serpentine*, $H_4Mg_3Si_2O_9$; *meerschaum* or *sepiolite*, $H_4Mg_2Si_3O_{10}$; and *talc* or *steatite*, $H_2Mg_3Si_4O_{12}$. There are a few others whose individuality is less well established: *gymnite*, $Mg_4Si_3O_{12}$—*vide* deweylite; *aphrodite*, $H_6Mg_4Si_4O_{15}$—from ἀφρός, foam—of N. J. Berlin, A. Schrauf, and H. Fischer; *spadaite*, $H_2Mg_5Si_6O_{18}.3H_2O$, of F. von Kobell and others which may be mixtures of magnesium silicates with opaline silica, etc. In nature, the magnesium oxide may be replaced by ferrous oxide, nickel oxide, etc.

It is highly probable that the λίθος ὄφιτης of Dioscorides' *Materia medica* (**5**. 161), written about A.D. 50, and the *ophites of* Pliny's *Historia naturalis* (**36**. 7), published about A.D. 70, referred to a mineral resembling that now known as *serpentine*. The Latin term was translated *serpentine* by G. Agricola; [2] *Serpentenstein, marmor serpentinum, marmor zeblicium,* or *lapis serpentinus,* by A. B. de Boodt. Analogous terms were used by J. G. Wallerius, A. Cronstedt, L. A. Emmerling, A. Estner, C. A. Hoffmann, etc., and they have crystallized into **serpentine** in allusion to the green, serpent-like cloudings of the serpentine marble. J. G. Wallerius used the term *lapis colubrinus*. R. J. Haüy regarded serpentine as a rock. In 1759, A. S. Marggraf [3] detected magnesia in serpentine; and about the end of the eighteenth or the beginning of the nineteenth century, the mineral was analyzed by R. Kirwan, C. A. Gerhard, P. Bayen, R. Chenevix, J. F. John, V. Hartvall, O. B. Kühn, C. G. Mosander, L. P. Lychnell, F. Stromeyer, etc. A large number of analyses have since been reported.[4]

Serpentine *in nature may* be associated with many other substances which can

be regarded as impurities. For instance, there may be much ferrous oxide present, and this may be due to admixed ferrous silicate. Serpentine has presumably been formed in nature by the metamorphosis of magnesian silicates—*e.g.* olivine—and it can but rarely be regarded as a one-phase mineral. It is associated with other magnesian silicates as well as ferrous silicates. Ferric oxide and alumina may be present, probably as a result of the serpentinization of aluminous and ferruginous magnesian silicates. There is also a series of analyses with a higher water-content than the normal 13·04 per cent., and another series with a lower water-content. There are also calcareous serpentines; some contain fluorine; and some have up to 10 per cent. carbon dioxide—presumably derived in part from the breaking down of the serpentine itself by carbon dioxide—*vide infra*. In a few cases, the presence of nickel, cobalt, copper, chromium, and manganese oxides has been reported; likewise also the alkalies, sulphates, and phosphates. M. W. Travers found that serpentine from Zermatt contained 0·80 per cent. of hydrogen which was not present in the mineral as an inclusion, but was produced from the non-gaseous constituents by heat, say, $2FeO+H_2O=Fe_2O_3+H_2$.

The idealized mineral has the composition of a **magnesium tetrahydrodisilicate,** $H_4Mg_3Si_2O_9$. It is assumed that the hydrogen is not present as water of hydration because it is held so tenaciously when heated—*vide infra*. R. Brauns represents its formula $Mg(MgOH)_2H_2Si_2O_7$. J. Jakob applied the co-ordination theory and represented it by

$$\left[SiO_2.SiO_6\right]^{Mg_4}_{H_2.OH_2}$$

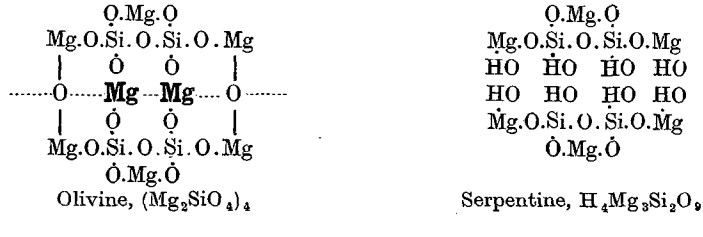
F. W. Clarke, and F. W. Clarke and E. A. Schneider regarded serpentine as a derivative of a polymerized magnesium orthosilicate, $Mg_4(SiO_4)_2$, namely, $Mg_2(SiO_4)_2H_3(MgOH)$. The assumption that some magnesium is present as hydroxide fits observations on the ultra-red transmission spectrum—*vide infra*. S. Hillebrand regarded serpentine as a salt of the acid $H_4Si_2O_8$; and chrysotile as a salt of the acid $H_{10}Si_4O_{13}$. He considers these two minerals to be related with olivine as:

| $(MgOMg)_2Si_2O_6$ | $(MgOH)_6H_2Si_4O_{12}$ | $(MgOMg)(MgOH)_4H_4Si_4O_{13}$ |
|---|---|---|
| Olivine. | Serpentine. | Chrysotile. |

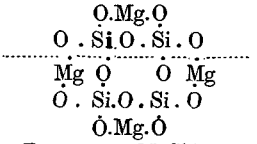
He represented serpentine and chrysotile by the formula $Mg_6H_8Si_4O_{18}$, and considered them to be isomeric forms of the same silicate. G. Tschermak,[5] and R. Scharizer showed that the serpentine formula can be represented in two ways—one symmetrical and the other unsymmetrical:



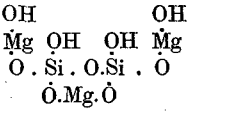
The genesis of serpentine has been investigated by A. Quenstedt, M. Websky, etc. The general result shows that serpentine may be formed from any silicate rich in magnesia—*e.g.* olivine, pyroxene, amphibole, garnet, etc. It can also be produced by the action of percolating magnesian waters on minerals like the felspars, which are non-magnesian. G. Tschermak represents the transformation of olivine into serpentine by the equation: $2Mg_2SiO_4+CO_2+2H_2O=H_4Mg_3Si_2O_9+MgCO_3$; and of diopside $3MgCa(SiO_3)_2+3CO_2+2H_2O=H_4Mg_3Si_2O_9+3CaCO_3+4SiO_2$. R. Scharizer represents the serpentinization of olivine by the structural formulæ:



The carbonated water attacks the magnesium atoms indicated in the above formula, forming magnesium carbonate. The olivine mol. simultaneously splits into two parts; each part furnishes a mol. of serpentine. Compare this with the formation of talc—*vide infra*. Similarly, also in the serpentinization of a pyroxene or amphibole:



Pyroxene, $(MgSiO_3)_4$



Serpentine, $H_4Mg_3Si_2O_9$

V. Iskyul said that the serpentines are metasilicates, and compact serpentine and chrysotile are pyroxene silicates similar to enstatite, while antigorite is similar to anthophyllite. The colloidal origin of the minerals of the serpentine family has been discussed by F. Cornu. A. Gages claimed to have made serpentine as a transparent amorphous mass by allowing gelatinous magnesium silicate to remain in contact with dil. potash-lye for some months. J. Lemberg also made a serpentine by the action of a soln. of sodium silicate on magnesite for 10 days at 100°, by heating in a sealed glass tube monticellite with a soln. of magnesium chloride for 18 hrs.; and in other ways.

Serpentine may occur massive, lamellar, foliated, fibrous, and crystalline. Serpentine as a rock may constitute whole mountains, and it is then associated with dolomite, magnesite, calcite, etc. The variety which makes a clouded green sometimes with white or pale green veins furnished the *vert antique* or *ophiolite* of the ancients. It is used for interior decorative work, but if exposed outside, it soon tarnishes by weathering. Some varieties take a high polish, and can be turned in a lathe, making ornaments of various kinds. The so-called *precious or noble serpentine* is a rich green of various shades, and more or less translucent. G. P. Merrill called a banded serpentine from Mexico, *ricolite*—from *rico*, in allusion to its rich green colour.

The texture of serpentine can thus be very varied; many of the varieties have received special names. G. T. Bowen [6] described what he regarded as a massive and granular nephrite, and J. D. Dana called it *bowenite*. J. L. Smith and G. J. Brush proved it to be serpentine. A massive serpentine, yellow to green in colour, was described by T. Thomson and named *retinalite*—from ῥητίνη, resin—in allusion to its waxy or resinous lustre. It is thought to be a mixture of serpentine and deweylite. T. S. Hunt regarded it as compact serpentine. G. A. Kenngott described a brown or greenish-black variety which he named *vorhauserite* after J. Vorhauser. A. des Cloizeaux regarded it as a compact serpentine. J. D. Dana called a variety resembling compact lithomarge *porcellophite*, and this is possibly the meerschaum of Taberg and Sala, Sweden. The *antigorite* of E. Schweizer is a thin lamellar variety from Antigorio Valley, Piedmont. It was also studied by G. J. Brush, and by G. A. Kenngott. V. Iskyul investigated the action of hydrochloric acid. A lamellar apple-green variety from Texas was named *williamsite* by C. U. Shepard; it was shown by R. Hermann, and by J. L. Smith and G. J. Irish, to be serpentine. T. Nuttall described a thin foliated variety from Hoboken, New Jersey; and he called it *marmolite*—from μαρμαίρω, I shine—in allusion to its pearly and somewhat metallic lustre. L. Vanuxem, and F. A. Genth and G. J. Brush showed that it is a foliated serpentine. J. R. Blum's marmolite was shown by A. Breithaupt to be a variety of mica. A. E. Nordenskjöld found a scaly variety of serpentine at Hopansuo, Finland, which exfoliated when heated, and which was hence named *thermophyllite*—θέρμη, heat; φύλλον, a leaf.

F. von Kobell applied the name *chrysotile* to a delicately fibrous serpentine from Reichenstein, in Silesia. It is named from χρυσός, golden; τίλος, fibrous. Its colour is greenish-white, green, yellow, and brown. According to J. F. Hausmann, the term includes most of the silky *amianthus* or schiller asbestos of serpentine rocks. V. Iskyul examined the action of hydrochloric acid on chrysotile. J. F. Hausmann applied the term *picrolite* to a fibrous and columnar variety of serpentine from Taberg, Sweden. The term is derived from πικρός, bitter, in allusion to its containing bitter-earth or magnesia. It was studied by F. Stromeyer, L. P. Lychnell, M. Websky, R. Brauns, C. List, C. Almroth, etc. The *baltimorite* of T. Thomson was shown by C. F. Rammelsberg to be a chrysotile; and R. Hermann, G. A. Kenngott, and C. von Hauer described impure varieties. L. F. Svanberg's

*hydrophite*—named in allusion to the water present—is a dark green fibrous serpentine from Taberg, Sweden. H. Fischer found it to be impregnated with magnetite. M. Websky regarded it as a ferruginous metaxite. A fibrous greenish-black crust, found by C. U. Shepard on the magnetite of Monroe, New York, was named *jenkinsite*, after J. Jenkins. It was shown by J. L. Smith and G. J. Brush to be a form of hydrophite. A. Breithaupt described a silky fibrous mineral from Schwarzenberg; and he named it *metaxite*—from *μέταξα*, silk. A. Delesse, R. Brauns, and M. Websky showed that it is a fine-fibred serpentine. A. E. Arppe, K. Hällsten, F. J. Wiik, and G. A. Kenngott have examined the mineral. A. E. Arppe's *picrofluite* proved to be a mixture of fluorite, magnetite, and metaxite.

A. Frenzel obtained a serpentinous mineral from Zöblitz, Saxony, and hence termed *zöblitzite*. It was also described by C. F. Rammelsberg. R. Brauns described the mineral *radiotine* from Wallenfels, Nassau; and named on account of its radial structure. R. Brauns named a serpentinous mineral from Amelose, Hessen, after M. Websky, *websk yite*. It was also studied by F. Cornu, and is probably an alteration product of serpentine. The mineral *limbachite*, from Limbach, Saxony, was shown by A. Frenzel to be an aluminous serpentine. F. P. Dunnington obtained a similar mineral from Webster, N. Carolina. A. Schrauf described the mineral *enophite*, from Kiemze, Bohemia, as a chlorite-like serpentine. A. Breithaupt obtained from Waldheim, Saxony, a green massive mineral with a resinous lustre; he called it *dermatine*—from *δέρμα*, skin—in allusion to its occurrence as an incrustation on serpentine. It is probably colloidal. M. F. Heddle obtained a fawn-coloured serpentinous mineral from Totaig, Scotland, and hence he called it *totaigite*. W. Haidinger described a mineral from Engelsberg, Bohemia, which he named *picrosmine*—from *πικρός*, bitter; *ὀδμή*, odour. It has some relationship with talc, and W. F. Foshag classes it with the talcs. It was discussed by G. Magnus, A. Frenzel, H. Fischer, and C. F. Rammelsberg. M. F. Heddle found in various parts of Scotland a kind of mountain cork or mountain leather as *pilolite*—from *πῖλος*, felt. Its composition corresponded with $4MgO.Al_2O_3.10SiO_2.15H_2O$. J. Henderson also described a specimen from New Zealand. C. U. Shepard found a serpentinous substance which he called *pelhamine—pelhamite*—in the asbestos mine of Pelha. Mass. N. Nordenskjöld described a serpentinous mineral from Zermatt, Schweiz (Switzerland), and he called it *zermattite*, while A. von Fersmann called it *schweizerite*. A. Breithaupt found a mineral in Frankenstein, Silesia, which he named *cerolite*—from *κηρός*, wax—in allusion to its vitreous, resinous appearance. It was also described by O. B. Kühn, R. Hermann, and F. A. Genth. F. Fock called a variety from Zillerthal, Tyrol, *memaphyllite*; it contained 2 per cent. of soda.

E. Emmons reported amorphous brown or yellow granules, resembling the appearance of gum arabic, from Barc Hills, Md. The mineral was called *deweylite* after C. Dewey; and T. Thomson called it *gymnite*—*γυμνός*, naked—in allusion to the locality when the mineral was found. Specimens were described or analyzed by C. U. Shepard, T. Thomson, J. Oellacher, F. von Kobell, K. Haushofer, V. Widtermann, A. Bukovsky, F. A. Genth, W. Haidinger, F. von Richthofen, L. Liebener and J. Vorhauser, E. Hatle, E. Hatle and H. Tauss, and E. F. Smith and D. B. Brunner. The composition corresponds with $Mg_4Si_3O_{10}.nH_2O$; and it is usually represented as **magnesium tetrahydrotriorthosilicate,** $H_4Mg_4(SiO_4)_3$. W. W. Coblentz found the ultra-red transmission spectrum of deweylite gave strong bands at $3\mu$ and $6\mu$, making it appear that the water is present as water of crystallization; in the ultra-red reflection spectrum there are maxima at $9{\cdot}65\mu$ and $10{\cdot}5\mu$. F. Cornu found the moistened mineral reacted alkaline towards litmus. M. Websky said the structure is like that of chalcedony. F. Zambonini regards it as an adsorption product. J. Jakob applied the co-ordination formula:

$$\begin{bmatrix} SiO_2 \\ SiO_2 \end{bmatrix} \begin{matrix} SiO_6 \end{matrix} \Big]^{Mg_2}_{(H_2O,Mg)_2}$$

to deweylite. Another mineral like deweylite in many respects was examined by D. Fogy, F. A. Genth, and F. Zambonini. The composition corresponds with $Mg_3Si_2O_7.3H_2O$. F. Zambonini called it pseudodeweylite, and he considered it to be a hydrogel. Their optical behaviours are similar. A. Breithaupt described a translucent yellowish or greenish-white mineral which was rather different from deweylite, and he called it *melopsite*—from *μῆλον*, apple; *ὄψον*, meat. It was analyzed by F. Goppelsröder. F. Zambonini, and D. Fogy examined the loss of water under various conditions. A ferruginous gymnite—*iron-gymnite*—was examined by T. Thomson, and E. Hatle and H. Trauss.[7]

Serpentine may be nearly white or coloured various shades of green, brownish-red, or brownish-yellow. On exposure to air, the lighter shades may become grey. The **crystals** are pseudomorphs after chrysolite, pyroxene, amphibole, spinel, garnet, titanite, chromite, etc. G. Friedel argued that the pseudocubic crystals found at Brewster belong to serpentine itself, and are not pseudomorphs after an unknown mineral. The properties of the crystals correspond with those of the

monoclinic system. P. Groth regards antigorite as monoclinic, and chrysotile as rhombic; H. Michel also says fibrous serpentine is rhombic. These two varieties are regarded as isomeric forms of serpentine. The crystalline structure has been discussed by M. Websky, A. des Cloizeaux, E. Reusch, F. J. Wiik, E. Hussak, H. Rosenbusch, A. Michel-Lévy and A. Lacroix, G. Tschermak, H. B. Patton, R. Brauns, T. G. Bonney and C. A. Raisin, A. Hamberg, R. B. Hare, etc. According to W. H. Miller, the **optic axial angle** is $2E=22°\ 20'$ for thermophyllite; and, according to A. des Cloizeaux, $2E=36°\ 26'$ at 26°, it is reduced about 2° by raising the temp. to 196°. H. Michel gives for the axial angle of fibrous serpentine, $2E=16°$–$50°$; and for antigorite, $2E=16°$–$98°$. G. Tschermak said that the axial angle depends on the iron content of the mineral.

The **specific gravity** was determined by many of those who analyzed the mineral —*vide supra*. Specimens low in iron oxide and alumina have a sp. gr. ranging from 2·55–2·59; and the sp. gr. is raised by iron oxide, and lowered by alumina. The **hardness** of fresh serpentine is 3–4. Specimens with a hardness approaching 5 are supposed to be admixed with opaline or chalcedonic silica. L. H. Adams and E. D. Williamson found the compressibility of **serpentine** to be $\beta=1·80\times10^{-6}$ at 2000 megabars and $1·38\times10^{-6}$ at 10,000 megabars; or $\beta=0·0_5 1804-0·0_{10}532(p-p_0)$. The **specific heat** of serpentine was found by A. S. Herschel and G. A. Lebour to be 0·27–0·28; by P. W. E. Oeberg, 0·2586; by J. Joly, 0·2529; by H. Hecht, 0·251 between 0° and 100°; by G. Stadler, 0·2439. $k$ denotes the **heat conductivity**; $c$, the sp. ht.; and $D$, the sp. gr., $a^2=k/cD$, and H. Hecht found $a^2=0·0113$, and G. Stadler, 0·0128. The **thermal dehydration** of serpentine has been studied by J. Lemberg, C. F. Rammelsberg, and others. A small proportion of water is expelled at 105°, but the bulk is lost only at a red heat. Thus, F. W. Clarke and E. A. Schneider found the percentage loss with four samples of serpentine:

| | | | | | |
|---|---|---|---|---|---|
| Water lost at 105° | 0·96 | 1·53 | 2·04 | 2·26 |
| ,, ,, 250° | 0·55 | 0·44 | 0·71 | 1·01 |
| ,, ,, 383°–412° | 0·27 | 0·62 | 0·27 | 0·98 |
| ,, ,, 498°–527° | 0·23 | — | 0·56 | 0·42 |
| ,, ,, red heat | 12·37 | 10·58 | 11·81 | 11·32 |
| ,, ,, white heat | 0·28 | 0·04 | 0·25 | 0·17 |

F. Zambonini found that with chrysotile confined over conc. sulphuric acid of sp. gr. 1·835:

| | | | | | |
|---|---|---|---|---|---|
| Hours exposed | 2 | 6 | 25 | 73 | 121 |
| Per cent. water lost | 1·71 | 1·98 | 2·18 | 2·37 | 2·18 |

The serpentine so dehydrated readily absorbs water again. He also measured the water lost at different temp. in a current of humid air by chrysotile with 15·4 per cent. of water, and bowenite with 13·20 per cent. of water:

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| | 125° | 250° | 320° | 345° | 480°* | | |
| Chrysotile lost | 2·62 | 2·87 | 3·18 | 3·35 | 3·32 per cent. | | |
| | 115° | 160° | 250° | 300° | 395° | 440° | 465° |
| Bowenite lost | 0·28 | 0·47 | 0·59 | 0·69 | 0·76 | 0·81 | 0·94 per cent. |

A. Daubrée, and V. Iskyul believed that when melted, serpentine breaks down into enstatite and olivine: $H_4Mg_3Si_2O_9=2H_2O+Mg_2SiO_4+MgSiO_3$. According to H. Leitmeier, measurements of the **melting point** showed that serpentine from Snarum softened at about 1480° and was quite liquid with rapid heating at 1550°. The f.p. was 1400°, and olivine crystallized out, but no enstatite appeared. A. Michel-Lévy and A. Lacroix gave for the **indices of refraction** of antigorite $a=1·560$, $\beta=1·574$, and $\gamma=1·571$. A. des Cloizeaux gave $\beta=1·574$ for red light. H. Michel gave 0·013 for the **birefringence** of fibrous serpentine, and 0·011 for antigorite; he found the birefringence of villarsite to be strong, and that of radiatine to be medium. The

optical character of fibrous serpentine was positive, and those of antigorite and radiotine, negative. The optical properties of serpentine minerals have been studied by J. R. Schnell, K. Schuster, M. Websky, R. B. Hare, E. Reusch, F. Becke, H. Wiegel, R. Brauns, W. H. Miller, A. des Cloizeaux, G. Tschermak, M. Stark, etc. A. Michel-Lévy and A. Lacroix said that antigorite is feebly **pleochroic** in that $\alpha$ and $\beta$ are a paler green than $\gamma$. H. Michel also said villarsite is strongly pleochroic. W. W. Coblentz found that serpentine has absorption bands in the **ultra-red transmission spectrum** at 1·4$\mu$, 3$\mu$, 5$\mu$, 6·6$\mu$, 7·4$\mu$, 8·1$\mu$, and 8·5$\mu$. The large absorption band at 3$\mu$ corresponds with the assumption that hydroxyl groups are present. There are maxima at 9·7$\mu$ and 10·5$\mu$ in the reflection spectrum. W. Suida observed that serpentine is readily stained with aniline dyes—*e.g.* fuchsine, and methylene blue—and F. Cornu noted that the stained mineral is strongly pleochroic.

According to G. A. Kenngott, powdered and moistened, calcined or uncalcined, serpentine has an alkaline reaction. The mineral is readily attacked, and partially dissolved by **water** with carbon dioxide in soln. R. Müller found 1·24 per cent. passed into soln. H. Leitmeier found 3·68 per cent. was dissolved by the action of carbonated water on serpentine from Kraubath, Steiermark; and the soln. contained 3·07 per cent. of magnesium oxide, 0·38 of ferrous oxide, and 0·23 of silica. C. R. van Hise represents the action of water by: $H_4Mg_3Si_2O_9+H_2O=3Mg(OH)_2+2SiO_2$; and the action of **carbon dioxide** by $H_4Mg_3Si_2O_9+CO_2=MgCO_3+2Mg(OH)_2+2SiO_2$. F. W. Clarke and G. Steiger heated serpentine with **ammonium chloride** in a sealed tube for 5 or 6 hrs.; and leached the cold product with water. They found 0·18 per cent. of silica and 5·53 per cent. of magnesia passed into soln. A. Lindner also studied this reaction. F. W. Clarke and E. A. Schneider said that a soln. of **sodium hydroxide** does not attack serpentine, but if the mineral has been strongly calcined, from 2·00–6·23 per cent. of silica passed into soln. A. Lindner studied the action of **potassium hydroxide.** F. W. Clarke and E. A. Schneider found that when heated to 383°–412° in a stream of dry **hydrogen chloride,** serpentine, unlike talc, is attacked, and when afterwards treated with water, from 9·98–16·73 per cent. of magnesia was extracted as chloride. The iron silicate is also attacked. A. Lindner, and R. Brauns also investigated the action of hydrogen on serpentine. Serpentine is attacked by **hydrochloric acid,** and more readily by **sulphuric acid**, with the separation of gelatinous silica; fibrous serpentine—*e.g.* chrysotile—yields fibrous silicic acid. A. Terreil found that all the magnesia and iron oxide dissolved by boiling with conc. hydrochloric acid. V. Iskyul studied the action of hydrochloric acid, and the solubility of silica in serpentine, antigorite, and chrysotile. A. Lindner examined the effect of **acetic acid**. H. Ota and M. Noda found that powdered serpentine does not show the **indophenol reaction.** The weathering of serpentine has been studied by A. Schrauf, and C. R. van Hise; and A. Lacroix investigated the action of the vapours from fumaroles on serpentine.

In his *Historiæ naturalis* (**19.** 4; **36.** 31, *c.* 77 A.D.), Pliny refers to a rare and costly cloth, the cremation cloth of kings, which he called *linum vivum*. He thought that it was of vegetable origin, and gave an imaginary description of its growth in the deserts of India. He said that it was called by the Greeks *asbestinon* —from *a*, not; and *σβέννυμι*, to extinguish—in allusion to its incombustibility. He also mentions the *amianthus* or the *ἀμίαντος λίθος* of Dioscorides, *De materia medica* (**5.** 155)—from *a*, not; *μιαίνειν*, to stain—also indestructible by fire. Near the beginning of our era, Strabo, in his *Geographica* (**10.** i, 6), described the occurrence of the mineral at Carystus, Eubœa; Pausanias, in his *Græcia descriptis* (**1.** 26), written in the third century, also mentions the properties of the mineral occurring at Carpasius, Cyprus; and Plutarch, in his *De defectione oraculorum* (**5.** 2), in the first century of our era, said that the asbestos was used in ancient times for making the wicks of the lamps used by the vestal virgins. In the thirteenth century, Marcus Polo in his *Travels* (**1.** 39) mentioned an indestuctible cloth made

by the Tartars which was said to be made from the skin of the salamander, supposed to live in fire, but which was found to be woven from a fibrous mineral called amicanto. The knowledge of asbestos possessed by the ancients appears to have been forgotten. Apart from a few isolated cases, the industrial applications of asbestos did not attract serious attention until towards the middle of the nineteenth century.[8]

The term **asbestos** includes two distinct minerals—actinolite and chrysotile—both of which have a fibrous structure, silky lustre, and a more or less pronounced green colour. Tremolite, actinolite, crocidolite, serpentine, and the palygorskite minerals can form fibrous asbestos. Crocidolite is also known as blue asbestos. Actinolite, and tremolite are varieties of *hornblende asbestos*, or *amphibole asbestos ;* and chrysotile is a variety of *serpentine asbestos*. Both are hydrated magnesium silicates, but actinolite is usually associated with more impurities, chiefly lime and iron oxide. Analyses of commercial samples gave :

| | $SiO_2$ | $Al_2O_3$ | FeO | MgO | CaO | $H_2O$ |
|---|---|---|---|---|---|---|
| Actinolite . . . . | 61·82 | 1·12 | 6·55 | 23·98 | 1·63 | 5·45 |
| Chrysotile . . . . | 40·18 | 2·24 | 1·01 | 41·75 | 0·00 | 3·81 |

The sp. gr. of actinolite varies from 3·02–3·17, and that of chrysotile from 2·2–2·3. Chrysotile fibres are much more elastic than those of actinolite. When rubbed between the finger and thumb, actinolite splits into harsh brittle fibres, whereas chrysotile fibres are elastic and tough, so much so that it can be spun into articles of various kinds. Crocidolite is more elastic and possesses a greater tensile strength than chrysotile. Chrysotile-asbestos is decomposed by hydrochloric or sulphuric acid ; tremolite is not attacked by acids ; while crocidolite or blue-asbestos is fairly resistant to acids, chemical soln., and sea-water. C. Matignon and G. Marchal examined the corrosive action on asbestos of water in the presence of carbon dioxide under 10 atm. press. during 3 years. R. E. Wilson and T. Fuwa measured the water adsorbed by asbestos from air of different degrees of humidity.

Chrysotile-asbestos loses water at a red heat, not below, and thin fibres can be fused in the Bunsen flame ; tremolite-asbestos fuses with difficulty ; and crocidolite readily fuses to a black glass. When the water of hydration has been expelled, the fibres become brittle, and crumble to powder when rubbed. Asbestos fireproofing and building materials have been the subject of numerous patents. The heat-insulating qualities of asbestos have been tested by W. R. Degenhardt, H. Pratt, C. R. Darling, C. G. Lamb and W. G. Wilson, F. Bacon, W. Nusselt, etc. G. Sever found that asbestos is a better non-conductor than magnesite, but the latter has a greater electrical resistance and " break-down " voltage. The electric conduction and dielectric capacity of asbestos were discussed by W. S. Flight.

Spun asbestos is used for steam packing, fireproof curtains, etc. ; as cloth, twine, and rope it is used as an insulator for steam and hot-water pipes and cold-storage plants ; and as a lining for safes, stores, and furnaces. Along with other materials asbestos is made into bricks, tiles, millboards, plasters, and paints. Some of the preparations have special trade-names—*e.g. uralite, manderite, ceilinite, asbestolite*, etc. Uralite is a mixture of asbestos fibre, chalk, sodium carbonate, and water-glass moulded and heated in a stove. Asbestos in fibrous powder mixed with powdered clay or other refractory earth can be made into a paste with water and moulded into retorts, crucibles, or bricks ; then dried ; and fired. The Société Méran make an asbestos " porcelain " from a mixture of about 70 per cent. of powdered asbestos and 30 per cent. of powdered steatite which is plastic enough to mould into bricks and larger quarries. When fired below 1400° the mass is firm and porous, and as the temp. approaches 1400°, the biscuit becomes more and more translucent and porous as the individual particles contract ; between 1400° and 1650°, incipient vitrification occurs, the porosity diminishes ; above 1650°, the mass fuses. Asbestos " porcelain " is used for diaphragms, and porous cells for electro-chemical work since the material is not attacked by ordinary acids and bases.

The mineral **meerschaum** has long been known. J. L. Smith [9] described it as occurring in earthy or alluvial deposits at the plains of Eskibisher,

Asia Minor; and as being formed by the decomposition of the magnesium carbonate embedded in the serpentine of the adjacent mountains. More or less magnesium carbonate is often found in meerschaum, so that R. J. Haüy could call it *une variété silicifère spongieuse de magnésie carbonatée.* A. Brongniart, indeed, under the term *magnésite* included (i) the carbonate, (ii) the hydrated silicate or meerschaum, and (iii) a siliceous carbonate from Piedmont, but F. S. Beudant reserved the term *magnésite* for meerschaum, and called magnesium carbonate, *gioberite.* Many French mineralogists adopted this nomenclature, but it is not justifiable on historical grounds. The name meerschaum was applied by A. G. Werner in 1788; it is the German word for sea-foam; which in French becomes *l'écume de mer.* The term may have been intended to emphasize the porosity and colour of the mineral, or the fact that when freshly dug it is soft, and forms a lather with water; or, as A. Estner expressed it, because it *eine schaumartige Leichtigkeit hat, und meistens von der Seeküste zu uns gebracht wird;* he also said the term may be a corruption of the local word Myrsen. E. F. Glocker proposed the term *sepiolite* from σηπία, cuttle-fish, which has a light and porous bone-like structure, and being also a product of the sea *deinde spumam marinam significabat.* R. Kirwan called the mineral *keffekill.*

The mineral is used commercially for making tobacco pipes, and cigar- and cigarette-holders. In Spain, it is used as a building stone. The mineral in Morocco is used in place of soap in the Moorish baths of Algeria—hence the term *pierre de savon de maroc.* Descriptions of the Asia Minor deposits have been made by C. C. von Leonhard, L. A. Emmerling, X. Landerer, A. Damour, etc.; and deposits in other localities have been reported by M. von Hantken, J. R. Blum, V. von Zepharovich, etc. Analyses of meerschaum were made by J. C. Wiegleb, M. H. Klaproth, L. P. Lynchnell, T. Scheerer, A. Damour, A. Schrauf, F. von Kobell, X. Landerer, P. A. Dufrénoy, P. Berthier, A. H. Chester, A. Lacroix, A. von Fersmann, F. Zambonini, M. Kispatic, F. Katzer, J. W. Döbereiner, D. Fogy, W. T. Schaller, C. F. Rammelsberg, H. B. von Foullon, A. Liversidge, E. Weinschenk, F. Kovar, G. P. Merrill, P. H. Walker, etc.

The water of the analyses is significant. A. H. Chester found that about half of the 19–20 per cent. of water passed off below 110°, and the remainder between 200° and a red heat. Observations on this subject were made by E. Weinschenk, D. Fogy, and F. Zambonini. D. Fogy found that over conc. sulphuric acid, the mineral loses 6·53 per cent. of water, and 5·14 per cent. over calcium chloride. According to F. Zambonini, the loss of water at different temp. is:

| | 120° | 165° | 200° | 280° | 340° | 400° | 475° | |
|---|---|---|---|---|---|---|---|---|
| Loss . . . | 18·69 | 19·21 | 19·33 | 19·92 | 20·92 | 21·74 | 21·96 | per cent. |

In T. Scheerer's analysis, the ratio $SiO_2 : MgO = 9 : 4$; and C. F. Rammelsberg gave 3 : 2. The latter is the value usually accepted. This makes meerschaum **magnesium tetrahydrotrisilicate,** $H_4Mg_2Si_3O_{10}$, or $Mg_2Si_3O_8 + 2H_2O$; F. Zambonini gave $Mg_2Si_3O_8.nH_2O$. H. Michel, and B. Sterett regarded the mineral as a colloid, and this agrees with F. Zambonini's observations on the dehydration and the substitution of the water by alcohol and other substances as in the case of the zeolites (*q.v.*). D. Fogy obtained metasilicic acid when the mineral is treated with acid, and hence argues that it is a metasilicate, $(MgOH)MgH_2Si_3O_9$; and C. Doelter assumed that the water removed by conc. sulphuric acid is physically bound, and wrote $2(MgSiO_3).H_2SiO_3.nH_2O$, where $n$ is one or more than one. L. Colomba gave $H_8MgSi_3O_{12}$. J. W. Döbereiner said that an artificial meerschaum can be made by precipitating a very dil. soln. of magnesium sulphate with one of potassium silicate, well washing the pasty precipitate, and drying it in air.

Meerschaum is found in irregular nodules which are opaque, with a dull lustre somewhat resembling ivory in appearance. The colour is white, pale grey, or cream, and sometimes pale green. The mineral is dull and earthy in appearance, but it can be polished by rubbing with the finger-nail which presses the particles close

together. Meerschaum is so porous that it adheres to the tongue, and floats on water. It rarely occurs fibrous. A. Lacroix said that the so-called compact amorphous mineral is composed of minute scale-like crystals. A. von Fersmann applied the term *para-sepiolite* to meerschaum, which is largely crystalline. W. Vernadsky called it *α-sepiolite;* and the colloidal gel meerschaum is called *β-sepiolite—vide infra.* They gelatinize differently when treated with hydrochloric acid. F. Zambonini says that the gelatinization of the sepiolites depends on the conditions of the experiment and not on the constitution of the mineral. He also studied the dehydration of the mineral, and found about half the water is lost at 100° over conc. sulphuric acid; and most is expelled at 500°. When melted, enstatite and silica are produced. L. Colomba said that the crystals of meerschaum are pseudo-hexagonal. H. Michel gave for the optic axial angle $2V=40°–50°$. The sp. gr. of meerschaum depends on the water content, and is about 2; the hardness is also about 2. H. Michel found the indices of refraction to be $\alpha=1·515–1·519$, and $\gamma=1·525–1·529$; the birefringence is $\gamma-\alpha=0·009$. F. Tucan found that the fibres of meerschaum become pleochroic after taking up organic agents. F. Cornu said that when moistened with water it reacts alkaline. The mineral is gelatinized by hydrochloric acid. W. Suida found that meerschaum is readily stained by basic aniline dyes. According to H. Michel, the behaviour of the meerschaums towards aniline dyes, show that they are mixtures of a fibrous, crystalline silicate with constant optical properties, and of a gel. The crystalline constituent is basic and absorbs acid dyes, whilst the isotropic substance is acidic and adsorbs basic dyes. When a finely powdered sample of meerschaum is subjected to the action of a soln. containing methylene-blue and magenta, it is found that the mineral becomes blue and the soln. red. This is attributed to the much greater rate at which the basic dye is absorbed by the gel. It is used like fuller's earth for absorbing grease. The variable water content of the meerschaums is probably connected with the varying proportion of the two constituents, for the constancy of the optical properties of the crystalline constituent would seem to show that the proportion of water in this is quite constant.

A soft earthy mineral from Längban, Sweden, was named by N. J. Berlin [10] *afrodite*, or *aphrodite*—from *ἀφρός*, foam. It was examined by A. Schrauf, T. S. Hunt, and H. Fischer. It resembles sepiolite or meerschaum; its composition, according to C. F. Rammelsberg, approximates $H_6Mg_4Si_4O_{15}$. The sp. gr. is 2·21. T. Scheerer obtained masses of stellate fibres from Arendal; and compact masses have been obtained from Eisenack, and Riesengebirge. The mineral was named *neolite*—from *νέος*, new. The colour is green or brown; the sp. gr. 2·625–2·837; and the hardness 1–2. Observations on the mineral have been made by C. M. Kersten, P. Herter and E. Porth, A. Frenzel, and V. von Zepharovich. F. von Kobell found a flesh-red amorphous mineral filling the spaces among the crystals of wollastonite in the leucitic lava at Capo di Bove, Rome. He called it *spadaite*—after Medici Spada. The analysis corresponds with $5MgO.6SiO_2.4H_2O$, or, according to C. F. Rammelsberg, $H_2Mg_5Si_6O_{18}.3H_2O$. H. Fischer said the mineral is not amorphous but cryptocrystalline.

In his Περὶ λίθον, Theophrastus refers to the *μαγνῆτις λίθος* as being a white mineral with a silvery lustre, and easily cut into any shape or figure. This description applies to steatite or talc, but the word "talc" does not occur in the writings of Theophrastus, Dioxorides, or Pliny. G. Agricola [11] gave *Talck, Silberweiss, Katzensilber*, and *Glimmer* as synonyms for *magnetis*. Glimmer is the present-day German term for mica; and probably talc was confused with some of the micas. G. Agricola referred to the fire-resisting qualities of talc, and referred to it as *lapis scissilis*. The name talc is generally considered to be of Arabic origin, and, according to C. Hintze, talc frequently appears in the recipes of the Arabian writers of the tenth to twelfth centuries. J. H. Pott quoted Avicenna: "the *aster samius* is tallz." U. Aldrovandus stated that the term is of Moorish origin, and that *hoc nomen appud Mauritanos stellam significare dicitur*. The term *star* or *star of the earth* is an old name for the mineral, suggested by the silvery lustre. A. Breithaupt suggested that the term talc is derived from the Swedish *tälja*, to cut with a knife;

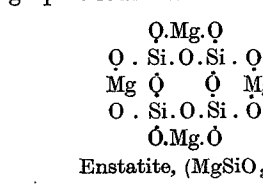
but this is very doubtful. J. H. Pott added that the word cannot be of German origin because there is nothing to show that Avicenna, who first used the term, ever came into contact with the Germans. In 1636, B. Cæsius used the word *talchus* for the mineral. A. B. de Boodt used *talcum;* J. G. Wallerius, *creta Brianzonia, creta Hispanica, creta Sartoria,* and *telgstein* or *lapis ollaris;* A. Cronstedt, *Talcum, tälgsten, Speckstein,* and *steatite.* The word *steatitis* occurs in Pliny's *Historia naturalis* as the name of an unctuous stone. A. B. de Boodt also employed the term steatite. J. B. L. Romé de l'Isle classed talc and steatite with the argillaceous minerals, and, like R. J. Haüy, regarded steatite as *une variété de espèce talc.*

The mineral was analyzed by M. H. Klaproth [12] in 1797, and by L. N. Vauquelin in 1800. Since then numerous analyses have been made, and many occurrences reported. Alkalies are usually present in very small proportions, if at all. Lime may be genetically connected with the derivation of talc from dolomites. In some cases the lime is present as admixed carbonate. Ferrous and manganese oxides are commonly present, possibly as silicates in solid soln. Nickel oxide is not uncommon—may be as a solid soln. of the oxide or silicate. Magnesium silicate is coloured green by nickel oxide. Chromic oxide is sometimes present, and the green colour of some specimens of talc is attributed by F. Cornu and K. A. Redlich to the tinctorial properties of that oxide. Alumina may be present in talc derived from chlorites and aluminous magnesium minerals. M. W. Travers found that talc from Greiner gave off, when heated, 0·04 per cent. of a mixture of carbon monoxide and hydrogen, and 0·07 per cent. of carbon dioxide. These gases are supposed to be produced by the action of ferrous oxide, water, and carbonate, and are not included in the mineral: $2FeO+H_2O=Fe_2O_3+H_2$; and $2FeO+CO_2=Fe_2O_3+CO$. From the collection of over a hundred available analyses, it is not quite clear what is the composition of the idealized mineral. E. Weinschenk gives MgO, 31·72 per cent.; $SiO_2$, 63·52 per cent.; and water, 4·76 per cent. This comes near to the generally accepted formula: $3MgO.4SiO_2.H_2O$. The analyses exhibit a variation in the Mg : Si ratio from about 1 : 1 to 4 : 3; and the water ranges from 3 to over 7 per cent. C. F. Rammelsberg gave for the ratio Si : Mg, 4 : 5; and for the ratio H : Si, nearly 1 : 2. The above formula makes talc to be **magnesium dihydrotetrasilicate,** $H_2Mg_3Si_4O_{12}$; but the formulæ, $H_2Mg_4Si_5O_{15}$, and $H_4Mg_4Si_5O_{16}$, have also been used to represent the composition of talc. W. F. Foshag found a sample from Russell, Mass., to lose 0·5 per cent. of water after standing over sulphuric acid for 23 days; 4·04 per cent. was lost at a dull red heat, and 3·4 per cent. of water was retained. The loss of the water at dull redness is not attended by any essential change in the optical properties, but when the firmly bound water is driven off the material loses its homogeneity. The water is assumed to be an integral part of the mol. because it is expelled only at comparatively high temp. In accord with F. W. Clarke and E. A. Schneider's observation that soda-lye extracts about 17·36 per cent. of the silica from talc which has been calcined, the formula can be written, $3MgSiO_3.H_2SiO_3$, which makes the compound a tetrametasilicate, or, regarding $Si_3O_8$ as a quadrivalent radicle:

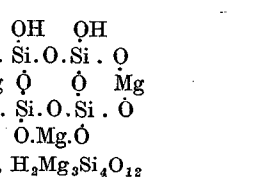
$$\begin{matrix} Mg \\ Mg \\ H_2 \end{matrix} \gtrless SiO_4 \\ \gtrless Si_3O_8 > Mg \qquad \text{or} \qquad \begin{matrix} H_2 \\ Mg \\ Mg \end{matrix} \gtrless SiO_4 \\ \gtrless Si_3O_8 > Mg$$

Talc appears to be formed in nature in many ways, most commonly by the hydrolysis of the pyroxenes or amphiboles: $4MgSiO_3+H_2O+CO_2=H_2Mg_3Si_4O_{12}+MgCO_3$; and $Mg_3CaSi_4O_{12}+H_2O+CO_2=H_2Mg_3Si_4O_{12}+CaCO_3$. The reactions resemble those involved in the formation of serpentine. F. Cornu and K. A. Redlich trace the talc of Mautem, Styria, to the action of magnesian waters on the neighbouring schists. This subject has been investigated by C. H. Smyth, J. H. Pratt, A. A. Julien, A. Gurlt, C. H. Hitchcock, E. Weinschenk, J. Rumpf, J. Roth, F. Cornu and K. A. Redlich, etc. C. Doelter discusssd the colloidal origin of talc.

R. Scharizer likens the formation of talc from enstatite to the formation of serpentine from olivine, and of kaolinite from orthoclase. The idea is illustrated by the graphic formulæ:




Enstatite, $(MgSiO_3)_4$




Talc, $H_2Mg_3Si_4O_{12}$

when the conversion of enstatite to talc simply involves the removal of an atom of magnesium and the substitution of eq. hydrogen atoms. There is no change in the type of salt since both minerals are regarded as metasilicates, and both resist attack by acids.

Talc has not been unequivocally synthesized in the laboratory. J. Lemberg[13] allowed a dil. soln. of sodium silicate to act on magnesite at 100° or 200°, and he obtained a mixture of magnesium carbonate and silicate by what C. Doelter and E. Dittler consider to be a reversible reaction: $3MgCO_3+4Na_2SiO_3+H_2O=3MgSiO_3.SiO_2+3Na_2CO_3+2NaOH$. C. Doelter and E. Dittler tried if talc is formed by the action of steam on a mixture of magnesium chloride and silicic acid. The reaction was symbolized: $3MgCl_2+6H_2O+4SiO_2+3H_2O=3MgO.4SiO_2.H_2O+6HCl+Aq.$, but it was not clear whether talc was or was not formed. When $3MgSiO_3.SiO_2$ is hydrolyzed, enstatite is produced. Attempts to make talc by molten fluxes—magnesium chloride and ammonium fluoride—were not successful.

Talc occurs in foliated or lamellar masses which can be readily separated into thin scaly crystals. These flakes are easily bent, but, unlike mica, the flakes do not spring back to their original position when released. Hence, the mineral is flexible, but not elastic like mica. The thin cleavage flakes are white, yellowish, or more commonly of a pale green colour, with a silvery lustre. Talc does not occur in distinctly developed crystals. Thin cleavage flakes are transparent; their optical properties resemble those of mica and the chlorites, and, like them, probably belong to the monoclinic system. J. R. Schnell[14] measured the crystal angles of talc. Talc or steatite occurs in crystals which are pseudomorphs after various minerals—quartz, dolomite, enstatite, topaz, etc. The original crystals have been largely replaced by steatite formed by the reaction of hot soln. of magnesium salts on the original mineral.

The mineral occurs in a compact massive form which feels greasy or fatty; it is then called *steatite, soapstone,* or *Speckstein.* The coarse and granular steatite is grey, greenish-grey or brownish-grey in colour, and, when more or less impure, usually owing to admixed chlorite, it is called *potstone, lapis ollaris, Topfstein, Lavenzstein,* and *Giltstein.* The fine granular or crypto-crystalline steatite may be soft like chalk. The so-called *French chalk,* or *craie de Briançon,* is milk-white steatite with a pearly lustre. An indurated or slaty talc is called *talc schist; talcose slate* is a dark argillaceous rock containing more or less talc, which gives it a greasy feel. The so-called *rensselaerite* is a crypto-crystalline or wax-like mineral pseudomorphous after salite or pyroxene. It was described by E. Emmons, and L. C. Beck. It was named after S. von Rensselaer. E. Repossi found a talc-like mineral in the Valle della Gava, and he called it *gavite.* The analysis corresponds with $H_4(Mg,Fe)_4Si_5O_{16}$. It resembles talc excepting for its ready solubility in hydrochloric acid, and in its water content. W. F. Foshag says that it is not a mineral species different from talc. A. R. Leids described a variety of talc pseudomorphous after pectolite, which he called *stevensite;* M. L. Glenn, and A. F. Rogers regard it as a colloidal magnesium silicate. L. W. Hubbard called a fibrous variety resembling asbestos, *beaconite;* and R. L. Packard, a variety with the appearance of vivianite, from Silver City, New Mexico, *native ultramarine.* The *pyrallolite* of A. E. Nordenskjöld—from πῦρ, fire; ἄλλος, other—appears to be a pseudomorph after pyroxene. According to A. E. Arppe, it is not homogeneous, but is a pyroxene partially transformed into steatite. A variety of pyrallolite was found in Sibbo, Finland, by J. J. N. Huot and named *vargasite* after Count Vargas. The so-called *strakonitzite* of V. von Zepharovich is a kind of steatite. The *talcoid* of C. F. Naumann is a white foliated talc which T. Scheerer called *neutraler Kieselsauer Hydrotalc.* According to J. D. Dana, it is a mixture of talc and quartz.

M. H. Klaproth found the steatite from Göpfersgrün contained rather less silica and rather more water than usual, and he called it *hydrosteatite*. R. Hermann applied the term *hampshirite* to steatitic pseudomorphs after quartz. Analyses were made by C. Dewey. It is probably not a homogeneous mineral. A. E. Arppe found a greyish-green talc with 7·83 per cent. of ferrous oxide, and 1 per cent. of cupric and zinc oxides. He called it *Eisentalk*, or *liparite*—from λιπαρός, fat.

The sp. gr. of talc has been determined by many of those who have analyzed the mineral. The values vary from 2·6–2·8. The hardness is very small; talc is one of the softest of minerals and represents No. 1 on Mohs' scale. It is scratched even by the finger-nail. F. Malt[15] found the sp. gr. rose from 2·78 to 3·19 on calcination; and the hardness rose to about 6. P. J. Holmquist, and A. Rosiwal investigated the hardness; if the hardness on the (0001)-face of quartz is 1000, the abrasive hardness of talc parallel to (001) is 2·6, and perpendicular to (001), 9·3. The heating curve is normal up to 875°, and at about 960° an acceleration appears, and the ferrous oxide simultaneously oxidizes. Enstatite appears to be formed. J. Joly found the sp. ht. to be 0·2168. A. Dannholm studied the sp. ht. of soapstone. C. Doelter gave 1530° for the m.p.; W. S. Howat, 1380°. When melted, talc breaks up into enstatite or anthophyllite, quartz, and water: $H_2Mg_3Si_4O_{12}=3MgSiO_3+SiO_2+H_2O$. Only hygroscopic water is lost at 110°; all the constitutional water is evolved only at a white heat. F. W. Clarke and E. A. Schneider found that at 105° talc lost 0·07 per cent. of water; at 250°–300°, 0·06 per cent.; at a red heat, 4·43 per cent.; and at a white heat, 0·35 per cent. E. Löwenstein found that over conc. sulphuric acid at 25° with a partial press. 21·58, 8·82, and 0·18 mm., the losses of water for equilibrium were respectively 0·10, 0·35, and 0·38 mol. A. des Cloizeaux found the optic axial angle $2E=19°\ 1'$ for the red ray, and 19° 56′ for the blue ray at 21·5°, and there is no perceptible change when the temp. is raised to 171°. W. F. Foshag obtained $2E=20°\pm5°$; and M. Bauer, $2E=13°$ for green talc. A. Michel-Lévy and A. Lacroix found $2Y=7°$. K. Zimanyi found the indices of refraction for Na-light to be $\alpha=1·539$, $\beta=1·589$, and $\gamma=1·589$. W. F. Foshag obtained $\alpha=1·540–1·545\pm0·005$; and $\beta=\gamma=1·575–1·585\pm0·003$. The birefringence is negative and strong $\alpha-\gamma=0·050$; A. Michel-Lévy and A. Lacroix obtained $\alpha-\gamma=0·038–0·043$. W. W. Coblentz found no hydroxyl band at $3\mu$ in the ultra-red transmission spectrum of talc. There are absorption bands at $5·6\mu$, $5·95\mu$, and $7·15\mu$. The reflection spectrum shows sharp maxima at $9·05\mu$ and $9·75\mu$. The percussion figures were studied by A. Michel-Lévy and A. Lacroix, and H. Rosenbusch; the resulting six-rayed star is oriented as with the micas. P. W. Bridgman represented the compressibility of talc by $dv/v_0=0·0_9104p-0·0_{12}63p^2$; and the thermal conductivity at a press. $p$, by $0·00733+0·0_6115p$ at 30°. He could not make finely powdered talc weld even at 30,000 kgrms. per sq. cm. press., possibly owing to films of air. A. V. Henry found the resistivity, $R$, in ohms per c.c., of Maryland, Italian, and Indian talcs, for a 45-volt, 1000-cycle alternating current, to be

| | 500° | 600° | 700° | 800° | 900° | 1000° |
|---|---|---|---|---|---|---|
| Maryland | $282\times10^5$ | $719\times10^4$ | $219\times10^4$ | $861\times10^3$ | $389\times10^3$ | $238\times10^3$ |
| Italian | $159\times10^5$ | $350\times10^4$ | $970\times10^3$ | $353\times10^3$ | $157\times10^3$ | $749\times10^2$ |
| Indian | $670\times10^5$ | $178\times10^5$ | $544\times10^4$ | $179\times10^4$ | $760\times10^3$ | $340\times10^3$ |

Talc is considered to be a very stable mineral at low temp. G. A. Kenngott, and F. Cornu found that talc moistened with water reacts alkaline whether the mineral has been calcined or not. E. W. Hoffmann made some observations on this subject. F. W. Clarke and E. A. Schneider heated talc for 15 hrs. at 383°–412° in a stream of hydrogen chloride, and observed no change in weight. Talc is not decomposed by acids other than hydrofluoric acid. F. W. Clarke and E. A. Schneider found that with fuming hydrochloric acid on a water-bath, about 1·05 per cent. of magnesia passes into soln. They also found that when calcined talc is boiled with soda-lye, about a fourth of the silica presses into soln., but with uncalcined talc, there is no perceptible change. Hence, talc suffers a chemical

change on calcination: $H_2Mg_3Si_4O_{12}=3MgSiO_3+SiO_2+H_2O$. C. Matignon and G. Marchal examined the corrosive action on talc of water in the presence of carbon dioxide under 10 atm. press. during ten years. E. C. Sullivan observed a basic exchange occurs when talc is treated with a soln. of cupric sulphate. H. Ota and M. Noda found that powdered talc does not show the indophenol reaction. The metamorphoses of talc in nature have been investigated by A. M. Finlayson, J. Roth, and E. Weinschenk.

Talc or steatite is used as a toilet-powder; for smoothing the floors of dancing rooms; and as a dry lubricant. Potstone can be turned in a lathe, and fashioned into fire-resisting vessels, and slabs. Steatite is used in making the tips of gas-burners, since it can be readily cut to the desired shape, and it becomes harder in use without fusing. Steatite was one of the fluxes used in making porcelain in England in former times; it is now used as a flux for clays, etc., in making sparking plugs;[16] it is also used in making furnace linings. The powdered mineral is used as a filler for paper, tailor's chalk, crayons, slate, pencils, shoe powder, wall plasters, etc.

A. Cronstedt[17] referred to *terra porcellanea particulis impalpabilibus mollis*; M. H. Klaproth, to a *soapstone* or *Seifenstein* from Cornwall; R. Kirwan, to a *steatite* from Cornwall; R. J. Haüy, to *mountain soap*, or *pierre à savon*; L. F. Svanberg, to *saponite*—from *sapo*, soap—and also to *piotine*—from πιότης, fat; R. Owen, to *thalite*; J. B. Hannay, to *birolingite* from Bowling, Scotland; and J. J. Dobbie, to *cathkinite* from Cathkin, Scotland; all these minerals, grouped as saponites, are probably different varieties of the same species, and represent variable mixtures of clay and hydrated magnesium silicates. The analyses are, as would be anticipated, very variable. According to M. F. Heddle, T. Thomson's *prasilite* is a variety of saponite, but is usually regarded as a chlorite (*q.v.*). E. W. Hilgard described a magnesian clay from Santa Lucia. Its analyses corresponded with an impure magnesium silicate which he called *lucianite*.

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## § 32. Zinc, Cadmium, and Mercury Silicates

In 1830, A. Lévy [1] described crystals of a mineral which he found at Altenberg, near Moresnet. The analysis corresponded with **zinc orthosilicate,** $Zn_2SiO_4$ ; and the mineral was named **willemite** after Willem I, King of the Netherlands ; A. Breithaupt proposed to call it *hebetine*—from ἡβητικός, youth. The term willemite is generally adopted, though it has been variously mis-spelt—*williamsite*, *wilhelmite*, and *villemite*. L. Vanuxem and W. H. Keating had previously reported a ferruginous "siliceous oxide of zinc" from New Jersey which C. U. Shepard had designated *troostite* after G. Troost. This is of course not the troostite constituent of steel. At Mine Hill and Sterling Hill, New Jersey, the mineral occurs in such quantities as to constitute an important zinc ore. Analyses in agreement with the above composition have been reported by T. Thompson, K. Monheim, A. des Cloizeaux, J. Lorenzen, V. M. Goldschmidt, G. Tschermak, F. A. Genth, etc. Manganese often replaces part of the zinc, and ferrous oxide is usually present. Analyses of troostite in agreement with the view that it is an isomorphous mixture of zinc, manganese, and ferrous orthosilicates were made by R. Hermann, A. Delesse, W. G. Mixter, C. H. Stone, G. A. König, H. Wurtz, G. Tschermak, and H. B. Cornwall. The sample called by G. A. König *tephrowillemite* is a brownish-grey troostite.

The fusion temp. of mixtures of silica and zinc oxide is so great that it is difficult to make vessels to withstand the temp. G. Rupprecht[2] overcame the difficulty by making a paste of the mixture to be fused and forming it into a bar, which is then heated in an oxyhydrogen flame so that it is progressively melted, and so that each molten globule falls on to a surface covered with the substance under treatment. A. Daubrée synthesized willemite by the action of silicon chloride on red-hot zinc oxide; but H. St. C. Deville repeated the experiment and found that willemite is decomposed by silicon chloride. He obtained the mineral by passing hydrogen fluosilicate over heated zinc; by the action of silicon fluoride on zinc oxide; and by the action of zinc fluoride on silicic acid. J. J. Ebelmen obtained relatively large crystals by heating a mixture of zinc oxide and silica in molar proportions, with boric oxide in a platinum crucible for 5 days. A. Gorgeu obtained the crystals by fusing a mixture of one part of silicic acid with 30 parts of an intimate mixture of an eq. of sodium sulphate and 0·5–1 eq. of zinc sulphate. The soluble matter was removed by leaching with water. G. Stein, and J. M. Jäger and H. S. van Klooster made crystals of zinc orthosilicate by simply fusing the component oxides. With rapid cooling, a glass was formed. According to K. Endell, the temp. of formation is much below the temp. of fusion, and he noted that 45–60 per cent. of zinc orthosilicate is formed when a dry mixture of zinc oxide and silica is heated for 24 hrs. between 1075° and 2000°. M. Rüger obtained zinc orthosilicate by heating a mixture of the constituents in theoretical proportions for 2 hrs. at 1200°, and heating the product on a water-bath to remove soluble matters. P. Groth, A. Schulze and A. W. Stelzner, A. Scott, and W. M. Hutchings noted the formation of willemite in the masonry of zinc furnaces, or in slags from ores containing zinc. For colloidal zinc silicates, *vide supra*, water-glass.

Crystals of a zinc silicate have also been reported in glazes highly charged with zinc oxide.[3] They were mentioned by C. Lauth and G. Dutailly in 1888, and ten years later they were adapted as a decorative glaze effect by A. Clément. J. W. Mellor's analysis of a large crystal, more or less contaminated with glaze, correspond better with willemite than with the metasilicate. K. Endell believes the crystals are those of zinc metasilicate. If the glaze contains a small proportion of cobalt oxide in soln., the crystals will abstract the colouring matter from the glaze and be stained a deep azure blue; with nickel oxide, free from cobalt, the crystals will be stained a fine turquoise blue; and with manganese oxide, brown.

The **colour** of the purer specimens is white, greyish-white, or greenish-yellow, but when contaminated with iron and other colouring oxides, it may be apple-green, flesh-red, yellowish-brown, and dark brown. It may occur in hexagonal prismatic **crystals**—long and slender or short and stout; it may also occur massive, in disseminated grains, and in fibrous masses. The crystals belong to the trigonal system, and, according to C. Palache,[4] $a:c=1:0{\cdot}6679$; and, according to A. des Cloizeaux, troostite has the axial ratio $a:c=1:0{\cdot}66975$, and $\alpha=107°\,46'$. Measurements have also been made by A. Arzruni, M. Bauer and R. Brauns, S. L. Penfield, A. Lévy, J. Lorenzen, C. Palache, etc. According to C. F. Rammelsberg, the crystals of willemite, troostite, phenacite, and dioptase are isomorphous. A. Arzruni observed the **twinning** of the crystals; and H. Traube the **corrosion figures.** A. von Lasaulx found microscopic inclusions of franklinite in the crystals. A. Schleede and A. Gruhl obtained **X-radiograms** of phosphorescent zinc silicate.

The general properties of willemite and troostite are similar. J. Lorenzen gave 4·11 for the **specific gravity**; T. Thomson, 3·935; F. A. Genth, 4·10; W. G. Mixter, 4·11–4·16; and C. H. Stone, 4·132–4·188. A. Gorgeu's crystals had a sp. gr. 4·25; and G. Stein's 3·7—in the latter case, probably less zinc was present than was thought because of volatilization at the high temp. of the furnace. The **hardness** is between 5 and 6. F. M. Jäger and H. S. van Klooster gave 1509·5° for the **melting point.** G. Stein gave 1484° for the **freezing point.** E. Jannetaz found the ratio of the **heat conductivities** in the $a$ and $\gamma$ directions to be $\sqrt{a/\gamma}=0{\cdot}854$. O. Mulert calculated the **specific heat** to be 0·14; the **heat of solution** of the

amorphous orthosilicate in *N*-HF, to be 99·54 ± 1·17 Cals. per mol; and of the crystalline, 90·5 ± 0·296 Cals. per mol. Hence, the **heat of crystallization** is 9·04 Cals. per mol, or 0·0405 Cal. per gram. The **heat of formation** of the glassy orthosilicate is −23·74 Cals. per mol; and the heat of formation of crystalline zinc orthosilicate from the crystalline metasilicate and zinc oxide is −17·20 Cals. per mol. The **indices of refraction** have been measured by O. B. Böggild, P. Gaubert, and C. Palache, and they respectively found for sodium light $\omega$=1·6928, 1·6931, and 1·6939; and $\epsilon$=1·7234, 1·7118, and 1·72304; and C. Palache gave for lithium light, $\omega$=1·68897 and $\epsilon$=1·71812. F. M. Jäger and H. S. van Klooster gave 1·719 and 1·697 for the indices of refraction of the artificial crystals. The **birefringence** is positive. V. M. Goldschmidt found for daylight $\gamma-\alpha$=0·0237; for red light, 0·0236; for green light, 0·024; and for blue light, 0·025. The birefringence decreases as the contained manganese and ferrous oxides increase; thus:

| Per cent. MnO+FeO | 0·5 | 4·6 | 6–13 |
|---|---|---|---|
| $\gamma-\alpha$ | 0·0306 | 0·0237 | 0·0187 |

G. Cesaro made some observations on this subject. A. Ehringhaus and H. Rose compared the dispersion and double refraction of the orthosilicates of copper, beryllium, and zinc with their mol. wts. According to J. D. Dana, willemite from New Jersey is **triboluminescent** since it glows with a blue light in a dark room when struck with a hammer. W. Crookes noted the phosphorescence of willemite when exposed to **cathode rays**—*vide* **4.** 25, 5. G. F. Kunz and C. Baskerville noted the **fluorescence** and **phosphorescence** of troostite—particularly the green varieties—when exposed to ultra-violet light, X-rays, and radium radiations. Each $\alpha$-particle striking against willemite produces a scintillation—*vide* radium. A. Schleede and A. Gruhl, and M. Curie studied the luminescence of zinc silicate containing traces of manganese; and obtained X-radiograms of the compound. T. Tanaka inferred the presence of manganese, iron, thallium, samarium, and ytterbium from the spectrum of the cathodoluminescence. The decay of the phosphorescence was studied by E. L. Nichols and E. Merritt; and the brightness of the luminescence by E. L. Nichols. C. Baskerville and L. B. Lockhardt and others noted that willemite phosphoresces under the action of **radium emanations**; and artificial as well as natural willemite phosphoresces if it contains small proportions of foreign oxides. E. Marsden noted the phosphorescence of willemite under the influence of **$\alpha$-rays** and **$\beta$-rays**—*vide* **4.** 26, 4. T. Liebisch observed neither phosphorescence nor fluorescence with the brown crystals of Altenberg when exposed to **ultra-violet light.** He found the emission **spectrum** of troostite at ordinary temp. to be continuous from 620–510$\mu\mu$ with a maximum in the green. At the temp. of liquid air, the spectrum is resolved into two parts separated by a small gap in the yellow at 575$\mu\mu$. W. W. Coblentz found the ultra-red transmission spectrum of willemite has bands at 5·9$\mu$ and 6·75$\mu$. The reflection spectrum has maxima at 10·1$\mu$, 10·6$\mu$, and 11$\mu$, and a band at 11·6$\mu$. He infers that the banding of the silica in willemite is different from what it is in quartz. M. Bauer and R. Brauns studied the **pyroelectric** properties of willemite. Willemite is soluble in cold dil. **hydrochloric acid,** and, according to G. Tschermak, orthosilicic acid separates out. J. D. Dana said that it is not gelatinized by **acetic acid.** H. C. Bolton found that willemite is not attacked by a cold sat. soln. of **citric acid.** A. H. Erdenbrecher studied the action of **hydrogen dioxide** on zinc silicate.

F. M. Jäger and H. S. van Klooster made **cadmium orthosilicate,** $Cd_2SiO_4$, by fusing a mixture of finely powdered quartz and cadmium oxide or carbonate. The m.p. was about 1252°, and the indices of refraction over 1·739. M. Rüger obtained cadmium orthosilicate by heating a mixture of the constituent oxides in theoretical proportions as in the case of zinc orthosilicate.

J. J. Ebelmen [5] made what he regarded as **zinc metasilicate,** $ZnSiO_3$, in *groupes de cristaux assez volumineux mais peu mets de forme,* by heating a mixture of the required proportions of zinc oxide and silica, and boric oxide, in a platinum crucible

for 5 days. H. Traube also said that when amorphous zinc silicate, prepared by precipitating a soln. of zinc sulphate with sodium silicate, is heated with boric acid for 10 days at a high temp., it is converted into a white crystalline powder, which has the composition $ZnSiO_3$. G. Stein made the metasilicate by heating a mixture of the component oxides in a porcelain tube. O. Mulert, and H. S. van Klooster employed a similar process. H. Schulze and A. W. Stelzner, and V. Steger reported crystals of the metasilicate in the walls of used zinc retorts. K. Endell—*vide supra*—said that the metasilicate is found in crystallized zinciferous glazes. The occurrence of the metasilicate in nature has not been reported. A. Gorgeu was unable to prepare the metasilicate by the processes just indicated. M. Rüger made zinc metasilicate by heating a mixture of zinc oxide and silica in the molar proportions 1 : 2 for an hour at 900°, and digesting the product with alkali-lye on a water-bath for several hours to remove soluble matters. Cobalt oxide is dissolved by zinc metasilicate when a mixture of the two is heated for 2 hrs. at 900°. R. Schwarz and G. A. Mathis made hydrated zinc metasilicate, $ZnSiO_3.H_2O$, by mixing dil. soln. of sodium metasilicate and zinc sulphate; and they converted this into hydrated **zinc monamminometasilicate,** $ZnSiO_3.H_2O.NH_3$. A. H. Erdenbrecher obtained *zinc peroxysilicates* by precipitating a zinc salt with sodium metasilicate in the presence of hydrogen dioxide.

H. Traube said that the optical properties of the **crystals** show that they belong to the rhombic system, and that zinc metasilicate is accordingly a zinc-pyroxene isomorphous with enstatite. H. S. van Klooster said that the crystals are hexagonal. F. M. Jäger and H. S. van Klooster gave 3·52 at 25°/4° for the **specific gravity.** G. Stein gave 3·42 for the sp. gr. of the crystals, and 3·86 for the sp. gr. of the glass. It is very rare to find the sp. gr. of a glassy silicate greater than that of the same substance in the crystalline state. G. Stein gave 1429° for the **melting point;** H. S. van Klooster, 1419°; and F. M. Jäger and H. S. van Klooster, 1437°; and the last-named added that there is a regular decrease in the m.p. as the at. wts.—magnesium, zinc, cadmium—increase. O. Mulert estimated the **specific heat** to be 0·16; and he found the **heat of solution** of the crystals in *N*-HF to be 51·48 ± 0·49 Cals. per mol.; the **heat of formation** of the crystalline metasilicate from amorphous silica and zinc oxide is 2·49 Cals. per mol. F. M. Jäger and H. S. van Klooster gave 1·623 and 1·616 for the two refractive indices. H. S. van Klooster observed with zinc metasilicate uniaxial positive interference figures; the **double refraction** was high. K. Endell found the metasilicate to exhibit fluorescence and phosphorescence when exposed to **X-rays** and to **radium rays.** H. Traube said that the metasilicate is insoluble in hydrochloric acid.

H. S. van Klooster prepared **cadmium metasilicate,** $CdSiO_3$, by the direct union of the constituent oxides at a high temp. He said that while the crystals of zinc metasilicate are hexagonal, those of cadmium metasilicate are rhombic. The m.p. is 1155°. F. M. Jäger and H. S. van Klooster gave 1242° for the m.p., 4·928 at 25°/4° for the sp. gr., and the indices of refraction over 1·739. Cadmium and zinc metasilicates form an unbroken series of mixed crystals with a minimum at 1052°, with 25 per cent. of zinc metasilicate, Fig. 104. G. Rousseau and G. Tite found that in preparing basic cadmium nitrate a layer of a solid product appears on the inner surface of the glass tubes. This can be freed from the cadmium salt by treatment with alcohol, and is removed from the glass

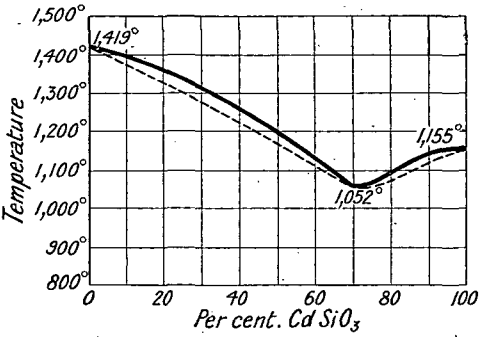



FIG. 104.—Freezing-point Curve of the Binary System: $ZnSiO_3$–$CdSiO_3$.

by prolonged treatment with warm water. It forms long scales which, when rubbed between the fingers, break up into microscopic needles, showing longitudinal extinction in parallel light. It has the composition, **trihemihydrated cadmium metasilicate,** $2CdSiO_3.3H_2O$, and is soluble in hydrochloric acid with separation of pulverulent silica. At a dull red heat it loses very little water, but when heated to orange-redness it melts and then intumesces in consequence of the escape of water. If the heating is continued, cadmium oxide is volatilized, and after prolonged heating a residue of silica alone remains. It would seem that the presence of water is essential to the stability of the mol.

A. Schrauf [6] reported that *ein Cadmium enthaltendes Silikate* occurred in minute triclinic crystals associated with the calamine of Altenberg. It was called *eggonite*—from ἔγγονος, a grandson—because it was supposed to be the third generation in a series of cadmium zinc silicates. According to J. D. Dana, the supposed cadmium silicate is really heavy spar or barite.

What may be *monohydrated zinc orthosilicate*, $Zn_2SiO_4.H_2O$, but is more probably **zinc dihydroxydisilicate,** $Zn_2(ZnOH)_2Si_2O_7$, occurs in nature as the mineral **calamine,** but has not been made artificially. H. and W. F. Lowe [7] found a boiler scale consisting chiefly of a hydrated zinc silicate which may have been an impure form of this compound. As indicated in connection with the history of our knowledge of zinc, the *cadmia* of Pliny and other ancient writers included the native silicate, the native carbonate, and the oxide—*cadmia fornacum*—which accumulated in the flues of zinc furnaces. Both J. G. Wallerius, and A. Cronstedt refer to *lapis calaminaris, cadmia officinalis, zincum naturale calciforme*, and *Galmeja*. The term *Galmei* is now a miner's term applied to ores containing calamine, and zinc spar. The word "calamine" appears in the French translation of J. G. Wallerius' book, and it was also used by J. B. L. Romé de l'Isle. T. Bergman in his *De mineris zinci* (Upsala, 1779) showed that two minerals are in question; the one contained zinc oxide and silica, and the other zinc oxide and carbon dioxide. B. Pelletier found silica in a zinc mineral from Breisgau which had previously been called *zeolite of Breisgau* because it gelatinized with acids; and M. H. Klaproth found silica in a zinc ore from Scotland. J. Smithson, however, cleared up the subject in 1803, by showing clearly that the mineral from Rezbanya is a silicate, and the zinc spar from Derbyshire and Somerset is a carbonate. He called the silicate *electric calamine*. The distinction established by J. Smithson was recognized by R. J. Haüy, and A. Breithaupt. C. C. von Leonhard called the silicate *Galmei*, and the carbonate *Zinkspath*. J. F. L. Hausmann called the silicate *Zincglas*: D. L. G. Karsten, *Zinkglaserz;* and A. Breithaupt, *Kieselzinkspath*, and *Kieselzinkerz*. In 1807, A. Brongniart called the silicate calamine, and this term was adopted by F. S. Beudant, who called the carbonate *smithsonite* after J. Smithson. In 1852, H. J. Brooke and W. H. Miller reversed these names; and in 1853, G. A. Kenngott suggested *hemimorphite* for the silicate in order to avoid any confusion, and to emphasize a most interesting feature of the mineral, *viz.*, its hemimorphism.

Clays carrying various proportions of zinc silicate are common in the zinc regions of south-western Missouri and Arkansas and in Virginia. They may be red, tough, but non-plastic; or yellow, grey, or brown with a greasy feel, and plastic when wet. In drying, they shrink and crumble into fragments. They have been called *tallow clays*.[8] They were described by W. H. Seamon, J. C. Branner, T. M. Chatard and H. N. Stokes, W. F. Hillebrand, F. Schönichen, and B. H. Heyward. H. Rose reported a leek-green or emerald-green mineral from Altenberg near Moresnet, and hence named it *moresnetite*. G. A. Kenngott showed that it is a mixture of calamine and clay. C. U. Shepard obtained an ocherous aggregate associated with the zinc ores at Sterling Hill, N.J., and named it *vanuxemite*—after L. Vanuxem. J. D. Dana regards it a mixture of a zinc silicate and clay. E. E. Libman studied the products obtained by sintering mixtures of silica, alumina, and zinc oxide.

Numerous analyses [9] have been made, and many occurrences reported.

C. F. Rammelsberg,[10] J. F. Wiik, W. Vernadsky, and G. Tschermak favoured the hypothesis that calamine is *monohydrated zinc orthosilicate*, $Zn_2SiO_4.H_2O$. The water, however, is given off only at a red heat, and hence P. Groth, and F. W. Clarke and G. Steiger thought that the water must be an integral part of the mol., and assumed that calamine is *zinc dihydroxymetasilicate*, $(ZnOH)_2SiO_3$. F. Zambonini showed that the contained water is present in two forms, since about half the water is lost continuously up to about 500°, and this loss is not attended by any marked change in the optical homogeneity of the crystal. He assumes that it is present as " dissolved water." The second half requires a very high temp. for its expulsion, and it is to be regarded as " constitutional water." He therefore assumes that the composition is best represented by the formula, $2(2ZnO.SiO_2)H_2O+H_2O$; or $Zn_2(ZnOH)_2Si_2O_7.H_2O$, thus making the compound *zinc dihydroxydisilicate*. This view shows how *clinoedrite*, $(CaOH)(ZnOH)SiO_3$, has no crystallographic resemblance to calamine, which would not be so clear if calamine has the formula, $(ZnOH)_2SiO_3$. F. Zambonini emphasized the crystallographic relationship observed by K. Vrba between calamine and bertrandite, $Be_2(BeOH)_2Si_2O_7$.

The **colour** of calamine is usually white, but it may have a delicate blue or green tinge; the colour may also pass through various shades of yellow to brown. The mineral may occur massive in nodules and fibrous. The *wabite* from Nijni-Jagurt, Ural, has been described by O. Radochoffsky, G. A. Kenngott, A. des Cloizeaux, and G. J. Brush; it is considered to be a pale blue or green concretionary calamine. The mineral may also occur in **crystals.** These were described by J. B. L. Romé de l'Isle as prismatic with dihedral summits, whereas the carbonate was said to be scalenohedral like dog-tooth spar; but he did not appreciate the importance of this difference as a distinguishing test. R. J. Haüy described only the crystals of the silicate, and he regarded native *carbonatée zinc* as an impure calcareous *zinc oxydé*. The crystals were examined by F. Mohs, A. Lévy, H. Dauber, F. Hessenberg, A. des Cloizeaux, H. Schulze, M. Bauer and R. Brauns, G. Cesaro, G. A. F. Molengraaff, K. Monheim, J. R. Blum, G. Rose, H. Traube, P. Groth, etc. According to A. Schrauf, the crystals belong to the rhombic system, and have the axial ratios $a:b:c=0{\cdot}78340:1:0{\cdot}47782$. The crystals exhibit **twinning** and have hemihedral forms. The **hemimorphism** was studied by M. Seebach and F. P. Paul. The **corrosion figures** were studied by H. Baumhauer. The **cleavage** according to (001) is imperfect, and perfect according to (110). V. von Lang found the **optic axial angle** for the red, yellow, and green rays to be respectively $2V=47°\ 30'$, $46°\ 9'$, and $44°\ 42'$; while A. des Cloizeaux found for the yellow ray $45°\ 57'$. V. von Lang measured $2E=81°\ 3'$, $78°\ 7'$, and 76° respectively for the red, yellow, and green rays, while A. des Cloizeaux gave 82° 30′, 80°, and 75°. By raising the temp. from 8·8° to 121°, the latter found the optic axial angle changed from $85°\ 21'$ to $76°\ 32'$. The **specific gravity** was determined by many of those who analyzed the mineral; A. Lévy gave 3·379; K. Monheim, 3·43–3·49; G. Rose, 3·435–3·871; F. P. Dunnington, 3·40; J. R. MacDirby, 3·338; etc. The **hardness** is 4–5. G. Spezia was able to melt the mineral to a white enamel, by feeding the flame with hot air. A. des Cloizeaux gave for the **indices of refraction** for yellow light, $\alpha=1{\cdot}615$, $\beta=1{\cdot}618$, and $\gamma=1{\cdot}635$; U. Panichi, $\alpha=1{\cdot}61376$, $\beta=1{\cdot}61673$, and $\gamma=1{\cdot}6355$; and V. von Lang, $\alpha=1{\cdot}61358$, $\beta=1{\cdot}61696$, and $\gamma=1{\cdot}63597$; the last-named also gave for red light, $\alpha=1{\cdot}61069$, $\beta=1{\cdot}61416$, and $\gamma=1{\cdot}63244$; and for green light, $\alpha=1{\cdot}61706$, $\beta=1{\cdot}6202$, and $\gamma=1{\cdot}63916$. U. Panichi found that the values of $\alpha$ and $\gamma$ at the temp. of liquid air are but slightly reduced, while $\beta$ is decreased by 0·0032. The decrease of $\beta$ is attended by an increase in the optic axial angles. The **birefringence** is strong. V. von Lang gave for red light, $\gamma-\alpha=0{\cdot}02175$; and for green light, $\gamma-\alpha=0{\cdot}02210$; and U. Panichi gave for yellow light, $\gamma-\alpha=0{\cdot}02174$. The optical character is positive. T. Liebisch observed the **fluorescence** of the mineral under the influence of **ultra-violet light.** The **emission spectrum** at −180° behaves like that of troostite. The mineral is also **triboluminescent.** P. Riess and H. Rose, F. Köhler, and A. Lévy found the mineral is strongly

**pyroelectric.** M. Bauer and R. Brauns noted that with a fall of temp., the electrification is stronger the longer the heating. J. and P. Curie noted the **piezoelectric** effects of compression—the ends with (001), (011), and (101) are negatively electrified, and the end with (121) is positively electrified. Calamine is soluble in **acids,** and, according to G. Tschermak, gelatinous orthosilicic acid separates out. J. D. Dana said that the mineral gelatinizes with **acetic acid ;** and is soluble in a conc. soln. of **sodium hydroxide.** H. C. Bolton said that a cold sat. soln. of **citric acid** attacks the mineral; and H. Brandhorst found that it is insoluble in an ammoniacal soln. of **ammonium carbonate.**

H. Bornträger [11] mixed an aq. soln. of a zinc salt (1 : 10) with an equal vol. of a soln. of sodium silicate of sp. gr. 1·357 dil. with half its vol. of water. The mass was washed with hot water. It melted when heated, forming a transparent glass with a composition corresponding with *zinc trisilicate*, $ZnO.3SiO_2$. The description includes no trustworthy evidence of chemical combination.

L. Bourgeois [12] made **cadmium orthosilicate,** $Cd_2SiO_4$, by heating mixtures of cadmium oxide and amorphous silica for several hours. It resembled cobalt orthosilicate (*q.v.*). A. Duboin first calcined a mixture of cadmium oxide, silica, and potassium fluoride ; and remelted the product with an excess of potassium chloride for 72 hrs. He thus obtained crystals of the orthosilicate, and **cadmium oxyorthosilicate,** $Cd_2SiO_4.CdO$. A. I. Walcker found a soln. of sodium silicate gives a white precipitate with mercurous nitrate soln.—possibly *mercurous silicate.* Soln. of mercuric chloride give no precipitate of *mercuric silicate*, and when the soln. is evaporated, crystals of mercuric oxychloride are formed.

H. S. van Klooster [13] found that no *lithium zinc silicate* is formed in the binary system with lithium and zinc metasilicates. The eutectic temp. is nearly 990°, and the eutectic mixture has nearly 52 per cent. of lithium metasilicate. The dotted portion of the curve, Fig. 105, was not determined thermally, but was estimated from optical observations on the solid products. R. Schindler said that a *potassium zinc silicate* separates in white flakes when zinc in contact with iron is dissolved in potash-lye containing silica in soln. He said that the flakes contain water ; dissolve in an excess of potash-lye, and in acids with the separation of gelatinous silica. There is here no evidence of the formation of a chemical individual. A. Duboin found that if precipitated zinc oxide is added to a soln. of silica in molten potassium fluoride, contained in a platinum crucible, and the cold mass remelted with the addition of potassium chloride, and maintained in that state for 72 hrs., two potassium zinc silicates are formed. These may be separated by a heavy liquid made by dissolving mercuric iodide in an aq. soln. of lithium or sodium iodide. The heavier silicate has a composition $K_2O.6ZnO.4SiO_2$, and it forms small prismatic crystals of sp. gr. 3·68 at 0° ; the lighter silicate has a composition $8K_2O.9ZnO.17SiO_2$, and it forms large prismatic crystals of sp. gr. 2·96 at 0°. Both are readily decomposed by hydrochloric acid. The constitution is not analogous to that of the potassium magnesium silicates. The data as to homogeneity are scarcely sufficient to justify naming the two products.

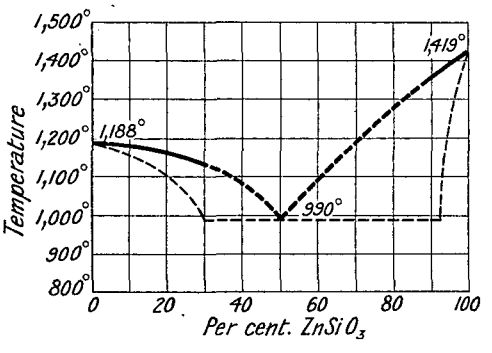



FIG. 105.—Freezing-point Curve of the Binary System: $ZnSiO_3$–$LiSiO_3$.

J. E. Wolff reported a white mineral from Franklin, N.J., which had a composition corresponding with the idealized formula $Ca_2ZnSi_2O_7$, or **zinc dicalcium orthodisilicate,** and it was called *hardystonite.* The crystals are tetragonal ; the index

of refraction for Na-light $\omega$=1·6691, and $\epsilon$=1·6568; or $\epsilon-\omega$=0·0123; for Li-light, $\omega$=1·6758, $\epsilon$=1·6647, and $\epsilon-\omega$=0·0111. The birefringence is negative. The sp. gr. is 3·396 and the hardness 3–4. The mineral gelatinizes with hydrochloric acid. K. Hofmann-Degen found a tetragonal silicate which he called *justite* in the slag at the Clausthal silver works. The composition approximates $(Mg,Fe,Zn,Mn,Ca)_3Si_2O_3$, where Ca : (Mg,Fe,Zn,Mn)=1 : 1. The refractive indices for Na-light are $\epsilon$=1·6581, and $\omega$=1·6712. Justite is isomorphous with hardystonite. A slag from Bochum contained tetragonal crystals of a member of the hardystonite family with the composition $R''_3Si_2O_{37}$, where R represents Ca : (Mg,Fe,Mn)=1 : 1. A. Duboin found crystals of **potassium cadmium triterosilicate,** $K_2CdSi_4O_{10}$, among those of the cadmium silicates indicated above.

S. L. Penfield and H. W. Foote obtained a colourless, white, or amethyst-blue mineral from Franklin, whose composition agreed with formula $H_2ZnCaSiO_4$, or **zinc calcium dihydrometasilicate,** $(CaOH)(ZnOH)SiO_3$, and he called it *clinohedrite*. The monoclinic crystals had the axial ratios $a : b : c$=0·68245 : 1 : 0·3226, and $\beta$=76° 4′. The birefringence is small. The optical character is negative. The sp. gr. is 3·33; and the hardness 5·5. The mineral gelatinizes with hydrochloric acid. Several cases in which zinc can replace more or less magnesium and calcium in the silicates have been indicated in connection with the magnesium silicates. G. A. König analyzed one with five basic elements—magnesium, zinc, manganese, calcium, and iron (ferrous)—present in appreciable quantities.


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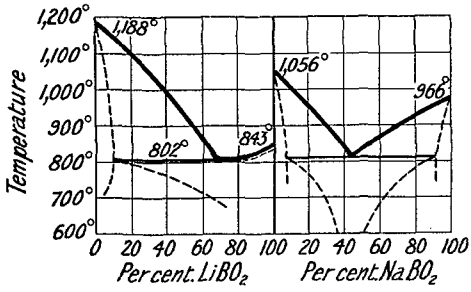
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## § 33. The Borosilicates

M. Faraday,[1] and W. V. Harcourt prepared a number of borosilicate glasses ; and W. Guertler showed that silica is insoluble or only slightly soluble in fused boric oxide. A. V. Bleininger and P. Teetor prepared fused mixtures of boric

oxide and silica, presumably homogeneous, with a composition ranging between $B_2O_3$ and $B_2O_3.3SiO_2$. The properties of various borosilicate glasses were investigated by W. E. S. Turner and co-workers—*vide* glasses. The constitution of the boratosilicate minerals was investigated by G. Cesaro and described in his memoir: *Sur le rôle du bor dans les silicates.* He considers that the boron is best regarded as part of the acid radicle, in which silicon is replaced by $B_2O''$.

H. S. van Klooster [2] measured the f.p. curves of mixtures of lithium metasilicate and metaborate, and found that no *lithium borosilicate* is formed, but mixed crystals were produced with up to 24 per cent. of lithium silicate and with up to 9 per cent. of lithium metaborate—Fig. 106. In the case of mixtures of sodium metasilicate and sodium metaborate, no *sodium borosilicate* is formed, but the product is immiscible in the solid state when between 4 and 95 per cent. of sodium metaborate is present. E. S. Larsen and W. B. Hicks [3] obtained a mineral from Searles Lake, San Bernadino, California, whose composition approximated to $Na_2O.B_2O_3.4SiO_2.2H_2O$, when what appear to be accidental impurities are eliminated. The composition of **searlesite**—as the mineral was called—is thus analogous with that of analcite—*vide infra*—$NaB(SiO_3)_2.H_2O$, or **sodium borodimetasilicate.** The crystals are probably monoclinic. The optic axial angle $2E$ is very large, and the indices of refraction $\alpha=1{\cdot}520$, and $\gamma=1{\cdot}528$. The mineral is fairly soluble in water, and is decomposed by hydrochloric acid. After treatment with dil. acid, the index of refraction fell to 1·47, and the optic axial angle also decreased.




FIGS. 106 and 107.—Freezing-point Curves of the Binary Systems: $Li_2SiO_3$–$LiBO_2$, and $Na_2SiO_3$–$NaBO_2$.

H. Erni [4] detected boric acid in a mineral from Danbury, Connecticut. C. U. Shepard found no boric acid, and named it **danburite.** J. L. Smith and G. J. Brush found about 27 per cent. of boric oxide. Analyses were made by G. J. Brush and E. S. Dana, J. E. Whitfield, E. Wittich and J. Kratzert, A. Schrauf, and E. Ludwig. It has also been found at Russell, N.Y., and C. Hintze, G. vom Rath, and G. Seligmann observed the mineral at Piz Valatscha, Switzerland; A. Lacroix in Maharitra, Madagascar; and N. Fukuchi in Obira, Japan. According to G. A. König, some slender prismatic crystals of danburite, associated with chlorite and tourmaline, were called *bementite*, after C. S. Bement. A. Lacroix estimated the composition of the idealized mineral to be 22·8 per cent. CaO; 28·4 per cent. $B_2O_3$; and 48·8 per cent. $SiO_2$, in agreement with the formula $CaB_2Si_2O_8$. W. Kupferbürger obtained a similar result. The constitution has been discussed by C. F. Rammelsberg. P. Groth compares the danburite with barsovite, $CaAl_2Si_2O_8$; and W. C. Brögger with hellandite, barsovite, abdalusite, and topaz. According to G. Cesaro, danburite is a neutral tricalcium metaboratosilicate with part of the silica replaced by the dyad radicle $B_2O''$. F. W. Clarke regards it as **calcium diborylmetasilicate,** and barsovite as an orthosilicate:

$$Ca<\begin{matrix}SiO_3{-}B{=}O\\SiO_3{-}B{=}O\end{matrix}$$

Danburite, $Ca(SiO_3)_2(BO)_2$

$$Ca<\begin{matrix}SiO{\equiv}Al\\SiO{\equiv}Al\end{matrix}$$

Barsowite, $Ca(SiO_4)_2Al_2$

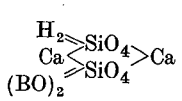
The mineral occurs massive and crystalline; and its colour is pale yellow or white. The crystals have been studied by H. Buttgenbach, G. J. Brush and E. S. Dana, C. Hintze, A. Lacroix, V. M. Goldschmidt and J. Philipp, H. L. Ungemach, etc. The crystals belong to the rhombic system, and, according to M. Schuster, they have the axial ratios $a:b:c=0{\cdot}54446:1:0{\cdot}48006$. The cleavage

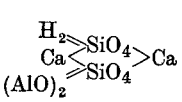
is distinct. G. J. Brush and E. S. Dana found the optic axial angle $2V$ to be 87° 37′ withLi-light; 88° 23, with Na-light; and 90° 56, with light filtered through a soln. of a copper salt. A. Lacroix gave $2V=86°\ 54'$. M. Kawamura gave $2V=89°\ 50'$. G. J. Brush and E. S. Dana gave for Li-light $2H=100°\ 33'$ and 100° 35′; for Na-light, 101° 30′ and 105° 36′; and for light transmitted by a copper salt, 107° 36′ and 102° 13′. A. des Cloizeaux, and E. Wittich and J. Kratzert made similar measurements. The sp. gr. found by G. J. Brush and E. S. Dana was 2·95–2·97; by C. Bodewig, 2·986; by E. Ludwig, 2·985; by W. T. Schaller, 2·98; by W. Kupferbürger, 2·95; and by A. Lacroix, 3·10. The hardness is about 7. The mineral readily fuses to a colourless glass. The indices of refraction, given by C. Hintze, are for the Li-, Na-, and Tl-rays respectively, $\alpha=1·6258$, 1·6317, and 1·6356; $\beta=1·6293$, 1·6340, and 1·6375; and $\gamma=1·6331$, 1·6363, and 1·6393. M. Kawamura obtained $\alpha=1·6303$, $\beta=1·6333$, and $\gamma=1·6363$; W. Kupferbürger, for Na-light, $\alpha=1·630$, and $\gamma=1·636$; and E. S. Larsen, $\alpha=1·632$, $\beta=1·634$, and $\gamma=1·636$. The optical character is negative. The mineral exhibits thermoluminescence, glowing with a reddish light. The mineral is attacked slightly by hydrochloric acid; but if it is previously ignited, gelatinous silica is formed by the action of this acid.

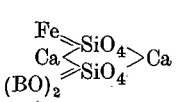
J. Esmark[5] obtained a boriferous mineral from Arendal, Norway, and he called it **datolite**—from δατέομαι, to divide—in allusion to the granular structure of the massive variety. The mineral was analyzed by M. H. Klaproth, and L. N. Vauquelin. A. G. Werner, and A. Brongniart called it *datholite*, but C. C. von Leonhard emphasized that this spelling is wrong. R. J. Haüy called it *chaux boratée siliceuse*: and J. F. L. Hausmann, *esmarkite*.

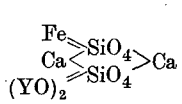
J. F. L. Hausmann, and R. J. Haüy stated that the crystals of datolite belong to the rhombic system, and A. Lévy found crystals of a mineral which belonged to the monoclinic system, and he named it *humboldite*. F. Mohs and others showed that humboldite and datolite are of the same mineral species. J. F. L. Hausmann called a fibrous form of datolite, *botriolite* or *botryolite*—from βότρυς, a grape. M. H. Klaproth, C. F. Rammelsberg, and A. Lacroix showed that botryolite is of the same mineral species as datolite. The *haytorite* from Hay Tor, Devonshire, described by C. Tripe, C. le Neve Foster, A. Volkmann, W. Haidinger, F. Hessenberg, C. S. Weiss, E. Geinitz, E. F. Glocker, J. R. Blum, J. F. L. Hausmann, P. A. Dufrénoy, H. J. Brooke and W. H. Miller, J. Phillips, A. Lévy, and D. Brewster appears to be datolite altered to chalcedony. O. Ludecke has published a monograph on datolite.

Various occurrences and analyses of datolite have been reported.[6] V. Goldschmidt gave for the loss on ignition of a specimen from Bologna, 1·0 per cent.; Arendal, 3·0 per cent.; and Bergenhill, 5·0 per cent. C. F. Rammelsberg said that the boron behaves as an electropositive element. The composition of the idealized mineral corresponds with $H_2Ca_2B_2Si_2O_{10}$; and P. Groth wrote the formula $Ca(B.OH)SiO_4$, calcium hydroxyboro-orthosilicate; and V. Goldschmidt represented it by $Ca_2(H_2B)Si_2O_{10}$. A. Himmelbauer found the silicic acid liberated by hydrochloric acid corresponded with G. Tschermak's $H_2Si_2O_5$, or *datolitic acid*. He assumed that the calcium is joined in part to the boron and in part to the silicon, $(H.B.Ca)_2(Si_2O_5)_2$. G. Cesaro supposed that datolite is calcium acid metasilicate with some silicon replaced by $B_2O''$. E. Baschieri made some observations on this subject. F. W. Clarke represents datolite as **calcium dihydrodiboryldiorthosilicate,** and shows its relation to humite, euclase, and gadolinite by the formulæ:


Datolite.


Euclase.


Homilite.


Gadolinite.

A. de Gramont[7] synthesized datolite in the form of long acicular crystals by heating in a closed steel tube a mixture of 5 grms. of precipitated calcium metasilicate and 25 grms. of borax for 36 hrs. at 400°. Less satisfactory results were

obtained with mixtures of soda water-glass and calcium borate at 300°, or of calcium oxide, boric oxide, and a soln. of alkali at 400° for 18 hrs.

Datolite occurs massive, botryoidal, and in crystals. The **colour** is white or it may be tinted grey, green, yellow, red, or blue; or the mineral may be a dirty olive-green, or yellow. The crystals have been studied by O. Luedecke, W. Schulze, E. V. Shannon, J. Lehmann, R. Riechelmann, V. M. Goldschmidt, L. Brugnatelli, H. P. Whitlock, M. F. Heddle, B. K. Emerson, C. U. Shepard, A. des Cloizeaux, A. C. Hawkins, O. C. Farrington, T. Nocca, R. Görgey and V. M. Goldschmidt, H. L. Ungemach, S. G. Gordon, F. H. Schröder, C. W. Cooke and E. H. Kraus, E. S. Dana, R. Köchlin, etc. The crystals belong to the monoclinic system, and, according to C. F. Rammelsberg, and H. Dauber, they have the axial ratios $a:b:c = 0{\cdot}63287:1:0{\cdot}63446$, and $\beta = 89° 51' 20''$. The cleavage is distinct. H. Baumhauer studied the **corrosion figures.** The **optic axial angles** have been determined by C. Bodewig, F. Sansoni, O. Luedecke, etc. L. Brugnatelli gave:

| | Li-line. | *C*-line. | *D*-line. | Tl-line. | *E*-line. | *F*-line. |
|---|---|---|---|---|---|---|
| $2H$ . . . . | 74° 44′ | 74° 34′ | 74° 6′ | 73° 27′ | 73° 25′ | 72° 31′ |
| $2V$ . . . . | 74° 39′ | — | 74° 21′ | — | — | — |

A. des Cloizeaux found a rise of temp. from 17°–171·5° had no perceptible effect on the optic axial angles. C. Bodewig found $2H = 89° 31' 7''$ at 20°; $89° 28' 13''$ at 126°; $89° 27' 36''$ at 130°; and $89° 26' 28''$ at 222°. F. Ulrich gave $2V = 74° 11'$ to 74° 16′. When cooled to 21°, $2H = 89° 29' 41''$, indicating a slight change. The **specific gravity** was found by G. A. Kenngott to be 2·968; J. Fromme gave 2·950–2·952; T. Nocca, 2·995 at 18°; F. Ulrich, 2·993; L. Brugnatelli, 2·907; G. C. Hoffmann, 2·985; and A. Himmelbauer, 3·003. G. A. Kenngott found the **hardness** to be between 5 and 6. The mineral fuses to a clear glass before the blowpipe flame. According to C. F. Rammelsberg, the water is expelled from datolite only at a high temp. The **indices of refraction** were determined by A. des Cloizeaux, L. Brugnatelli, O. Luedecke, T. Nocca, etc. W. F. P. MacLintock found $\alpha = 1{\cdot}626$, $\beta = 1{\cdot}653$, and $\gamma = 1{\cdot}670$. A. des Cloizeaux gave for the red and yellow light, $\alpha = 1{\cdot}6248$ and 1·6260 respectively; $\beta = 1{\cdot}6510$ and 1·6535; and $\gamma = 1{\cdot}6670$ and 1·6700. L. Brugnatelli gave for Li- and Na-light, $\alpha = 1{\cdot}6217$ and 1·6246 respectively; $\beta = 1{\cdot}6492$ and 1·6527; and $\gamma = 1{\cdot}6659$ and 1·6694. F. Ulrich gave $\alpha = 1{\cdot}654$, $\beta = 1{\cdot}654$, and $\gamma = 1{\cdot}670$. U. Panichi investigated the action of low temp. on the refractive index of datolite. W. W. Coblentz found that in the ultra-red transmission spectrum of datolite the hydroxyl band appears at $2{\cdot}8\mu$. There are other bands at $2\mu$, $3\mu$, $5{\cdot}3\mu$, and $6{\cdot}3\mu$. The reflection spectrum has small sharp maxima at $8{\cdot}8\mu$, $9{\cdot}2\mu$, $9{\cdot}5\mu$, $10\mu$, and $10{\cdot}8\mu$. W. G. Hankel studied the **pyroelectric** behaviour of datolite. According to G. A. Kenngott, when the powdered mineral, calcined or uncalcined, is moistened with **water,** it reacts alkaline. With **hydrochloric acid,** gelatinous silica separates. A. Himmelbauer found that the mineral is decomposed by cold **acetic acid,** and by **ammonium chloride** at 100°. F. W. Clarke and G. Steiger also investigated the action of ammonium chloride. The geological changes have been discussed by J. Roth.

S. R. Paijkull [8] described a black or brown mineral found on the Stockö, Brevig, Norway; and he named it **homilite**—from ὁμιλέω, to occur together—in allusion to its accompanying melinophane and erdmannite. Analyses were made by S. R. Paijkull, and A. des Cloizeaux and A. Damour. They correspond very well with the formula $Ca_2FeB_2Si_2O_{11}$; and are thus related with those of datolite. G. Cesaro supposes homilite to be like datolite but containing some iron. The graphic formula given by F. W. Clarke—*vide supra*—is closely akin to that of datolite. This makes the mineral **calcium ferrodiboryldiorthosilicate.** A. E. Nordenskjöld emphasized the close similarity between the crystals of datolite and of homilite. The crystals are monoclinic, and, according to A. des Cloizeaux, the axial ratios are $a:b:c = 0{\cdot}6249:1:1{\cdot}2824$, and $\beta = 89° 21'$. The cleavage is indistinct. A. des Cloizeaux found the optic axial angle $2H = 97° 5'$ to $98° 22'$ with

red light. The sp. gr. given by S. R. Paijkull is 3·28; and that given by A. des Cloizeaux and A. Damour is 3·34. The hardness is 4·5–5·5. A. des Cloizeaux and A. Damour said that some of the crystals are throughout doubly refracting; others have a green doubly refracting kernel surrounded by a yellowish crust of a singly refracting substance; and still others are entirely singly refracting. The composition of the singly refracting material is like that of erdmannite. E. S. Larsen made observations on the optical characters of homilite.

The complex mineral **erdmannite** has been treated among the rare earth minerals. It was first described by N. J. Berlin. It is dark brown without a sign of crystallization. Analyses were reported by A. des Cloizeaux and A. Damour, C. A. Michaelson, and N. Engström. W. C. Brögger gave it the formula $3RO''.R'''_2O_3.2SiO_2$, where RO represents mainly calcium, ferrous, and beryllium oxides; $R'''_2O_3$ represents ferric and boric oxides; and the rare earth sesquioxides. He called it *cer-homilite*.

Rounded nodules of a calcium borosilicate mineral were found by H. How [9] at Brookville, Nova Scotia. The mineral was called **howlite** by J. D. Dana. Analyses were made by H. How, S. L. Penfield and E. S. Sperry, A. S. Eakle, and W. B. Giles. The composition corresponds with $H_6Ca_2B_5SiO_{14}$. C. F. Rammelsberg gave for the formula $Ca_4B_{10}Si_2O_{23}.5H_2O$, and he regarded the mineral as a complex of calcium borate, calcium silicate, and boric acid. P. Groth assigned to it the formula $H_3Ca(BO_2)_5.H_2CaSiO_4$, and thus regarded it as a complex of metaborate and orthosilicate. G. Cesaro regards howlite as an orthosilicate with some silicon replaced by $B_2O''$. W. and D. Asch represented it by $4CaO.2SiO_2.5B_2O_3.5H_2O$. C. F. Rammelsberg found the water was expelled at 350°, and hence regarded it as water of crystallization. The acicular or prismatic crystals belong to the rhombic system. Howlite may also occur in white earthy masses. The sp. gr. is 2·55, and the hardness 3–4. H. How also described a white crystalline calcium borosilicate from Winkworth, Nova Scotia. He called it *winkworthite*. It is regarded as a mixture of gypsum and howlite. W. G. Giles obtained from San Bernadino, California, an amorphous mass of what he called *bakerite*—after R. C. Baker. The analyses corresponded with $8CaO.6SiO_2.6B_2O_3.6H_2O$. The sp. gr. was 2·73; and the hardness $4\frac{1}{2}$. It is readily soluble in dil. hydrochloric acid. A. S. Eakle claims that *camsellite*—*vide* **5.** 32, 12—is a *magnesium borosilicate*, $2(MgO,FeO).B_2O_3.SiO_2.H_2O$.

A. Lacroix [10] found a white basic lithium borosilicate near the Manandona river, Madagascar; and he named it *manandonite*. The analysis corresponds with $Li_4Al_{14}B_4Si_6O_{41}$. It occurs in lamellar aggregates or mammillary crusts of hexagonal plates.

M. Faraday [11] melted a mixture of 112 parts of lead oxide, 16 of silica, and 24 of boric oxide, and obtained a *lead borosilicate*; K. Beck and co-workers found that 5 per cent. of boric acid made lead silicate glasses more fusible—the monosilicate melted at 460°, the disilicate at 540°, and the trisilicate at 600°. The boric oxide increases the attack by one per cent. nitric acid, or 4 per cent. acetic acid. P. Bartel obtained an analogous result. *Axinite* may be a borosilicate—*vide* the iron silicates.

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## § 34. Aluminium Silicates

N. G. Sefström [1] obtained a sintered mass by heating a mixture of 3 mols of silica and 2 mols of alumina in the strongest heat of a blast furnace. P. Berthier, W. A. Lampadius, and A. Gaudin made observations on fused mixtures of silica and alumina; but no definite combinations were produced, although several were reported. Thus, N. G. Sefström reported $2Al_2O_3.3SiO_2$; P. Berthier, $Al_2O_3 : SiO_2$;

4 : 3, 2 : 3, 1 : 3, and 2 : 9; and C. F. Plattner, $2Al_2O_3.9SiO_2$. W. Vernadsky obtained $Al_4Si_3O_9$ and $Al_2O_3.SiO_2$ by strongly heating aluminosilicates—*vide infra*, andalusite and sillimanite; H. St. C. Deville and H. Caron, $4Al_2O_3.3SiO_2$ by heating alumina in silicon tetrafluoride; S. Meunier, $5Al_2O_3.6SiO_2$, by heating aluminium in silicon tetrachloride; H. St. C. Deville, by heating alumina in the same gas; E. Frémy and C. Feil, $2Al_2O_3.3SiO_2$, by heating silica in the vap. of aluminium fluoride; and F. Singer, $Al_2O_3.2SiO_2$, by calcining ammonium zeolite. With the exception of sillimanite, $Al_2O_3.SiO_2$, the chemical individuality of none of these products has been established. There is evidence of the existence of another compound, $3Al_2O_3.2SiO_2$, on the f.p. curve. H. A. Seger [2] made some observations on the fusibility of mixtures of alumina and silica. He found evidence of a eutectic with about 17 mols of silica per mol of alumina. H. A. Seger's results were replotted by B. Neumann; and verified by L. Bradshaw and W. Emery. For colloidal aluminium silicates, *vide supra*, water-glass.

S. Kozu [3] and co-workers reported a mineral from Kochi-mura, Rikuchu, Japan, which they called **kochite.** It formed a granular aggregate of cubic crystals, with the composition $2Al_2O_3.3SiO_2.5H_2O$, or $Al_4(SiO_4)_3.5H_2O$, or normal **aluminium orthosilicate.** Its sp. gr. at 15° was 2·929; and its index of refraction for the *D*-line, 1·590. The water is rapidly evolved when the mineral is heated in air at 725°–800°; and in water-vap. at atm. press. it is given off at 775°–790°. G. A. Rankin and co-workers, and N. L. Bowen and J. W. Greig, have studied the general behaviour of the binary system, $Al_2O_3$–$SiO_2$, illustrated by Fig. 108. Only one compound appears in the system at these temp., and its composition is represented by $3Al_2O_3.2SiO_2$. There is no evidence of the formation of sillimanite, $Al_2O_3.SiO_2$, under these conditions. The observations by G. Shearer, and J. W. Mellor and A. Scott show that the X-radiograms of kaolinite, and of a mol of kaolinite mixed with a mol of alumina fired at 1700°, are quite different from the X-radiogram of a mixture of a mol of kaolinite with two mols of alumina. The inference is that there are two distinct compounds, sillimanite, $Al_2O_3.SiO_2$, and what N. L. Bowen and J. W. Greig propose to call **mullite,** $3Al_2O_3.2SiO_2$, in allusion to the fact that the "best described examples" of sillimanite are those of H. H. Thomas from the Island of Mull. It is probable that the two compounds can form solid soln. R. Ballo and E. Dittler also found only the one aluminium silicate to be stable in contact with molten lithium silicate. R. C. Wallace observed the formation of sillimanite when silica and alumina are melted together—*vide infra*. P. J. Holmquist discussed this subject.

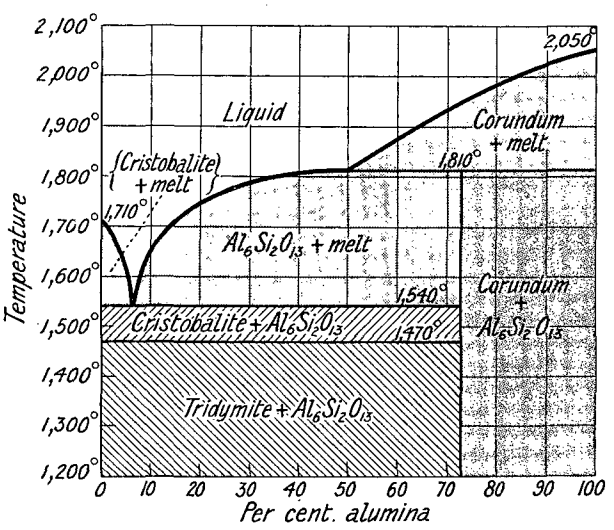



FIG. 108.—Freezing-point Curves of the Binary System: $Al_2O_3$–$SiO_2$.

Three distinct crystalline minerals can be represented by the empirical formula $Al_2O_3.SiO_2$, and this aluminium silicate is therefore trimorphous. The three forms are called sillimanite, andalusite, and cyanite or disthene. As shown by W. Vernadsky, and E. H. M. Beekmann, sillimanite is the only form stable at a

high temp., and presumably has the simpler constitution. Cyanite has the highest sp. gr., and sillimanite the lowest. The metasilicates are usually more stable than the orthosilicates. P. Groth therefore argued that andalusite is probably an orthosilicate: $Al{\equiv}SiO_4.Al:O$; or $SiO_4{\equiv}Al_2:O$—provided the molecules are not polymerized. Cyanite and sillimanite can thus be regarded as metasilicates—*i.e.* **aluminium dioxymetasilicate:**

$$SiO_3(AlO)_2, \text{ or } Al:O_2:Al:(SiO_3), \text{ or } (O:Al:O.Al)SiO_3$$

If the mols. have a higher mol. wt. than is represented by the formula $Al_2O_3.SiO_2$, the possibilities of isomeric forms are multiplied. F. W. Clarke and J. S. Diller gave for sillimanite:

$$\begin{matrix} Al{\equiv}SiO_4 \\ Al{\equiv}SiO_4 \end{matrix}\!\!>\!Al-SiO_4{\equiv}(AlO)_3$$

K. Zulkowsky found that disthene gives off $1\frac{1}{2}$ mols of carbon dioxide when a mol is fused with 3 mols of alkali carbonate. He thinks that this is not in accord with P. Groth's disthene formula, $(AlO)_2SiO_3$. He represents the three forms by

$$O<\begin{matrix} SiO.O.Al:O_2:Al \\ SiO.O.Al:O_2:Al \end{matrix}>O$$

Andalusite or Cyanite.

$$O<\begin{matrix} SiO.O.Al:O_2:Al \\ Al.O_2:Al.O.SiO \end{matrix}>O$$

Sillimanite.

K. Zulkowsky has separate formulæ for andalusite and cyanite, but when expressed in this way, they both give the same result. Since topaz and andalusite readily form muscovite mica, F. W. Clarke suggests that the empirical formulæ of the two former minerals should be tripled so as to keep the formulæ of all three minerals of the same type:

| $Al_3(SiO_4)_3(AlO)_3$ | $Al_3(SiO_4)_3(AlF_2)_3$ | $Al_3(SiO_4)_3KH_2$ |
|---|---|---|
| Andalusite. | Topaz. | Muscovite. |

This subject was discussed by L. Grünhut without relevant evidence. Sillimanite, $Al_2O_3.SiO_2$, can be represented as **silicon oxydialuminate,** $O{=}Si{=}Al(O_2)_2$, which is related to mullite, $3Al_2O_3.2SiO_2$, as indicated by the formula $(AlO_2)_3Si-O-Si(AlO_2)_3$ for **silicon oxyhexaluminate.** In the absence of more definite facts, there is no profit in pursuing the subject further. R. B. Sosman suggested a possible parallelism between cyanite and quartz, cristobalite and sillimanite, and between tridymite and andalusite.

Sillimanite occurs in separate crystals—usually long and slender—or in aggregates of fibres arranged in a diverse or radiating manner. There are several varieties differing simply in texture, and more or less contaminated with quartz, corundum, etc. The mineral may be colourless, white, or tinged brown, grey, or green. A dense compact form is one of the many different minerals which have been called *jade;* and, according to A. Damour,[4] F. W. Clarke, and F. Quiroga, it was sometimes used by prehistoric man in Western Europe for making implements and utensils.

In 1792, B. von Lindacker described a fibrous mineral from Bohemia which he called *Faserkiesel*, and which, according to A. G. Werner, and C. C. von Leonhard, might be a mixture of tremolite and quartz. J. L. Bournon called a variety which he found in some Asiatic corundum, *fibrolite*. J. A. H. Lucas proposed the name *bournonite*. Fibrolite was analyzed by R. Chenevix, and B. Silliman. According to C. N. von Fuchs, fibrolite is a mixture of disthene and quartz. L. J. Spencer reported a blue fibrolite from Burma and Ceylon; it had the indices of refraction with Na-light: $\alpha=1{\cdot}6584$, $\beta=1{\cdot}6596$, and $\gamma=1{\cdot}6789$; and birefringence $\gamma-\alpha=0{\cdot}0205$. The optic axial angles were $2E=52°\ 2'$, and $2V=28°\ 2'$. R. Brandes called a variety which he found in Tyrol, *bucholzite*—after C. F. Bucholz. These three terms were regarded by E. F. Glocker, C. Hartmann, and J. F. L. Hausmann as synonyms for the same mineral species. A mineral from Saybrook, Connecticut, was described by G. T. Bowen; it was called **sillimanite,** after B. Silliman, who showed that it is chemically and crystallographically like fibrolite. A. Erdmann called a mineral from Bamle, Norway, *bamlite*. L. Saemann, and P. A. von Sachsen-Coberg showed that it is a

mixture of sillimanite and quartz. N. Nordenskjöld named a mineral from Peterhof, Finland, *xenolite*—from *ξένος*, stranger. A. Lacroix showed that it resembles fibrolite. *Xenolite* accompanied the mineral *wörthite*—named after M. von Wörth, by H. Hess. Wörthite is a partially hydrated and altered sillimanite. The *monrolite* from Monroe, N.Y., described by B. Silliman is a mixture of sillimanite and quartz. The *Glanzspath*, or *glance spar*, of H. von Dechen, and G. vom Rath, was shown by W. Vernadsky to be impure sillimanite. C. Hintze takes the same view. The mineral *westanite* from Westana, Sweden, was described by C. W. Blomstrand. It is regarded as a hydrated fibrolite; P. Groth suggested that it is an altered andalusite. T. Thomson mentioned *hydro-bucholzite*, probably from Sardinia. A. des Cloizeaux said that mineral is a doubtful species and has little in common with bucholzite.

Analyses of the different varieties have been reported; and various occurrences recorded. The mineral is mined at Assam, India. A compound resembling sillimanite was made by H. St. C. Deville and H. Caron [5] by the action of silica on aluminium fluoride, or of alumina on silicon fluoride at a high temp. Similar results were obtained by E. Frémy and C. Feil, and by A. Reich. Andalusite and cyanite were shown by W. Vernadsky to be each transformed into sillimanite between 1320° and 1380°, with the disengagement of heat. He obtained sillimanite by fusing together silica and alumina. R. C. Wallace, and G. Stein obtained sillimanite crystals in a similar manner. When fused sillimanite is rapidly cooled, said E. S. Shepherd and G. A. Rankin, it always crystallizes as sillimanite. Soln. of sillimanite in fused calcium vanadate, borax, albite, etc., always give crystals of sillimanite. W. Vernadsky said that better crystals are produced if 2 to 4 per cent. of magnesia is present in the magma. J. Morozewicz studied the conditions under which sillimanite can form magmatically; in a fused magma of the composition $RO.mAl_2O_3.nSiO_2$, if magnesia and iron oxide are absent, and $m=1$, sillimanite is always developed if $n$ be greater than 6. Artificial sillimanite was discussed by C. E. Sims and co-workers, O. Rebuffat, A. Malinovszky, etc.

The formation of crystals of sillimanite in porcelain was observed by C. G. Ehrenberg, A. Bünzli, A. Zöllner, E. Plenske, G. N. White, M. Glasenapp, E. Rosenthal, A. Oschatz and A. Wächter, H. Behrens, E. Hussak, W. Vernadsky, J. W. Mellor, P. Sustschinsky, P. A. Schemjatschensky, A. S. Watts, A. A. Klein, A. Scott, H. Ries and Y. Oinouye, L. Bertrand, etc.; and in firebricks by J. W. Mellor, A. H. Cox, H. M. Kraner, and others. It also appears when china clay has been heated to a high temp. short of fusion. The temp. of formation must be lowered in the presence of felspar, because A. Heath and J. W. Mellor observed them in pottery bodies fired below 1200°. W. Eitel observed their formation in alumino-thermic processes. From the observations of N. L. Bowen and J. W. Greig, it is probable that mullite has not always been distinguished from sillimanite in these reports of sillimanite; and F. H. Riddle, and T. S. Curtis said that the crystals they obtained had the composition of mullite, not sillimanite. In some cases, the artificial crystals have been analyzed, and the results are in agreement with the mullite ratio, but it is not always clear that the isolation of the crystals by hydrofluoric acid does not leave an aluminous residue behind, since there are no indications that this has been removed by washing—preferably with a soln. of ammonium acetate. The use of sillimanite as a refractory material was discussed by A. Malinovszky, A. F. Greaves-Walker, and S. English; and of andalusite for sparking plugs, by A. B. Peck. Sillimanite makes a very good refractory brick when mixed with 10–20 per cent. of a good type of plastic clay as a bond.

According to E. Taubert, the **crystals** of sillimanite belong to the rhombic system, and they have the axial ratios $a:b:c=0{\cdot}9696:1:0{\cdot}7046$; A. des Cloizeaux gave $0{\cdot}6873:1:—$. G. A. Rankin and F. E. Wright said that sillimanite crystallizes from the melt in fine-grained, fibrous, or lath-shaped individuals, which, like the natural mineral, are often in close parallel columns. It is difficult to cool molten sillimanite quickly enough to prevent crystallization, but the glass can be obtained by dropping the fused mass from the tip of a perforated conical crucible directly from the electric furnace into cold water. The glass

readily crystallizes into sillimanite when heated to 1200°, or when heated to 350°–400° in bombs containing a 10 per cent. soln. of sodium chloride. The **cleavage** with the natural crystals is well defined; and in the artificial crystals the cleavage is distinct in the direction of elongation of the fibres. The **optic axial angle** of the artificial crystals is not large. A. des Cloizeaux found the optic axial angle at 18° is $2E=49°\ 9'$ for the red ray; 42° 30′ for the yellow ray; and 38° 41′ for the blue ray. For white light, $2E=35°$–40°. The effect of temp. is as follows:

| | 12° | 15° | 47° | 95·5° | 121° | 146·5° | 175° |
|---|---|---|---|---|---|---|---|
| $2E$ | 44° 4′ | 44° 4′ | 44° 28′ | 45° 0′ | 45° 18′ | 45° 54′ | 46° 8′ |

A. Lacroix found $2V=26°$ for yellow light; G. Melczer, 31° 11·5′; and A. Michel-Lévy and P. Termier about 20°; W. Eitel, 43°; and E. S. Larsen, 20°. The **X-radiograms** were examined by G. Shearer, and F. Renne. The **specific gravity** of the mineral is 3·235–3·248. E. H. M. Beekmann gave 3·152 for the sp. gr. before calcination, and 3·157 after calcination. E. S. Shepherd and G. A. Rankin gave 3·031 for the sp. gr. of the artificial crystals, and 2·54 for the glass. I. I. Saslavsky studied the mol. vol. of sillimanite. The **hardness** is between 6 and 7. G. Spezia tried the action of the oxygenated blowpipe flame on sillimanite. The **melting point** of artificial sillimanite is 1811°, according to E. S. Shepherd and G. A. Rankin; and 1816°±10°, according to G. A. Rankin and F. E. Wright. As indicated in Fig. 108, N. L. Bowen and J. W. Greig found that mullite melts incongruently at 1810°, forming corundum and liquid. Natural sillimanite though unstable at higher temp. does not suffer any change when heated for several days at 1545°, but above this temp. it breaks up into crystals of mullite and liquid. The passage of cyanite and of andalusite into sillimanite appear to be monotropic changes, for E. S. Shepherd and G. A. Rankin were quite unable to produce either cyanite or andalusite from sillimanite. They add that it seems reasonably certain that andalusite and cyanite are formed by crystallization from soln. at low temp. G. A. Rankin and F. E. Wright state that terminal sections of the fibres of artificial sillimanite are square in outline, and that the centre of nearly every section has a minute inclusion in the shape of a cross with arms parallel to the sides. Minute inclusions of a lower refracting isotropic substance are almost always present in artificial sillimanite. It is postulated that at its m.p. sillimanite is dissociated into alumina and this glass. The temp. of dissociation is so high—above 1800°—that the hypothesis has not been tested. O. S. Buckner gave 0·00432 for the coeff. of **thermal conductivity** in C.G.S. units.

A. des Cloizeaux gave for the **index of refraction** of the mineral for the red ray, $\beta=1·660$; A. Lacroix gave for the yellow ray $\alpha=1·659$, $\beta=1·661$, and $\gamma=1·680$; E. S. Larsen, $\alpha=1·659$, $\beta=1·660$, and $\gamma=1·680$; and G. Melczer, $\alpha=1·6562$, $\beta=1·65765$, and $\gamma=1·6766$. G. A. Rankin and F. E. Wright found for the artificial crystals with Na-light, $\alpha=1·638$, $\beta=1·642$, and $\gamma=1·653$, each $\pm0·003$; and W. Eitel, $\alpha=1·648$, $\beta=1·652$, and $\gamma=1664$. These values are lower than those of the mineral. E. S. Shepherd and G. A. Rankin gave for the index of refraction of sillimanite-glass, 1·625. N. L. Bowen and J. W. Greig gave the following comparison of the properties of mullite and sillimanite:

| | Mullite. | Sillimanite. |
|---|---|---|
| Crystal system | rhombic | rhombic |
| Prism angle (110)–($1\bar{1}0$) | 89° 13′ | 88° 15′ |
| Cleavage | (010) | (010) |
| Refractive indices | $\alpha=1·654$, $\gamma=1·642$ | $\alpha=1·677$, $\gamma=1·657$ |
| Axial angle, $2V$ | 45°–50° | 25° |

The **birefringence** of the artificial sillimanite crystals is about $\gamma-\alpha=0·014$. The **optical character** is positive. Observations on the optical constants were also made by F. Grünling, and by E. Taubert. A. des Cloizeaux found the mineral to be **pleochroic,** being colourless when viewed in one direction, and pale rose-red in another; H. Rosenbusch found a sample from Saybrook to be dark brown in

the direction *c*, and pale brown in the directions *b* and *a*. A. Lacroix also made some observations on this subject. F. Haber said that porcelain containing a large proportion of sillimanite does not conduct electricity below 900° ; but beyond that the **electrical conductivity** increases with the temp. A. V. Henry found the electrical resistivity, *R* ohms per c.c., of sillimanite refractories with a 45 volt, 1000-cycle alternating current to be

| | 400° | 600° | 800° | 1000° | 1200° | 1400° | 1500° |
|---|---|---|---|---|---|---|---|
| *R* . . | $358\times10^5$ | $148\times10^4$ | $179\times10^3$ | $363\times10^2$ | $115\times10^2$ | 4290 | 3150 |

Sillimanite, as prepared by G. A. Rankin and co-workers, is not affected by hot or cold **water ;** and is but slowly attacked by **acids** or **alkalies.** It is practically unaffected by hot or cold hydrochloric, sulphuric, or nitric acid, or by cold hydrofluoric acid. It is slowly decomposed by mixed hydrochloric and hydrofluoric acids, and by fused **sodium carbonate.** P. Sustschinsky studied the action of sodium carbonate on sillimanite. H. Hanemann found that molten **cast iron** reduces silicon from the aluminosilicates.

The mineral **andalusite** was first obtained from Andalusia, Spain, and this name was first applied by J. C. Delamétherie.[6] Previously, J. L. Bournon referred to it as *spath adamantin d'un rouge violet*, and L. B. G. de Morveau as *felspath du Forez.*

R. J. Haüy called andalusite *feldspath apyre ;* J. Brunner, *micaphilite*—from φίλος, loved—not *micaphyllite.* M. Flurl called a variety from Stanzen, Bavaria, *stanzaite.* The so-called *chiastolite*—from χιαστός, arranged diagonally, from *chi*, the old Greek name for the letter χ—has been under observation from early times. J. J. Bernhardi, F. S. Beudant, R. Bunsen, and G. Landgrebe showed that it is a variety of andalusite which was so named by D. L. G. Karsten because it exhibits in cross-section a coloured cross, or mosaic pattern. It was referred to by C. Gesner in 1565. M. Mercati called it *lapis crucifer* ; C. P. G. de Robien, *pierre de macle ;* J. Hill, *cross-stone*, or *Spanish shirl ;* U. Aldrovandi, and J. B. L. Romé de l'Isle, *pierre de croix ;* J. C. Delamétherie, *crucite ;* R. J. Haüy, *macle ;* and A. G. Werner, *Hohlspath.* The term *macle*, said C. P. G. de Robien, is from the Latin *macula*, a spot, and refers to the *mascle* or *macula* in heraldry, where it means a design with a lozenge-shape or a rhomb with an open centre. It has been suggested that the macula in the armorial bearings of the family of the Vicomte de Rohan was taken from the chiastolite of their neighbourhood. H. F. Link's *maranite* is andalusite, which occurs on the Serra de Maras. J. J. Sederholm called a variety of chiastolite from Ladoga Lake, Finland, *maltesite ;* H. Bäckström, a variety of andalusite with about 7 per cent. of manganese oxide, *manganandalusite.* G. Klemm's green variety *viridine* from Darmstadt is andalusite containing iron and manganese.

Many analyses of andalusite have been made, and various occurrences reported.[7] Andalusite is commonly found in the zones of contact of clay slate near dykes of granite or divrite. It is also found in many metamorphic schists. A. Knopf reported a large body of rock, almost entirely andalusite, at Inyo Range, California. The earliest analyses by C. F. Bucholz, L. B. G. de Morveau, etc., appear to have been made on specimens contaminated with quartz because their formulæ—*e.g.* $Al_8Si_9O_{30}$ and $Al_6Si_7O_{23}$—deviate from the $Al_2SiO_5$ of later analysts with clean homogeneous samples. The constitution has been discussed in connection with sillimanite. One plausible hypothesis makes it *aluminium monoxyorthosilicate*, or **aluminium aluminoxyorthosilicate,** $Al_3(AlO)_3(SiO_4)_3$, or $Al(AlO)SiO_4$. The alleged syntheses of andalusite by H. St. C. Deville,[8] E. Frémy and C. Feil, and S. Meunier have not been established—*vide* sillimanite. E. Baur prepared a product with optical properties similar to andalusite excepting a different refractive index. He heated to 300°–500° in an autoclave a mixture of silicic acid, alumina, and potassium silicate ; or a mixture of silica, aluminium hydroxide, and potassium aluminate. Other silicates were formed at the same time—possibly pyrophyllite and muscovite.

The **colour** of natural andalusite may be white, grey, red, violet, brown, or green. It occurs massive and crystalline. The **crystals** have been studied by W. Haidinger,[9] A. Schrauf, V. M. Goldschmidt, P. E. Haefele, J. Krejci, E. S. Dana,

etc. According to A. des Cloizeaux, the axial ratios of the rhombic crystals are $a:b:c=0{\cdot}98613:1:0{\cdot}70238$. The (110) **cleavage** is perfect, while the (100) and (010) are less well defined. The **optic axial angle**, $2V$, was found by A. des Cloizeaux to be 84° 30′; P. von Jeremejeff gave $2V=87°$ and $2H$ from 96° 30′ to 113°. E. Bertrand gave $2H=96°\ 32'$. A des Cloizeaux found that the optic axial angle is reduced about $2\frac{1}{2}°$ by a rise of temp. from 21°–191°. E. E. Schmid gave 3·07–3·11 for the **specific gravity**; C. M. Kersten, 3·152–3·154; J. Roth, 3·401; A. von Hubert, 3·103; G. Grattarola, 2·86; M. F. Heddle, 3·121; P. von Jeremejeff, 2·944–3·14; G. F. Kunz, 3·2–3·4; W. Haidinger, 3·170; and A. Damour, 3·160. E. H. M. Beekmann gave 3·158 for the sp.gr. of the mineral before calcination, and 3·150 after calcination. The **hardness** is generally rather less than 7. G. Lindner found the **specific heat** to be 0·1684 at 50°; 0·1731 at 100°; 0·1774 at 150°; 0·1819 at 200°; and 0·1861 at 250°. R. Cusack gave 1209° for the **melting point.** This value is far too low. A. L. Fletcher gave 1259°; and C. Doelter gave 1330°–1395°. The m.p. of the pure compound must be like that of sillimanite if, as W. Vernadsky said that andalusite changes into sillimanite at 1300° with the evolution of heat. E. S. Shepherd and G. A. Rankin found the change takes place so slowly at that temp. as to mask completely the character of the corresponding heat change. They found that no sillimanite is produced by heating the mineral for 28 days at 900°, or 168 hrs. at 1150°; but there is much alteration after 4 days at 1500°. Sillimanite was observed after heating andalusite with sodium chloride at 800° for 168 hrs. or with calcium vanadate for 48 hrs. at 100° or 216 hrs. at 900°. At higher temp., the andalusite is decomposed by reacting with the *agent minéralisateur*. The change of andalusite to sillimanite is monotropic, for the reverse change did not occur under any of the numerous conditions tried. This agrees with W. Vernadsky's observation that andalusite does not occur in igneous rocks. A. B. Peck, and N. L. Bowen and J. W. Greig represent the change, not into sillimanite, but into mullite, $Al_6Si_2O_{13}$, at about 1350°. A. des Cloizeaux found the **indices of refraction** for the red ray to be $\alpha=1{\cdot}632$, $\beta=1{\cdot}638$, and $\gamma=1{\cdot}643$; and E. Taubert obtained respectively for the *C*-, *D*-, and *F*-lines, $\alpha=1{\cdot}6300$, 1·6361, and 1·6410; $\beta=1{\cdot}6326$, 1·6390, and 1·6440; and $\gamma=1{\cdot}6386$, 1·6453, and 1·6511. The **birefringence** $\gamma-\alpha$ is 0·011; $\gamma-\beta=0{\cdot}005$; and $\beta-\alpha=0{\cdot}006$. The optical character is negative. M. Lewitskaja found that although each of the principal refractive indices of andalusite has a maximum absorption of light near $485\mu\mu$, yet only $\beta$ has an absorption maximum in this region. According to A. Bertin, E. Mallard, and W. Haidinger, sections of andalusite normal to an optic axis are idiophanous, or show polarization brushes distinctly. The crystals are strongly **pleochroic.** W. Haidinger found crystals showing, *a*, olive-green; *b*, green; and *c*, dark blood-red. A. des Cloizeaux, E. Bertrand, P. von Jeremejeff, and W. Haidinger made observations on this subject. The red and green dichroism of andalusite from Minas Geras, Brazil, is remarkable; and sections cut from the mineral may be so facetted that the light obliquely reflected from the sides may be differently coloured from light more directly reflected from the centre. According to O. Mügge, **radium radiations** do not affect andalusite; but, according to C. Doelter, **X-rays** affect this mineral more than they do quartz. Stout crystals of chiastolite or macle often have the axis and angles a different colour from the remaining mass. This is due to a regular arrangement of the impurities in the interior. The crystals may therefore show a coloured cross, or a tesselated structure when viewed transversely. J. J. Bernhardi found the central column sometimes widens from the middle towards each end. C. T. Jackson made similar observations. Observations on this subject have been made by the early mineralogists—*vide supra*—and by J. F. L. Hausmann, H. Rosenbusch, W. Cross, F. Zirkel, J. Durocher, A. des Cloizeaux, H. Fischer, G. A. Kenngott, A. von Lasaulx, F. E. Müller, C. E. M. Rohrbach, A. Gramann, E. Weinschenk, R. Rüdemann, etc. The peculiar structure is supposed to indicate a skeletal growth of the crystals in which the carbonaceous residue has followed the lines of growth during the conversion of slate into crystals of andalusite.

Andalusite is insoluble in acids ; but it is decomposed by fused alkali hydroxides or carbonates. It is slowly attacked by fused borax. P. Jannasch [10] said that unlike most silicates andalusite is only partially decomposed by fused boric oxide. G. A. Binder studied the behaviour of andalusite towards water at 160°. F. Cornu found the moistened mineral reacted alkaline towards litmus. W. Suida found the mineral feebly adsorbed aniline dyes. C. Doelter heated andalusite with potassium carbonate and fluoride for several weeks at 250°, and observed the formation of scales of mica. He also compared the effect of a number of chemical agents on andalusite and cyanite. With fused potassium hydroxide no measurable difference was observed; a similar result was obtained when dry hydrogen chloride was passed over the heated minerals, which were afterwards leached with water to find what proportion was made soluble. When heated in a stream of chlorine, cyanite lost but a slight amount more than andalusite. Ten per cent. hydrofluoric acid dissolved 84 per cent. from cyanite, and 44·4 per cent. from andalusite. The amount of alumina dissolved in both cases was nearly the same, namely, 40·2 per cent. from cyanite, and 43·1 per cent. from andalusite. When digested at 180° in an autoclave with a soln. of sodium hydroxide, andalusite lost an unweighably small amount, while cyanite lost 1·23 per cent. The conclusion is that, although in particular cases there might be a difference, in general, the two minerals behave very much alike towards these reagents. J. Lemberg heated andalusite or cyanite with alkali silicates or carbonates under press.; and found that zeolitic substances were formed. K. Zulkowsky studied the action of fused sodium carbonate on andalusite.

The change of andalusite into muscovite was observed by A. Gramann ; and into chlorite and kaolinite by P. E. Haefele. The reaction for muscovite is symbolized by C. R. van Hise: $6Al_2Si_3O_5+K_2CO_3+11H_2O=6Al(OH)_3+2H_2KAl_3Si_9O_{12}+CO_2$; and for kaolinite, $2Al_2SiO_5+5H_2O=2Al(OH)_3+H_4Al_2Si_2O_9$. Analyses of transformation products have been reported by C. G. C. Bischof, P. von Jeremejeff, J. Roth, J. R. Blum, G. Grattarola, E. Hussak, J. Romberg, etc. M. Weibull showed that the so-called *westanite* or *vestanite* is an altered andalusite. F. Slavik found pseudomorphs of chiastolite after mica near Pribram.

A blue mineral from Botiphinie, Scotland, was called by B. G. Sage [11] *talc bleu*, and later *beril feuilleté*. When the mineral is blue and transparent, and in large enough pieces, it can be used as a gem, and it then resembles sapphire. N. T. de Saussure, by a misreading of a label " sapphire," called it *sappare*. A. G. Werner designated it **cyanite** or rather *kyanite*—from κυάνος, blue. R. J. Haüy called it *disthene*—from δίς, twice ; and σθένος, strong—in allusion to the unequal hardness and electrical properties in two different directions. C. A. S. Hofmann called a white variety of cyanite *rhaetizite*—from Rhætia, the ancient name of Pfitschthal where the mineral occurs.

Cyanite occurs principally in gneiss, mica slate, and crystalline schists. It does not occur as a pyrogenetic mineral in igneous rocks. Various occurrences and analyses [12] have been reported. The results agree with the formula $Al_2O_3.SiO_2$. The constitution has been discussed in connection with sillimanite. A. Daubrée thought that he had synthesized cyanite by the action of silicon tetrachloride on alumina at a red heat, but H. St. C. Deville showed that he was mistaken—*vide* sillimanite and andalusite. The colour is white, blue, grey, green, or black ; the crystals may be blue along the centre of the blades, and the margins may be white. It may occur in transparent crystals which are usually long-bladed crystals ; the crystals may also be coarsely bladed columnar, or subfibrous. The first measurements were made by R. J. Haüy. The angles were also measured by W. Phillips. Observations on the crystals have been also made by T. Liebisch, A. des Cloizeaux, J. Plücker and A. Beer, G. Cesaro, G. Rose, A. Böhm, etc. The **crystals** belong to the triclinic system, and M. Bauer's values for the axial ratios $a:b:c$ are 0·89912 : 1 : 0·69677 ; $\alpha=90°\ 23'$, $\beta=100°\ 18'$, and $\gamma=106°\ 1'$ ; G. vom Rath gave 0·89942 : 1 : 0·70898, and $\alpha=90°\ 5\frac{1}{2}'$, $\beta=101°\ 2\frac{1}{4}'$, and $\gamma=105°\ 44\frac{1}{2}'$. F. Rinne has

studied the **X-radiogram** of cyanite. The (100) **cleavage** is perfect, the (010) is less so, and the (0$\bar{1}$1) imperfect. M. Bauer, and O. Mügge studied the **gliding planes** of the crystals. H. Traube, and T. L. Walker studied the **corrosion figures**; and E. S. Federoff, the orientation of the crystals. The **twinning** of the crystals is common; and the crystals may be so combined as to make right- or left-handed twins analogous to those of orthoclase; the twins may also occur in staurolite-like forms crossed at an angle of 60°. F. von Kobell studied the axial figures in twin crystals; he said that the right- and left-handed twins may be easily distinguished by means of the polariscope. In polarized light, they give a cross in an oblique position, but the principal optical section does not revolve with the revolution of the crystal. The colours with right- and left-handed twins change in different order with the revolution. The **optic axial angles** were found by A. des Cloizeaux to be $2H=101°\ 6'$ and $2V=82°\ 16'$ for red light. O. Korn gave for different samples $2H=99°\ 18'$–$101°\ 2'\ 30''$ for Li-light, and $98°\ 55'$–$100°\ 45'$ for Na-light. A. des Cloizeaux found that there is no perceptible change in the optic axial angle between 12° and 17·8°. A. Michel-Lévy and A. Lacroix made some observations on this subject.

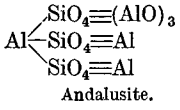
The **specific gravity** was found by F. Oswald[13] to be 3·057; by G. C. Hoffmann, 3·6005; and by E. H. M. Beekman, 3·56–3·59 before calcination, and 3·236–3·240 after calcination. The **hardness** on the (100)-face parallel to the *c*-axis, 4–5; on the (100)-face and parallel to the (100) (001)-edge, 6–7; and on the (010)-face, 7. R. Cusack gave 1090° for the **melting point** of cyanite; A. L. Fletcher, 1140°; and A. Brun, 1190°–1210°; C. Doelter observed no fusion at 1340°, and gave 1370°–1430° for the m.p. A. Brun stated that at 1310° there is a mol. change. W. Vernadsky found the mineral changed to sillimanite above 1300°, with the evolution of heat. E. S. Shepherd and G. A. Rankin found the change to be very slow, but more rapid than in the case of andalusite. Cyanite was decomposed after heating half an hour at 1500°, but no sillimanite could be detected. Similar remarks apply after 48 hrs.' heating in calcium vanadate at 1000°. There was very little change in cyanite after being 7 days at 1150°, 2 days at 1000°, or 28 days at 900°. Similar remarks apply after heating cyanite 72 hrs. in the presence of sodium chloride at 800°. Under no condition tried could sillimanite be converted to cyanite. A. B. Peck, and N. L. Bowen and J. W. Greig say that cyanite changes to mullite, not sillimanite, at about 1350°. R. Lorenz and W. Herz studied the relation between the m.p. and the critical temp. A. des Cloizeaux obtained for the **index of refraction** with the red ray, $\beta=1·720$. E. Taubert gave for the *C*-, *D*-, and *F*-lines, $\alpha=1·7101, 1·7131$, and 1·7201 respectively; $\beta=1·7189$, 1·7201, and 1·7219; and $\gamma=1·7256$, 1·7282, and 1·7372. E. Wülfing gave for the Na-light, $\alpha=1·7171$–$1·7124$; $\beta=1·7222$; and $\gamma=1·728$–$1·729$. For the **birefringence** $\gamma-\alpha=0·0119$; $\gamma-\beta=0·0068$; and $\beta-\alpha=0·0051$. Observations were also made by A. Michel-Lévy and A. Lacroix, and by O. Korn. The former gave $\alpha=1·712$; $\beta=1·720$; and $\gamma=1·723$; and $\gamma-\alpha=0·011$. E. Mallard and H. le Chatelier found at $\theta°$ between 0° and 300°, for the change in the double refraction $(225·7+4·68\lambda^{-2})(1+0·0000475\theta)\times10^{-5}$; and between 300° and 600°, $(221+5·56\lambda^{-2})(1+0·0000744\theta)\times10^{-5}$. The optical character is negative. Cyanite is feebly pleochroic; this is noticeable in strongly coloured crystals between colourless and blue. C. Doelter found that cyanite is almost transparent to **X-rays**; nor did he obtain any colour change by exposing the mineral to **cathode rays** or to **radium rays.** O. Mügge obtained no result with radium rays. J. Plücker investigated the **magnetic properties** of cyanite.

Cyanite is not decomposed by acids; hydrofluoric acid attacks it very slowly. The action of chlorine, hydrogen chloride, hydrofluoric acid, alkali hydroxides, boric oxide, etc., are indicated in connection with andalusite. K. Zulkowsky studied the action of fused sodium carbonate on cyanite; J. Lemberg noted that a soln. of sodium silicate at 200°–210° forms a substance like analcite. F. Cornu said that the moistened powdered mineral gives a feeble alkaline reaction with litmus.

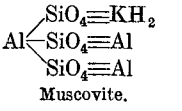
Cyanite does not decompose so readily as andalusite, and the transformation products, in nature, are potash mica, talc, steatite, and pyrophyllite.

Z. Weyberg [14] in his experiments on the action of fused barium chloride on china clay obtained besides the hexagonal crystals of $4BaO.4Al_2O_3.7SiO_2$, isotropic irregular grains with the composition $2Al_2O_3.15SiO_2$, or $Al_4Si_{15}O_{36}$.

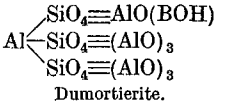
The fibrous mineral **dumortierite** was discovered by F. Gonnard [15] in 1881, and named after E. Dumortier. It was found embedded in the felspar in the gneiss blocks near Beaunan, France; and other localities have been reported by G. vom Rath, H. Traube, A. Michel-Lévy and A. Lacroix, R. B. Riggs, J. S. Diller and J. E. Whitfield, J. Romberg, E. Wittich, H. A. Weber, W. E. Ford, and A. Damour. In most of these cases analyses were also given, and the results of the earlier analyses agree with the formula $Al_8Si_3O_{18}$. W. E. Ford gave $Al_{20}Si_7O_{44}$, and he assumed that it is a basic orthosilicate, $(AlO)_{16}Al_4(SiO_4)_7$, corresponding with heptaorthosilicic acid, $H_{28}Si_7O_{28}$. The later analyses show that up to about 6 per cent. of boric oxide may be present. W. T. Schaller then represented the composition of the boriferous mineral by $HAl(AlO)_7(BO)(SiO_4)_3$, *i.e.* **aluminium heptaluminyl-borohydroxytriorthosilicate,** and that of the boron-free mineral—if such really exists—by $HAl(AlO)_8(SiO_4)_3$, *i.e.* **aluminium octoaluminyl-hydroxytriorthosilicate**. W. F. Clarke represents andalusite, muscovite, and dumortierite by the related formulæ:



Andalusite.



Muscovite.



Dumortierite.

In place of the bivalent BOH-group, W. T. Schaller introduced the two univalent radicles, BO and H'. The mineral usually occurs in fibrous or columnar aggregates; rarely in distinct crystals. The colour is ultramarine-blue or greenish-blue —rarely colourless, white, or green. According to J. S. Diller and J. E. Whitfield, the axial ratios of the rhombic crystals $a:b:c=0{\cdot}5317:1:-$; the prismatic angle approximates 56°. The (100) cleavage is distinct. A. Damour gave 3·36 for the sp. gr.; G. Linck, 3·22; and J. S. Diller and J. E. Whitfield, 3·265. The hardness is 7. The index of refraction is moderately high; A. Michel-Lévy and A. Lacroix gave $\beta=1{\cdot}65$; and G. Linck, $\alpha=1{\cdot}678$, $\beta=1{\cdot}686$, and $\gamma=1{\cdot}689$. The former gave for the birefringence $\gamma-\alpha=0{\cdot}010$, and the latter, 0·011. The optical character is negative. The pleochrosim is strong; $a$ is deep ultramarine-blue; $\beta$, reddish-violet; and $\gamma$, colourless. It shows idiophanous figures analogous to those of andalusite. Observations on the optical properties were made by E. S. Larsen, E. Wittich and J. Kratzert, and E. Rimann.

The so-called *serendibite* is a dark bluish-green mineral occurring in triclinic crystals in the moonstone pits near Kandy, Ceylon. According to A. K. Coomaraswamy,[16] its composition corresponds with $10(Fe,Ca,Mg)O.5Al_2O_3.6SiO_2.B_2O_3$; its sp. gr. is 3·42; and hardness 7. The pleochroism ranges from pale yellowish-green to deep indigo-blue.

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## § 35. Hydrated Aluminium Silicates—Clays

The hills are shadows, and they flow
From form to form and nothing stands ;
They melt like mists, the solid lands
Like clouds they shape themselves and go.—T. HUTCHINSON (1889).

Rocks show striking differences in behaviour when exposed to the weather for long periods of time. Some remain hard and firm, others crumble and powder in a comparatively short time. Many ancient Egyptian and Grecian monuments show relatively slight symptoms of decay, whereas in many other countries buildings made from apparently similar rocks soon deteriorate, and are saved from disintegration only by continued renovation. Calcareous building stones decay comparatively quickly when exposed to the moist, acidic vapours which prevail in the atmospheres of towns.[1]

Felspar and felspathic rocks are rather susceptible to weathering agents. The mineral is rarely found pellucid and clear ; it appears to be first attacked along the cleavage cracks. The felspar becomes turbid or opaque, due to the formation of innumerable particles of what appears, in some cases, to be white clay. When the change is advanced the felspar becomes friable. A granitic rock with its constituents originally bonded by the felspathic matrix, may thus disintegrate and leave behind the clay mixed with the more resistant varieties of mica, quartz, and other minerals which originally formed the granitic rock. It is, however, probable that the product of the weathering of these rocks is not always kaolinite or clayite.

In the extraction of china clay, the products[2] formed by the weathering of the less ferruginous granitic rocks are leached from the sides of the mine by streams of water. The velocity of the stream of water carrying the clay, mica, quartz, etc., in suspension is allowed to slow down gradually whereby all the coarser particles of sand and mica settle. The fine-grained clay, together with a very small amount of fine-grained mica and quartz, is allowed to settle in suitable pits ; part of the water is syphoned off ; part is removed by evaporation ; and the clay is finally dried in suitable kilns. The water may also be removed by filter press. ; by electrical deposition on the anode of a suitable electrical cell ; by centrifuge ; etc. The product is known as **china clay** and is sometimes called **kaolin**—generally outside the industry. The disintegrated granite from which china clay is washed is called **china clay rock ;** a crystalline form of china clay is called **kaolinite,** and non-crystalline particles are called **clayite**—the chief impurities are very fine-grained particles of mica, and quartz. Analysis of the purer varieties approximate to $Al_2O_3.2SiO_2.2H_2O$. Many of the impurities in the commoner clays can be removed by washing. Some of the "iron" in some clays cannot be removed in this way, and Y. Ichikawa claimed to have removed it by the action of chlorine on the clay at 100°–110°. Chlorine attacks metallic iron or ferric oxide plus charcoal at this temp., but not iron oxide without the carbon. The process though costly is sometimes effective, sometimes not. The same remark applies to other modes of purification—*vide infra.* A more or less decomposed form of granite is called *Cornish stone,* which contains more or less undecomposed felspar, and it is graded for the market according to the stage of weathering—*purple stone* is hardest,

least weathered, and the most fusible; *dry white and buff stones* are most weathered, softest, and least fusible; while *mild purple* represents an intermediate stage of weathering. The Cornish stone is ground to powder and used as a flux in the manufacture of pottery.

D. G. de Dolomieu [3] said the rock in which the change is in progress is affected by *la maladie du granat*. The action is extremely slow, but nature is in no hurry. While the decomposition of silicates by weathering furnishes colloidal silica—opal, the weathering of the aluminosilicates furnishes colloidal clay—clayite. There are many intermediate products of the decomposition. The transformation of felspar to china clay in nature was recognized by J. B. L. Romé de l'Isle as early as 1783, by A. G. Werner in 1791, and by R. J. Haüy in 1801. The last-named called the china clay *feldspath décomposé*. The plagioclase felspars highest in lime are attacked most readily, orthoclase is more resistant. Both E. Mitscherlich,[4] and C. G. C. Bischof have remarked that when soda- and potash-felspars are together present, the former is frequently found decomposed and friable when the latter is but slightly affected.

The mechanical disintegration [5] of rocks by the alternate freezing and thawing of water in fissures and cracks; and the crazing of the surface by the diurnal variations of temp.—as illustrated by the fact that some buildings show most signs of weathering on the sunny and not the shady side—facilitate the weathering of rocks by bringing fresh surfaces into contact with the agents which produce chemical changes; mainly water carrying various agents in soln.—carbon dioxide, oxygen, organic acids, hydrogen sulphide, and sulphuric acid. The products of the chemical decomposition of rocks are very varied; but with felspathic and related rocks, the hydrated aluminium silicates, known as clays, are produced. Among the clays, the so-called kaolin or china clay is perhaps the most important. Consequently, the conversion of felspar and related rocks into clay, by weathering, is sometimes called the *kaolinization* of these rocks.

Kaolin or china clay is not to be regarded as a primary mineral, as M. H. Klaproth [6] assumed, but is always a secondary product formed by the chemical decomposition of other rocks. J. Hawkins [7] even suggested that china clay rock is the original or parent rock; granite the derivative. He maintained that the lapidifying influence has acted from below upwards. The arguments are quite inadequate. J. Fournet's [8] ideas are difficult to understand; he suggested that those minerals which at the time of their formation have a tendency to crystallize in two different forms, are least stable, and rocks containing such minerals readily decompose. The felspar was supposed to be partly kaolinized during the cooling of the granitic magma, and more complete decomposition was supposed to be induced by local electric currents set up by contact with rocks of different kinds. Following up a suggestion by A. F. Gehlen,[9] A. Brongniart and J. Malaguti, in 1841, attributed the kaolinization of felspathic rocks to a kind of electrolysis because they were able to decompose felspar by passing an electric current through water holding ground felspar in suspension. A. S. Cushman and J. Hubbard's process for the extraction of the alkali from potash-felspar is based on the same reaction.

There are three recognized hypotheses on the kaolinization of felspar all of which have given rise to much discussion. For example, H. Rösler [10] maintains that the china clay of Halle, and indeed all clays, are produced by the operation of thermal waters with their gaseous emanations; E. Wüst considers that the Halle clay has been produced by the action of humus acids; and V. Selle ascribes the kaolinization of the Halle clay to the chemical activity of water containing carbonic acid.

1. *Volcanic gases and vapours, or pneumatolytic actions*—from πνευματικός, air or gas; λύειν, to loosen. G. Forchhammer [11] showed the possibility of the formation of clay by the action of water-vapour at a high pressure upon felspar. This view was generally adopted by L. von Buch, F. H. Butler and J. H. Collins, who emphasized the effects of fluorides and borates in the vapours of fumaroles. The assumption that the clay in Cornwall has been in many cases formed by pneumatolytic action, from below upwards, is supported by the facts: (i) the

deep-seated disintegrated granite or china-clay rock—extending sometimes over 600 ft.—is often most affected in the lower parts of the bed, and tongues of clay pass upwards into granite much less affected; (ii) boriferous and fluoriferous minerals—tourmaline, topaz, and fluoro-apatite are common in the clay localities; and (iii) the quartz grains are etched [12] or altered into rounded grains owing to the attack by the acidic vapours. J. H. Collins found that vapours of hydrofluoric acid acting on felspar produced a white amorphous powder which has some analogies with clay; and he further noticed that potash-felspar was more susceptible to attack than soda-felspar, or soda-lime-felspar. Some investigators [13] have perhaps over-emphasized the action of fumarole discharges from below upwards, and assumed that all china clay has been so produced. A summary of the available evidence shows that the kaolinization of felspathic rocks may also proceed by surface weathering acting from above downwards. According to this interpretation, the rotting or weathering of the rock will gradually diminish downwards until finally fresh rock is reached. The surface weathering of some of the rocks in South Brazil and in the Transvaal is considered deeper than usual,[14] and here it extends downwards about 200 ft. Again, according to H. Ries,[15] the Brandywine Summit clay deposits were worked for a number of years, and abandoned when the surface clay gave out; the mine was afterwards worked for the felspar lower down. Presumably, the surface layers of felspar had been kaolinized. According to H. Ries, all the beds of china clay hitherto exploited in the United States have been formed by surface weathering from above downwards.

2. *The action of surface waters charged with carbon dioxide.*—Numerous observers [16] have demonstrated the decomposition of felspar, mica, and related minerals by the action of water, and particularly water charged with carbon dioxide. W. P. Headden, for instance, said that water holding carbon dioxide in soln. is nearly nine times as active as distilled water when in contact with felspar (*q.v.*). Water can work its way into the body of granite rocks through pores and cleavage cracks; for, according to C. R. van Hise,[17] granite rocks have a porosity of 0·2–0·5 per cent. According to C. G. C. Bischof, one of the springs in the vicinity of Lake Leach (Germany) discharged nearly 176,000 lbs. of water carrying 0·13 per cent. of sodium carbonate in 24 hrs.; assuming that the sodium in felspar is converted into soluble sodium carbonate, this would represent the decomposition of nearly 18,000 lbs. of soda-felspar per annum. A few centuries would thus suffice to decompose enormous masses of granitic rock. It does seem curious to find a dil. soln. of carbon dioxide has sufficient chemical strength to decompose a combination like felspar which is fairly resistant to the most powerful mineral acids; but H. Rose [18] pointed out, in 1842, the enormous quantities of carbonic acid which are brought into contact with the rock make up for its deficiency in chemical strength. According to L. von Struve and H. Müller,[19] carbon dioxide under compression is more active than it is at ordinary press. A. Stahl [20] considers that the clay deposits of Passau, Mederschlesien, and Odenwald have been formed from gneiss rocks by the action of the carbon dioxide. The china clay at Auvergne (France) is supposed to have been formed in this way; W. S. Bayley found the china clay in the Piedmont Plateau, North Carolina, gradually merges downwards into felspar. The effect of carbonated waters can be easily over-estimated, in contrast with the action of organic acids which are probably more powerful than carbonic acid. I. Ginsberg,[21] however, claims that the formation of china clay by the action of organic acids in natural waters has not been demonstrated. H. Stremme [22] considers that the efficiency of all the different weathering agents is really due to the chemical activity of aq. soln. of carbonic acid—cold or hot; and K. Endell has shown that the acidity of moor-waters is largely due to the carbonic acid they contain.

E. Mitscherlich [23] suggested that the pyrites occurring in carboniferous strata is oxidized by the percolating water holding oxygen in soln. Sulphuric acid is formed. This decomposes the underlying felspathic rocks into kaolin, and other

products. Since most china clay beds do not occur in the vicinity of carboniferous strata, the hypothesis is inadequate. According to R. Bunsen, aq. soln. of hydrogen sulphide, derived from neighbouring sulphide ores, can kaolinize felspathic rocks more vigorously than soln. of carbon dioxide. There is a little evidence to show that dil. soln. of sulphuric acid derived from the oxidation of neighbouring sulphide ores, can kaolinize felspathic rocks.

3. *The action of water draining from peat bogs, etc., containing organic acids in solution.*—According to E. Wüst,[24] and V. P. Smirnkoff, organic acids—humic and crenic acids—derived from vegetable matter have a far greater corrosive action on minerals than has carbonic acid. Water is the agent which brings the acid in contact with the rocks. The drainage from bogs and peat beds, water percolating through soils, river and other surface waters, carry in soln. ammoniacal salts and organic acids—humic, oxyhumic, crenic, apocrenic, and other acids. E. Wüst claims that humic acid is the important agent in the kaolinization of felspathic rocks; and A. Stahl [25] has shown that the majority of the deposits of china clay in Germany—Saxony, Thuringia, Silesia, etc.—occur near beds of lignite—*Braunkohle*—and in many cases underneath these beds. The drainage-water—*Moorwasser*—from the bogs, peat, and lignite has presumably been the active agent in the kaolinization of the underlying rocks. The china clays which have been formed in this way are usually more pure and more free from ferruginous impurities than clays formed in other ways, because, as F. Senft has pointed out, organic acids have a solvent action on these impurities.

According to K. D. Glinka, it is very probable that the products obtained by the weathering under different conditions are not the same.[26] There are also many hydrated aluminium silicates—such as pyrophyllite, $Al_2O_3.4SiO_2.H_2O$; halloysite, $Al_2O_3.2SiO_2.4H_2O$; etc.—whose mode of formation has not been made clear. In tropical and subtropical regions—India, Malabar, Surinam, Seychelle Islands, Hawaiian Islands, Madagascar, British Guiana, etc.—the chemical action seems to proceed further than in temperate zones. The silicates are more thoroughly decomposed, and lateritic earth, and gibbsite are produced. Laterite appears to be a variable mixture of ferric and aluminium hyroxides with free silica.[27] E. E. Schmid, and H. Herold consider kaolinite to be the end-product of the change, and the former designates the intermediate products as $\alpha$, $\beta$, $\gamma$, and $\delta$-kaolins: thus he said that **$\alpha$-kaolin** is $Al_2O_3.2SiO_2.2H_2O$; **$\beta$-kaolin,** $Al_2O_3.2SiO_2.1\frac{1}{2}H_2O$; **$\gamma$-kaolin,** $Al_2O_3.2SiO_2.H_2O$; and **$\delta$-kaolin,** $Al_2O_3.3SiO_2.2H_2O$. H. Rösler, however, considers that E. E. Schmid was working with mixtures, and not with chemical individuals. J. M. van Bemmelen determined the ratio $Al_2O_3 : SiO_2$ dissolved when clays are treated with acids, and from the results inferred that clays produced by ordinary weathering are probably hydrogels with the ratio 1 : 3–5; those formed by kaolinitic weathering, have the ratio 1 : 1–2; and in lateritic weathering free gibbsite is formed as indicated by R. Lenz. M. Bauer obtained similar results. As shown below, it is doubtful if the solubility test is of much value.

The transformation of felspar into kaolin or china clay is usually symbolized: $K_2O.Al_2O_3.6SiO_2+2H_2O+CO_2=Al_2O_3.2SiO_2.2H_2O+4SiO_2+K_2CO_3$; after representing the action by an equation eq. to $K_2O.Al_2O_3.6SiO_2+nH_2O=Al_2O_3.2SiO_2.2H_2O+K_2SiO_3+3SiO_2.nH_2O$, G. Forchhammer said: "It is highly probable that the second product of the decomposition, water-glass, will be found somewhere in nature," and he succeeded in establishing the existence of this salt in the water of the geysers in Iceland. The bases and soluble silicic acid derived from the decomposition of felspathic rocks are partially retained by the soil and partially washed into the sea. The formation of gibbsite or laterite has been symbolized in an analogous manner. The formation of *sericitic mica*, $K_2O.3Al_2O_3.6SiO_2.2H_2O$, a common intermediate product of the conversion of felspar into kaolin, is symbolized: $3(K_2O.Al_2O_3.6SiO_2)+2H_2O+2CO_2=K_2O.3Al_2O_3.6SiO_2.2H_2O+12SiO_2+2K_2CO_3$. W. W. Hutchings,[28] for instance, inferred that the sericitic mica in some fireclays was produced from the decomposition of the felspar. The experiments of

A. E. Tucker on the action of carbonated water on felspar resulted in the formation of white scaly crystals. Magnesium and iron salts may also take part in the degradation of felspar forming biotite, epidote, etc.

The clay may be leached by natural streams of water from the place where it was formed, transported from the hills, and deposited at lower levels where the velocity of the stream slackens down. All kinds of *débris* from the rocks and soils, etc., over which the clays are carried may be transported along with the clay. Hence, many clays are the washings and sweepings of the hills which Nature has accumulated as her rubbish-heaps in convenient places. Transported clays are usually, but not always, less pure than the residual clays. The term *clay* is applied industrially to a fine-grained mixture of various minerals which has these qualities: (i) It is plastic enough to be moulded when it is wet; (i) it retains its shape when dried in spite of a certain amount of contraction; and (iii) when the moulded mass is heated to a high enough temp. it sinters together, forming a hard coherent mass without losing its original contour. These properties have given clays an important place—probably third or fourth—in the world's industries. Clays are used in the manufacture of building bricks, tiles, firebricks, crucibles, gas retorts, sanitary goods, pottery, etc. China clay is also extensively employed for filling paper, cotton, etc. It is used in making white paints, alum, ultramarine, wall-plasters, etc.; and it appears as an ingredient in some pharmaceutical preparations. The agriculturalist's definition of clay is quite different from that employed in ceramics, because he arbitrarily selects from a mixture of grains of various sizes a particular fraction and calls it clay. Some of the definitions would apply equally well to pulverulent coal, cocoa, and clay.

The discovery of china clay in Europe is usually considered to date from the beginning of the eighteenth century when J. F. Böttger[29] made porcelain in imitation of that brought to Europe from China by Eastern traders. It is said that J. F. Böttger had acquired a good knowledge of the properties of clays in making crucibles for his alchemical experiments; and that he wanted only a white burning clay to produce the desired result. With the coloured clays then available, he made red stoneware or a vitreous body known as *Bottger's red porcelain*. He is said to have accidentally discovered the white clay which he desired at Aue near Schneeberg. This white clay is now known as porcelain clay, china clay, or *kaolin*. The term "kaolin" is said to be a corruption of the Chinese *kao*, high; and *ling*, hill, in allusion to the Kaoling Mt., North China, whence much of the clay used by the Chinese for the manufacture of porcelain was obtained. As a matter of fact, the white clays were known in Europe long before J. F. Böttger's time, and E. W. von Tschirnhausen, before J. F. Böttger, made experiments with the white clays, and came very near to the discovery of porcelain. H. Peters, indeed, claimed that E. W. von Tschirnhausen actually made porcelain before J. F. Böttger, but E. Zimmermann showed that H. Peters was probably mistaken, and that the first porcelain was made by J. F. Böttger in 1709, a year after the death of E. W. von Tschirnhausen.

In early days, a white clay from the islands of Lemnos and Samos was known in Europe as *Diana's earth*, and *terra sigillata*, and used as a medicine. The beneficent virtues of this *edible clay* were extolled by Homer, and Herodotus. The *Lemnian earth* was mentioned by Theophrastus, and Dioscorides; and Pliny confused the terra sigillata, which he called *sphragis*, with the *Lemnian red earth* used as a pigment. The edible clay occurred in the Lemnian hills, and the mine, so to speak, was in charge of the priests of Diana. They alone had the right of access to the mine. A supply of clay was extracted once a year as a solemn religious ceremony. The temple priests mixed the clay with the blood of goats, moulded it into pastils, and impressed the slabs with the sacred symbol of Diana. In the Middle Ages, the edible clay was obtained from other localities, and the tabloids were stamped with various symbols and legends. The earth was used as a panacea against all kinds of diseases. Copies of the different stamps which were employed in the

marketing of *terra sigillata* will be found in D. C. G. Ludwig's *Terræ musei regii Dresdensis* (Lipsiæ, 1749). Through some confusion, the red *Samian pottery* of the Romans has been called *terra sigillata*—*e.g.* F. Oswald and T. D. Davis, *An Introduction to the Study of Terra Sigillata* (New York, 1920); and many others. M. B. Valentini, J. J. Wagner, A. Bertold, J. T. Schenck, J. Montanus, J. G. Geilfusius, L. F. Jacobi, D. Richter, and G. A. Volkmann wrote memoirs on the *terra sigillata*. C. Gesner, J. R. Speilmann, A. Baumé, and several others wrote monographs about clays before the eighteenth century. Clay was also in use by the Chinese, about 536 A.D., as a therapeutic agent; and edible clays have been discussed by E. G. Love, C. Schmidt, C. W. C. Fuchs, C. Hebberlung, M. M. P. Muir, etc.

B. Palissy experimented with *terra sigillata* for pottery purposes before J. F. Böttger's work, but there is no evidence that he made porcelain. Had he been looking for porcelain, however, he would probably have found it because it is scarcely conceivable that some of his trial mixtures were not adapted for the work; but they were probably rejected as over-fired. In the official deed providing for the manufacture of porcelain at Meissen, reproduced by E. Zimmermann, it is specified that the ware is to be made *von sogenannter Terra Sigillata*. The discovery of a white clay at Allençon, France, in 1758, enabled J. E. Guettard, and B. Lauraguais to make porcelain; and the subsequent discovery of a deposit of this clay at St. Yriex, Limoges, by M. H. Vilaris, in 1766–68, led to the manufacture of porcelain at Sèvres and elsewhere. Likewise also the discovery of china clay in Cornwall, by W. Cookworthy, enabled him in 1768 to apply for a patent for the manufacture of porcelain, and this resulted in factories being started at Plymouth and Bristol. The manufacture of hard porcelain, for some reason or other, has never flourished in England.

The term *bole*—from βῶλος, a clod of earth—is applied to a number of clay-like earths used medicinally. The more common varieties occur in yellowish-brown masses, with a greasy feel, and crumble to powder when placed in water. The composition of boles from different localities is very variable; the silica, for example, may range from 20–65 per cent. C. F. Rammelsberg gave a number of analyses. The red earth of Lemnos was probably a bole. It is alluded to by Theophrastus, Dioscorides, and Pliny. D. L. G. Karsten called a variety *sphragid*, and E. F. Glocker, *sphragidite*. The *oropion* of E. F. Glocker is a dark brown or black bole, and the *Bergseife* of A. G. Werner from Olkutsch, Poland. The colour is due to the presence of some bituminous matters. Oropion was analyzed by C. F. Bucholz. A. Breithaupt's *ochran* is a yellow bole from Orawitza of sp. gr. 2·4–2·5. It was analyzed by C. M. Kersten. E. Löwenstein measured the vap. press. of a number of boles. The red clay referred to by Theophrastus as *σύνοψις*, by Pliny as *sinopsis*, by M. H. Klaproth as *sinopische Erde*, and by J. F. L. Hausmann as *sinopite*, is a bole. A honey-yellow clay from Amberg, Bavaria, etc., was called by E. F. Glocker *melinite*—from μέλι, honey; and a variety from Vierzon, France, was called *vierzonite*. It appears to be the *Gelberde* referred to by C. A. S. Hofmann. Melinite was analyzed by O. B. Kühn; and analyses of boles were reported by C. C. von Leonhard, H. W. F. Wackenroder, E. Zellner, etc. P. Dwojtschenko obtained a mineral resembling kaolinite from Aluschta, Krim, and it was called *aluschlite*.

The old German term *Steinmark*—from *Mark*, marrow—was applied by G. Agricola [30] to a firm compact clay occurring in fissures in rocks, was likened to marrow in bones. The same kind of clay was called *lithomarge*—from λίθος, stone; and *marga*, marl—and A. Breithaupt called it *lithocolla*—from λίθος, stone; and κόλλα, glue or cement. J. G. Wallerius called it *leucoargilla*, as well as *marga porcellana*; and A. Cronstedt, *terra porcellana*. The general properties of these varieties of clay resemble those of compact, more or less indurated, kaolinite. J. F. L. Hausmann called the hard compact china clay *Steinmark*, and the friable clay *porcelain earth*. The older mineralogists seem to have regarded this variety of clay as a magnesian earth or an earth allied to talc. A. G. Werner, for instance, said it was a *Talkerde* composed of scaly particles. C. A. S. Hofmann, and D. L. G. Karsten also called it *earthy talc*; and R. J. Haüy, *talc granuleux*. A *green lithomarge* from Oravicza, coloured with ferrous oxide, was called by A. Breithaupt [31] *oraviczite*. A little zinc oxide is sometimes present. The sp. gr. may rise to about 3·1. C. M. Kersten, H. Naschold, M. H. Klaproth, and A. Frenzel analyzed a white or reddish-white variety from Rochlitz, Saxony, called by J. C. Freiesleben *Falksteinmark*; it had a sp. gr. 2·488–2·505; A. Breithaupt called it *myelin*—from μυελός, marrow—and a *flesh-red* variety with a sp. gr. 2·543 was called *carnat*—from *carnis*, flesh. Analyses show that these

substances are varieties of clay associated with more or less iron oxides, in place of alumina. A lavender-blue, grey, or dark red earth was called by A. Breithaupt [32] *Eisensteinmark*. It appears to be the old *sächsische Wandererde* of D. Richter, and J. E. de Schütz ; it was called *teratolite*—from *τέρας*, wonder—by E. F. Glocker. It was analyzed by J. C. Freiesleben, who found that about 12 per cent. of alumina was replaced by ferric oxide. A. Knop, and A. Frenzel described the clay, and H. Fischer, the crystalline structure.

W. A. Ross [33] described a yellowish-white mineral obtained from Simla, India, which appeared like meerschaum, and had an earthy or conchoidal fracture. He called it *meerschaluminite ;* and A. Schrauf, *simlaite*. Its sp. gr. is 1·5–2·0. N. S. Maskelyne and W. Flight analyzed it and found the composition : $2Al_2O_3.3SiO_2.4H_2O+H_2SiO_3$. The white or grey clay from the diaspore rocks at Dillin, Hungary, was called *dillnite* by A. Hutzelmann.[34] It has an earthy or conchoidal fracture ; its sp. gr. is 2·574–2·835. Analyses by A. Hutzelmann, and J. L. Smith agree with $4Al_2O_3.3SiO_2.9H_2O$. W. Haidinger thought it to be a mixture of diaspore and clay. M. H. Klaproth's *Bildstein* is regarded as a mixture of dillnite and aluminium hydroxide. G. Ulrich [35] described silver-white, or greenish *talcosite* as a mineral resembling talc occurring in the selwynite of Heathcote, Victoria. Its sp. gr. is 2·46–2·50, and the hardness over 1. Its composition approximates $Al_2O_3.2SiO_2.\frac{1}{2}H_2O$. P. Termier [36] described vermiculitic aggregates of a related mineral which he obtained from St. Etienne, France, etc., and called *leverrierite—vide infra*. C. F. Rammelsberg [37] described a straw-yellow clay from Schlackenwald, Bohemia, which he called *carpolite*. The composition approximated $2Al_2O_3.3SiO_2.3H_2O$, with some alumina replaced by ferric and manganese oxides. The sp. gr. was 2·935. T. Thomson described a brownish-red earth from Antrim, Ireland, which he called *plinthite*. Its composition approximated $2Al_2O_3.3SiO_2.6H_2O$, with up to half the alumina replaced by ferric oxide. M. F. Heddle analyzed a sample from Skye. A soft rose-red earth from the same locality was called by T. Thomson *rhodalite*.

A very large number of analyses of china clay have been published,[38] and analyses are made every day. From the very way in which clays have been formed in nature it might be anticipated that they are particularly liable to be contaminated with impurities. Even supposing the clay in china-clay rock to be fairly pure, its subsequent transport by currents of water may be attended by the introduction of *débris* carried by other streams. Thus, there are arenaceous clays, calcareous clays, micaceous clays, ferruginous clays, felspathic clays, etc. The analyses in Table XVII will give an idea of the composition of some clays used in the manufac-

TABLE XVII.—THE COMPOSITION OF SOME CLAYS.

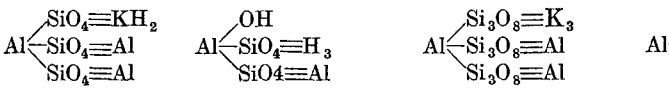
| — | Stourbridge siliceous clay. | Ruabon clay. | Leeds clay. | Devon clay. | Kingswinford clay. | Kilwinnig clay. |
|---|---|---|---|---|---|---|
| $SiO_2$ | 80·86 | 72·46 | 67·24 | 62·24 | 54·86 | 41·44 |
| $TiO_2$ | 1·00 | 1·31 | 1·00 | 1·00 | 1·42 | 1·56 |
| $Al_2O_3$ | 11·92 | 17·28 | 20·45 | 25·56 | 29·01 | 33·71 |
| $Fe_2O_3$ | 0·81 | 0·77 | 2·19 | 0·94 | 1·70 | 1·87 |
| MgO | 0·11 | 0·36 | 0·27 | 0·16 | 0·40 | 0·19 |
| CaO | 0·10 | 0·26 | 0·18 | 0·24 | 0·24 | 0·44 |
| $K_2O$ | 0·32 | 1·74 | 0·90 | 3·74 | 0·78 | 0·40 |
| $Na_2O$ | 0·40 | 0·48 | 0·30 | 0·58 | 0·48 | 0·26 |
| Loss on ignition | 4·40 | 5·30 | 7·40 | 5·80 | 10·87 | 20·60 |
| Refractoriness | 1660° | 1650° | 1660° | 1690° | 1710° | 1770° |

ture of firebricks. The refractoriness refers to the squatting temp. A. Brongniart and J. Malaguti gave $2Al_2O_3.3SiO_2.4H_2O$ for the best representative value of the composition of the ideal clay base ; L. F. Bley, $2Al_2O_3.3SiO_2.3H_2O$ ; J. N. von Fuchs, $4Al_2O_3.9SiO_2.12H_2O$ ; R. Fresenius, $Al_2O_3.3SiO_2.2H_2O$ ; and G. Forchhammer, $Al_2O_3.2SiO_2.2H_2O$. The last result is the generally accepted formula. It is in close agreement with the analysis of the purer types of china clay, and with analyses of crystalline kaolinite. Assuming that this hydrate occurs in all true clays, and is the cause of their plasticity, A. Brongniart and J. Malaguti called it *le véritable argile ;* and F. Senft called it *Thonsubstanz* or *clay substance*, a term much in use for the clayite or kaolinite in clays. The method of estimating the amount

of clay substance in clays by finding the amount soluble in hot conc. sulphuric acid was shown by J. W. Mellor to be fallacious. H. le Chatelier assumed that halloysite is the clay-base in some clays, montmorillonite in others; and J. W. Gregory, and D. P. McDonald assumed a halloysitic base in Glenboig clay.

Attempts have been made to find the constitution of china clay by observations on the effects of acids, alkalies, and heat. S. J. Thugutt [39] stated that one-third of the alumina is more rapidly dissolved by hot sulphuric acid than the other two-thirds. J. H. Collins said that half the alumina is dissolved relatively quickly by hot sulphuric acid, and the other half slowly. The retardation of the reaction is partly due to the formation of a protective layer of silica over the unattacked cores of the granules. There is nothing to show that the rate of decomposition and dissolution differ from those of other heterogeneous reactions. According to A. Brongniart and J. Malaguti, and C. F. Rammelsberg, aq. soln. of potassium hydroxide extract a quarter of the silica from kaolinite. The kaolinite was probably impure because P. Berthier showed that caustic alkalies scarcely attack the fired or unfired clay. The action is really determined by the conc. of the soln. and the temp. since J. Lemberg showed that by digesting china clay with aq. soln. of alkali silicates, hydroxides, or carbonates, natrolite, $K_2O.Al_2O_3.3SiO_2.3H_2O$, is formed. The action is represented, $3(Al_2O_3.2SiO_2.2H_2O)+6KOH \rightarrow 2(K_2O.Al_2O_3.3SiO_2.3H_2O)+3H_2O+K_2O.Al_2O_3$. This led R. Brauns to assume that the molcule of kaolinite should be symbolized $2(Al_2O_3.SiO_2.3H_2O)Al_2O_3.3SiO_2$. If the argument were valid, the action of chlorine on potassium hydroxide: $3Cl_2+6KOH \rightarrow 5KCl+KClO_3+3H_2O$, might be cited as evidence for a more complex formula for potassium hydroxide. However, the original experiment, if modified a little, gives quite a different result. There is no worthy evidence that the aluminium atoms of kaolinite have different characteristics; a similar remark applies to the silicon atoms. W. Vernadsky assumed that the water in kaolinite is held half by the alumina and half by the silica; only that held by the alumina is driven off at low redness leaving a partially dehydrated molecule which is readily decomposed by hydrochloric acid—*vide infra.* As a matter of fact, no reliable evidence justifying this conclusion is available. All the water can be driven from kaolinite below redness. The action is slow at low temp., more rapid at high temp. It will be shown later on that there is no evidence of two breaks in the dehydration curve, and both the molecules of contained water behave similarly.

Until suitable evidence is forthcoming, undue emphasis should not be placed on constitutional formulæ which assume dissymmetrical atoms like R. Brauns' formula, $H_2(AlOH)_2Si_2O_7$; or the metasilicate formula, $HO.Al(HSiO_3).SiO_3.Al(OH)_2$. P. Groth's formula is $\{Al(HO)_2\}_2Si_2O_5$, or $\{SiO.O.Al(OH)_2\}_2O$; R. Scharizer's $O\{Si(OH)_2.O.Al:O\}_2$ or $O(Al{=}SiO_4{=}H_2)_2$; K. von Haushofer's, W. Pukall's, and F. Hundeshagen's $O(HO.Si{=}O_2{=}Al.OH)_2$; and C. Simmonds's $(HO.O)_2Si:Si(O.O.AlOH)_2$. H. C. McNeil, K. D. Glinka, Y. V. Samoiloff, W. and D. Asch, and W. Vernadsky have also recommended formulæ for kaolinite. F. W. Clarke emphasized the relation between kaolinite and muscovite, and between kaolinite and felspar by means of the graphic formulæ:




Muscovite. Kaolinite. Felspar. Kaolinite.

With these and other possibilities, the choice is largely a matter of temperament; but if there be any weight in (i) the continuity in the rates of dissolution of kaolinite by acids and alkalies; and (ii) the continuity in the rate of decomposition at different temp., the aluminium and hydroxyl groups are symmetrically placed in the molecule, and P. Groth's formula is preferable. This may be written as a **dialumino-disilicic acid,** the so-called *kaolinic acid:*

$$\begin{matrix}(HO)_2{=}Al{-}O.SiO\\(HO)_2{=}Al{-}O.SiO\end{matrix}\!\!>O, \quad i.e. \quad \begin{matrix}(HO)_2\\(HO)_2\end{matrix}\!\!>Al_2<\begin{matrix}O.SiO\\O.SiO\end{matrix}\!\!>O$$

in harmony with F. Ullfers's idea that kaolinite is derived from an hypothetical *anhydrid der Tonerdemonokieselsäure*, Al(OH).O.SiO.O . . ., by analogy with chromomonoxalic acid. B. Kosmann regarded kaolinite as one member of a family of aluminium silicates which he represented $Al_2O_3.SiO_2$; $Al_2O_3.Si_2O_4$; and $Al_2O_3.Si_3O_6$, in which part of the silica may be hydrated. In the case of kaolinite he wrote $Al_2O.Si_2O_4(OH)_4$.

R. Schwarz and A. Brenner [40] studied the action of sodium silicate on soln. of aluminium chloride. The precipitates were filtered off, dried in a steam-oven, and washed successively with water, alcohol, and ether. The influence of conc. was such that the mol. ratio of silica to aluminium hydroxide diminished with increasing dilution, but was always slightly in excess of the proportion, 1·5 : 1, thus showing that silica was invariably adsorbed by the primary product, $2Al_2O_3.3SiO_2$. The proportion of silica in the precipitate increased with increasing conc. of sodium silicate, although the latter never entered quantitatively into the reaction; when 6–10 mol. proportions of silicic acid were present, a compound corresponding in composition with natural kaolinite, $Al_2O_3.2SiO_2.2H_2O$, was invariably produced. Normal *aluminium metasilicate*, $Al_2(SiO_3)_3$, appears incapable of existence. The primary product of the action is the compound, $2Al_2O_3.3SiO_2.nH_2O$, which absorbs silicic acid when left in contact with the soln. and tends to pass into the compound, $Al_2O_3.2SiO_2.2H_2O$. If the precipitate is heated in contact with the soln., the substance $Al_2O_3.2SiO_2.2H_2O$ (after desiccation at 110°) is obtained. X-radiograms of the products show that the primary compound, $2Al_2O_3.3SiO_2.6H_2O$, is amorphous, and that from it there is formed in course of time a crystalline material, $Al_2O_3.2SiO_2.2H_2O$, which is similar or closely related to natural kaolin in structure. The natural product loses its two molar proportions of water continuously above 360°, and becomes anhydrous at 640°. The artificial material loses one molar proportion below 260°, and the second proportion between 360° and 640°. It appears that in the neutral ternary system, $Al_2O_3$–$SiO_2$–$H_2O$, a single compound, $Al_2O_3.2SiO_2.nH_2O$, is capable of formation, and it is uninfluenced by the presence of an excess of silica, or by the period of the reaction; this compound is formed with particular readiness when at least six mols of silica are present for each mol of aluminium oxide.

The hydrated aluminium silicates resembling kaolinite behave very like acids in many reactions, for, as P. A. Schemjatschensky [41] showed, the hydrogen is partly or wholly replaceable by a metal. Again, when fused with alkali carbonates, kaolinite displaces carbonic anhydride, and probably forms aluminosilicates soluble in a large excess of water. Kaolinite gives off hydrogen sulphide when heated with many sulphides; it displaces sulphuric anhydride from sulphates; and A. Gorgeu showed that it reacts in a similar manner with chlorides, bromides, and iodides. Z. Weyberg found that by the prolonged fusion of a mixture of kaolinite, and potassium carbonate or chloride, the silicate $K_2O.Al_2O_3.2SiO_2$ is formed; and with potassium dichromate at a low temp., $K_2O.Al_2O_3.2SiO_2$ is produced, but at a high temp. $K_2O.Al_2O_3.SiO_2$ is formed. He also found that when fused with barium or strontium chloride a product $4RO.4Al_2O_3.7SiO_2$ is formed. The work of J. Lemberg, H. P. Armsby, E. C. Sullivan, etc., shows that the salts of alumino-silicic acids resemble the salts of the ordinary acids in that the bases can be interchanged in accord with the laws of mass action—*vide* zeolites.

If china clay, free from soluble salts, be boiled with distilled water and allowed to stand 24 hrs., extremely fine particles of solid remain in suspension, and pass through porous earthenware filters. It is not possible to separate this suspended matter by settling; but it can be sedimented by the addition of lime-water or sodium chloride. The addition of the salt causes the fine particles of clay to aggregate or flocculate into masses which settle rapidly. The finest particles are invisible

under a $\frac{1}{12}$th objective. The suspended matter from china clay can also be isolated by evaporation, when a pale brown mass is produced; that from ball-clay is dark brown. Like glue, the mass shrinks enormously when dried, and furnishes a horny mass which adheres tenaciously to the tongue. The glue-like mass was termed by T. Schloesing [42] *argile colloïdale*, or *colloidal clay*. When wetted, the colloidal clay swells enormously, furnishing a sticky plastic mass. Only about 0·50 per cent. was obtained from china clay. This amount probably represents a small fraction of the colloidal clay which is present. The colloidal non-crystalline particles of clay were termed *clayite* by J. W. Mellor. S. Kasai found no colloidal matter in the clay from Zettlitz. J. Splichal, and R. C. Wallace and J. C. Maynard determined the colloidal matter in a number of clays; A. Vasel found 3 per cent. in Meissen clay.

The china clay or kaolin formed by the decomposition of aluminium silicate rocks is usually a mixture of amorphous granules of clayite, and crystalline plates, termed by S. W. Johnson and J. M. Blake,[43] **kaolinite.** C. G. Ehrenberg, A. Knop, A. Safarik, W. Cross and W. F. Hillebrand, and R. C. Hills regarded the crystals as hexagonal or rhombic; and H. Reusch, as triclinic; but A. B. Dick, and H. A. Miers proved that they belong to the monoclinic system, and this was confirmed by E. Hussak. Kaolinite occurs in minute hexagonal plates, Fig. 109, with edges at 60° and 120°. H. A. Miers, and A. B. Dick gave for the axial ratios

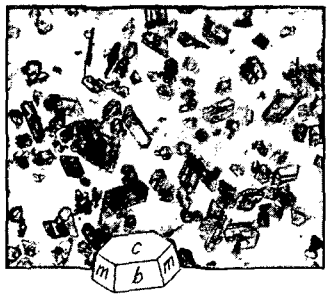



FIG. 109.—Crystals of Kaolinite from Amlwch (Anglesey) × 50.

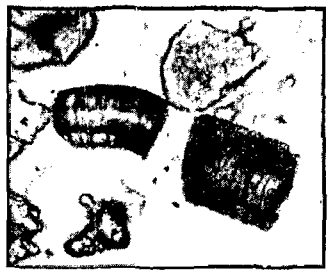


FIG. 110.—Vermiculites or Rouleaux in Clay.

$a : b : c = 0{\cdot}5748 : 1 : 1{\cdot}5997$; and $\beta = 83° 11'$. In Fig. 109, $b(010)$, $c(001)$, $m(110)$; and $b : m = 60° 16'$; $c : m = 84° 16'$. The thinnest plates are at most 0·000002 mm. in thickness.

Well-formed crystals of kaolinite are not common; they are regarded as a mineralogical curiosity. Pockets or veins have been found at Silverton, Colorado; Porth-yr-hwch, near Amlwch, Wales; Bolton Abbey, Yorkshire; Congleton Edge, Cheshire; Newcastle-on-Tyne; Glamorganshire; Diendorf, Bavaria; Ziesigwald, Chemnitz; Schlan, Bohemia; Altenberg, Saxony; Tuolomne, California; Mount Savage, Maryland; Bradon, Vermont; Richmond, Virginia; Perth Amboy, New Jersey; Reading, Chester; Tamaqua, and Pottsville, Pennsylvania; etc. The crystals may occur in aggregates of plates piled one above the other so that by screwing the cover-glass under slight press., it is possible to spread out the plates much as if a pack of cards were spread out fan-wise by pressing and screwing with the thumb at the other end. Curious vermicular—*vermis*, a worm—aggregates or rouleaux of plates, Fig. 109, have been found in many clays.[44] A. B. Dick [45] found that the chlorite-like form of kaolinite has the same refractive index and behaviour when heated as kaolinite; and the optical character is negative like that of nacrite. The **X-radiograms** have been examined by G. Shearer, and F. Rinne. The **cleavage** of kaolinite is perfect and parallel to the face $c(001)$. Some of the larger grains —0·0005 mm. in diameter—of china clay give with polarized light pale bluish-white gleams of light, but particles less than 0·0001 mm. do not show polarization effects.

The **index of refraction** of kaolinite is 1·563, very near to that of Canada balsam; A. B. Dick gave 1·56–1·57; W. T. Schaller and R. K. Bailey, and E. T. Wherry and G. V. Brown, and E. S. Larsen gave $\alpha$=1·561, $\beta$=1·565, and $\gamma$=1·567. The **double refraction** is low, approximately 0·008. Both the index of refraction and double refraction of kaolinite are very close to those of mica, so that the one mineral is frequently mistaken for the other, but, as A. Michel-Lévy and A. Lacroix pointed out, the refractive index and birefringence of kaolinite are less than those of mica or talc. A. Johnsen gave $2E$=1·563 for the optic axial angle. H. Zocher found that suspensions of clay in water are birefringent.

Varieties from different localities have received different names—nacrite, and pholerite. The term **nacrite**—from *nacre*, mother-of-pearl—was applied by A. Brongniart [46] to a mineral which resembled lepidolite in composition, but differed in its extreme unctuousness; later on A. Breithaupt employed the term for what appeared to be "an earthy talc" which occurred in snow-white or yellowish, six-sided plates aggregated in fan-shaped or reniform masses of sp. gr. 2·63. The pearly lustre sometimes approaches that of adamantine. The plates are flexible and non-elastic, with a soft soapy feel. The pearly lustre appears to be due to strata of air included between the separate crystalline plates forming a crystalline mass. The lustre can be seen under the microscope by oblique reflected light. Analyses of the mineral correspond closely with those of kaolinite. According to F. Sandberger, the mineral can be decomposed by hydrochloric acid. The sp. gr., hardness, and refractive index also approach the values for kaolinite. According to A. B. Dick, the crystals of nacrite are optically negative, those of kaolinite positive. Summarizing these results:

| | | | |
|---|---|---|---|
| Kaolinitic minerals | Crystalline | optically negative | *Nacrite.* |
| | | optically positive | *Kaolinite.* |
| | Non-crystalline or colloidal | | *Clayite.* |

A. Breithaupt also claimed that the mineral "with white pearl-like scales; soft and friable to the touch; with the property of sticking to the tongue when wetted; and of forming a plastic mass with water" which J. Guillemin [47] called **pholerite**—from φολίς, a scale—was identical with nacrite. A. Ledoux studied the pholerite and nacrite from St. Vincent. Pholerite was formerly regarded as a distinct mineral species with analyses in agreement with $2Al_2O_3.3SiO_2.4H_2O$; and, accordingly, H. A. Wheeler assumed that the *flint clays* of Missouri are variable mixtures of kaolinite and pholerite. Analyses by S. W. Johnson and J. M. Blake, with samples likely to be freest from impurities, correspond with those of kaolinite. On similar grounds, T. S. Hunt suggested that pholerite is an impure variety of kaolinite. O. Koch called an impure variety of kaolinite from Ancud, Island of Chiloë, *ancudite*. F. Wöhler described a similar product occurring at Schneckstein "in shining laminæ which when magnified 200 times appeared as transparent rhomboidal plates. The mass had an earthy fracture, and became lustrous when rubbed. The sp. gr. was 2·6." S. W. Johnson and J. M. Blake considered this substance to be kaolinite. The white claystone at Chemnitz was thought by A. Knop to be pholerite; it consists of aggregates of scaly crystals.

The "clay" of ordinary china clay is a mixture of particles of clayite and kaolinite; and, with respect to the **grain-size of the particles**, J. Stark [48] found that the particles of Zettlitz china clay had a mean diameter of 4·8$\mu$, and those of a more plastic clay, 3·6$\mu$. The former clay contained 32 per cent. of coarser particles 11$\mu$–49$\mu$, and the latter 21 per cent. ranging from 9$\mu$ to 40$\mu$. Both clays contained some very fine particles—suspensoids. There were approximately $6·6\times10^9$ particles per gram of the Zettlitz clay, and $15·8\times10^9$ particles per gram of the plastic clay. A. B. Dick found the **hardness** of kaolinite to be 2·0–2·5 on Moh's scale; and the **specific gravity** 2·60–2·63. The reported values for the sp. gr. of china clay range from 2·2–2·6. The former number is too low—due probably to the presence of entangled air bubbles, and possibly to the presence of hydrogels.

The sp. gr. alters when the clay is calcined, the magnitude of the change depends on the temp. of calcination. A. Laurent found the sp. gr. increased from 2·47 (dried at 100°) to a maximum 2·70 after calcination at *rouge sombre*—perhaps 500°; and then dropped to 2·64 at *rouge vif*—perhaps 800°; and finally to 2·48 at the temp. *de essais de fer*. The clay must have been rather impure, and fluxing must have occurred, because J. W. Mellor and A. D. Holdcroft found that the sp. gr. of china clay and of alumina behave in quite the opposite way. For instance, the sp. gr. of alumina and china clay calcined at different temp. are :

| | 110° | 600° | 700° | 800° | 900° | 1200° |
|---|---|---|---|---|---|---|
| China clay . . . | 2·615 | 2·473 | 2·489 | 2·497 | 2·560 | 2·734 |
| Alumina . . . | — | 2·824 | 2·828 | 3·394 | 3·525 | 3·914 |

G. H. Brown and E. T. Montgomery working up to 700° obtained analogous results with a number of different clays. The apparent volume of clay, corresponding with the contraction which occurs when clays are heated, was measured by J. Burton, P. Braesco, R. Wallach, J. M. Knote, H. Hecht, R. Lucas, E. Berdel, etc. The results show that a slight contraction occurs up to about 300°; and an increase in the volume occurs between 450° and 500°, which attains a maximum between 550°–600°. Above this temp., contraction sets in. Thus, E. Berdel found with a 4 hrs.' heating of china clay slabs at the indicated temp., the percentage linear contraction—**fire-shrinkage,** or *fire-contraction*—and porosity are :

| | 970° | 1150° | 1170° | 1190° | 1230° | 1290° |
|---|---|---|---|---|---|---|
| Contraction . . . | 2·1 | 2·4 | 3·1 | 4·2 | 8·2 | 9·5 |
| Porosity . . . | 41·6 | 41·9 | 42·1 | 31·6 | 26·3 | 20·8 |

The actual results vary with different clays; with different methods of making the slabs; with the rate of rise of temp.; and with the time of firing. The pyrometer of J. Wedgwood in 1782 was based on the definite contraction of clay bits when heated to definite temp. under constant conditions. There have been several modifications in the method of measurement, but the fundamental principle is extensively employed to-day.

Wo. Ostwald and F. Piekenbroek found that the viscosities of wet china clay, and ordinary clays differ in that the value for the latter increases rapidly to a maximum with age and mechanical working, but that of china clay increases slowly. The presence of 1·0 per cent. of quartz in clay, after mechanical treatment, gave a higher viscosity than did the untreated clay. The optimum quartz content varies with the grain-size. It is inferred that in china clay suspensions, the viscosity is determined by the grain-size, and the hydration and swelling of the particles.

The contraction which occurs when slabs made of wet clays are dried is called the **drying-shrinkage** or *drying-contraction*. B. A. Keen, and E. A. Fisher studied the drying of wet masses of clay which was conditioned by evaporation from the surface, and the movements of water in the capillary pores. J. Aron [49] showed that there are three stages in the drying : (i) as the water evaporates from the wet clay the volume-shrinkage is equal to the volume of water lost. This means that the space vacated by the water is taken up by the clay. After a time (ii) air spaces begin to appear and the volume-shrinkage is then less than the volume of water, since the space vacated by the water is not all reoccupied by the clay. Finally, (iii) the volume-contraction virtually ceases although water is still being lost by the clay. The shrinkage of the clay is due to the work of capillary attraction by films of water surrounding the clay particles. These results were in the main confirmed by W. J. Jackson and E. M. Rich, and C. Bischof. The ceramic journals teem with observations on these various properties of clay. The **tensile strength** of slabs made with wet clay varies with the amount of moisture present, and on drying, W. Jackson and E. M. Rich found that the tensile strength slowly increases to a maximum of about 3 kgrms. per sq. cm. when about 20 per cent. of water is present. The clay is then " white-hard," or " leather-hard." The subsequent evaporation of the water lowers the tensile strength to a minimum value of about 1·5 kgrms. per

sq. cm. with about 1–2 per cent. of water. The tensile strength then rapidly increases until the clay is quite dry and reaches 5 kgrms. per sq. cm. E. Orton found that the tensile strength of clay admixed with a given proportion of sand increases as the grain-size of the non-plastic material decreases. A. V. Bleininger gave for the tensile strength, the transverse modulus of rupture and the compressive strength in pounds per square inch:

| | Tensile strength. | Transverse modulus. | Compressive strength. |
|---|---|---|---|
| English ball clay | 210 | 558 | 1148 |
| English china clay | 41 | 98 | 228 |
| American ball clay | 125 | 380 | 635 |
| Florida china clay | 104 | 239 | 539 |
| Georgia china clay | 147 | 325 | 455 |
| North Carolina china clay | 69 | 166 | 349 |

W. Schumacher [50] gave for the **specific heat** of dried clay, 0·1784; H. Platter, 0·2231 if dried at 100°, and 0·3063 if air-dried; V. C. Lang, 0·233; and R. Ulrich, 0·2243 between 20° and 98°. J. M. Knote gave for raw clay between 22° and 150°, 0·237, for clay previously heated to 650°, 0·204; and for clay previously heated to 1050°, 0·200. C. F. Howe and C. B. Harrington gave for bricks made from clay $0·196+00533\theta$ between 0° and 1100°; S. T. Wilson and co-workers, $0·193+0·00006\theta$ between 0° and 1300°; and L. Bradshaw and W. Emery, $0·193+0·000075\theta$ between 0° and 1400°. Observations were also made by E. Heyn and co-workers, M. Kinoshita, A. Bigot, W. Steger, Y. Tadokoro, J. K. Moore, L. Navias, etc. L. Navias found that the heat absorbed per gram per degree on heating air-dried clays from 25°–1200° is 0·50–0·55 cal. per gram per degree, whereas the heat evolved on cooling the final product is 0·23–0·29 per gram per degree. The former includes the latent heat of evaporation of the water adsorbed by air-dried clays, the combined water, etc. The **thermal conductivity** of clay is small. A number of determinations have been made on bricks made from clays. The results therefore represent the conductivity of the fired clay plus pore-spaces. O. S. Buckner found 0·00169–0·00251 in standard units, and S. Wologdine 0·0035 at 1050° to 0·0042 at 1300° for the coeff. for different fired fireclays. J. W. Cobb and co-workers gave for the thermal conductivity $K$ at $\theta°$, $K=0·00155+0·0_525\theta$. The literature has been summarized by P. Gilard, and A. T. Green. Observations on commercial firebricks were made by H. A. Wheeler, G. H. Brown, A. S. Watts and R. M. King, A. T. Green, R. A. Homing, J. W. Cobb and co-workers, V. Tadokoro, E. Heyn and co-workers, P. Goerens and J. W. Gilles, B. Dudley, S. M. Marshall, S. Wologdine, J. D. Pennock, M. Simonis, F. Tschaplowitz, P. Rosin, and J. K. Clement and W. L. Egy. The porosity of the sample tested is an important factor. As predicted in 1914 by J. W. Mellor, A. T. Green found that while a high porosity is unfavourable to thermal conductivity below red heat, there is an inversion near 1100°, so that at higher temp. a high porosity enhances the thermal conductivity. The coeff. of **thermal expansion** of bricks made from clays have been measured, and the results have been summarized by J. W. Mellor. H. Kohl gave $0·0_5419$ for the mean linear coeff. at 1150°; $0·0_5520$ at 1250° of a china clay, and for a plastic clay, $0·0_5729$ at 1000° to $0·0_41079$ at 1250°. Recalculating the results of H. J. Hodsman and J. W. Cobb for the coefficient of thermal expansion of china clay at different temp.

| | 195° | 450° | 700° | 900° |
|---|---|---|---|---|
| Coeff. expansion | $0·0_5571$ | $0·0_5495$ | $0·0_5477$ | $0·0_5469$ |

In one case there is an increase with rise of temp. and in the other a decrease. The results must be greatly influenced by the presence of quartz. G. Tammann and H. Diekmann found that when dry clay is warmed to 48°, superimposed mercury begins to pass through.

W. C. Heraeus gave between 1667° and 1680° for the **melting point** of china

clay. H. A. Seger showed that the curve for the softening temp. of mixtures of clay and quartz has the **U**-form with a minimum at about 1650°, and a ratio $Al_2O_3 : SiO_2 = 1 : 16$; L. Bradshaw and W. Emery confirmed these results. The results with mixtures of commercial fireclay and silica are shown in Fig. 111. See also aluminium silicates, Fig. 108. The effect is greater with fine-grained than it is with coarse-grained silica. J. W. Mellor and B. J. Moore found that the effect of load is to depress the softening temp. in accord with the expression: Squatting temp. $=35c^{-0{\cdot}0082w}$, where $w$ represents the load in lbs. per sq. in. for loads up to 112 lbs. per sq. in., when the softening temp. are expressed in terms of Seger's cones. This corresponds with a depression of one cone per 5¼ lbs. per sq. in. press. With mixtures of silica, the difference between the softening temp. is less marked the higher the proportion of silica. This result was confirmed by L. Bradshaw and W. Emery. L. Bertrand studied the effect of the proportion of alumina in natural clays on the softening temp. H. Hirsch and M. Pulfrich examined the behaviour of a large number of clays when heated under load. E. L. Dupuy found the resistance to crushing on a rising temp. at first decreased, then rapidly increased to a maximum at about 1000°, being then sometimes double or triple the value at atm. temp., at still higher temp., the strength rapidly diminished until fusion was complete. A felspathic china clay exhibited two maxima, the second being near 1400°. Many other observations have been reported.[51]

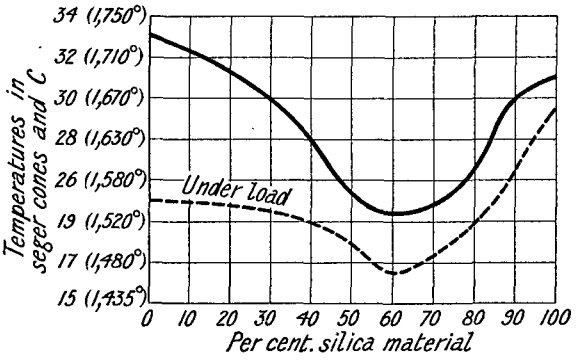



FIG. 111.—The Effect of Silica on the Softening Temperature of Fireclay.

The action of heat, etc., on various mixtures of clay and *silica* or *quartz* has been discussed by M. Simonis,[52] E. Berdel, F. Kraze, R. Lucas, S. L. Galpin, etc. An indefinitely large number of observations have been reported in the ceramic

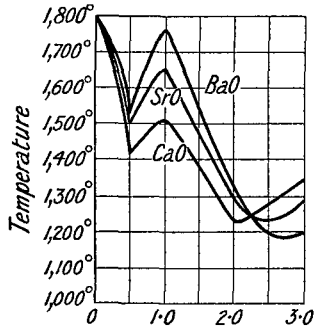



FIG. 112.—The Effect of Alkaline Earths.

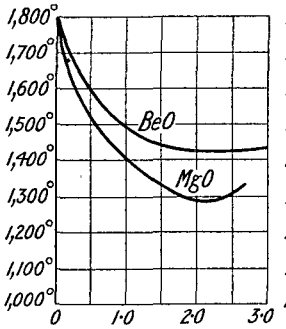



FIG. 113.—The Effect of Beryllia and Magnesia.

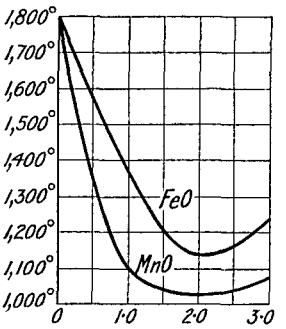



FIG. 114.—The Effect of Ferrous and Manganous Oxides.

journals. The effect of heat on mixtures of clay with felspar, and mica is discussed in connection with these minerals. The effect of *lithium oxides* on the fusibility, etc., of clay was investigated by R. Rieke; of *potassium and sodium oxides*, by R. Rieke, and G. Flach; of *calcium oxide*, by G. Flach, and R. Rieke, Fig. 112—*vide infra*, cements; of *strontia*, and of *baryta*, by G. Flach, and R. Rieke—Fig. 112; of *beryllia*, by R. Rieke—Fig. 113; of *magnesia*, by H. Mäckler, A. F. Hottinger,

L. E. Barringer, G. Flach, and R. Rieke—Fig. 113; of *iron oxide*, by R. Rieke, and J. W. Mellor—Fig. 114; of *manganese oxide*, by R. Rieke—Fig. 114; of *chromic oxide*, by K. Dornhecker, and S. Sandlund; of *uranium oxide*, by O. Kallauner and J. Hruda; and of *zirconia*, by R. Rieke. The effect of *titanic oxide* on the fusibility of clay was shown by H. A. Seger and E. Cramer to be greater than is the case with silica. The subject was investigated by H. Ries, C. Bryce, and R. Rieke. The latter showed the fusibility with the following percentage amounts of titanic oxide was:

| $TiO_2$ | 0 | 10 | 20 | 30 | 50 | 70 | 80 | 90 | 100 |
|---|---|---|---|---|---|---|---|---|---|
| Temp. | 1770° | 1670° | 1580° | 1530° | 1525° | 1530° | 1565° | 1580° | 1610° |

G. Tammann studied the effect of alkaline earths on clay. E. Richter examined the influence of different fluxes on the fusibility of clay, and concluded with what has been called Richter's law: *Chemically equivalent quantities of magnesia, lime, ferrous oxide, soda, and potash exert the same influence in lowering the fusibility of a clay.* The subject was discussed by C. Bischof, and it was found that at high temp. silica itself acts as a flux with clay, and should not be present in excess; the presence of an excess of silica also intensifies the effect of other fluxes. E. Cramer also found that the fluxes do not act according to E. Richter's law in the presence of free silica. T. Ludwig inferred that E. Richter's rule is a special case of the law of dil. soln.: *Equimolar quantities of different substances dissolved in equal amounts of the same solvents, lower the m.p. to the same extent.* R. Rieke tested the rule with additions of baryta, beryllia, magnesia, ferrous oxide, and manganous oxide to a mol of china clay, $Al_2O_3.2SiO_2.2H_2O$, with a softening temp. of about 1790°. Using 0·25 mol of the base, the corresponding softening temp. were:

| $Li_2O$ | $Na_2O$ | $K_2O$ | CaO | SrO | BaO | BeO | MgO | FeO | MnO |
|---|---|---|---|---|---|---|---|---|---|
| 1380° | 1520° | 1530° | 1690° | 1720° | 1730° | 1660° | 1700° | 1660° | 1670° |

With 0·25 mol $TiO_2$ and 0·25 mol $ZrO_2$ the softening temp. were respectively 1700° and 1690°. The results with still higher proportions of lime, strontia, and baryta showed that the oxide with the lowest mol. wt. lowered the m.p. most. Similarly with the alkali family. The effect with beryllia is less than with magnesia; and with ferrous oxide less than with manganous oxide. The atm. of the furnace was strongly reducing, and it was assumed that the last two oxides were in the lower state of oxidation. The general results show that the alleged law is inapplicable and the analogy with dil. soln. is invalid. A. S. Watts also made some observations on this subject.

Several observers—J. Burton,[53] F. W. Clarke, H. C. McNeil, J. M. Knote, H. E. Ashley, etc.—have attempted to find a **dehydration temperature.** E. Lovejoy said the dehydration temp. is near 630°; A. E. Brown gave 565°, and W. M. Kennedy, 475°, while A. B. Dick observed no loss of water with crystals of kaolinite at 275° or at 400°, and W. H. Hillebrand none at 330°. W. Vernadsky, and F. Hundeshagen affirmed that dehydration takes place in two stages: one half the water is said to be evolved at one temp. and the other half at a higher temp. Hence, J. M. van Bemmelen, and S. J. Thugutt inferred that one half the water is Si-hydroxyl, and the other half Al-hydroxyl, and they wrote the formula $H_2Al_2Si_2O_8.H_2O$. E. Löwenstein considered that 0·5 mol is driven off at the lower temp. and 1·5 mol at the higher temp., and he wrote the formula $2Al_2O_3.4SiO_2.3H_2O+Aq$. There is, however, no satisfactory evidence of the evolution of water in two stages. J. W. Mellor and A. D. Holdcroft found that above 300°, the evolution of water is a continuous process, and that the rate which the water is expelled rises with the temp. Thus, the percentage losses were:-

| | | 300° | 400° | 425° | 450° | 500° | 550° | 600° |
|---|---|---|---|---|---|---|---|---|
| China clay | Vacuum | 0·24 | 0·89 | 1·43 | 3·38 | 8·48 | — | — |
| | Atm. press. | 0·26 | 0·57 | 0·68 | 0·80 | 1·19 | — | 11·92 |
| Kaolinite | Vacuum | 1·66 | 1·70 | 1·80 | 2·72 | 4·96 | 8·20 | 11·58 |
| | Atm. press. | 1·82 | 1·91 | — | — | 2·41 | 6·00 | 10·08 |

The 13–14 per cent. of combined water is rapidly given off as the temp. rises beyond 500° under ordinary atm. press., although most is given off below this temp. under reduced press. It requires a high temp. to expel the last traces of water. The decomposition of the mineral which is attended by the evolution of water is an endothermal reaction and produces a terrace in the heating curve. D. Tschernobéeff, and J. W. Mellor and A. D. Holdcroft's rough estimates of the **heat of dehydration** range from 11–28 Cals. per mol, and D. Tschernobéeff's estimate of the **heat of formation** of kaolinite is $(Al_2O_3,2SiO_2,2H_2O)$=43·8 Cals., but these data are of little value. E. Löwenstein measured the **vapour pressure** of a number of clays at ordinary temp., and J. W. Mellor and co-workers found that with a partial press. of water-vap., $p$ mm., when confined over sulphuric acid, the loss in weight for crystals of kaolinite, china clay, ball clay, and halloysite was at 25° :

| $p$ | 18·0 | 13·5 | 8·8 | 4·3 | 1·8 | 0·6 | 0·0 mm. |
|---|---|---|---|---|---|---|---|
| Kaolinite | 0·06 | 0·08 | 0·12 | 0·18 | 0·24 | 0·38 | 0·46 |
| China clay | 0·01 | 0·06 | 0·13 | 0·16 | 0·23 | 0·36 | 0·50 |
| Ball clay | 0·08 | 0·24 | 1·63 | 2·31 | 2·44 | 3·29 | 3·54 |
| Halloysite | 0·06 | 0·44 | 1·67 | 1·96 | 3·26 | 3·62 | 4·03 |

The water is restored when the clay is exposed to a moist atm. L. Navias measured the velocity at which clays give off their combined water, and he suggested that the evolution of water is rapid at 745°, and the speed falls in a decisive manner, while the temp. rises 200°–300° more. Only clays containing organic matter develop an appreciable press. between 900° and 1200° in air. V. Agafonoff and W. Vernadsky raised the objection that the product obtained by dehydrating clay below 550° is homogeneous, because it cannot be separated into parts by separating liquids, and it appears homogeneous under the microscope. Neither test is at all an adequate proof of the conclusion. W. T. Schaller and R. K. Bailey described hexagonal plates of a kaolinite from Oklahoma which, unlike ordinary kaolinite, intumesced strongly when heated.

H. le Chatelier observed a retardation in the heating curve of crystalline kaolinite ending at 770°, and a slight acceleration at 1050° ; he also found a marked retardation with halloysite ending at 700°, and a sudden acceleration at 1000°. As a matter of fact, the actual temp. observed under these conditions depends on the rate of rise of temp., the physical state of the powdered material, etc. It is also possible that the alleged halloysite was really colloidal clayite, since J. W. Mellor's observations show no marked retardation with halloysite at the above temp. J. W. Mellor and A. D. Holdcroft found that china clay and crystalline kaolinite give a terrace in the **heating curves** just over 500°, and a hump in the curves between 800° and 1000° ; china clay, like the colloidal aluminosilicates gives a terrace at about 150°, indicating that it contains clayite as well as crystals of kaolinite (shown by the microscope). The hydrogels of silica and alumina also give a terrace just over 100°, and alumina gives a hump at 800°–1000°. The curves are illustrated in Figs. 119, 120, and 122. Endothermal reactions are represented by terraces ; exothermal reactions by humps. There is a remarkable likeness in the 800°–1000° hump in the heating curves of the hydrated aluminium silicates in conformity with the suspicion that all are due to one cause—the polymerization of alumina. It is inferred from the chemical and physical properties of dehydrated kaolinite or clayite that it is decomposed into free silica and free alumina above 500°, and the uniformity in the hump between 800° and 1000° with all these minerals corresponds with the inference that a mixture of silica and alumina is involved. Confirmatory results were obtained by R. Rieke, G. Keppeler, R. Wohlin, C. E. Moore, H. S. Houldsworth and J. W. Cobb, R. Wallace, A. M. Sokoloff, G. Tammann and W. Pape, A. Zöllner, J. V. Samoiloff, and S. Satoh. At higher temp., in the vicinity of 1200°, cristobalite, and sillimanite crystals are formed—presumably by the recombination of silica and alumina. If the clay breaks down into water and a disilicate, $Al_2O_3.2SiO_2$, it is necessary to assume that this compound has properties

parallel with those of alumina, and that it breaks down at higher temp. into sillimanite (fibriolite) and silica (cristobalite). W. Vernadsky calls this residue leverrierite, and invests it with all the properties required to explain the assumption that the final products of the reaction are $Al_2O_3.2SiO_2+2H_2O$. O. Rebuffat supports this hypothesis. The above-mentioned observations on the vap. press., coupled with the low temperature dehydration of clays in vacuo, probably mean that the clay loses its water before breaking down into free silica, and alumina (possibly sillimanite). J. Matejka went further than G. Tammann and assumed that several aluminium silicates are formed; he also used the break on the heating curve as a means of detecting kaolinite in soils. A. V. Henry found the **electrical resistance**, $R$ ohms per c.c., of china clay—*vide infra*, pottery—with a 45-volt, 1000-cycle alternating current, to be

| | 300° | 500° | 700° | 900° | 1100° | 1300° | 1500° |
|---|---|---|---|---|---|---|---|
| $R$ . . . | $133\times10^5$ | $269\times10^3$ | $302\times10^2$ | 7440 | 2350 | 1060 | 681 |

Clays in suspension in water are rapidly flocculated and made to settle by carbon dioxide, hydrochloric acid, many ammonium salts, the sulphates and chlorides of the alkalies and alkaline earths, ferrous and ferric sulphates, zinc chloride, etc. On the contrary, humic matters, sodium carbonate, water-glass, sodium and potassium phosphate, borax, potassium or ammonium oxalate, etc., have the converse effect, for they deflocculate clays and retard their settling. This subject has been discussed by W. Durham,[54] and many others. The observations of J. Murray and R. Irvine show that the clay matters carried by rivers to the sea are quickly deposited on reaching salt water, and only a small fraction is carried to deep waters. O. M. Smith found that salts containing bivalent ions aided the flocculation of clay suspensions by alum, but that it was hindered by sodium hydroxide or carbonate. N. M. Comber showed that clay suspensions were flocculated most readily in an alkaline medium, but that the degree of alkalinity above that of $0{\cdot}005N$-$NH_4OH$ had no effect; he also determined the relative flocculating powers of different electrolytes by observing the rate of settling of the coagulum formed by a decided excess of the electrolyte. Observations by O. Arrhenius, E. F. Burton, etc., show that the addition of certain electrolytes in excess of the minimum required for flocculation yields a coagulum that settles much more slowly than that obtained when just enough is added to bring the colloid to its iso-electric point. R. Bradfield found that with an amount of potassium hydrophosphate just below that required to cause flocculation, the addition of a larger amount of other electrolytes is required to cause coagulation than is the case with the untreated clay. The protective action may be due to an absorption of negative phosphate ions and hydroxyl ions by the negative clay particles, thus increasing the negative charge, and consequently also the amount of positive ions required to bring it to the iso-electric point. The protective action may also be due to the higher conc. of the potassium hydrophosphate required for flocculation when used alone might be due to its weakly basic reaction, larger quantities being required to bring the colloid to its critical value than is the case with a strong base like potassium hydroxide. M. A. Rakuzin and A. N. Nesmejanoff found that mercuric chloride is not adsorbed by china clay. R. Bradfield measured the effect of the acidity of a soln. on the flocculation of clay in suspension, and found that hydrochloric, sulphuric, phosphoric, and acetic acids flocculate the clay at about the same H'-ion conc., but a greater acidity is needed with citric acid. Flocculation involves a decrease in the electric charge; peptization an increase. The acidity or hydrogen ion conc. of clays was found by F. P. Hall to range from $10^{-3{\cdot}1}$ to $10^{-7{\cdot}27}N$, when results with clays containing appreciable quantities of soluble salts are rejected. The iso-electric point with clays corresponds with a hydrogen ion conc. of $10^{-2{\cdot}7}$ to $10^{-4{\cdot}0}N$. The maximum electric charge acquired in the presence of soluble salts represents maximum deflocculation; and the maximum rate of settling takes place at the iso-electric point. R. Schwarz

said that flocculation occurs only when the acidity is eq. to an hydrogen ion conc. of $10^{-4.5}$ to $10^{-5.2}N$. This subject has been discussed by S. E. Mattson. A. Fodor and B. Schönfeld, and F. P. Hall also studied the effect of acids on clays.

The hygroscopicity of china clay—*i.e.* the property for absorbing moisture from humid air—is greater if it has been pre-heated to between 500° and 800°, than if the raw clay be used, and, like alumina, it loses this property if it has been calcined over 800°. L. Gurvich[55] measured the heat of wetting clay, and he found that oxygen compounds have a greater heat of wetting and are more adsorbed by adsorbents containing oxygen—or they are *oxyphilous*, while hydrocarbons are more attracted by charcoal and are *carbophilous*. With increasing mol. wt. in a series, the oxyphilous effect decreases to a minimum, and increases again with increasing mol. wt.—*vide* charcoal. E. Reichardt and E. Blumtritt found that 100 grms. of dry and moist clay respectively absorbed 33 and 29 c.c. of gas from the atm., and the gas contained respectively 65 and 60 per cent. nitrogen; 21 and 6 per cent. oxygen; and 14 and 34 per cent. carbon dioxide. A. von Dobeneck showed that 100 grms. of china clay absorbed 0·023 grm. of carbon dioxide at 0°, and practically the same amount at 10°, 20°, and 30°. In 1825, M. Faraday noted that china clay which has been heated to redness and exposed to the air for a week, absorbs, during that time, much ammonia from the air. B. von Ammon observed that china clay at 20° absorbed 0·42 per cent. of its dry weight of ammonia, and he, and A. von Dobeneck found the amount absorbed is less the higher the temp. above zero. R. E. Wilson and T. Fuwa found that with

| | | | | | | |
|---|---|---|---|---|---|---|
| Humidity of air . . . | 15 | 30 | 50 | 70 | 90 | per cent. |
| Moisture in clay . . . | 0·30 | 0·60 | 0·92 | 1·06 | 1·27 | ,, |

According to W. Suida, china clay absorbs the colouring matter from aq. soln. of acid and basic aniline dyes. E. Dittler and C. Doelter observed that an alcoholic soln. of fuchsine does not dye kaolin. 2·5 grms. of a kaolinized granite containing about 70 per cent. of china clay absorbed 0·0176 grm. malachite-green, 0·0211 acid fuchsine, and 0·0211–0·0218 grm. of methylene blue from a litre of the soln. containing half a gram of the dye, and H. E. Ashley proposed to estimate the plasticity of clays by measuring the amount of malachite-green adsorbed by a given quantity of clay from a standard soln. of the dye. The adsorption of salts from their aq. soln. has been studied by F. Rautenberg, E. C. Sullivan, M. Rakuzin, S. Wosnessensky, H. Hirsch, T. O. G. Wolff, G. Moressée, A. S. Cushman, E. Kohler, J. M. van Bemmelen, A. Fodor and B. Schönfeld, K. Kobayashi, T. Okazawa, A. Bencke, H. Kohl, R. Bradfield, and others. E. Kohler, and E. C. Sullivan showed that when an aq. soln. of copper sulphate or lead nitrate is filtered through china clay, the basic constituent is largely retained by the clay. Neutral soln. of sodium chloride or sulphate, or of magnesium sulphate or chloride, give a filtrate which is distinctly acid. The acidity is thought to be partly due to the exchange of the bases for the aluminium (and iron) of the clay; and partly to the greater speed of the acid component when the salt is hydrolyzed, $MgSO_4+2H_2O=Mg(OH)_2+H_2SO_4$. E. C. Sullivan studied the action of cupric sulphate and silver sulphate soln. on clay. P. Rohland described a clay which was permeable to crystalloids—*e.g.* sodium chloride, barium chloride, cupric sulphate, potassium dichromate, etc.—and impermeable to colloids—*e.g.* ferric hydroxide, silicic acid, dissolved starch, etc. S. Lagergren found that china clay, dried at 160°, increased the conc. of soln. of chlorides and bromides—in some cases as much as one per cent. The results require confirmation. H. Udluft showed that clay adsorbs ferric oxide and manganese dioxide from the colloidal sol; both the clay and manganese dioxide sols are negatively charged.

J. Lemberg's observations showed that sodium silicates or aluminosilicates are less stable in aq. soln. than the corresponding potassium salts. The replacement of potassium by sodium in the silicates does not proceed nearly so readily

as the reverse reaction. He also noted that the displacement of magnesium by calcium is more difficult than the reverse change. C. G. C. Bischof, and J. Lemberg suggested that the need of plant life for potassium rather than sodium may be due to the fact that the potassium salts are held more tenaciously by soils than those from sodium salts; and accordingly the plant finding more potassium than sodium available in the soils, has developed the habit of assimilating potassium rather than sodium. Again, the reason sodium salts accumulate in the ocean has been explained by showing that the potassium salts are retained more tenaciously by the soil while the sodium salts are washed into the rivers and seas.

J. M. van Bemmelen found that 100 grms. of china clay adsorbed 2·3 eq. of potassium chloride from 250 c.c. of a soln. containing 10 eq. of the salt; and H. Hirsch, that 100 grms. of clay adsorbed $w$ grms. of barium chloride from a litre of soln. containing $C$ grms. of salt:

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| $C$ | 0·1 | 0·5 | 1·0 | 3·0 | 5·0 | 10·0 | 15·0 | 20·0 | 25·0 |
| $w$ | 0·096 | 0·424 | 0·701 | 1·087 | 1·231 | 1·412 | 1·527 | 1·535 | 1·551 |

R. Gallay found that clay with adsorbed bivalent ions is more sensitive to coagulation than clays with adsorbed univalent ions. The clay with adsorbed bivalent ions is more sensitive towards univalent ions than is a clay with adsorbed univalent ions towards bivalent ions. This indicates that the bivalent ion released by exchange from the clay exerts a coagulating influence; and that coagulation is complementary to adsorption. In 1859, C. Bödeker concluded from his observations that the amount of adsorption is proportional to the sq. root of the conc. T. O. G. Wolff said that the final, not the initial, conc. of the salt should be alone considered in discussing this relation, for a soln. percolating through a colloid will give up the solute to the colloid until equilibrium is attained, and it will then pass through unchanged. Conversely, a more dil. soln. will abstract salt from the colloid until equilibrium is attained. W. Ostwald, and H. Freundlich showed that the form of the function connecting adsorption with conc. will be exponential. For further work on the relation between adsorption and conc., *vide* carbon.

**The plasticity of clay.**—The fictile qualities of a clay are primarily dependent on its plasticity. Plasticity is a property of wet clay which enables it to change its shape without cracking when it is subjected to a deforming stress. The elasticity of the wet clay is negligibly small. Clay is peculiar in possessing another quality which is as important as plasticity. It has a high binding power when dried and fired, so that the form impressed on the plastic clay is retained more or less persistently when the clay is dried and fired. As shown by A. Baumé,[56] G. Vogt, S. Kasai, E. Bourry, E. Orton, F. F. Grout, A. Leppla, H. A. Wheeler, etc., very fine powders—barium sulphate, glass, quartz, etc.—acquire a kind of plasticity when wetted, but when dried, the binding power is exceedingly small. They are plastic, but their plasticity cannot be used in the fictile arts because the second quality is wanting. Many definitions of plasticity confuse these two distinct properties, and assume that the binding power of the dried clay is implied in the term plasticity. Indeed, many methods proposed for measuring plasticity are based on the binding power of the dried clay—*e.g.* those of W. Olzschewsky, and H. A. Wheeler. It is assumed that the tenacity of the dried clay is proportional to the plasticity of the wet clay. This is generally, but not always, true. No known property of the *dry* clay can be used as an infallible index of the plasticity of the *wet* clay, and measurements of plasticity dependent on some property of the dried clay can therefore be dismissed, because even though they may measure an important property of clay, that property is not plasticity.

It is really difficult to measure the plasticity of clay because the property is somewhat complex. In 1844, A. Brongniart recognized its elusive character. He said: *On a souvent parlé de cette propriété, on semble la connaître, mais on n'en a qu'une vague idée.* The potter's thumb under working conditions is one of the most sensitive tests at present known, but that is not always decisive. B. Zschokke

regarded plasticity as a complex property which could be analyzed into four simpler qualities: (i) the deformability; (ii) the cohesion; (iii) the adhesion; and (iv) the viscosity or internal friction of the clay. A. Martens assumed that the plasticity, $P$, is proportional to the toughness, $T$, of the material, and inversely as the modulus of rupture, $R$, such that $P \propto T/R$; and H. Fischer added that the plasticity also varies inversely as the elasticity, $e$, of the material, so that $P \propto T/eR$. The subject was discussed by H. Fischer, A. Rejtö, F. Kick, H. Tresca, and L. von Tetmajer. In estimating plasticity there is first the internal friction which can be otherwise represented as the resistance which the clay offers to changing its shape; and second, there is the cohesion, *i.e.* the amount of deformation which the clay can suffer without cracking. F. F. Grout worked on these lines; he assumed that, with suitable units, the product of (1) the resistance the clay offers to deformation, Fig. 115; and (2) the amount of deformation the clay can suffer without cracking, Fig. 116; represents the plasticity, Fig. 117. E. C. Bingham regards plasticity as a complex property involving a definite shearing stress and the viscosity determined by measuring the quantity of clay flowing through a capillary tube at various press. The subject has also been discussed by F. P. Hall, and A. de Waele.

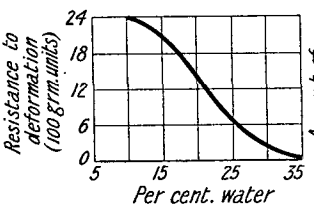



FIG. 115.—Relation between Water Content and Resistance to Deformation.

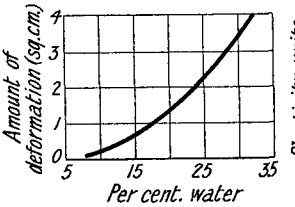



FIG. 116.—Relation between Water Content and the Amount of Deformation.

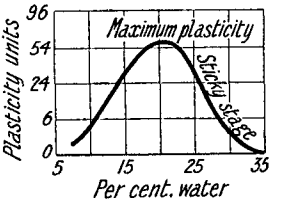



FIG. 117.—Relation between Water Content and Plasticity.

The plasticity of a clay varies with the proportion of water in a curious way. As water is progressively added to a dry clay, the plasticity continually increases and attains a maximum value. Any further addition of water reduces the plasticity; the clay acquires another quality. The particles no longer have a marked tendency to cohere together, rather does the clay become "sticky," and it adheres to anything it touches which water can "wet." In the sticky stage the clay is no longer workable. This represents a break in the continuity between plasticity and viscosity. As more and more water is added, the clay assumes the form of slip, and can then be poured like a liquid. J. W. Mellor and A. D. Holdcroft were able to restore a small proportion of water to completely dehydrated clay by heating it under pressure in steam. It was assumed that the silica and alumina of the decomposed clay are hydrated. J. S. Laird and R. F. Geller repeated the experiment and obtained analogous results. The restored plasticity is of a totally different kind to that possessed by the original clay.

There are different qualities in plasticity. The deformation pressures of some clays are greater than others, and such clays are said to be "stiff" or "strong." Some strong clays offer a high resistance to changing their shape and yet cannot be deformed very much without cracking. In other words, the clay is "strong" and "short"—*e.g.* London clays. There are other clays which have a low deformation pressure, and can suffer little deformation without rupture. They are "weak" and "short"—*e.g.* many siliceous pipe-clays. Other "fatty" clays offer a low resistance to change of shape, and yet suffer a comparatively large deformation without rupture—*e.g.* the black ball-clays.

*Plasticity is a mechanical property, the resultant effect of a deformation and a pressure.*—The deformability of a clay is probably determined by the distances the particles can move without loss of cohesion; and the deformation pressure represents the magnitude of the cohesive or attractive forces as shown by the

resistance offered by cohesion to the movements of the particles under the influence of an impressed force. The deformability of the clay is then conditioned by the size and shapes of the particles ; and the deformation pressure is determined by the magnitude of the cohesion between the clay particles and the water, and by the thickness of the water film.

Until it has been shown that plasticity is a definite function of some other quality—salt-absorbing property of H. Hirsch, dye-adsorbing property, viscosity of slip, etc.—it cannot be assumed without reservations that measurements of these qualities measure plasticity. The claims made on behalf of such indexes of plasticity are examples of the logical fallacy *circulus in probando*. Take the dye-absorbing test. Plasticity is assumed to vary with the amount of colloid in a clay ; the amount of colloid in the clay is then assumed to be proportional to the amount of dye the clay can absorb from a standard soln. Hence, dye-absorption measures plasticity. The viscosity test—used by M. Simonis, M. Chatenet, F. P. Hall, R. F. MacMichael, E. van der Bellen, etc.,—is another example. Some methods which have been proposed for measuring plasticity really measure only one of the two components—deformation and pressure—into which plasticity has been resolved. For example, L. J. Vicat's needle test—used by P. Langenbeck ; A. Brongniart's wad-box test—used by C. Bischof, R. Biedermann and H. Herzfeld, E. C. Stover and J. Lindley, etc. ; G. E. Ladd's tensile test ; P. Jochum's bending test ; and K. Dummler's spiral test, ultimately measure deformation, not pressure ; and they give comparable results under constant conditions for a particular type of clay when the pressure is constant, but not necessarily so for different types of clay.

The plasticity of a clay was assumed by G. Keppeler, and others, to be inversely proportional to the grain-size. H. E. Ashley made this an essential part of his formula. The observation has been qualitatively recognized for a couple of centuries. In 1770, A. Baumé attributed the high plasticity of clays to their extremely fine state of subdivision, and to their containing some saline matter. He said :

> On doit attribuer le liant des argilles à l'extrême division de leurs parties qui les rend propres à retenir l'eau, et à leur état salin qui leur donne la faculté d'être presque dissolubles dans l'eau. Leurs molécules sont beaucoup plus dans l'état de division, que celui qu'on pourroit procurer à une pierre quelconque par des moyens mécaniques.

A. Baumé's *l'état salin* approaches near to the modern idea of matter in a colloidal state. The meaning is clear ; superposed on the plasticity exhibited by fine grained powders, clays have a plasticity in virtue of their contained saline or colloidal matter. A. Baumé's assumption thus approximates to that made by T. Way, T. Schlösing, H. Kaul, F. Förster, E. W. Hilgard, E. Podszus, S. Odén, A. Benecke, E. van der Bellen, W. H. Brewer, A. S. Cushman, R. C. Wallace and J. E. Maynard, A. Bigot, G. Keppeler, P. Rohland, and by H. E. Ashley, that plasticity is connected with the amount of colloidal matter in the clay—*l'argile colloïdale* of T. Schlösing—and inversely as the state of subdivision. If, as appears highly probable, the plasticity of clay is proportional to the amount of colloidal matter in the clay, the dye-absorption test is probably invalid because there is nothing to show that the colloidal matters in different clays have the same absorption power. It is fairly certain that the colloidal matter in different clays—say ball clay and china clay—is not the same, for this must be largely determined by the nature of the organic matters associated with the clay at the time of its deposition, or which have been afterwards acquired from extraneous sources. Neither J. Splichal, nor C. D. B. y Escuder found the dye-absorbing test to be a satisfactory method of measuring plasticity. Clays have qualities which might be predicted from the known properties of matter in the colloidal state. It is therefore assumed that clays contain $x$ per cent. of colloidal matter possessing qualities like those possessed by the clay itself.

The evidence for the statement that plasticity is inversely proportional to grain-

size is not to be accepted without reservations. B. Zschokke, and F. F. Grout have both shown that the plasticity of some clays is not always influenced by finer grinding, and that the plasticity of other clays may be lessened by fine-grinding. This shows that close-packing is also concerned in the action. It follows that closer packing is possible with mixed fine and coarse grains than with all fine or all coarse grains, and V. Alexiejeff, and P. A. Schemjatschensky have shown that both extremely fine-grained and extremely coarse-grained clays are less plastic than clays containing mixed fine and coarse grains. Hence, if grinding makes the particles more uniform in size, the clay will become less plastic; and it is probable that, other things being equal, the distribution of grain-sizes which permits the closest packing of the particles, will be the most favourable to high plasticity.

Plasticity *per se* can be readily explained by the known properties of films of water, and theories have been devised which postulate special shapes for the predominant particles in the clay; *e.g.* H. le Chatelier, R. Biedermann and H. Herzfeld, G. H. Cook, A. Leppla, H. A. Wheeler, R. F. MacMichael, G. Vogt, S. W. Johnson and J. M. Blake postulated flattened particles; J. Aron, and E. Linder, spherical particles; and W. Olzschewsky, spongy particles. There are, however, a number of cognate properties possessed by wet clays, which are of assistance in the clarification of the concept of plasticity. For example, the slow development of plasticity during the weathering or ageing of clays; the action on clay-slip of alkalies, hydrolysable salts, acids, and certain organic compounds like tannin; the high tenacity of dried clays, etc. H. A. Seger emphasized that the increased plasticity due to ageing is accompanied by an increased acidity in the clay. The acidity is due to the decomposition of the organic matters in the clay. It does not necessarily follow, as E. Rohland supposed, that increasing the acidity—*i.e.* the conc. of the $H^{\cdot}$-ions—will increase the plasticity of clays. It might be anticipated that the bacteria which decompose the organic matters may accelerate the development of plasticity by ageing and weathering. E. G. Stover said that the *bacillus sulphureus* is the active agent, but this is not proved. The subject was discussed by O. Beck, and F. F. Grout, etc. The facts connected with the action of alkalies, etc., on clay-slip have been worked out by many investigations on the sedimentation of clay, etc., suspended in water. It has been observed that there are three classes of substances concerned in these effects: *I. Flocculants*—Acids, acid salts, lime, calcium sulphate, sodium chloride, and most neutral salts cause the fine particles in suspension to flocculate or coagulate into groups and settle; these agents also enhance the plasticity of clays. *II. Deflocculants*—A small proportion of ammonia, alkali hydroxide, alkali carbonate, borate, silicate, or a salt of other weak acids deflocculate, decoagulate, or peptize the clay, causing it to assume a more finely divided condition than in water, and thus to remain in suspension for a longer period. These agents also diminish the plasticity of clays. *III.* An excess of the deflocculating agents may produce the converse effect giving the same result as if an acid had been added; and perhaps also with some flocculants.

The attractive forces exerted on the molecules at the surface of a liquid are smaller than on a molecule in the interior, so that there is a tendency for the surface mols. to move inwards. The general result is that the surface tends to contract so as to leave the smallest number of molecules on the surface. K. Fuchs, M. Whitney, and W. J. A. Bliss have pointed out that with fine-grained particles of a solid suspended in a liquid, when the surface attraction of the liquid for the liquid predominates over that of the clay for the liquid, the shell of liquid about the clay will diminish, and flocculation will set in. This case is characterized by acids and other flocculants of the first class. When the surface attraction of the clay for the liquid predominates over that of liquid for liquid, the shell of liquid about the clay will enlarge, and the grains of clay will be kept apart and deflocculation will occur. This case is typical of dil. soln. of the alkalies, and other deflocculants of the second class. The behaviour of substances in the third class shows that there is a critical concentration below which the surface attraction of

clay for the liquid predominates, and above which the attraction of liquid for liquid is predominant.

The effect of alkalies on clay suspended in water is to keep the clay particles apart, the effect of acids is to make them form aggregates. The result is rather remarkable. Clay-slip prepared with about 0·3 per cent. of a mixture of sodium carbonate and silicate, can be readily poured in casting operations, and yet it may contain less water than a stiff mass of clay without the alkali. The addition of a little acid to the former so as to neutralize the alkali is attended by an immediate "solidification" of the slip. The vessel can then be turned upside down without interfering with the contents. The addition of more alkali will again make the slip pour readily. The amount of the alkali mixture required to give the maximum fluidity with the minimum proportion of water varies from clay to clay. The phenomenon has important industrial applications. It has been discussed by C. Goetz, A. Schmidt, A. Johnson, M. Simonis, O. M. Smith, J. W. Mellor, E. Weber, H. E. Ashley, B. Kosmann, A. V. Bleininger and C. E. Fulton, G. Keppeller, M. Rosenoff, M. Böttcher, H. Hirsch, A. Spangenberg, H. G. Schurecht, S. Wossnessensky, A. Fodor and B. Schönfeld, R. C. Wallace and J. E. Maynard, etc.

The above hypothesis shows how the plasticity of a clay can increase with increasing proportions of water so long as the average thickness of the surface films of water on the particle of clay is not greater than the average range of the mol. attraction of the clay for water. When enough water has been added to produce thicker films, part of the water will be outside the range of this attraction, and the clay will be less coherent, and become "sticky." The high surface attraction of clay for water is illustrated by the magnitude of the **Pouillet effect** observed by C. S. M. Pouillet, C. G. Jungk, F. Meissner, and S. Lagergren. According to A. Mitscherlich, with approximately the same surface area, the maximum effect is nearly 1·50 cals. per gram with china clay; 0·03 cal. with ground quartz; and 0·01 cal. with ground flint. J. G. Bouyoucos found the heat of wetting quartz sand is zero; with fine sand, 0·8 cal. per 50 grms. of material; and 607·5 for clay. The heat of wetting is reduced when the materials are preheated, and this the more the higher the temp., until, at 750°, the effect with soils vanished. Attempts by J. Aron, B. Kosmann, O. Bock, W. H. Brewer, P. Rohland, E. Orton, A. Scheid, H. A. Seger, F. Kraze, etc., to refer plasticity to the hydration of the clay mols. have not been very successful because no direct relation has been observed between the plasticity and the water of hydration *per se*. It is, however, noticeable that the greater the plasticity of the clay, the greater the proportion of water required to develop maximum plasticity. Thus, a highly plastic clay may take up 30 per cent. of water before becoming sticky, while less plastic clay requires 20 per cent., and a short clay may become sticky after 10 per cent. of water has been added. O. Ruff contrasted the plasticity obtained by kneading a solid in a viscous fluid—*e.g.* putty—with the plasticity obtained by the concentration of lyophile substances—*e.g.* clays—thus attributing the plasticity of clays to the affinity between the clay particles and the water. E. Bourry, and R. Biedermann and H. Herzfeld showed that liquids like absolute alcohol, ether, petroleum, benzene, turpentine, olive oil, glycerol, etc., do not make dry clays plastic in the same sense that water makes them plastic.

In analyzing the effect of acids, bases, and salts on clays, it is necessary to take adsorption into consideration. The relation of the clay particles to the liquid may be drastically modified when the clay particles contain adsorbed salts, acids, etc. R. C. Purdy specially emphasized the function of adsorbed salts. This, however, does not affect the qualitative explanation of the effects just outlined; nor is it necessary to make any assumption as to the nature of the attractive forces. The gravitational attraction of solid for solid has been neglected because it can be regarded as a constant under these conditions. L. Wolff has built an explanation based on T. Schniedel's application of the gravitational law to molecular attraction. C. Tomlinson made a similar hypothesis. The particles of clay are assumed

to attract one another according to the gravitational law; but any other assumed law of attraction would apply equally well.

The remarkable effects of gum and other mucilages in enhancing the plasticity of clay has been utilized by potters for an indefinitely long time. In 1903, E. G. Acheson patented the use of aq. soln. of the tannins and gallotannins, *e.g.* decoctions of oak-bark, etc.; and in 1918, G. Keppler, and A. Spangenberg patented the use of decoctions of humic acid, peat, etc. These plasticizing agents probably act indirectly by adsorption. The clay particles adsorb the organic colloid, and, judging by results, this probably augments the surface attraction between the particles and the surrounding liquid. The plasticity of china clays, practically free from organic matter, shows that adsorbed organic colloids are not always the source of their plasticity. Clays which have been sodden with ground waters rich in organic matter are usually highly plastic; and those clays which can be shown geologically to have been deposited in swamps and bogs, or which have been in contact with such waters, are usually very plastic unless other metamorphic changes have occurred. Many such clays, however, are not plastic when freshly dug, but they become plastic during weathering. When first mined, some of the clays are hard, but if they be moistened and exposed to sunshine and frost they more or less quickly disintegrate and crumble to fine-grained plastic clays. Clays which are allowed to stand for a long time in contact with moisture become more plastic, or, as the workmen express it, more "buttery." Clays which have been boiled with water also become more plastic. Clays prepared by fast processes—filter-press—are not so "buttery" as when prepared by a slower process—slip-kiln. China clays prepared by the elaborate, apparently primitive Cornish process—by slow sedimentation and slip-kiln—are more plastic than when the process of dewatering the clay is accelerated by filter-press. There is thus an intimate connection between the plasticity of a clay and its past history with respect to water. All this looks as if the clay in contact with water is being hydrated to form a colloidal gel.

Attempts have been made to establish the colloidal theory of plasticity by adding artificially-prepared colloids to feebly plastic clays. A. S. Cushman, for example, found that when colloidal silica is added to such a clay, the air shrinkage and the tensile strength of the clay are increased, but not the plasticity; but with colloidal alumina, neither the air shrinkage nor the tensile strength were increased but the plasticity was augmented. F. F. Grout, however, pointed out that unlike the plasticity of clays, the plasticity acquired by the addition of colloidal alumina is lost when the clay is dried. Similar remarks apply to the colloids prepared by precipitation from a mixed soln. of alum and water-glass. If the plasticity of clays is due to the presence of a colloidal aluminosilicate, it is therefore necessary to assume that it is due to a form which has not yet been recognized. J. Stewart assumed that an organic aluminium component is *the* colloid, but this is unlikely. From his study of the action of acids and alkalies on the colloidal fractions of clay, R. Bradfield inferred that *the* colloid is a complex aluminosilicate and not a mixture of hydrated oxides. The properties of T. Schloesing's *l'argile colloïdale* simulate, in a highly exaggerated form, the behaviour of clays on drying, and it is probable that the colloid plays an important part in the drying of clay. The "felting" action *per se* of the particles of the drying clay is scarcely an adequate explanation of the comparatively high tenacity of dried clays. The impermeability of wet puddled clay to water is also difficult to understand on the "felting" hypothesis *simpliciter*.

Clay suspended in water is negatively charged. W. S. Jevons,[57] and W. Durham said that the electrification is excited by the friction of the clay particles falling in the water, and the water in the vicinity acquires an equal and opposite charge. Hence water and clay are mutually attracted. The latter said that the dissipation of the charge is prevented by the non-conductivity of the water. In the presence of acids or salts the water becomes a good conductor, the charges are neutralized,

and the clay settles. This does not explain the action of peptizing agents which make the water a good conductor and yet keep the clay in suspension—*vide* **3.** 23, 8. The acceleration of the sedimentation of clays by electrification whereby the clay is deposited on the anode has been discussed in connection with hydrated silica. The action has also been examined by A. V. Bleininger and C. S. Kinnison, R. D. Kleeman, A. Muentz and H. Gaudechon.

**Some chemical properties of clays.**—According to F. Cornu,[58] moist kaolinite reacts more or less acid to litmus. H. F. Kriege studied the rate of chlorination of different clays when mixed with carbon and heated in chlorine gas. According to R. van der Lieden, china clay from Zettlitz is slightly soluble when shaken with distilled water at room temp., but it is possible that a colloidal suspension was mistaken for a soln., or the clay was impure, and it is doubtful if china clay is really soluble in water. The attempts made to find the constitution of kaolinite by the action of acids and alkali-lye have been previously discussed; and the action of sulphuric acid in connection with the preparation of alum—**5.** 33, 20. H. St. C. Deville [59] examined the solubility of china clay in soda-lye; and he also found that the clay is decomposed by hydrofluosilicic acid (*q.v.*) so that alumina passes into soln. He also removed iron and pyrites from clays by means of hydrochloric acid. China clay is slightly soluble in acetic and hydrochloric acids at ordinary temp.; the former dissolved 1·26 and the latter 0·34 per cent. China clay is still more soluble in hydrochloric or nitric acid at the b.p. when the former dissolved 3·91 and the latter 1·37 per cent. More alumina is dissolved than silica so that the clay is partially decomposed by the acid. Hot conc. sulphuric acid breaks down the clay completely and aluminium sulphate can be obtained from the soln. The action of sulphuric acid was considered by S. Kasai. If the china clay has been heated at temp. between 500° and 800°, it becomes much more soluble in acids. If the calcination be higher than 800°, the solubility again decreases. R. van der Lieden studied the action of acetic acid. The solubility curve of kaolinite calcined at different temp., Fig. 118, is by A. M. Sokoloff. Alumina also becomes much more soluble after it has been preheated to between 500° and 800°, and less soluble after heating above 800°. The solubility curve for alumina alone is analogous to that for china clay at these temp. A. Gyemant studied the ionic conc. of china clay in soln. of sodium chloride; and R. Bradfield measured the H·-concentration of colloid clay. K. D. Glinka studied the action of boiling soln. of potassium hydroxide. J. Lemberg, and S. J. Thugutt found that with a soln. of sodium carbonate, cancrinite is formed; with potassium carbonate, a potassium aluminium silicate; and with a soln. of sodium silicate, analcite is produced. H. Schneiderhölm studied the action of various salt soln. on china clay. J. H. Davidson, and W. E. S. Turner studied the solubility of clay in molten glass, and G. V. Wilson showed that crystals of felspar, magnetite, and biotite may be formed in the soln. W. E. S. Turner and co-workers studied the action of fused glasses on fireclays. The disintegrating influence of furnace gases—*e.g.* carbon monoxide—on firebricks was investigated by B. M. O'Harra and W. J. Darby, T. Holgate, F. Firmstone, J. Pattinson, L. Bradshaw and W. Emery, J. W. Mellor, C. E. Nesbitt and M. L. Bell, R. M. Howe, L. P. Ross, and A. C. Fieldner and co-workers. The absorption of sulphurous gases by clays was studied by F. G. Jackson; and the adsorption of ammonia from the atmosphere, by J. Bouis, and M. Faraday. For the action of the vapours of ammonium or sodium chloride, *vide* silica. H. Ota and M. Noda found that china clay does not show the indophenol reaction. The polymerizing

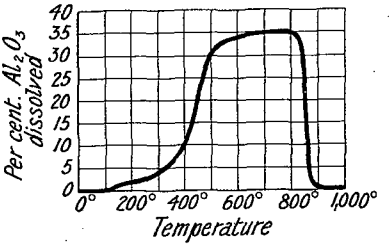



FIG. 118.—Hydrochloric Acid Solubility of Kaolinite Calcined at Different Temperatures.

effect of healed clay on some unsaturated hydrocarbons was discussed by S. W. Lebedeff and E. P. Filonenko, and L. G. Gurvitsch. H. Freundlich and F. Oppenheimer found that the presence of particles of china clay increased the rate of crystallization of water, and various aq. soln. The subject was also studied by A. Brann and co-workers.

R. N. Brackett and J. F. Williams [60] found a soft white mineral, occurring as plates or leaves resembling mountain leather, in the sandstone of the Blue Mountain, Arkansas. They called the mineral **rectorite**—after E. W. Rector. The folia are flexible and inelastic, separating with an easy cleavage; and they are softer than talc. The crystals are possibly monoclinic; they are biaxial, and have the optical axial angle $2E=5°–20°$. The refractive index is low. The composition of the mineral dried at 110° is $Al_2O_3.2SiO_2.H_2O$. F. W. Clarke wrote $Al_3(SiO_4)_3H_3$. The mineral is sometimes stained with iron oxide. R. N. Brackett and J. F. Williams also found at Sneed's Creek, Newton, Arkansas, soft compact masses of a white powder which they called **newtonite.** The powder consists of minute rhombs with angles 88°–89°. The extinction is parallel to the diagonals of the rhombs, and the crystals are thought to belong to the trigonal system. The composition approximates $Al_2O_3.2SiO_2.5H_2O$. F. W. Clarke wrote $Al(OH)_2(H_3SiO_4)$. The sp. gr. is 2·37. Newtonite resembles halloysite in many respects. It is slightly soluble in hydrochloric acid; decomposed by sulphuric acid with the separation of gelatinous silicic acid; decomposed by boiling soda-lye, leaving a residue insoluble in hydrochloric acid. These two minerals have not been closely investigated, and their relation to the better-known hydrated aluminium silicates remains to be elucidated.

P. Termier [61] described a clay-like, colourless or brown mineral which he called **leverrierite**—after U. J. J. Leverrier. Analyses made by A. Carnot, P. Termier, and E. S. Larsen and E. T. Wherry, do not agree. P. Termier gave $Al_2O_3.5SiO_2.5H_2O$, as the best representative value; W. Vernadsky gave $Al_2O_3.2SiO_2$, corresponding with calcined kaolinite. Leverrierite occurs in vermiculate aggregates in the black shales of the Departments de la Loire, France. The crystals are hexagonal prisms—possibly rhombic. The form and twinning resembles that of the micas. The sp. gr. is 2·3–2·598; the hardness 1·5; the indices of refraction $\alpha=1·554$, and $\gamma=1·582$; the dispersion $\gamma-\alpha=0·028$; and the optical character is negative. E. S. Larsen and E. T. Wherry gave $\omega=1·470$, and $\epsilon=1·515$. F. W. Clarke, and E. S. Larsen and E. T. Wherry regard the group of minerals leverrierite, batchelorite, kryptotile, and delanouite as belonging to the same family—probably the micas. According to W. F. Petterd, **batchelorite** is a green, foliated, clay-like mineral from the Mt. Lyell mine, Tasmania, which was named after W. T. Batchelor; its composition approximates to that of rectorite: $Al_2O_3.2SiO_2.H_2O$.

There is usually a difficulty in assigning formulæ calculated from the analyses of the hydrated aluminium silicates because the minerals are so often contaminated with silicic acids, aluminium hydroxides, etc. These hydrates are often colloidal or amorphous. Many of them have been given specific names owing to trifling and accidental differences such as the occurrence in a different locality, or a variation in the colour, state of aggregation, etc., without any attempt being made to correlate the essentials with those of other known minerals. This may be due to excessive zeal in the discovery of new minerals. To the onlooker of descriptive mineralogy it would appear as if the co-ordination of facts has not always been kept in view as the ultimate goal. The colloidal hydrated aluminium silicates have generally been formed by the weathering of crystalline aluminosilicates to which they are related much as china clay is related to felspar. Many of the hydrated aluminium silicates are mixtures of the hydrogels of silica and alumina, and many of them have been artificially synthesized by the simultaneous precipitation of these two gels from aq. soln. of their salts. J. Splichal [62] measured the refractive index of various mixtures of the hydrogels of silica and alumina after calcination, and found for the $SiO_2 : Al_2O_3$ ratio:

| $SiO_2 : Al_2O_3$ | 0·9 : 1 | 1·9 : 1 | 2·8 : 1 | 4·3 : 1 | 6·5 : 1 |
|---|---|---|---|---|---|
| Ref. index | 1·580–1·595 | 1·535–1·545 | 1·520–1·535 | 1·495–1·505 | 1·48–1·49 |

when 1·68 was obtained for alumina alone, and 1·480–1·485 for silica alone. The

three minerals halloysite, allophane, and montmorillonite may be regarded as types of colloidal or gel minerals. P. Groth, for instance, suggested that allophane and montmorillonite are "loose" compounds of colloidal silicic acid and colloidal aluminium hydroxide, and S. Kasai found that mixtures of these two gels have properties like those of allophane. The work of B. Aarnio, F. Cornu, R. Gans, T. A. Nikolajewsky, H. Stremme, and G. Wiegner shows that these minerals are adsorption compounds of silica gel and alumina gel, although S. J. Thugutt, and E. Löwenstein hold the view that they are definite compounds.

H. le Chatelier examined the thermal changes which occur when halloysite, allophane, and montmorillonite are heated, and considered that each curve is specific and characteristic. J. W. Mellor showed that the heating curves of all three minerals are the same if allowance be made for the presence of kaolinite impurities, and for small variations in the position of the critical points due to differences in the lag determined by differences in the rates of heating. A terrace in the heating curve at about 150° is a characteristic of colloidal silicates and silicic acid; a terrace at about 500° is characteristic of kaolinitic clays (kaolinite or clayite); and a hump in the curve at about 900° is characteristic of alumina (Figs. 51–5, 33, 10) and of aluminium silicates, which are assumed to have broken down at some lower temp. into free silica and free alumina (Figs. 119–120, *vide supra*). Variations in sp. ht.,

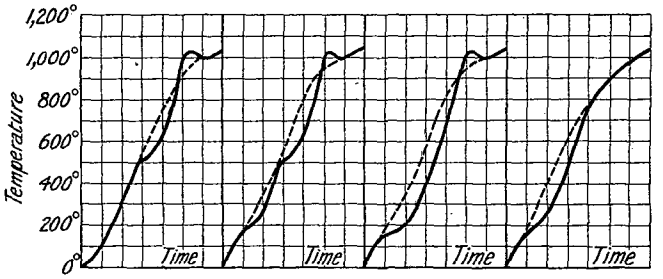



FIG. 119.—Crystals of Kaolinite.

FIG. 120.—China Clay (Clayite and Kaolinite).

FIG. 121.—Halloysite, Allophane, and Montmorillonite.

FIG. 122.—Silicic Acid.

thermal conductivity, and compactness of the mineral may produce small variations in the positions of the singularities on the heating curves. There is no terrace at 500° with silicic acid, opal, aluminium hydroxide, halloysite, allophane, indianite, lenzinite, schrötterite, collyrite, smectite*, montmorillonite, severite*, cimolite* razoumoffakite*, anauxite*, and confolensite*. Those marked with an asterisk showed a faint terrace, presumably owing to the presence of impurities; and all of them showed the colloid terrace near 150°, and the alumina hump near 900°. This is in agreement with H. Stremme's suggestion that halloysite, allophane, and montmorillonite are mixtures of hydrogels of silica and alumina; and not chemical individuals. With these views of the nature of these hydrates, the graphic formula representing them as alumino-silicates lose their significance. Summarizing these results, the heating curve of these hydrated aluminium silicates has

| | | | |
|---|---|---|---|
| Hump at 900° | Terrace near 500° | No terrace about 150° | Kaolinite. |
| | | Terrace about 150° | Clayite. |
| | No terrace near 500° | Terrace about 150° | Halloysite, etc. |

The so-called *clay-base* or *clay substance* may contain one or more of these constituents.

P. Berthier[63] described a friable hard mineral from Angleur, etc., which he called **halloysite**—after J. B. J. d'Omalius d'Halloy, who first noticed the

mineral. Its colour is white, grey, bluish-green, yellow, red, or brown according to the nature and proportion of impurities which are present. The more pure varieties are sometimes translucent particularly near the edges, and the translucency is more pronounced when the mineral is wet. Halloysite occurs massive and earthy. It has a soapy feel. The sp. gr. ranges from 1·92–2·20; and P. Philipenko gave 2·45 at 19°. The hardness is 1–2, and P. Philipenko gave 2·5–3. J. Splichal gave for the index of refraction 1·54–1·57, and after calcination, 1·555–1·595.

Analyses of halloysite were reported by P. Berthier, P. A. Dufrénoy, P. Philipenko, F. Ostwald, V. Monheim, C. Sauvage, M. Thomson and M. Binney, H. le Chatelier, R. Helmhacker, F. Pisani, C. F. Rammelsberg, C. von John, F. W. Clarke and T. M. Chatard, M. F. Heddle, D. Pedro, F. Koch, F. L. Ransome, E. S. Simpson and C. G. Gibson, A. F. Rogers, and H. Stremme. The results are divergent, but the best representative value approximates to $Al_2O_3.2SiO_2.nH_2O$, with $n$ varying from 3 to 5, usually nearer 3. An air-dried sample from Styria contained 22·42 per cent. of water of which 9·43 per cent. was lost at 110°, and the remainder was lost as the temp. rose gradually above 300°. Air-dried halloysites from various localities were found by A. Lacroix to have from 17·6 to 26·5 per cent. of water. The possible constitutional formulæ are as varied as in the case of kaolinite. E. S. Larsen and E. T. Wherry regard halloysite as an amorphous mineral corresponding with kaolinite, but holding extra water either by adsorption or capillarity. As an example of a possible constitution, assuming that halloysite is a chemical individual, the following may be quoted, $O : Al.O.Si(OH)_3$. H. le Chatelier found that halloysites lost between 3·5 and 12·5 per cent. of water when heated to 250°. The heating curve shows a rapid evolution of water between 150° and 200°, Fig. 121, and the residue has the composition $Al_2O_3.2SiO_2.2H_2O$, the same as kaolinite; but the loss of the remaining water at about 500° does not show the kaolinite terrace. There is the alumina hump at about 900°. H. le Chatelier believes that the sedimentary clays do not contain kaolinite, but rather halloysite. J. W. Gregory, and D. P. McDonald adopted a similar hypothesis. J. W. Mellor showed that the results are better interpreted by assuming that these clays contain colloidal kaolinite, *i.e.* clayite, because the heating curves have the kaolinite terrace at about 500°. E. Löwenstein found that when confined at 25° over sulphuric acid of vap. press. $p$ mm. of mercury, the molar loss of water for equilibrium was as follows:

| $p$ | 23·55 | 19·60 | 13·45 | 4·41 | 0·56 | 0·18 |
|---|---|---|---|---|---|---|
| Halloysite | 0 | 0·25 | 0·91 | 2·32 | 3·34 | 3·44 |
| Collyrite | 0 | 0·14 | 0·42 | 0·71 | 0·98 | 1·14 |
| Montmorillonite | 0 | 1·05 | 1·93 | 3·41 | 4·74 | 5·16 |

J. W. Mellor and co-workers obtained analogous results with halloysite. A. B. Dick found the refractive indices of the opaline halloysites ranged from 1·522 to 1·544. When boiled in water, and afterwards dried spontaneously in air, their refractive indices were not changed; but if dried for a fortnight at ordinary atm. press., over conc. sulphuric acid, the refractive index rose to 1·555. Dry air decomposes the minerals because, when placed in damp air for some days to regain the lost water, they do not regain their original refractive index. There are some museum specimens of halloysite with a refractive index a little over 1·56. They have a cryptocrystalline structure and a faint double refraction. A. B. Dick said that these specimens may be kaolinite or restormellite, or an alkaline earth silicate. J. Splichal gave 1·54–1·57 for the refractive indices of the halloysites from Angleur, Belgium, and Radzionkow, Silesia; and after ignition, 1·555–1·595. Halloysite is partly decomposed by cold conc. hydrochloric acid, and completely decomposed by the boiling acid. Similarly also with sulphuric acid.

A. Breithaupt called ordinary compact halloysite from Angler, *galapectite*, and a dense gum-like variety which does not adhere to the tongue, *gummite*. A gum-like clay from Budapest was called halloysite by F. Koch. P. A. Dufrénoy's *argile chimique* is probably halloysite. A compact, earthy, white, translucent variety of halloysite from La Vilate, France, was called by J. F. John, *lenzinite* or *lenzite*—after D. G. J. Lenz; its composition

is $Al_2O_3.2SiO_2.3H_2O$; and a brownish variety from Call, Eifel, had a composition $3Al_2O_3.5SiO_2.11H_2O$. C. C. von Leonhard regarded it as a decomposed semiopal. It is said not to gelatinize with acids. For the heating curve, *vide* Fig. 121. The term lenzinite has also been applied to white clay with a large proportion of silica. The lenzinite from St. Sévére was called by F. S. Beudant *séverite*. It was analyzed by J. Pelletier; and discussed by C. von Hauer. For the heating curve, *vide* Fig. 121. A white clay with a conchoidal fracture from Lawrence, Indiana, resembling halloysite, was called by E. T. Cox *indianite*. The sp. gr. is 2·31–2·53, and the hardness 2–2½. Indianite was discussed by W. N. Logan, A. M. Gibson, H. A. Wheeler, etc. For the heating curve, *vide* Fig. 121. The term indianite has been also applied to a brown anorthite from India. A white or yellowish-white earth from Bergenrsreuth, Bavaria, was called by A. Breithaupt *glagerite*—from γλαγερός, milk coloured. There are two varieties, one is earthy, with a sp. gr. 2·355, and a composition $2Al_2O_3.3SiO_2.6H_2O$; the other is compact, with a sp. gr. 2·331, and a composition $2Al_2O_3.2SiO_2.6H_2O$. Glagerite was analyzed by J. F. John, and A. Sajtzeff. A. B. Dick gave 1·544 for the refractive index. J. Fikenstein found that A. Breithaupt's glagerite is halloysite. A variety of halloysite from Condé-sur-Végre, France, was called by A. Salvétat, *smectite*—from σμηκτις, detersive earth. It has a greenish colour, and a greasy appearance; and in certain states of humidity appears almost transparent and gelatinous. It was examined by L. A. Jordan. For the heating curve, *vide* Fig. 121. A. Breithaupt applied the term smectite to a kind of fuller's earth from Styria. C. U. Shepard called a milk-white variety of halloysite from Dade, Georgia, *glossecollite*. It was analyzed by F. Pisani. M. Thomson and M. Binney applied the term *pseudosteatite* to an impure green halloysite from Bathgate, Scotland. A white or bluish-white earth obtained at Nertschinsk was called *nertschinskite* by E. F. Glocker, who considered it to be a variety of lenzite. E. Tietze called a white earth from Maidanpek, Serbia, *milanite*. An opaque milk-white slightly lustrous clay from the red sandstone on the banks of the Tweed, Scotland, was called by T. Thomson *tuesite*—from the Latin *Tuesis*, the Tweed. C. F. Rammelsberg gave a number of analyses. The sp. gr. is 2·434–2·624. P. A. Dufrénoy, J. Nicol, and J. W. Gregory regard tuesite as a variety of halloysite. It is amorphous and practicallly isotropic.

Cimolian earth referred to by Theophrastus [64] as κιμωλία; by Pliny as *cimolia*; and by M. H. Klaproth as *cimolite*, is a greyish-white clay when freshly dug, but it acquires a reddish tint on exposure to air. It was originally obtained from Kimlos, *i.e.* the island of Argentiera, and a similar earth has been reported from other localities. Cimolian earth has a slaty fracture; and is difficult to powder. E. Dittler and J. E. Hibsch gave $2Al_2O_3.9SiO_2.6H_2O$ for the formula. Cimolite is a structureless powder. Its sp. gr. is 2·18–2·30. It sticks to the tongue, and on immersion in water, it splits into flakes and forms a cream-like slip when ground with water. In this form it has been used for removing oils and fats from wool and silk. Analyses were reported by M. H. Klaproth, C. F. Rammelsberg, R. B. Riggs, F. W. Clarke, R. Scharizer, and A. Liversidge; the results are not concordant; the average approximates $2Al_2O_3.9SiO_2.6H_2O$. The mineral is probably a mixture of the hydrogels of silica and alumina. For the heating curve, *vide* Fig. 121. F. W. Clarke gave for cimolite, $Al_4(Si_3O_8)_3.6H_2O$. A. Breithaupt described a greenish-white cimolite in the weathered basalt of Bilin, Bohemia, which he called *anauxite*—from ἀναύξης, not softening—in allusion to its behaviour in the blowpipe flame. Its sp. gr. is 2·26; E. Dittler and J. E. Hibsch gave 2·524. It was analyzed by C. von Hauer. E. Dittler and J. E. Hibsch gave the formula $3Al_2O_3.10SiO_2.8H_2O$. They say the crystals are rhombic and unlike those of kaolinite. The heating curve is shown in Fig. 121. The *pelikanite* of N. Ouchakoff is a mixture of cimolite and quartz found at Kieff, Russia. The *hunterite* of S. Haughton is a similar earth.

J. J. Nöggerath described a rose-red earth from the trachyte of the Siebengebirges which he called *ehrenbergite*. It is almost gelatinous when freshly dug, and it becomes fragile and pulverulent when dried. It swells up like boiled starch when placed in water. W. C. Knight [65] discovered a soft fine-grained clay in the Benton formation of Wyoming, and he first named it *taylorite*—after W. Taylor—but the name was afterwards altered to **bentonite** when it was found that taylorite was already in use for something else. The mineral was also reported in other localities by N. H. Darton, C. E. Siebenthal, etc. In some respects bentonite resembles ehrenbergite. It is supposed in some cases to have been formed by the weathering of labradorite; in other cases, as shown by E. T. Wherry, and C. S. Ross and E. V. Shannon, it is considered to be derived from volcanic ash which has sometimes been reworked and mixed with detrital matters. Often it is made up of varying proportions of volcanic rock, phenocrysts, and a devitrification product of glass. There are, however, several varieties probably derived from different sources. The composition approximates $Al_2O_3.6SiO_2.5H_2O$. H. G. Schurecht and H. W. Douda consider that bentonite is a mixture of colloidal silicates and fine-grained kaolinite. The colour when freshly dug is yellowish-green, which changes to a pale cream on exposure to air. The sp. gr. is 2·132–2·180. When placed in water some varieties absorb more than three times their weight or up to eight times their own volume of water, swelling considerably, and producing a jelly-like mass which recalls some of the adhesive pastes. According to W. A. Nelson, when bentonite is boiled with sulphuric acid, nearly all the alumina passes

into soln. Bentonite has been used in the manufacture of soap, as a filler for paper, as a sizing for yarn, as a diluent for certain drugs, and as a raw constituent of glazes to help in keeping the materials suspended in water. Numerous possible uses have been suggested. It has high adsorptive powers resembling those of diatomaceous earth. H. F. Coward found bentonite is a typical negative suspensoidal colloid in that the particles are negatively charged, and the charge decreases with increasing quantities of electrolytes—acids, alkalies, or salts—until, with a sufficient concentration, the whole is sedimented in a gelatinized form. The flocculation is reversible.

Many kinds of clay-like substances have been called **fuller's earth**, in allusion to the fact that they have long been used for " fulling " or removing grease from woollen goods. Fuller's earth corresponds with the description of the *creta cimolia* or *cimolian earth* of Pliny's *Historiæ naturalis* (**17.** 4; and **35.** 57). The earth was used by the Romans for scouring cloth. The Metilian Law of the Romans had to do with the *ars fullonia*. In ancient times, the cloth was washed by stamping it with water and *creta fullonia* which acted partly by scouring and partly by absorbing greasy dirt. According to J. Beckmann,[66] the mill where cloth was scoured as it came from the loom was formerly called *fullencium*, or *molendium cum fullione*. A. G. Werner, L. A. Emmerling, etc., called a clay of this kind *Walkererde*, *Walkthon*, or *Walkerde*; A. J. M. Brochant, *la terre à foullon*; J. G. Wallerius, *smectis*; R. J. Haüy, *argile smectique*; and A. Breithaupt, *walkerite*, *smectite* (*vide* halloysite), and *malthacite*. Fuller's earth has been worked in Great Britain for very many years—at Reigate and Nutfield, Surrey; Bath, Somerset; etc. Various other occurrences have been reported by J. Woodward, J. C. Branner, A. E. Fersmann, A. H. Cox, G. M. Davies, J. Middleton, H. D. Miser, P. G. Morgan, F. J. Bennett, H. Ries, H. K. Shearer, R. Tate, D. J. Day, A. C. G. Cameron, J. T. Porter, T. W. Vaughan, E. H. Sellards and H. Gunter, L. E. Aubury, A. Duessen, W. C. Alden, O. Veatch, E. Sloan, etc. In the eighteenth century, a special Act was passed prohibiting its export from England; after the repeal of the Act, England was the chief producer for the world, but in recent years has been outstripped by the United States. The mining of fuller's earth is like that of other clays. The earth may or may not be washed by levigation as in the case of china clay. In the washing, the earth remaining suspended in water after the grosser impurities have settled, is finally dried in kilns. The drying temp. must be low, or the adsorbent qualities are impaired. The preparation of fuller's earth for the market was described by H. B. Woodward, W. C. Phalen, A. C. G. Cameron, C. L. Parsons, etc.

The first analysis was made by T. Bergman, and analyses were afterwards reported by M. H. Klaproth, T. Thomson, R. Sachsse and A. Becker, H. B. Woodward, P. G. Sanford, H. Ries, J. Brierley, L. A. Jordan, J. T. Porter, etc. The results range from 44·00–72·00 per cent. $SiO_2$; 5·00–33·38, $Al_2O_3$; 4·89–24·95, $H_2O$; 1·26–14·87, $Fe_2O_3$; 0·33–7·40, CaO; 0·43–4·36, MgO; alkalies, 0·45–5·00; with small amounts of organic matter $SO_3$, $P_2O_5$, and $TiO_2$. The variations in composition are so great that analysis alone does not determine whether a particular clay is to be classed as a fuller's earth. Fuller's earth contains hydrated aluminium silicates, incompletely decomposed mineral matters, and various detrital minerals. The petrology of fuller's earth has been discussed by A. H. Cox, and T. Crook. H. Ries said that hydrated silica is usually present. A. Breithaupt supposed *smectite*, $Al_2O_3.7SiO_2.12H_2O$, and *malthacite*, $Al_2O_3.7SiO_2.16H_2O$, to be primary constituents. The conclusion, however, is not very convincing. The origin of fuller's earth has not been elucidated. H. Credner said that while kaolinitic clays are derived from the decomposition of felspathic rocks, fuller's earth is probably derived from hornblende, amphibole, and augite rocks—*e.g.* gabbros, diorites, diabases, and basalts.

The colour of fuller's earth may be white, grey, green, or brown. It does not adhere to the tongue and it softens when placed in water. The sp. gr. ranges from 1·9–2·1. Some fuller's earths have an acid reaction, others are neutral. The so-called *Kambara clay* of Japan is like an acidic fuller's earth. Its properties were described by K. Kobayashi and S. Veno. The adsorbent quality of fuller's earth is determined by the constituent colloidal aluminium silicates. Most of the fuller's earths contain much water, but, as C. L. Parsons showed, some of the earths adsorb as well after the water has been expelled as they did before; others have their adsorbent power much weakened. Although still used as a kind of *argile savonneuse* in cleaning cloth, washing woollens, and fine-dyed goods, fuller's earth is still more extensively employed in refining oils, fats, lard, etc. J. E. Gilpin and O. E. Bransky found that the selective adsorption by fuller's earth is greatest for oils of high sp. gr. and viscosity, for unsaturated hydrocarbons, and for sulphur compounds. E. K. Rideal and W. Thomas believe that with the earths from Surrey, Somerset, and Florida, the adsorption of methylene blue from aq. soln. is approximately proportional to the sp. surface of the earths, while the catalytic activities in decomposing hydrogen dioxide are not dependent on the adsorption and may depend on the iron content. The specific adsorbent qualities of fuller's earth have been discussed by V. F. Herr, J. E. Gilpin and co-workers, L. G. Gurvitsch, D. Wesson, W. R. Jewell, T. G. Richert, A. Seidell, C. L. Parsons, J. J. Vollertson, etc. A little is used as a pigment for wall-papers, and the finest grades in toilet preparations.

F. Stromeyer and J. F. L. Hausmann[67] applied the term **allophane** to a mineral

occurring in cavities in a marl near Saalfeld, Thuringia. The name is derived from ἄλλος, other; φαίνεσθαι, to appear, in allusion to the change in the appearance of the mineral before the blowpipe flame. A. Breithaupt called it *riemannite*. Allophane is a hard, brittle, opaque, non-crystalline earth; the edges of the fragments are sometimes translucent. The colour may be white, but more commonly sky-blue, green, red, or brown. The fracture is conchoidal, and the lustre vitreous. The sp. gr. is 1·89–2·02. J. Splichal gave for the index of refraction 1·480–1·490; and after calcination, 1·505–1·570. The mineral has been found in different localities and described by W. D. Herman, J. Morris, J. Prestwich, R. H. Chandler, G. vom Rath, P. Berthier, A. B. Northcote, C. T. Jackson, B. Silliman, etc. Analyses were reported by F. Stromeyer, F. A. Walchner, J. Guillemin, R. Bunsen, P. Berthier, A. B. Northcote, B. Silliman, C. T. Jackson, E. F. Smith, J. Gamper, A. F. Rogers, C. F. Rammelsberg, F. Kretschmer, G. d'Achiardi, S. Kasai, A. Nikolavsky, etc. The results approximate to $Al_2O_3.SiO_2.nH_2O$, where $n$ may be 4, 5, or 6. F. W. Clarke gave $\{Al(OH)_2\}_2H_2SiO_4.3H_2O$, or, analogously to andalusite, $Al_2(SiO_4)_2.\{Al(OH)_2\}_2.12H_2O$. According to S. J. Thugutt, and H. Stremme, the mineral is probably a mixture of the hydrogels of silica and alumina. For the heating curve, *vide* Fig. 121. J. Splichal found the refractive indices of samples of allophane from Hromice, Bohemia; Bogsan, Banat; and Borovec, Moravia, to range from 1·480–1·490 before calcination, and after calcination, 1·505–1·570. Allophane is partly decomposed by cold conc. hydrochloric acid, and completely decomposed by the boiling acid. H. Schneiderhölm studied the action of various salt soln. on allophane; and R. van der Lieden, the action of acetic acid.

The blue variety looks like a copper ore, and presumably contains chrysocolla; the green variety contains malachite. C. Schnabel found a sample with nearly 19 per cent. CuO; and the yellow and brown varieties, iron oxides or hydroxides. B. Silliman found a sample with admixed gibbsite. The yellow variety from Kornwestheim contained aluminite, and M. van Groningen and A. Oppel called the mineral *siliceous aluminite*; L. Muck designated a similar variety from Schwelm, Westphalia, *sulphatallophane*; and L. Bombicci named a variety from Mt. Vocchio, Sardinia containing a little lead, *plumb-allophane*. A. L. Sach found a reddish allophane at Friesdorf, Bonn, and called it *elhuyarite*; it was described by E. F. Glocker, and R. Bunsen. F. L. Sonnenschein applied the term *carolathine*—after Prince Carolath—to a yellow allophane from Zabrze, Silesia. The white or yellow allophane found by J. D. Dana as stalactites and stalagmites in the lava caverns on the island of Upolu, Samoa, was styled *samoite*. F. W. Clarke gave the formula $Al_2(SiO_4)_3.12H_2O$. V. von Zepharovich reported a ferruginous variety. J. D. Dana considered that the samoite of B. Silliman is probably a labradorite.

D. L. G. Karsten [68] employed the term *collyrite*, for the white clay which he found near Schemnitz, Hungary, because it agrees well with Dioscorides' description of the Samian earth κολλύριον, and Pliny's *collyrium*. J. C. Freiesleben called it *Salpeter*, and M. H. Klaproth, *natürliche Alaunerde*. Collyrite is very like allophane in its general properties. Occurrences were reported by W. V. Vernon, A. Brongniart, J. C. G. de Marignac, J. Jacobson, etc. Analyses of collyrite were made by M. H. Klaproth, P. Berthier, C. M. Kersten, and J. H. and G. Gladstone. The best representative value is $2Al_2O_3.SiO_2.9H_2O$—F. W. Clarke gave $(AlO)_4.SiO_4.6H_2O$. It is probably a mixture of the hydrogels of silica and alumina. G. Vogt regarded the clay of Hesdain, France, as a mixture of 30 per cent. allophane and 70 per cent. kaolin. H. le Chatelier called the same clay collyrite. The collyrite found at Scarborough, Yorkshire, was called by W. V. Vernon, *scarboroite*; its nature was discussed by J. F. L. Hausmann. A greenish or yellowish clay resembling allophane, and found by A. Schrötter near Freienstein, Styria, was called *opaline allophane*; E. F. Glocker named it *schrötterite*. It was analyzed by A. Schrötter, and J. W. Mallet. Its composition is variable, for the ratios $Al_2O_3 : SiO_2 : H_2O$ range over 8 : 3 : 30, 7 : 3 : 36, and 5 : 2 : 20. The index of refraction is 1·584. F. Zambonini regarded a sample from Saalfeld as a mixture of $3(Al_2SiO_5.8H_2O)+8Al(OH)_3$; and R. Helmhacker believed a sample from Freienstein to be a mixture of halloysite and variscite. F. W. Clarke gave the formula $\{Al(OH)_2\}_4SiO_4.6H_2O$. The heating curves—Fig. 121—show that collyrite is a mixture of the hydrogels of silica and alumina. The vap. press. of collyrite is indicated above.

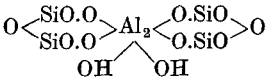
A. Salvetat [69] found a rose-red clay in pockets in the brown clay of Montmorillon, France, and he called it **montmorillonite**. The clay was reported from

other localities, and analyses have been made by A. Damour, L. Azénma, A. von Fersmann, D. Lovisato, H. Leitmeier, C. von Hauer, H. le Chatelier, R. Helmhacker, H. L. Wells, C. S. Ross and E. V. Shannon, and J. H. Collins. The analyses are not conçordant, but the best representative value is $Al_2O_3.4SiO_2.9H_2O$. The heating curve—Fig. 121—indicates that montmorillonite is a mixture of the hydrogels of silica and alumina. J. Splichal gave for the indox of refraction 1·50; and after calcination, 1·510–1·525. H. Leitmeier kept the isotropic hydrogel from Zogora, Bulgaria, for three years when it had acquired a feeble birefringence, indicating that it had become crystalline, with an index of refraction 1·51. This may be a chemical individual, or a solid soln. of silicic acid and of a simpler aluminium silicate. The vap. press. of montmorillonite has been indicated above. According to A. Salvetat, an aq. soln. of sodium carbonate dissolves a little silica from montmorillonite; the mineral is partially decomposed by cold, conc. hydrochloric acid, and completely decomposed by the boiling acid.

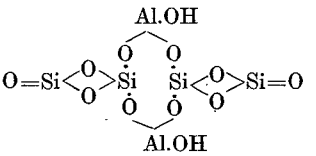
A number of varieties have been reported. A pale rose variety found at Confolens, and St. Jean-de-Cole (Thiviers), was called *confolensite* by A. P. Dufrénoy. It was analyzed by P. Berthier, and A. Salvetat. For the heating curve, *vide* Fig. 121. G. A. Kenngott, and C. von Hauer described a variety from Millac, France, and called it *delanouite*. It is rose-red when freshly dug, but the colour darkens on exposure to air. A. des Cloizeaux described white, yellow, or green varieties from Virolet, and Poitiers, France; and he called this mineral *steargillite* or *steatargillite*. A yellowish clay, resembling steargillite, found in the basalt of Stolpen, Saxony, was called *stolpenite*, or the *bole of Stolpen*, by G. A. Kenngott, C. F. Rammelsberg, A. von Fersmann, D. Lovisato, and C. F. Naumann, T. Thomson called a yellowish-red clay from Giant's Causeway, Ireland, *erinite*—from *Erin*, Ireland. A white or mottled green clay from the serpentine of Frankenstein and Kosemutz, Silesia, was called *razoumovskyn* by J. F. John and J. Zellner. R. Helmhacker reported a similar bluish clay from Lading, Carinthia. Some calcite and azurite were also present as impurities. For the heating curve, *vide* Fig. 121. J. Nicklès applied the term *saponite* to a white, plastic, soap-like clay occurring in the granite from which issues one of the hot springs at Plombières, France. R. P. D. Graham analyzed a sample from Montreal. C. F. Naumann named a similar clay *smegmatite*. This clay is one of a series called *mountain soap, pierre à savon*, or Bergseife referred to by C. F. Bucholz, H. O. A. Ficinus, and S. J. S. Beckmann. There is also a variety of meerschaum, or soapstone which is the true saponite. S. D. Villarello described what he called *paramontmorillonite* from Michoagan, Mexico, as a mineral with the composition $Al_2O_3.4SiO_2.5H_2O$, or $H_6Al_2Si_4O_{14}.2H_2O$. G. Friedel described a mineral from Miramont, France, which he called *termierite*; its composition approximates $Al_2O_3.6SiO_2.18H_2O$. Its sp. gr. is 1·54; hardness, 2; and index of refraction, 1·403. The partially dehydrated mineral takes up ether, benzene, or methylene iodide; but these are readily displaced by water.

M. H. Klaproth[70] employed the term *agalmatolite* for a talc-like mineral; C. A. G. Napione used *pagodite*, and for the Chinese mineral A. Breithaupt used *gemmahuji*. Some of the agalmatolites are not hydrated aluminium silicates, but rather nephelites, and hydrated magnesium aluminium silicates (*q.v.*). R. Hermann received a sample of the supposed talc from Ural, and showed that it is really an aluminium silicate which he designated **pyrophyllite**—from πῦρ, fire; and φύλλον, a leaf. K. G. Fieldler found a similar mineral at Berjosowsk, Ural. A. Breithaupt proposed to use the term *pyrauxite*—from πῦρ, fire; and αὔξω, to increase—in allusion to its behaviour when heated. The occurrence of pyrophyllite in various localities has been indicated by G. Rose, L. L. de Koninck, L. J. Igelström, H. Sjögren, E. Schumacher, G. A. Kenngott, H. Gorceix, G. J. Brush, F. A. Genth, V. von Zepharovich, R. Helmhacker, M. F. Heddle, W. I. Macadam, A. Frenzel, P. Groth, and F. von Richthofen. Analyses were made by R. Hermann, C. F. Rammelsberg, L. L. de Koninck, H. Sjögren, L. J. Igelström, H. Gorciex, J. L. Smith, G. J. Brush, F. A. Genth, A. H. Church, M. H. Klaproth, J. F. John, E. Walmstedt, M. F. Heddle, W. I. Macadam, C. W. von Gümbel, F. Dewalque, F. W. Clarke, J. Samojloff, J. Morozewicz, J. H. Pratt, T. Löwinson-Lessing, A. Huntzelmann, and A. Damour. The relation between agalmatolite and pyrophyllite was shown by G. J. Brush. The best representative formula was given by G. A. Kenngott, $Al_2O_3.4SiO_2.H_2O$, or $H_2Al_2Si_4O_{12}$, or $HAlSi_2O_6$. Other

formulæ were suggested by J. Morozewicz, and T. Löwinson-Lessing. The latter regarded the pyrophyllite of Pyshminsk as a mixture of pyrophyllite, $3Al_2O_3.11SiO_2.3H_2O$, which is optically negative, and *pseudo-pyrophyllite*, $3MgO.4AlO_2.9SiO_2.8H_2O$, which is optically positive. F. W. Clarke and G. Steiger, and H. C. McNeil proposed $HO.Al:Si_2O_5$; and R. Scharizer, and W. Vernadsky gave respectively:




R. Scharizer's formula.




W. Vernadsky's formula.

K. von Chroustschoff claimed to have obtained a zirconiferous pyrophyllite by heating a mixture of silicic acid, water, alumina, and zirconia to dark redness; and E. Baur, and M. Schläpfer, pyrophyllite, by heating a mixture of silicic acid, alumina, and potassium silicate in an autoclave. Pyrophyllite is a crystalline mineral belonging to the rhombic or monoclinic system. It occurs as a compact mass of small crystalline plates or radiating fibres. It is more or less translucent, and coloured white, grey, yellow, green, or brown. It has a greasy feel, and a dull matte or mother-of-pearl lustre. A. Michel-Lévy and A. Lacroix found the refractive index is 1·58; and the double refraction, 0·041. A. des Cloizeaux showed that the axial angle $2V=62°$; and $2E=110°\ 28'$ at 170, and this diminished with a rise of temp. to 105° 30′ at 135°. The hardness is nearly 1; and the sp. gr., 2·8–2·9. H. le Chatelier observed the variations of temp. when the mineral is heated; and J. W. Mellor's heating curve is indicated in Fig. 123. R. Wohlin, and J. L. Stuckey obtained a similar curve. Pyrophyllite loses an appreciable quantity of water at about 500°; thus after heating 2 hrs. at 500° the mineral lost 0·33 per cent., kaolinite under the same conditions lost nearly all its combined water. The combined water is given off at about 700°. G. Tammann found that when confined over sulphuric acid with a partial press. $p$ of water vap., pyrophyllite lost the following percentage amounts of water:

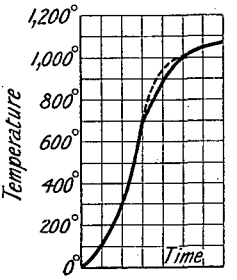



FIG. 123.—The Heating Curve of Pyrophyllite.

| $p$ | 15·72 | 14·55 | 12·48 | 9·11 | 6·05 | 2·93 | 0·11 |
|---|---|---|---|---|---|---|---|
| Loss | 0·000 | 0·027 | 0·035 | 0·039 | 0·050 | 0·059 | 0·060 per cent. |

J. W. Mellor and co-workers obtained higher values. Pyrophyllite swells to twice its bulk when heated. A. Johnsen studied the optical properties of the mineral. E. S. Larsen gave for the indices of refraction $\alpha=1·552$, $\beta=1·588$, and $\gamma=1·600$. F. Cornu found that the moist powder reacts alkaline to litmus. The mineral is but slightly attacked by aq. soln. of sodium carbonate, but, according to F. W. Clarke and G. Steiger, and H. C. MacNeil, when the pyrophyllite has been calcined, about 2·84 per cent. of the silica becomes soluble in that menstruum; and when calcined in ammonium chloride vap., about 6 per cent. becomes soluble. K. D. Glinka studied the action of potassium hydroxide on pyrophyllite. Pyrophyllite is but slightly affected by hydrochloric acid; while sulphuric acid decomposes it with the separation of gelatinous silica. Some varieties of agalmatolite were employed by the Chinese for carving figures; it has also been used for making slate-pencils since it leaves a white trace on slate—hence the name *pencil-stone*.

T. Scheerer[71] applied the term *lardite* to a greenish agalmatolite analyzed by T. Thomson. A light greenish-white variety of pyrophyllite was found by C. W. von Gümbel at Nord-

halben, Oberfranken. The mineral was analyzed by F. von Kobell, and A. Terreil, and named *gümbelite*. C. W. Blomstrand found reddish fibrous aggregates in the pyrophyllite of Vestana, Sweden, and named the mineral *vestanite* or *westanite*. The composition approximates $Al_2O_3.SiO_2.\frac{1}{3}H_2O$, and P. Groth regarded it as a hydrated andalusite. K. F. Peters found a granular microcrystalline mineral in the limestone of Biharberg, Hungary, and named it *biharite*. W. Haidinger considered it to be a variety of agalmatolite. A fibrous variety of agalmatolite was found by T. S. Hunt at Stanstead, Canada, and named *neurolite*—from *νεῦρον*, a fibre or tendon. T. S. Hunt, and T. Thomson analyzed the mineral, and the results show that it approximates in composition to pyrophyllite. A. H. Church described a massive greyish-green agalmatolite-like mineral from the Restormel Mine, Cornwall. He called it *restormelite*. The hardness was 2, the sp. gr. 2·58, and the analysis 45·66, $SiO_2$; 35·10, $Al_2O_3$; 1·11, FeO; 0·85, MgO; 2·30, $K_2O$; 4·39, $Na_2O$; 11·68, $H_2O$.

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## § 36. Pottery

The potter's art has been so universally practised that there is probably no nation, whether barbarous or civilized, which could not contribute some interesting pages to a general history of pottery; whilst in almost every country it would be found that the state of this art at any particular time is a tolerably fair test of the degree of civilization to which its people had attained.—S. W. BAKER.

The potter's art, in its more primitive forms, has been practised from the remotest of prehistoric times in various parts of the earth. Only a few peoples have been found to be unacquainted with the fictile art—*e.g.* the natives of Australia, New Zealand, and some Polynesian islands; the nomadic tribes of Siberia; the natives of the extreme south of South America, and South Africa; and of the north-western region of North America. The art as practised to-day in some parts of Africa represents a very early stage in the manufacture of pottery.

The *fossil pottery* found in the soil of the country from Hanover to Thuringia, and Bohemia, was once thought to grow naturally like truffles in the ground. J. Matthesius,[1] B. A. Balbinus, and others had no doubts and they quoted irrefutable proofs, if such were needed, that these pots, *ollæ fossiles* as B. A. Balbinus called them, were the result of nature's parturient forces. It was argued that to question the fact was nothing short of heresy; did not the Psalms (**139**. 15) refer to " the vessels formed within the earth " ? It was some time before the sceptics were able to show that the *ollæ fossiles* were really cinerary urns from the burial ground of indigenous tribes living in North Germany long before the Roman invasion. These vessels represent an early stage in the manufacture of pottery. According to L. von Ledebur, in 1838, about two thousand pamphlets and books had been written on the cinerary urns of Germany.

Fragments of fired bricks have been found by borings in the Nile basin. From their depth, and assuming that the rate of deposition of the Nile mud has been continuously the same in past times as it is at present, it has been estimated that the bricks are over ten thousand years old. The tombs of ancient Egypt,[2] however, furnish the earliest definite evidence of a refining of the technique of this fictile art. Terra-cotta vessels, common to most primitive civilizations, have been found in the tombs of Memphis, and these are estimated to belong to the period 5000–3000 B.C. The Egyptians practised the compounding of bodies, glazing, and enamelling long before these arts were acquired by any other nation. Scenes from Egyptian life in the period 3000–1700 B.C. have been found depicted on the walls of tombs at Thebes representing the making, Fig. 124, and the firing, Fig. 125, of vases in

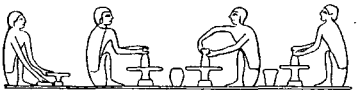


FIG. 124.—Throwing Pottery in Ancient Egypt.

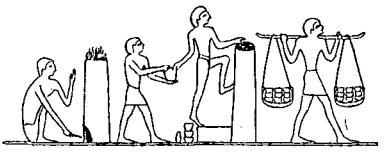


FIG. 125.—Firing Pottery in Ancient Egypt.

ovens. Glazed earthenware, made in the period 3000-1700 B.C., has been found in the pyramid of Saggareh. The decorations of the temple of Tell-el-Yadouai, built by Rameses III, show that the potter's art was well advanced between 1700 and 500 B.C. The Egyptian potter's wheel is not essentially different from that employed to-day. According to H. le Chatelier, samples of pottery from Saggarah (Memphis) show that the Egyptians made real porcelain. The description and analyses, however, agree better with the assumption that the pottery in question was a more or less opaque glass. Some statuettes found in Egyptian tombs are usually thought to have been carved out of natural sandstone, and covered with a cupriferous sodium silicate glaze. H. le Chatelier assumes that the body was artificially made. There are several biblical allusions to the potter's

art—*e.g. Jeremiah* **18.** 1–6. It may be added that the potter's ovens depicted in Fig. 125 seem to be of a type similar to many of those used by the Romans; and these in turn pass by an easy transition to the intermittent ovens used at the present day.

The bricks from Chaldean and Assyrian ruins show that these peoples were adepts at the work, but whether or not their knowledge was borrowed from Egyptian sources no one can say. The ruins of Nineveh and Babylon furnish bricks sometimes coloured with blue, grey, or yellow glazes. The traditions of the Assyrian potters seem to have stimulated the Persians, who acquired great skill in the art of glazing. The beautiful turquoise-blue cupriferous glaze of the Persian tiles has never been surpassed. The potter's art was carried to Greece. The Mycenean pottery is referred to in Homer's *Iliad* (**18.** 560).[3] Although the Grecian potters produced some magnificent ware, they did not specially develop the methods of glazing so well employed by their neighbours, the Persians. The term *ceramic* comes from Greece. The potteries of Athens were located at Keramis, and the inhabitants—mainly potters—were called Kerameis.[4] The term *ceramic* thus came to be employed for the potter's art; and by an easy transition the term *ceramic art* was applied to the clayworker's art generally. In Pliny's time, beautiful pottery was made in several towns both in Greece and in Italy. The Roman potters were stimulated by contact with the Greeks, and are noted for the Etruscan ware made in Etruria, and the red *samian ware* used for domestic purposes.

The secrets of the art of glazing[5] pottery passed from the Persians to the Arabians. The Moors carried the art into Spain, and it then passed on to the Island of Majorca. This gave rise to the name *majolica*—an old Tuscan name for the island. A similar kind of ware made at Faenza, Italy, in the thirteenth century, was called *faience*. The art of glazing pottery with plumbiferous and stanniferous glazes was practised in several places in Europe during the latter part of the Middle Ages. It has been suggested that in the twelfth-century Latin work, *De investigatione magisterii*, attributed to Geber, the instruction to evaporate a soln. of salt *in vase terreo plumbato* refers to an earthen vessel coated with a plumbiferous glaze. Albertus Magnus, in the thirteenth century, in his *De alchymia*, mentioned the use of red-lead for glazing pottery; in the fourteenth century, P. Bonus, in his *Margarita pretiosa* (1330), spoke of the use of tin and lead oxides in this connection; and in the sixteenth century, D. Agricola gave some glaze recipes; while J. B. Porta indicated the use of lead oxide in making glasses to imitate precious stones. According to B. Laufer,[6] the production of glazes in Western Asia stimulated the Chinese to develop the idea. It is probable that the Chinese were making porcelain towards the end of the sixth century, and they had attained a very high skill in the art during the Tang, Sung, and Yuan Dynasties, 618–1367 A.D. The importation of Chinese porcelain into Europe by Eastern traders acted as a great stimulus on the European potters.

According to A. Foresi,[7] the Venetian glass-makers imitated the Oriental ware by heating mixtures of an impure china clay, sand, and glass. R. A. F. de Reaumur likewise, in France, obtained an imitation by a similar method, and also by the devitrification of glass—*porcelaine par devitrification*. This subject was discussed by W. Lewis, A. Dartigues, and L. B. G. de Morveau. The discovery of the mode of manufacturing porcelain at Meissen early in the eighteenth century has been mentioned in connection with china clay. The two letters of Père d'Entrecolles, a Jesuit missionary in the pottery district of China, reached Europe about this time. The first letter is dated Sept. 1, 1712. These letters contained some acute observations on the methods employed for manufacturing porcelain in China. The art gradually spread through Europe in spite of the elaborate precautions at Meissen to keep the procedure a secret. The first clear description of the Meissen process was published by N. C. de Milly in his *L'art de la porcelaine*

(Paris, 1771). Experiments on the properties of the materials were made by J. H. Pott, L. L. B. de Lauraguais, J. P. J. d'Arcet, B. Palissy, J. E. Guettard, P. J. Macquer, etc. W. Cookworthy's discovery of china clay in Cornwall, about 1755, led to the manufacture of porcelain in England, about 1760.

The remains of Celtic pottery, made in England in pre-Roman times, consist mainly of sepulchral urns, drinking cups, vessels for food, and incense pots. The Romans established potteries in Kent, London, Essex, Buckinghamshire, Dorsetshire, Wiltshire, Hampshire, Norfolk, Cambridgeshire, Lincolnshire, Yorkshire, Shropshire, and Staffordshire. The ware produced in the different districts had its own characteristics determined largely by the character of the local clays. A red ware, sometimes called *English samian*, was made in Staffordshire, and in some other counties. After the departure of the Romans, the potter's art in England seems to have relapsed into its original barbarous state. The recovery was slow. About the middle of the seventeenth century, the importations of Oriental, Dutch, French, and German ware seems to have excited public taste and stimulated the curiosity of potters. The work of J. Dwight, J. P. and D. Elers, J. Astbury, J. Twyford, Josiah Wedgwood, etc., raised English pottery to the highest degree of excellence, which has ever since been maintained.

It is impossible to compile a set of mutually exclusive definitions of the various types of pottery, because one type merges into another by insensible gradations. Most types of pottery are made from mixtures of clay, felspar, and quartz. The right proportions of these components for the desired type of ware may occur naturally in the clays. Such clays are usually coloured buff or various shades of red, and in the latter case furnish the so-called *terra-cotta*, red and buff flooring tiles, flower-pots, varieties of *stoneware*, etc. The ware may or may not be glazed with a plumbiferous or with a leadless glaze, and certain colouring oxides may be mixed with the glaze to impart to it a desired colour. Drain-pipes, etc., may be glazed by introducing sodium chloride in the fire-mouths of the oven or kiln near the finish of the firing operation. The salt partly decrepitates and partly volatilizes; and part is hydrolyzed by the steam. The final result is to cover the ware exposed to the fumes with a glassy film—*salt-glaze*.

For white pottery, the scarcer white-burning clays are used. In one of the simplest cases, the clay may be intimately mixed with about twice its weight of felspar, moulded into the desired shape, and fired. This furnishes the so-called *parian* which has a translucent and vitreous body, and which may or may not be afterwards glazed. The body of English *earthenware* is made from a mixture of, roughly, Cornish stone, 15; flint, 30; ball clay, 25; china clay, 30. The colour of ball clay when fired is objectionable, but the clay is used because it is highly plastic. The available china clay is not sufficiently plastic if used alone. The Cornish stone contains enough felspar to serve as a flux or matrix. When the moulded and dried ware is fired in the biscuit oven in an oxidizing atmosphere to about 1100°, the flux acts as a cementing agent binding the whole into a durable body. The biscuit body may be decorated in suitable designs and colours—*underglaze decoration*—or it may be left white. The body is then dipped in a slurry or slip in which the powdered glaze is suspended. The molar composition of the glaze approximates:

$$\left.\begin{matrix}0{\cdot}4PbO\\0{\cdot}3CaO\\0{\cdot}3(K,Na)_2O\end{matrix}\right\}0{\cdot}28Al_2O_3\left\{\begin{matrix}3{\cdot}0SiO_2\\0{\cdot}5B_2O_3\end{matrix}\right. \qquad \left.\begin{matrix}0{\cdot}3(K,Na)_2O\\0{\cdot}7CaO\end{matrix}\right\}0{\cdot}38Al_2O_3\left\{\begin{matrix}3{\cdot}8SiO_2\\0{\cdot}9B_2O_3\end{matrix}\right.$$

according as a lead or leadless glaze is required. Some of the substances used in compounding the glaze are fritted with suitable proportions of some of the other materials. Part or all the "lead" may be included with the frit. The dried, and dipped ware is then fired in the glost oven at about 1500°. The glazed ware may be decorated by painting or printing on the glaze with mixtures of fusible frits and metal oxides to give the desired colour—*on-glaze decoration*. The ware is then

fired in muffles between 800° and 900°. Glazed ware may also be gilded with a kind of lustre-gold or with a form of gold which requires burnishing after being fired. *Lustres* may also be produced on the glaze by painting the glaze with bismuth nitrate, etc., suspended in a medium of oil, and afterwards firing.

As previously indicated in connection with china clay, *hard porcelain, porcelaine dur,* or *felspathic porcelain,* is made from a mixture of felspar, quartz, and clay in the approximate proportions 1 : 1 : 2. According to the analysis of W. L. Howat,[8] the so-called *Marquart's porcelain* used for making pyrometer tubes, has the composition 35·12 per cent. $SiO_2$; 63·20 per cent. $Al_2O_3$; and 1·65 per cent. $K_2O$. F. H. Riddle based a process of manufacturing these tubes on this analysis. The moulded and dried porcelain ware is baked at about 900° usually by the waste heat from another oven. The baked ware is dipped in the glaze which approximates in composition to felspar. The body and glaze are fired together up to the required temp., 1400°–1600°. The atm. is reducing, and this imparts a very faint bluish tinge to the white colour of the ware; if fired under oxidizing conditions, the colour is cream or pale yellowish-red. In some cases, the maturing temp. of body and glaze is lowered by mixing a small proportion of lime with the glaze and body; in rarer cases, magnesia is used. The effect of lowering the firing temperature of the body with additions of lime is to narrow the margin of safety between over-fired and under-fired ware. Some of the early porcelains had steatite for a flux, and the same flux, or its equivalent, is used as a constituent of the body of sparking plugs and some similar types of ware. In the *jasper* body, barium sulphate or carbonate is used as a flux.

The so-called *soft porcelain, porcelain tendre,* or *fritted porcelain,* was once a speciality of the Sèvres factory. The body was made from a calcareous marl admixed with an alkaline frit, and glazed with a plumbiferous glaze. Practically all the English porcelain, or *bone china,* is made from a body containing rather less than 50 per cent. of bone ash in admixture with nearly equal parts of china clay and Cornish stone. The body is fired near to 1200° in an oxidizing atm. There are special phenomena connected with the decomposition of the calcium phosphate when the ware is a little over-fired, if an excess of clay is present, or if reducing conditions obtain. A lead or leadless glaze is applied to the biscuit and fired at about 1050°.

The silicate industries are usually concerned with certain reactions which are not allowed to pursue their full course, but which are arrested at definite stages of their progress. The success or failure of the industrial operations is determined by the arrest being made at precisely the right stage. These *arrested reactions* were discussed **4.** 31, 33.[9] In the different kinds of pottery, the flux begins its work of dissolving the clay and quartz or flint in the vicinity of 1000°, and the speed of the action is greater the higher the temp. The result is that the particles of clay and quartz appear to be cemented together by a felspathic or other glassy matrix. The change has not progressed very far in earthenware and similar types of body, but in the porcelainic bodies, the proportion of glassy matrix is so large that it makes the body appear translucent in moderately thick layers. For the development of sillimanite crystals in pottery, *vide* aluminium silicate.

A series of so-called vitreous bodies come between porcelain and earthenware. These are represented by the *mortar bodies* used in making Wedgwood-ware mortars and pestles; *granite ware; ironstone-china; stone-ware; sanitary ware;* etc. The earthenware bodies are porous and absorb liquids, the porcelain bodies are glassy with a conchoidal fracture and are virtually non-absorbent. Those vitreous bodies approaching the porcelain stage pass the so-called red-ink test in which a drop of red ink placed on the body can afterwards be washed off without showing a stain. The distinction between the bodies of different types of ware is perhaps as much a question of time and temp. of firing, as of composition. Otherwise expressed, the different bodies represent different stages of progress in an arrested reaction. In order that the firing temp. may not be inconveniently high, and the time

inordinately long, the proportion of fluxes may be augmented. No particular value, however, can be attached to proofs that a given type of ware is porcelainic solely because its composition is like that of any particular type of porcelain. All the clay-felspar-quartz (or flint) bodies become porcelainic with the right firing conditions. The margin of safety represented by the percentage loss in manufacture may be greater with some mixtures than with others.

The measurements of some properties of what has been described as porcelain, probably refer to the less vitreous, more porous earthenware. The **colour** of porcelain depends on the nature of the atm. which obtains in the oven at different stages of the firing; and on the porportion of contained iron oxide. The effect of the small proportions of titanic oxide usually present in clays is not appreciable. A very small proportion of lime reduces the tinctorial power of iron oxide. The colour can be controlled by using blue smalt or its equivalent to mask the yellow colour produced by iron oxide in an oxidizing atm. K. H. Reichau, and others, have studied the minute structure of porcelain —*vide* sillimanite. The **specific gravity** of the porcelain body fired to about 700° is 2·60–2·62, but when fired at higher temp., the sp. gr. falls to about 2·3. This was shown by A. Laurent,[10] G. Rose, etc. A. V. Bleininger and J. K. Moore studied the sp. gr. of porcelain. The **hardness** of porcelain is nearly 7, and that of the glaze nearly 6. S. L. Bigelow measured the **permeability** of unglazed porcelain (earthenware) for liquids at different temp. and at different press.; and S. L. Bigelow and F. E. Bartell estimated the **size of the pores** in porcelain (earthenware). H. le Chatelier also made observations on the porosity. A. V. Bleininger and J. K. Moore studied the **porosity** of porcelain. Glazed porcelain should be impermeable to gases at temp. as high as 1300°. A. V. Bleininger and P. Teetor measured the **viscosity** of different porcelain bodies between 1100° and 1320° in terms of their deformation under tensile strain. According to R. M. Friese, and R. Rieke hard porcelain has a **tensile strength** equal to about 1000–2000 kgrms. per sq. cm. H. le Chatelier reported some measurements of the tensile strength. R. Rieke found china clay increased and felspar decreased the tensile strength of porcelain. E. Rosenthal studied the effect of composition on the **crushing strength** of porcelain. R. M. Friese, and R. Rieke found that the crushing strength is about 4000–5000 kgrms. per sq. cm.; the **compressibility** coeff., $1{\cdot}4\times10^{-6}$ or $1{\cdot}8\times10^{-6}$; and the **elastic modulus,** 54,000–71,000 kgrms. per sq. cm. H. le Chatelier reported some measurements of the coeff. of elasticity. The **velocity of sound** in porcelain approximates 5000 metres per sec. Many observations have been made on the **thermal expansion** of porcelain. H. St. C. Deville and L. Troost found the coeff. of cubical expansion of porcelain to be between 0·000016 and 0·000017 between 0° and 1500°. L. Holborn and W. Wien gave for the coeff. of linear expansion $0{\cdot}0_544$. R. C. Purdy and A. P. Potts found the coeff. of expansion ranged between $0{\cdot}0_525$ and $0{\cdot}0_565$. A. Weinhold gave $0{\cdot}0_5269$ between 0° and 100°; F. Henning, $0{\cdot}0_5177$ between —191° and 16°; $0{\cdot}0_5336$ between 16° and 250°; $0{\cdot}0_53645$ between 16° and 500°; and $0{\cdot}0_54340$ between 16° and 1000°; and A. E. H. Tutton $0{\cdot}0_52522$ at 0°; $0{\cdot}0_53265$ at 50°; $0{\cdot}0_54008$ at 100°; and $0{\cdot}0_54305$ at 120°. This shows that the higher the temp. the greater the coeff. of thermal expansion. T. G. Bedford gave $(3{\cdot}425+0{\cdot}00214\theta)10^{-6}$ up to 830°; and L. Holborn and E. Grüncisen found for two different samples $(3{\cdot}027+0{\cdot}0011770)10^{-6}$, and $(3{\cdot}188+0{\cdot}00036\theta)10^{-6}$ up to 625°. R. Rieke observed no relation between the composition and thermal expansion. Observations were also made by L. Holborn and co-workers, K. Scheel, H. le Chatelier, E. Damour, M. Coupeau, and M. Chantepie. T. G. Bedford gave for the linear expansion at $\theta°$ between 0° and 600°, $l=l_0(1+0{\cdot}03425\theta+0{\cdot}0_8107\theta^2)$; and for the cubical expansion, $v=v_0(1+0{\cdot}0_410275\theta+0{\cdot}0_8324\theta^2)$. F. Singer and E. Rosenthal gave for the linear coeff. of Berlin porcelain $0{\cdot}0_5177$ between —191° and 16°; $0{\cdot}0_5366$ between 16° and 250°; $0{\cdot}0_53645$ between 16° and 500°; and $0{\cdot}0_5434$ between 16° and 1000°. Porcelain from other sources gave $0{\cdot}0_5269$–$0{\cdot}0_54305$ from 0°–100°. R. Rieke also gave $0{\cdot}0_5343$ between 23° and 200°, and

$0{\cdot}0_5356$ between 23° and 700°. J. W. Mellor found that the higher the firing temp. of floor-tiles the smaller the coeff. of thermal expansion, and G. Vogt, and R. Rieke made a similar observation with respect to porcelain. R. Rieke found that the coeff. of expansion is lowered by increasing the proportion of felspar and lowering the quartz or flint, and keeping the clay constant. The expansion coeff. of porcelain is smaller than that of glass, and in consequence, such porcelain resists abrupt changes of temp. better than glass—*vide supra*, clays. The **thermal conductivity** of porcelain is about 0·04 when that of silver is 100; and the conductivity on the absolute scale is 0·2. The thermal conductivity increases with a rise of temp.—*vide supra*, clays. W. Steger found the mean **specific heat** of porcelain between 20° and 200° to be 0·202, and between 20° and 400°, 0·221. J. A. Harker gave between 15° and 912°; 0·2563 between 15° and 958°; and 0·2539 between 15° and 1075°. F. Singer and E. Rosenthal gave 0·202 from 20°–200°, and 0·221 from 20°–400—*vide supra*, clays. W. Steger discussed the **translucency** of porcelain. D. Hofmann, J. H. Pitt, and G. de Razoumowsky noted the **triboluminescence** of porcelain.

The **electrical conductivity** of porcelain at ordinary temp. is extremely small. The temp. coeff. is large and positive. G. Fossereau found that the **electrical resistance** approximates $215\times10^7$ megohms at 50° and 651 megohms at 210°. The subject is important in the manufacture of insulators for high-tension currents. As the temp. rises, the resistance decreases rapidly. H. F. Haworth gave for the sp. conductivity $c$ of porcelain at different temp.

| | 1·63° | 20·50° | 30·87° | 40·62° | 50·40° | 59·12° | 64·89° | 81·93° |
|---|---|---|---|---|---|---|---|---|
| $c\times10^{10}$ . . | 0·49272 | 1·9883 | 5·0210 | 11·288 | 26·693 | 65·273 | 110·75 | 485·67 |

F. Haber and co-workers found that the conductivity of porcelain is appreciable at 300°, and at higher temp. it conducts electrolytically, and it is therefore decomposed by the current. M. Pirani and W. von Siemens represented the relation between the resistance $R$ and the absolute temp. $T$ by $\log R=a+bT^{-1}$, where $a$ and $b$ are constants dependent on the type of porcelain in use. One sample had a resistance of 1·098 megohms at 613°, and 68,700 ohms at 900°; while another had a resistance of 100,000 ohms at 727°, and 3400 ohms at 1292°. R. G. Allen found the results indicated in Fig. 126 for two samples of electric porcelain. Observations have been reported by W. Dietrich, F. Fleischmann, G. Stade, G. Benischke, E. Rosenthal, A. V. Bleininger and co-workers, B. S. Radcliffe, E. F. Northrup, E. F. Earhart, A. V. Henry, E. Watkin, F. H. Riddle, F. Wernicke, H. F. Haworth, J. Lustgarten, W. D. A. Peaslee, T. M. Feder, L. E. Barringer, E. E. T. Creighton, etc. Good insulators may deteriorate with use, and what appears a non-porous body may acquire a certain porosity. W. D. A. Peaslee attributes this to a piezoelectric effect in the quartz grains which have not been dissolved by the vitreous magma of the body in the firing. The alternating electrostatic field sets up a kind of vibratory movement in the crystals which may rupture them along the cleavage planes, or along the line of contact of the crystal with the surrounding magma. R. M. Friese found the **dielectric constant** of porcelain to be between 4·5 and 5·3. H. F. Haworth gave for the capacity $K$, of porcelain in microfarads at different temp.:

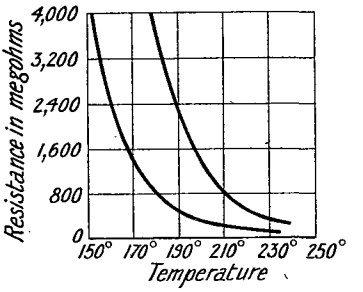



FIG. 126.—Effect of Temperature on the Electrical Resistance of Porcelains.

| | 0·38° | 19·92° | 44·04° | 60·50° | 79·88° | 99·00° |
|---|---|---|---|---|---|---|
| $K$ . . | 0·0011170 | 0·0013803 | 0·0023920 | 0·0035531 | 0·0063010 | 0 0098226 |

R. Rieke observed no relation between the dielectric strength and the composition

of porcelain. A. S. Watts found that the **puncture voltage** of vitreous bodies, the so-called electrical porcelain, varies but little with the composition or maturing temp. of the body. E. Rosenthal studied the influence of composition on the puncture voltage. A. S. Watts found that the resistance to puncture is much less when porcelain is under-fired than when properly vitrified. C. E. Henderson and G. O. Weimer observed that raising the temp. from 24°–525° lowered the puncture voltage from 60,700–20,000 volts. The properties of porcelain for high-tension insulators have been discussed by M. F. Dahl, etc.[11]

Porcelain, if not thoroughly vitreous, or well glazed, may be pervious to gases and air. J. Priestley[12] drew some wrong conclusions on the conversion of water into air by not allowing for this fact pointed out to him by J. Wedgwood. C. H. Pfaff discussed the permeability of retorts to gases. The fact that solid carbon diffuses into porcelain crucibles and cups has been established by the work of J. Violle, and S. Marsden. Porcelain is fairly resistant towards chemical reagents; and the glaze of hard porcelain is usually more resistant than glass. Acids other than hydrofluoric acid have but a slight action. The evaporation of hydrochloric acid soln. in glazed porcelain basins day after day causes an appreciable erosion; alkaline soln. attack rather more quickly than acids. A. Emmerling studied the action of water, dil. hydrochloric acid, aq. ammonia, soln. of ammonium chloride, etc., on porcelain glazes—*vide* glass. Fused alkali hydroxides and carbonates and lead oxide attack porcelain quickly producing, in the former case, a mass readily decomposed by acids. Porcelain is attacked by heated phosphoric acid, and more so by hypophosphorous acid. H. von Wartenberg found that many metals in a reducing atm. attack porcelain above 1200°, forming silicon and silicides; hydrogen alone above this temp. also forms silicon; and chlorine attacks the iron silicates in porcelain: $3Fe_2SiO_4+3Cl_2=2FeCl_3+Fe_4(SiO_4)_3$. W. Nernst and H. von Wartenberg found that water vapour also attacks the iron in porcelain above 1200°.


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## § 37. Glass

The manufacture of glass appears to have originated in Egypt. It is possible that the glass industry developed from the art of glazing pottery. Egyptian pottery was first glazed with the idea of making vessels water-tight and durable; and the glaze was afterwards employed for producing decorative effects. This view of the origin of glass appears to have been taken by H. B. Walters,[1] W. Fröhner, G. Perrot and C. Chipiez, A. C. Kisa, etc. How glasses or glazes came to be discovered is unknown. In the first century of our era, Pliny, in his *Historia naturalis* (**36.** 65), related the following story:

A ship laden with *nitrum* was moored beside the river Belus, in Phœnicia, and the merchants preparing their food on the sea-shore, used some lumps of nitre from the vessel to support their cooking-pot over the fire. The heat from the fire melted the *nitrum*, which combining with the sand formed transparent streams of an unknown liquid. This was the origin of glass.

Modified versions have been repeated by B. Palissy, A. Neri, etc. J. Beckmann discredited the legend, although there is nothing improbable in some such mode of discovery. According to J. du Halde, the Chinese made glass in the district of Yen-Tsching from very early times.

The ancient writers attributed the discovery of the art of making glass to the Phœnicians, but excavations in Egyptian tombs have shown that the Egyptians must have been adept glass-makers long before the Phœnicians practised the art. This indicates that the Phœnicians were probably distributors of Egyptian glass before their own factories were established at Sidon. In the work cited above, Pliny said that glass was made in Italy, and in the Gallic and Spanish provinces, by fusing sand with three times its weight of nitre; and he added that in India rock-crystal was used in place of sand. Bases other than the alkalies are needed to make the glass resist rapid attack by moisture. These might have been added deliberately, or brought in as impurities with the sand or alkalies. Pliny also mentioned that there were reports of a *vitrum flexible—malleable glass—vide* **5.** 33, 1. This recalls the Delhi flexible sandstone—*vide supra.* Pliny wrote:

It is said that in the time of Tiberius, a combination was devised which furnished malleable or flexible glass; but the workshop of the artist was totally destroyed in order to prevent the value of copper, silver, and gold from being depreciated. This report, however, was for a long time more widely spread than well authenticated.

Representations of the processes of glass-making are depicted on the walls of the tombs of Ben-Hassam near Thebus, 3000–1700 B.C., Fig. 127. These tombs also contain vessels, etc., showing that the artisans were not only acquainted with the making and working of glass, but also with the colouring and cutting of glass in imitation of the precious stones. F. M. de Rozière also found samples of coloured glass in early Egyptian tombs. W. M. F. Petrie collected at Tell-el-Amarna specimens illustrating all stages of the process of glass-making about 1400 B.C. F. Rathgen gave analyses of antique Babylonian glass. Theophrastus, in his Περὶ λίθων, about 300 B.C., mentioned the coloration of glass by copper; and in his *Clouds*, Aristophanes referred to a glass-lens used as a burning glass. From Cicero, it would appear that glass from Egypt was greatly prized by the Romans; so much so that when Augustus subdued Egypt, 29 B.C., a portion of the Egyptian tribute was ordered to be paid in glass. At the time of Tiberius, Egyptian workmen were imported to Rome, and Roman glass rivalling that from Egypt was soon obtained. Works were also established in Italy, France, and Spain at an early date. In the

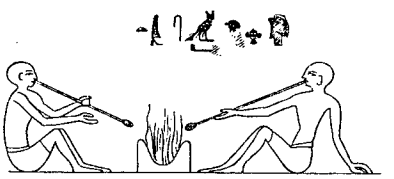


FIG. 127.—Egyptian Glass-makers at Ben-Hassam.

second century, H. Philo, in his *De legatione ad Caicum Caligulum*, alluded to the use of translucent stones as windows in the halls and chambers of the emperor's palace, and in the fourth century, L. C. Lactantius, in his *De opificio Dei*, mentioned the use of glass itself for windows. It is therefore probable that about the third century glass was employed in the construction of windows; but, according to L. Dutens,[2] the excavations of Pompeii, near Naples, show that at that time *les salles de bain étaient garnies de fenêtres en verre aussi belles que les nôtres*. After the fall of the Roman Empire the manufacture of glass was taken up in Byzantium (**1**. 1, 12), where it flourished for about five centuries. The fall of the Eastern Empire was attended by the migration of the glass-makers to other parts of Europe. Many were attracted to the Venetian Republic, and the Venetian glass became famous throughout the civilized world.

In the early Middle Ages, glass-making was taken up in Germany; and in his *De re metallica* (Basiliæ, 1546), G. Agricola gave a drawing of a glass-furnace; and shortly afterwards J. Mathesius, in his *Sarepta* (Nürnberg, 1562), described the practice employed in Venice, Germany, and Bohemia. A. Neri[3] published a number of recipes in 1612, and some years afterwards this work was elaborated by J. Kunckel.

The factories in different localities acquired fame for some peculiarity in manufacture; the Bohemian manufacturers, for example, excelled in the production of colourless glass rivalling that from Venice. The manufacture of glass in Bohemia suffered a relapse owing to the heavy import duties levied against it, and the inducements held out to Bohemian workmen by foreign countries. Both the Venetian and Bohemian glass industries were revived in more recent years. The manufacture of the better types of glass in France commenced in the eighteenth century in factories erected first at Paris and then at St. Gobain. The latter is now famous for the manufacture of plate-glass. According to H. J. Powell, it is possible that during the Roman occupation a few beads, small cups, and bottles were made in England; but the resemblance of the scattered vessels and fragments of vessels to those found elsewhere makes it probable that there were only a few centres of glass manufacture in the Roman empire, and that the vessels were distributed from these to various parts. Glass was manufactured in England in the thirteenth century, for the industry was in existence at Chiddingfold, Surrey, in 1226. The south-eastern counties—Surrey and Sussex in particular—were favourite spots for the native glass-makers from the thirteenth to the sixteenth centuries. Glass was manufactured in Russia in the seventeenth century; and, in the United States, near the beginning of the nineteenth century.

Theophilus, in the latter half of the eleventh century, related that, in Italy, flint glass was used for imitating gem-stones, and added that the Jews were engaged in the manufacture of these imitations. Towards the end of the eighteenth century, J. Strasser, of Vienna, was famous for his skill in this work. He made a flint glass very rich in lead, and of high refractive power and sp. gr., which was called *strass*, and which was tinted with the necessary colouring oxides—*e.g.* 0·8 per cent. of chromic oxide to imitate the emerald; a mixture with 0·8 per cent. of manganese oxide, 0·5 cobalt oxide, and 0·2 gold purple, to imitate the amethyst. A. B. Ryley, in his *Old Paste* (London, 1913), has discussed this subject.

Ordinary glass is a fused mixture of silicates of the alkalies and alkaline earths which has congealed without crystallization. The molten mixture on cooling passes through various stages of viscosity, until, when cold, it furnishes a hard and brittle solid. There is no sign of a f.p. on the cooling curve (**1**. 9, 6). The simple silicate of potassium or sodium, or a mixture of the two, even when a large proportion of silica is present, is attacked by water and acids; so also is calcium silicate glass. A mixture of alkali and calcium silicates is fairly fusible, but under ordinary conditions it furnishes a glass which resists the action of water and acids very well, and this the more the greater the proportion of silica and alumina which may be present. For special purposes, the calcium silicate may be wholly or

partly replaced by other silicates—*e.g.* those of barium, lead, magnesium, zinc, lithium, didymium, arsenic, antimony, etc.—and the silica may be in part replaced by boric oxide, phosphoric oxide, etc. For lead glasses, see pottery glazes, and lead silicates.

The more common types of glass are represented by (i) *soda-lime glass* with 71–78 per cent. $SiO_2$; 0–2, $K_2O$; 12–17, $Na_2O$; 5–15, $CaO$; and 1–4, $Al_2O_3+Fe_2O_3$. It fuses at a comparatively low temp., and can be easily worked. It is used in making glass tubes, laboratory apparatus, window glass, and plate-glass. In the latter case it is called *crown glass*; (ii) *potash-lime glass*, also called *Bohemian glass*, with 72–76 per cent. $SiO_2$; 12–15, $K_2O$; 0–3, $Na_2O$; 8–10, $CaO$; and about one per cent. of $Al_2O_3+Fe_2O_3$. It fuses at a higher temp. than soda-lime glass, and it is used for making chemical apparatus, combustion tubes, etc.

Common *bottle glass* is usually coloured yellow, brown, or green owing to the presence of a relatively high proportion of ferruginous and other impurities. The composition approximates: 60–65 per cent. $SiO_2$; 3–5 per cent. alkali oxides; 18–20, $CaO$; and 6–11, $Al_2O_3+Fe_2O_3$. The raw materials used in the manufacture of this glass are not selected with such care as is the case with other types. Common sand; wood-ashes; by-products from the alkali-works, soap-works, and gas-works; common salt; salt-cake; and felspathic rocks represent some of the cheap raw materials which have been used. A. F. Gehlen [4] discussed the use of Glauber's salt as a source of the alkali.

A third type of glass is represented by the *potash-lead glasses*, and *flint glass*. Such glasses have 40–50 per cent. $SiO_2$; 8–11, $K_2O$; 28–53, $PbO$; and about one per cent. $Al_2O_3+Fe_2O_3$. These glasses are very fusible and easily worked. Owing to the ready reduction of lead silicate to metallic lead, the heating of these glasses must be done in an oxidizing atm. The sp. gr. and index of refraction of these glasses are greater than is the case with the other types of glass. This glass is not suitable for laboratory apparatus, but it is employed for articles in common use, table glass, etc. In the so-called *crystal*, a higher proportion of lead is introduced. This glass is used for optical purposes. In *strass*, mentioned above, a still higher proportion of lead is added.

The so-called *boro-silicate glasses* have many special applications; such a glass is used for making high-temp. thermometers. The so-called *Jena glass* has zinc and barium oxides as bases; it is specially resistant towards water, and is used for laboratory beakers and flasks. A boro-silicate glass, free from alkali, but with zinc, barium, and aluminium oxides as bases, is used for photographic objectives. A *phosphato-silicate glass*, with alkali, baryta, and alumina as bases, is used for microscopic objectives. L. M. Dennis and A. W. Laubengayer made *glasses with germanium* oxide in place of silica. Glasses are thus made with the idea of enhancing particular properties—*e.g.* refractive index, resistance to attack by particular liquids, transparency or opacity to particular parts of the spectrum, resistance to abrupt temp. changes, high softening temp., etc. Much attention has been devoted to the so-called optical glasses.[5] An extraordinary number of analyses of ancient and modern glasses has been reported.[6] The analysis of a glass, plus an elementary knowledge of the available raw materials, soon enables the practician to imitate any particular glass; it may, however, take the workmen a longer time to master the idiosyncrasies of the imitation in order to make its manufacture a commercial success. E. Zschimmer, and G. W. Morey discussed the classification and nomenclature of glasses, glazes, and enamels.

The manufacture of ordinary glass is comparatively simple. Glass is made by intimately mixing the raw materials required to give the desired composition. The mixture may or may not be exposed to a low temp. to drive off moisture, etc., likely to cause spitting and frothing, in the subsequent melting of the glass. The mixture is then placed in large crucibles made from fireclay, and called *glass-pots*. These are arranged on ledges in a circular or oblong furnace, and exposed to a steadily rising temp. until the mass is free from bubbles, streaky patches, quartz granules, etc. The scum or glass-gall is skimmed off. A portion of the molten glass is gathered at one end of an iron rod and blown into the required shape. The glass vessels are annealed by slow cooling, or by reheating them in an annealing furnace or lehr. The melting of the glass may be done in a tank-furnace,

which is an adaptation of the reverberatory furnace. The heat is applied by gaseous fuel on the regenerator principle. The automatic blowing machines for shaping glass bottles are a triumph of mechanical skill.

These and related subjects are discussed by H. Benrath, *Die Glasfabrikation* (Braunschweig, 1875); F. Tscheuschner, *Handbuch der Glasfabrikation* (Leipzig, 1885); R. Gerner, *Die Glasfabrikation* (Wien, 1897); R. Dralle, *Die Glasfabrikation* (München, 1911); R. Müller, *Chemische Technologie des Glases* (Leipzig, 1911); F. W. Hodkin and A. Cousen, *A Textbook of Glass Technology* (London, 1925).

In spite of the most careful selection of the available raw materials, sufficient iron oxide is usually present to impart a pale yellow tinge to the glass matured in an oxidizing atm., or a pale green tinge in a reducing atm. Pliny, in his *Historia naturalis* (**36**. 26, *c.* 77 A.D.), spoke of the use of *magnes lapis* in making glass, and J. Beckmann believes that a manganese ore is here implied; while experimenting on the effects of different oxides on the colour of glass, it must have been noted that when a very small proportion of *magnes lapis* was employed, the yellow colour produced by iron was masked and a colourless glass obtained. Proportions of manganese oxide in excess of those required to mask the yellow tinge of iron give violet-reds and browns. Selenium compounds for the purpose of bleaching the yellow tinge of iron have been used in recent years.

In addition to ordinary, clear, colourless, transparent glass, and glasses with special colours for arresting particular kinds of rays from transmitted light, there are glasses stained with particular colouring oxides for ornamental effects. Thus, cobalt oxide dissolved in glass imparts a fine azure-blue; copper oxide in alkaline glasses gives a turquoise-blue, and in many glasses an emerald-green, both under oxidizing conditions. The ruby-red colour obtained by the use of very small proportions of copper oxide under reducing conditions, and the ruby colour obtained by the use of gold, have been described (**3**. 23, 11). A green and a red colour is obtained by means of chromic oxide. Manganese oxide furnishes a series of pink and violet colours in alkaline glasses and under oxidizing conditions; and in other varieties, manganese oxide produces a brown colour. A kind of Naples yellow is obtained by the use of antimony oxide, by the use of silver salts, and by iron oxide. Under reducing conditions, iron oxide may give a green colour; while under oxidizing conditions a reddish-brown, blood-red, or yellow colour may be obtained with ferric oxide. J. C. Hostetter and H. S. Roberts discussed the coloration of glass by iron oxide. K. Fuwa studied the yellow colours obtained with ceria. H. le Chatelier and P. Chapuy found that with glazes didymium oxide gave green, blue, or violet colours in a reducing atm.; erbium, violet or blue, in a reducing atm., and green or red, in an oxidizing atm.; lanthanum, violet or blue, in a reducing atm.; neodymium, violet, blue or green, in a reducing atm.; thallum or thorium, blue or green, in a reducing atm.; vanadium, blue, green, or yellow, in an oxidizing atm.; titanium, violet, blue, or green, in a reducing atm., and yellow or red, in an oxidizing atm.; molybdenum, blue or violet, in a reducing atm.; and tungsten, violet, blue, yellow, or red, in a reducing atm. A. Granger obtained a yellow with tungsten oxide, in an oxidizing atm. K. Fuwa has reported on the colours produced by manganese, antimony, molybdenum, chromium, tungsten, and vanadium oxides; S. D. Whitmer, F. K. Pence, H. Wicks and J. W. Mellor, and T. Perry, by nickel oxide; and K. Fuwa, and T. Cohn, cobalt and copper oxides. Sulphide impurities in the glass were shown by D. C. Splitgerber, E. Grieshammer, and R. Zsigmondy to produce a yellow colour. Thomas Aquinas, in his *De esse et essentia mineralium*, described a mode of preparing artificial topaz by using smoke obtained by placing a piece of aloe-wood over the pot in which the glass was melted. Selenium and cadmium oxide may give a red or yellowish-red colour to alkaline glasses, and for marking the coloration due to iron oxide. The selenium-red has been discussed by F. Kraze,[7] P. Fenaroli, E. Fränkl, and O. Witt; the effect of tellurium, by P. Fenaroli, and of bismuth and stannic oxides, by K. Fuwa. Combination tints may be obtained by using a mixture of oxides in the right proportions. A black glass is obtained by using a mixture of iron, copper, chromium, and manganese oxides in suitable proportions. The so-called opaque-white glass, or milk-glass, is translucent, and the opacity is produced by undissolved particles of calcium phosphate, tin oxide, sodium antimoniate, zirconia, or other suitable opacifying

agents. Matte effects are produced by a sand-blast, or by etching with hydrogen fluoride in aq. soln. or as a gas.

F. Leydolt [8] found that when the surface of clear, apparently homogeneous glass is etched with conc. hydrofluoric acid, and examined microscopically, evidence of crystalline formations can be detected. W. Jackson and E. M. Rich made similar observations; and H. E. Benrath said:

> Remembering that the content of silica in commercial glasses is very variable, and that at a higher temp. more of this acid can be taken up than can be retained by the glass as the temp. falls the further, felspathic minerals may be taken up and again separated by a molten glass; finally, also sulphates, phosphates, borates, metallic oxides, and metals (gold) may enter into the constitution of glasses, it would appear that these facts allow of no other explanation than that commercial glasses are quickly solidified soln. not only of different silicates in each other, but even soln. of basic oxides or silica and the other salts and metals, in molten silicate. Whether in all glasses some fundamental silicate, a compound—say, $Na_2O.CaO.6SiO_2$, or $Na_2O.CaO.4SiO_2$—is to be taken as the solvent or not, must remain a question so long as nothing more is known than at present; yet many of the observations appear to speak for such an assumption.

J. B. A. Dumas regarded glass as an indefinite mixture of definite silicates; W. Jackson and E. M. Rich powdered various commercial glasses, and separated the fractions of different sp. gr. by flotation in methylene iodide, or by elutriation. In both cases the fractions had a different composition. They therefore concluded that glass must be considered to be a mixture of various silicates and oxides more or less homogeneous according to the method of manufacture. In ordinary crown and flint glass the mixture is sufficiently imperfect to allow the constituents to be readily separated by grinding; but the optical glasses show a much greater degree of homogeneity. All this means that the congealed soln. of silicates (**1**. 9, 6) known as glass is not necessarily homogeneous. This may be largely due to the difficulty in adequately mixing such viscid soln. *L'analogie du verre avec une gelée* was discussed by P. Bary, C. Doelter, M. W. Travers, and A. Silverman; and the colloidal chemistry of glass by R. G. Liesegang. G. Quincke applied his theory of foam cells (**1**. 11, 4) to the structure of glass. T. T. Smith and co-workers found in optical glass a difference of $\pm 2$ in the fourth decimal between the indices of refraction of the striæ and the rest of the glass. L. N. G. Filon and F. C. Harris' experiments on the elasticity of glass indicated a two-phase system. H. le Chatelier believed that above 800°, glass is in a different "allotropic" state from glass below that temp. N. Seljakoff and co-workers regard glass as an amorphous undercooled liquid.

C. Zulkowsky reported that for a good serviceable glass, the relation of acids to bases should form approximately a trimetasilicate—*e.g.* KO.SiO.O.SiO.O.SiO.OK. C. Dralle could not confirm this. W. L. Baillie recommended a modification of the hypothesis. W. and D. Asch applied their hexite-pentite hypothesis to glasses, assuming that they are all chemical individuals. H. Fritz, F. Cedivoda, and O. Inwald discussed the formation of phosphate glasses without silica.

The various physical properties of glass naturally depend on the composition. Attempts to correlate the physical properties of glass with composition have given only empirical results. The results of much German work on the subject is summarized in H. Hovestadt, *Jenaer Glas und seine Verwendung in Wissenschaften und Technik* (Jena, 1900; London, 1902). Observations were made by J. W. Döbereiner,[9] W. H. Harcourt, E. Zschimmer, E. W. Tillotson, etc. S. Salpeter examined the properties of different glasses in the light of the periodic law. The **specific gravity** of alkali-lime crown glass is between 2·4 and 2·6; that of alkali baryta glass, 2·4–3·6. M. Faraday prepared flint glass with a sp. gr. 5·44, and the sp. gr. of flint glass may be as low as 2·9; and that of alkali-lead glass between 3·0 and 3·8. A. Lamy, and O. Schott prepared a thallium-lead glass of sp. gr. 4·18. K. Schall found for the sp. gr. of light crown glass, 2·49; phosphate glass, 2·58; crystal glass, 3·10; barium phosphate glass, 3·35; light flint glass, 3·44; heavy flint glass, 3·63; very heavy flint glass, 4·91; and the heaviest flint glass, 6·33. The sp. gr. of glass is primarily dependent on its

composition, and attempts have been made to find a relation between the two. A. Winkelmann and O. Schott found that if $a_1$, $a_2$, $a_3$, . . . represent the percentage amounts of the several oxides present in glass, and $z_1$, $z_2$, $z_3$, . . . the sp. gr. constants, then, the sp. gr. of the glass, $S$, is $100/S=a_1/z_1+a_2/z_2+a_3/z_3+$ . . . The sp. gr. constants are not the same as the sp. gr. of the individual oxides because, if these are employed, the calculated values of $S$ are smaller than the observed. Consequently, the total vol. is diminished by combination. They showed that the above formula is approximately fulfilled by taking the following values of $z$ :

| | $SiO_2$ | $B_2O_3$ | ZnO | PbO | MgO | $Al_2O_3$ |
|---|---|---|---|---|---|---|
| $z$ . . . | 2·3 | 1·9 | 5·9 | 9·6 | 3·8 | 4·1 |
| Sp. gr. . . | 2·17 | 1·46 | 5·65 | 9·32 | 3·40 | 3·85 |

| | $As_2O_3$ | BaO | $Na_2O$ | $K_2O$ | CaO | $P_2O_5$ |
|---|---|---|---|---|---|---|
| $z$ . . . | 4·1 | 7·0 | 2·6 | 2·8 | 3·32 | 2·55 |
| Sp. gr. . . | 4·09 | 5·0 | 2·55 | 2·66 | 3·15 | 2·38 |

C. J. Peddle studied the sp. gr. of the $SiO_2$–$Na_2O$–$K_2O$, binary and ternary glasses, of the $SiO_2$–CaO–$Na_2O$ or $K_2O$ glasses; $SiO_2$–BaO–$K_2O$– or $Na_2O$; and of the SiO–PbO–$Na_2O$ or $K_2O$ glasses. J. R. Clarke and W. E. S. Turner measured the sp. gr. of the lime-soda series of glasses. E. W. Tillotson found the additive rule for lime-magnesia glasses, lithia-baryta glasses, and lithia-lime glasses works better with the factors $SiO_2$, 2·3; CaO, 4·1; MgO, 4·0; BaO, 7·0; $Li_2O$, 3·7; and $Al_2O_3$, 2·75, than with A. Winkelmann and O. Schott's factors. S. English and W. E. S. Turner investigated the sp. gr. of the soda-lime glasses, soda-magnesia glasses, soda-magnesia-lime glasses, and aluminous and boriferous glasses; and W. L. Baillie examined the subject and proposed another set of factors. These factors are all purely empirical; and they must be dependent on the working conditions because each worker recommends his own set of factors, but in practice uses the observed data.

F. Auerbach[10] has measured the **pressure-hardness** of glass, and obtained numbers in agreement with H. Hertz's formula, $12p\epsilon/d^3E=(1-\sigma)$, where $p$ denotes the mutual press. between a plate and a lens with a radius of curvature, $\epsilon$; $d$, the diameter of the surface of contact; $\sigma$, the elastic modulus or Poisson's ratio; and $E$, Young's modulus. If $H$ denotes the absolute hardness of the glass; $a_1$, $a_2$, $a_3$, . . ., the percentage amounts of the several oxides in the glass; and $y_1$, $y_2$, $y_3$, . . ., the hardness coeff. of the several oxides, then $H=a_1y_1+a_2y_2+a_3y_3$ + . . ., when

| $SiO_2$ | $B_2O_3$ | ZnO | PbO | $Al_2O_3$ | BaO | $Na_2O$ | $K_2O$ | CaO | $P_2O$ |
|---|---|---|---|---|---|---|---|---|---|
| $y$=3·32 | 0·75 | 7·1 | 1·45 | 10·2 | 1·95 | −2·65 | 3·9 | 6·3 | 1·32 |

J. R. Rydberg, C. Benedicks, J. Schneider, and O. Schott studied the hardness of glasses; and F. Auerbach also determined the scratching-hardness of glass, but observed no regular relation between the two forms of hardness. A. Lecrenier concluded that soda glasses are usually harder than silica glasses containing an equal vol. of silica; with lime-soda glasses, the hardness increases with increase of lime and decrease of soda; boric oxide imparts great hardness to glass; and the addition of soda and lime to lead glasses increases the hardness.

K. Arndt[11] found the **viscosity** of glass at 1050° to be 36·0 (water at 20°=0·01); at 1100°, 17·0; and 1200°, 12·0. A. L. Field found that the temp.-viscosity curves of blast furnace slags always approximate to a rectangular hyperbola, and that replacing lime by magnesia lowers the viscosity at all temp. Alumina did not decrease the viscosity at high temp. F. Farup and co-workers found that increasing the alumina and silica decreases the viscosity. F. T. Trouton and E. S. Andrews gave $0{\cdot}0_{12}11$ for the viscosity coeff. of a soda glass at 575°; $0{\cdot}0_{10}23$, at 660°; and $0{\cdot}0_{9}45$, at 710°. S. English, C. E. Guye and co-workers, investigated the viscosity of various kinds of glass near the annealing temp.; and J. T. Littleton and E. G. Roberts suggested that the annealing temp. of a glass may be determined

by measuring its viscosity at various temp. H. le Chatelier represented the viscosity, $\eta$, of a number of glasses at the temp. $\theta°$ by $\log \eta = a - b\theta$, where $a$ and $b$ are constants. Observations on the viscosity of glass were made by C. Doelter and H. Sirk, E. Greiner, V. Vesely, C. E. Guye and S. Vassileff, A. Lecrenier and co-workers, H. F. Staley, G. Tammann, J. Masson and co-workers, and E. W. Washburn and co-workers. E. W. Tillotson, and A. Lecrenier and co-workers measured the **surface tension** of molten glasses. E. W. Washburn found the surface tension of the soda-lime-silica glasses between 1200° and 1450° to be of the order 150 dynes per cm.; and A. A. Griffith gave for the surface tension of a glass:

| | 15° | 745° | 801° | 852° | 905° | 1110° |
|---|---|---|---|---|---|---|
| $\sigma$ | (0·0031) | 0·00251 | 0·00257 | 0·00249 | 0·00239 | 0·00230 |

E. Warburg[12] discussed the **diffusion** of metals in glass; and A. Günther-Schulze, of silver in glass. H. Wessels observed the thermolysis or Soret's effect in glass.

The **elastic properties** of glass have been investigated by R. Reiger,[13] J. Salpeter, E. Stephan, A. Kundt, G. Quincke, L. Boltzmann, J. Salpeter, C. Brodmann, H. K. Onnes, L. Grenet, B. Halle, E. Warburg, G. Tamman, B. Halle, etc. The **tensile strength** of glass varies from 2·9–8·35 kgrms. per sq. mm. This constant has been measured by J. von Kowalsky, etc. J. von Kowalsky found that the greatest linear extension with a simple pull was 0·00131; with bending, 0·00132; with torsion, 0·00183; and with an end-pressure, 0·00129. Hence, glass can bear a much greater extension by torsion than by pull, bending, or end-pressure. A. Winkelmann and O. Schott represented the tensile strength, $T$, in kgrms. per sq. mm., by $T = a_1y_1 + a_2y_2 + a_3y_3 + \ldots$, where $a_1$, $a_2$, $a_3$, . . . represent the percentage amounts of the component oxides in the glass; and $y_1$, $y_2$, $y_3$, . . . the respective tenacity coeff. which are:

| | $SiO_2$ | $B_2O_3$ | ZnO | PbO | MgO | $Al_2O_3$ |
|---|---|---|---|---|---|---|
| $y$ | 0·09 | 0·065 | 0·15 | 0·025 | 0·01 | 0·05 |

| | $As_2O_5$ | BaO | $Na_2O$ | $K_2O$ | CaO | $P_2O_5$ |
|---|---|---|---|---|---|---|
| $y$ | 0·03 | 0·05 | 0·02 | 0·01 | 0·20 | 0·075 |

The term *elastische Nachwirkung*, or *elastic after-effect*, refers to a residual effect which occurs after glass has been deformed. The residual effect subsides only gradually when the body is left to itself. The subject was investigated by G. Weidmann, who found an after-effect after bending, or flexure, after compression, and after torsion. F. Kohlrausch represented the subsidence of the after-effect by $x = Ce^{-at^m}$, where $x$ denotes the amount of deformation after the time $t$ reckoned from the instant when the body is free, divided by the original deformation; and $C$, $a$, and $m$ are constants. J. Hopkinson studied the elastic after-effect after the release of a torsional strain. A. Pazziani and C. E. Guye studied the torsion modulus, and the effects of annealing on glass fibres. J. W. French, E. Thomson, F. W. Preston, and A. J. Dalladay and F. Twyman discussed the stresses produced in glass by cutting with a diamond, and by grinding. A. A. Griffith found the maximum tensile strength of glass in the corners of a crack may be more than ten times the tensile strength as ordinarily measured. Freshly prepared rods have a great tensile strength which reduces to the normal value in a few hours. This is attributed to the development of numerous ultramicroscopic cracks.

A. Winkelmann and O. Schott[14] measured the **crushing strength** or resistance to crushing and found numbers between 60·6 and 126·4 kgrms. per sq. mm. If $R$ denotes the crushing strength, $a_1$, $a_2$, $a_3$, . . ., the percentage amounts of the respective oxides in the glass; and $y_1$, $y_2$, $y_3$, . . . the crushing coeff. of the respective oxides, then $R = a_1y_1 + a_2y_2 + a_3y_3 + \ldots$, where

| | $SiO_2$ | $B_2O_3$ | ZnO | PbO | MgO | $Al_2O_3$ |
|---|---|---|---|---|---|---|
| $y$ | 1·23 | 0·9 | 0·6 | 0·48 | 1·1 | 1·0 |

| | $As_2O_5$ | BaO | $Na_2O$ | $K_2O$ | CaO | $P_2O_5$ |
|---|---|---|---|---|---|---|
| $y$ | 1·0 | 0·05 | 0·02 | 0·05 | 0·2 | 0·76 |

G. Berndt obtained for the mean crushing strength of borosilicate glass with cubes 5 mm. edge, 1200 kgrms. per sq. cm. for 10 mm. cubes, 9000 kgrms. per sq. cm.; and for 15 mm. cubes, 8700 kgrms. per sq. cm. For unannealed cylinders with the press. continually increased 15,000 kgrms. per sq. cm., for annealed glass the numbers are respectively 14,200 and 12,500 krgms. per sq. cm. P. B. Galitzin found that the **bursting pressure of glass tubes** (i) is independent of the rapidity of compression of the contained water; (ii) varies with the ratio of internal and external diameters; (iii) increases at first with the radius to a maximum value and then slowly decreases; and (iv) is independent of the absolute thickness of the walls—although the thicker the walls the more likely are flaws to be present. Observations were also recorded by D. I. Mendeléeff, and W. P. Bradley and A. W. Browne. A. A. Griffiths found the **breaking stress,** $S$, of glass fibres, of diameter $d$ inches, to be in lbs. per sq. in.:

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| $d$ | 0·040 | 0·004 | 0·002 | 0·00115 | 0·00050 | 0·00026 | 0·000130 |
| $S$ | 24,900 | 42,300 | 79,600 | 88,700 | 195,000 | 332,000 | 491,000 |

A. Föppl tested the **brittleness** of glass by letting a hammer fall from a definite height on a cube of glass. The ratio of the brittleness to the crushing strength varied with different glasses. P. Gaubert attributed to internal strains the regular system of cracks and regular shape of fragments sometimes found in glass ruptured *par les explosions*. J. Wolf reported on shock-resisting glasses; and E. E. Schumacher, on the cracking tendency of glasses.

The elasticity of glass or **Young's modulus** of glass was investigated by A. Winkelmann and O. Schott,[15] A. E. Williams, etc. They found that the elasticity ranges from 4802 –7971 kgrms. per sq. mm.; and if $E$ denotes Young's modulus; $a_1$, $a_2$, $a_3$, . . ., the percentage amounts of the respective components; and $y_1$, $y_2$, $y_3$, . . . the elasticity coeff. of these oxides, $E=a_1y_1+a_2y_2+a_3y_3+$ . . ., where the values of $y$ are different for different types of glass. A. Winkelmann found for the silicate glasses, without boric or phosphoric oxide, baryta or magnesia:

| | $SiO_2$ | ZnO | PbO | $Al_2O_3$ | $As_2O_5$ | $Na_2O$ | $K_2O$ | CaO |
|---|---|---|---|---|---|---|---|---|
| $y$ | 70 | 52 | 46 | 180 | 40 | 61 | 40 | 70 |

for leadless borosilicates free from phosphoric oxide:

| | $SiO_2$ | $B_2O_3$ | ZnO | MgO | $Al_2O_3$ | $As_2O_5$ | BaO | $Na_2O$ | $K_2O$ | CaO |
|---|---|---|---|---|---|---|---|---|---|---|
| $y$ | 70 | 60 | 100 | 40 | 150 | 40 | 70 | 100 | 70 | 70 |

and for the remaining types comprising borates, lead borosilicates, and phosphates:

| | $SiO_2$ | $B_2O_3$ | PbO | MgO | $Al_2O_3$ | $As_2O_5$ | BaO | $Na_2O$ | $K_2O$ | $P_2O_5$ |
|---|---|---|---|---|---|---|---|---|---|---|
| $y$ | 70 | 25 | 55 | 30 | 130 | 40 | 30 | 70 | 30 | 70 |

A. Winkelmann found that if $E$ denotes Young's modulus at $\theta°$ up to nearly 482° and $E_{20}$, the value at 20°, $E=E_{20}\{1-\alpha(\theta-20)^\beta\}$, where $\alpha$ and $\beta$ are constants for a given type of glass. It was found that if a glass be first tested at ordinary temp. and then at the higher temp., on its return to ordinary temp. it exhibits a greater resistance to bending than before. If it undergoes only one such heating, the enlarged elasticity decreases with time. Several heatings and coolings are needed before the elasticity becomes constant. Corrections are needed for the thermal expansion of glass. A. Winkelmann found that the simultaneous presence of large amounts of soda and potash favour the change of elasticity with temp.; but if boric oxide be simultaneously present, the change is in the opposite direction. E. Wandersleb found that Young's modulus is smaller in the normal condition than in the *accommodation condition* observed by A. Winkelmann; and Hooke's law is fulfilled in the normal condition of glass up to the breaking point, but in the accommodation condition the ratio of the bending to the stress is increased. The effect of temp. on Young's modulus is $E=E_{15}\{1-\alpha(\theta-15)+\beta(\theta-15)^2\}$ in the

accommodation condition, and $E=E_{15}\{1-\alpha(\theta-15)^{\beta}\}$ in the normal condition. A. E. Williams measured for the modulus of rupture and Young's modulus of 5000 samples of various types of glass, and found for window glass 7000 lbs. per sq. in. and 11,000,000 lbs. per sq. in. respectively; and for plate glass, respectively 6500 and 10,000,000 lbs. per sq. in. L. N. G. Filon and F. C. Harris studied the effect of temp. on the elastic constants of glass.

The ratio of the lateral contraction to the longitudinal extension with a longitudinal pull or thrust furnishes the so-called **Poisson's ratio,** $\sigma$—*vide* **1.** 13, 17. Measurements were made by F. Twyman and J. W. Perry,[16] G. Wertheim and E. Chevandier, W. Pscheidl, J. Kieweit, A. Winkelmann and O. Schott, A. Winkelmann, W. Ludwig, J. D. Everett, A. Cornu, H. T. Jessop, W. Voigt, M. Cantone, J. von Kowalsky, and E. H. Amagat. R. Straubel found that the observed values range from 0·197–0·239; and if $a_1$, $a_2$, $a_3$, . . . denote the percentage amounts of the respective oxides, and $y_1$, $y_2$, $y_3$, . . . the Poisson coeff., then $\sigma=a_1y_1+a_2y_2+a_3y_3+$ . . ., where

| | $SiO_2$ | $B_2O_3$ | ZnO | PbO | $Al_2O_3$ | BaO | $Na_2O$ |
|---|---|---|---|---|---|---|---|
| $y$ . | 0·001533 | 0·002840 | 0·003460 | 0·002760 | 0·001750 | 0·003560 | 0·004310 |

| | $K_2O$ | CaO | $P_2O_5$ | $Sb_2O_5$ | MgO | $As_2O_5$ | $Mn_2O_3$ |
|---|---|---|---|---|---|---|---|
| $y$ . | 0·003969 | 0·004163 | 0·002147 | 0·002772 | 0·002500 | 0·002500 | 0·002500 |

F. Auerbach calculated indirect values for Poisson's ratio and obtained a relation between the hardness and Poisson's ratio. R. Straubel showed that the supposed relation is invalid.

R. Straubel[17] used the formulæ indicated **1.** 13, 17, and calculated values for the **rigidity** or **resistance** to shearing and the **compressibility,** vol. elasticity, or resistance to compression from Young's modulus, and Poisson's ratio. He obtained values for the rigidity ranging from 1840–3140 kgrms. per sq. mm., and for the compressibility 3470–7520 kgrms. per sq. mm. J. E. P. Wagstaff found for the coeff. of rigidity of a glass plate $2·576\times10^{11}$ to $2·59\times10^{11}$ dynes per sq. cm. per unit shear. P. W. Bridgman represented the compressibility of pyrex glass at a press. $p$, by $dv/v_0=0·0_93027p-0·0_{12}99p^2$. L. H. Adams and E. D. Williamson found the compressibility of plate glass to be $\beta=2·27\times10^{-6}$ at atm. press., $2·23\times10^{-6}$ at 2000 atm. press., and $2·05\times10^{-6}$ at 10,000 atm.; or $\beta=0·0_52226-0·0_6220(p-p_0)$. J. Y. Buchanan gave for the linear compressibility of flint glass, $0·0_72$, and for ordinary glass tubing, $0·0_6846$. Observations were made by E. Madelung and R. Fuchs. G. Ercolini found that a tension, compression, and a shearing force in an electric field produced no variation in the elastic constants.

J. Cardanus,[18] in 1557, noted that when glass is kept for some time near the temp. of liquefaction, it loses its transparency and becomes opaque. Glass when cooled has all the characteristics of a congealed soln., but some glasses are very liable to crystallize or devitrify during the cooling; all depends on the nature and proportions of the different components, and on the time occupied in the cooling. Other glasses must be kept in the temperature zone of crystallization for hours in order to obtain crystals. J. B. A. Dumas found by analysis of a piece of devitrified glass:

| | $Na_2O$ | CaO | $Al_2O_3$ | $SiO_2$ |
|---|---|---|---|---|
| Crystallized portion . . | 14·9 | 12·0 | 4·0 | 68·2 per cent. |
| Vitreous portion . . | 19·8 | 12·0 | 3·5 | 64·7 ,, |

Analyses and observations on devitrification were made by B. G. Sage, F. Hundeshagen, E. Péligot, H. Schwarz, M. Gröger, and A. Terreil. Some of the alkali-lime glasses furnish crystals of wollastonite. H. le Chatelier observed the formation of tridymite. As previously indicated, a small proportion of alumina is inimical to the process of devitrification. The subject has also been discussed in connection with Reaumur's porcelain. The first signs of devitrification are a faint turbidity and the appearance of a bluish tinge by reflected light. Observations were made by W. Lewis, A. Dartigues, D. C. Splitgerber, N. L. Bowen, L. B. G. de Morveau,

J. Fournet, J. B. A. Dumas, J. Pelouze, S. F. Cox, L. Appert, M. Bontemps, H. Knoblauch, J. W. Mellor, J. Fowler, N. Heaton, D. Herman and F. Rutley, N. L. Bowen, H. Insley, C. N. Fenner and J. B. Ferguson, Lord Rayleigh, F. Gelstarp, H. le Chatelier, C. J. Brockbank, Y. Amanomiya, R. Wietzel, A. F. O. Germann, etc. The alleged devitrification of old glass has not been clearly established, for it is probably due to a kind of surface weathering—*vide infra*. A. F. O. Germann removed the surface film by washing with hydrofluoric acid, and found the underlying glass to be quite normal.

E. Kochs and F. Seyfert[19] obtained an empirical formula to calculate the **melting point** of a silicate. Let $[SiO_2]$ denote the percentage amount of silica; $[Al_2O_3]$, the percentage amount of alumina; $K$, their ratio; $A$, $B$, $C$, . . ., the percentage amounts of various fluxes; and $M_a$, $M_b$, $M_c$, . . ., the mol. wts. of the various fluxes. If $F$ represents the sum $A/M_a+B/M_b+C/M_c+\ldots$, what they call the fusibility quotient, $Q$, then $Q=0{\cdot}005767T^2/KF$. The fusibility quotient, $Q$, of potash-felspar is 0·153, of potash-lime glass 0·00004, etc. It will be observed that the assumption made is that the fusibility is solely determined by the mol. wts. of the constituent oxides. A. Granger used this formula. As shown by E. Zschimmer, etc., glasses have no definite m.p.; and F. Weidert and G. Berndt refer to the deformation temp. as the upper limit at which a piece of glass loses its form. F. Singer, R. L. Frink, R. Schaller, and F. Springer have discussed the effect of small additions of alumina in making soda-lime glasses more friable. A. Q. Tool and co-workers observed a small heat absorption shown on the heating curve of powdered glass just above the annealing temp. Observations were also made by J. W. Mellor and co-workers, L. Grenet, A. A. Lebedeff, K. Beck, H. and F. le Chatelier, etc. The thermal effect which occurs on heating glass was observed by A. Q. Tool and C. G. Eichlin, and it corresponds to the effect produced by a change of state, but is thought to be due to the formation of some molecular aggregate producing homogeneity, and relieving strains as in annealing.

P. S. Laplace and A. L. Lavoisier[20] measured the coeff. of **thermal expansion** of flint glass and found $0{\cdot}0_5812$–$0{\cdot}0_5872$; lead-free glass, $0{\cdot}0_5875$–$0{\cdot}0_5898$; and mirror glass, $0{\cdot}0_5891$. P. L. Dulong and A. T. Petit found the coeff. of cubical expansion up to 300° to be $0{\cdot}0000251+0{\cdot}0_42251+0{\cdot}0_{10}60°$. H. V. Regnault measured the coeff. for a number of glasses of different composition, and obtained for crystal-glass values ranging from $0{\cdot}0_42144$–$0{\cdot}0_42442$; and for ordinary white glass, values ranging from $0{\cdot}0_42324$–$0{\cdot}0_42758$. H. le Chatelier gave between 0° and 40°, $0{\cdot}0_4186$, and between 0° and 700°, $0{\cdot}0_4225$. O. Schott obtained values ranging from $0{\cdot}0_4110$–$0{\cdot}0_4337$; and A. Winkelmann and O. Schott found that if $a_1$, $a_2$, $a_3$, . . . denote the percentage amounts of the respective oxides, and $y_1$, $y_2$, $y_3$, . . . their expansion coeff., the coeff. of cubic expansion will be $a\times10^7=a_1y_1+a_2y_2+a_3y_3+\ldots$, where

| | $SiO_2$ | $B_2O_3$ | ZnO | PbO | MgO | $Al_2O_3$ | $As_2O_5$ |
|---|---|---|---|---|---|---|---|
| $y$ . | 0·8 | 0·1 | 1·8 | 3·0 | 0·1 | 5·0 | 2·0 |

| | BaO | $Na_2O$ | $K_2O$ | CaO | $Sb_2O_5$ | $Li_2O$ |
|---|---|---|---|---|---|---|
| $y$ . | 3·0 | 10·0 | 8·5 | 5·0 | 2·0 | 2·0 |

The additive character of the thermal expansion coeff. was confirmed by J. Mori, J. Salpeter, and S. English and W. E. S. Turner for soda-lime glasses, such that if the symbols of the constituents represent the percentage amounts, the coeff. of cubical expansion of these glasses is $0{\cdot}0_78[SiO_2]+0{\cdot}0_51[Na_2O]+0{\cdot}0_65[CaO]$. Similarly, for the magnesia-soda glasses, the results are given by the factors $SiO_2$, 0·15; $Na_2O$, 12·96; CaO, 4·89; and MgO, 1·35. With the soda-lime glasses the coeff. of linear expansion ranged from $0{\cdot}0_41138$–$0{\cdot}0_5801$; and for the soda-magnesia glasses from $0{\cdot}0_41138$–$0{\cdot}0_5594$. W. E. S. Turner and co-workers also determined the effects of silica, boric oxide, soda, titania, and alumina on the thermal expansion of glasses. J. Salpeter found a relation between the at. vols. of the elements and the coeff. of thermal expansion. H. Schönborn observed that different varieties

of glass have a critical zone of temp. in which there is a discontinuity in the curve representing the rate of expansion with temp. This zone corresponds approximately with a variation in the electrical resistance of the glass (*q.v.*). W. B. Pietenpol found the thermal expansion of glasses increased linearly with temp., up to 450° or 550°, during the next 60° or 100° increased 4–6 times more rapidly, and therefrom increased linearly to the softening point. With unannealed glass the rate of expansion decreased as the internal strain disappeared, and this indicates a method of finding the proper annealing temp. O. Schott showed that a sample of glass in a state of strain produced by rapid cooling, had a coeff. of cubical expansion $0{\cdot}0_42895$, while the unstrained glass had a coeff. $0{\cdot}0_42748$; and the result was confirmed by J. Wolf. C. Pulfrich found a rise in the value of the coeff. from $0{\cdot}0_4258$ *between* 4·85° *and* 18·7°, *to* $0{\cdot}0_4265$ *between* 18·7° and 90·5°. Measurements at different temp. were made by M. Thiessen and co-workers, who gave for the linear coeff., $(7797+3646)10^{-9}$; and for the cubical coeff., $(23391+10{\cdot}92\theta)10^{-9}$. For normal Jena glass, A. W. Warrington gave for the vol. at $\theta°$, $v=v_0\{1+(23714+10{\cdot}62\theta)10^{-9}\theta\}$, *when* $v_0$ *represents the initial vol. The subject has been discussed* by E. Reimerdes, F. C. H. Wiebe, F. C. H. Wiebe and G. Möller, E. Zschimmer, R. Rieke and W. Steger, H. Auffenberg, G. W. C. Kaye, W. B. Pietenpol, C. G. Peters and C. H. Cragoe, M. Meyer and B. Havas, F. E. Wright, etc. K. E. Guthe found the linear coeff. of a glass to be $0{\cdot}0_545$; J. T. Bottomley and W. J. Evans gave 0·00181 for the cubical expansion of Jena glass between 0° and 100°. C. Holborn and E. Grüneisen gave for the expansion of Jena borosilicate glass between 0° and 500°, $(5184\theta+0{\cdot}804\theta^2)10^{-9}$ and $(5852\theta+0{\cdot}959\theta^2)10^{-9}$. F. Henning found a rod of this glass, a metre long, contracted 0·877 mm. when cooled to −191°. C. G. Peters and C. H. Cragoe found for intervals approximately 19°–500°, $\alpha=0{\cdot}0_562-0{\cdot}0_4120$; and between 500° and 600°, $\alpha=0{\cdot}0_4205-0{\cdot}0_4649$. P. Lafon studied the irregularities which occur in the dilation of glass with rise of temp. O. Schott found a zinc borate glass with the small coeff. $0{\cdot}0_4110$, and an alumina-glass with the coeff. $0{\cdot}0_4337$, which is nearly that of iron or nickel, and a glass with the coeff. $0{\cdot}0_545$ is used for making lamp chimneys. A. Arnulf devised a machine for automatically recording the expansion of glass.

The glass of a newly-made glass thermometer only gradually resumes its original volume, so that the mercurial column gives continually higher indications for one and the same temp. A thermometer which has been allowed to season before calibration does not show this *rise of zero*, but if it be heated to a high temp. there is a *depression of zero* which gradually resumes its normal value as the original volume is restored. R. Weber stated the phenomena are due to what he called the *Nachwirkung*, or the *after-effect*, or the *thermal after-effect*. The phenomenon has been studied in its application to thermometry by W. Schlösser, F. C. H. Wiebe, O. Schott, B. Eckardt, F. Grützmacher, A. Böttcher, J. Pernet, C. E. Guillaume, M. Thiessen and co-workers, K. Scheel, F. Allihn, W. Pomplun, H. Lemke, A. Mahlke, P. Chappuis, M. Tonnelot, etc. O. Schott devised a kind of compensation for the after-effect by enclosing within the thermometer bulb a small rod of another kind of glass with the same coeff. of expansion, but with a much larger thermal after-effect, so as to correct the depression of the zero when the thermometer is heated. The subject was investigated by W. Hoffmann, and G. Müller. No exact relation was observed by G. Weidmann between the thermal and elastic after-effects. As indicated above, A. Winkelmann observed that the coeff. of elasticity was increased after heating and cooling; and the effect became stationary after a repetition of the treatment a number of times. The phenomenon was called the *thermo-elastic after-effect*, and it has also been observed with platinum. L. Marchis made observations on the subject.

If liquid glass is abruptly cooled, say, by falling drop by drop into cold water, the congealed droplets are called *Rupert's drops*, *lacrymæ vitreæ*, *Knallgläser*, or *guttis vitreis* (glass tears). When the thin tip is broken, the whole is converted into a fine powder with a feeble detonation. These drops were first brought to England

by Prince Rupert, but, according to J. Beckmann,[21] they were not invented by him; they appear to have been made prior to 1661, because they were mentioned by B. de Monconys in that year. Theses on glass drops by J. C. Schulenburg appeared in 1695, by J. G. Baier in 1708, and by S. Reyher in 1714. According to P. D. Huet, the first glass drops came from Germany; according to A. le Grand, they came from Prussia; and according to G. Montanari, and H. Regius, they came from Sweden. On the authority of B. de Monconys, J. Beckmann argued that the drops first came from Holland. A tumbler of the unannealed glass may shatter to fragments when slightly scratched, say, by dropping a small piece of flint into the glass. F. B. A. R. de la Bastie found that if glass articles are heated to redness, suddenly immersed in oil at 300°, and then allowed to cool very slowly, the product is the so-called *toughened glass*. It resists abrupt changes of temp. better than untoughened glass, and it is not readily broken when dropped; but if it once does break, it shatters into fine fragments. A crack may occur in toughened glass without shattering the whole; but it cannot be cut with a diamond. Glass is annealed in order to relieve the strains introduced during the cooling. This subject was investigated by L. H. Adams and E. D. Williamson, G. Guadet, H. Schuz, etc. A. Q. Tool and C. C. Eichlin examined the effect of annealing on the heating curves of glass.

Glass is a bad conductor of heat. The **thermal conductivity** of glass was measured by O. Paalhorn,[22] and he obtained numbers ranging from $k$=0·001082–0·002267 cal. per cm. per sec.; and H. Hecht obtained 0·0025. A. Winkelmann showed that the absolute conductivity can be calculated from $k=a_1y_1+a_2y_2+a_3y_3+\ldots$, where $a_1$, $a_2$, $a_3$, . . . denotes the percentage amounts of the constituent oxides; and $y_1$, $y_2$, $y_3$ . . . represents the conductivity coeff., *viz.*

| | $SiO_2$ | $Ba_2O_3$ | ZnO | PbO | MgO | $Al_2O_3$ |
|---|---|---|---|---|---|---|
| $y$ . . | $0{\cdot}0_4220$ | $0{\cdot}0_4150$ | $0{\cdot}0_4100$ | $0{\cdot}0_580$ | $0{\cdot}0_584$ | $0{\cdot}0_4200$ |
| $z$ . . | 0·34 | 0·66 | 15·0 | 16·0 | 5·0 | 2·5 |

| | $As_2O_5$ | BaO | $Na_2O$ | $K_2O$ | CaO | $P_2O_5$ |
|---|---|---|---|---|---|---|
| $y$ . . | $0{\cdot}0_520$ | $0{\cdot}0_4100$ | $0{\cdot}0_4160$ | $0{\cdot}0_510$ | $0{\cdot}0_4320$ | $0{\cdot}0_4160$ |
| $z$ . . | 3·0 | 13·0 | 10·5 | 13·3 | 6·0 | 6·7 |

A. Winkelmann obtained better results by using $b_1$, $b_2$, $b_3$, . . . as the vol. percentages instead of $a_1$, $a_2$, $a_3$, . . . percentages by weight; and using the corresponding coeff. $z_1$, $z_2$, $z_3$, . . . In that case the reciprocal of the conductivity $k^{-1}=b_1z_1+b_2z_2+b_3z_3+\ldots$ Measurements were also made by T. M. Focke, A. Eucken, J. Thoulet, C. H. Lees, H. Mayer, and O. Venske. J. Krüger studied the influence of temp. on the thermal conductivity of glass, and represented the value of $k$ at $\theta°$, when the conductivity at $\theta°$ is $k_0$, by $k=k_0(1+a\theta)$, where $a$ is a constant dependent on the type of glass. W. M. Thornton observed a relation between the thermal conductivity, $k_1$, the elasticity, $E$, and the sp. gr., $D$, such that $k=ED=V^2D^2$, where $V$ is the velocity of sound in the glass. J. R. Clarke could not confirm this relation. E. D. Williamson and L. H. Adams studied the distribution of temp. in glass during heating or cooling. P. W. Bridgman represented the thermal conductivity of pyrex glass at a press. $p$ by $0{\cdot}0261+0{\cdot}0_71p$ at 30°–75°.

A. Winkelmann [23] determined the **specific heat** of various glasses and obtained numbers ranging from 0·08174–0·2318. If $c$ denotes the sp. ht. of a glass, $a_1$, $a_2$, $a_3$, . . . the percentage amounts of the constitutional oxides, and $y_1$, $y_2$, $y_3$, . . . the sp. ht. of the component oxides, then $c=a_1y_1+a_2y_2+a_3y_3+\ldots$, where

| | ZnO | $B_2O_3$ | $Al_2O_3$ | $SiO_2$ | $As_2O_3$ | PbO | MgO |
|---|---|---|---|---|---|---|---|
| $y$ . . | 0·1248 | 0·2272 | 0·2074 | 0·1913 | 0·1276 | 0·05118 | 0·2439 |

| | BaO | $Mn_2O_3$ | $Na_2O$ | $K_2O$ | $Na_2O$ | CaO | $P_2O_5$ |
|---|---|---|---|---|---|---|---|
| $y$ . . | 0·06728 | 0·1661 | 0·2674 | 0·1860 | 0·5497 | 0·1903 | 0·1902 |

The sp. ht. of glass rises with temp., and the sp. ht. in the amorphous or glassy

state is slightly higher than in the devitrified or crystalline condition ; the difference is more marked with glasses with a high proportion of alkali. I. Iitaka found the sp. ht. of ordinary glass to be 0·212 at 133·3° ; 0·221 at 213° ; 0·231 at 318° ; and 0·236 at 405°. G. E. Gibson and W. F. Giauque showed that in the case of glycerol, the entropy of a glass exceeds that of a crystal of the same composition at absolute zero.

Thermal shock tests are made by heating the glass vessel containing a suitable liquid to progressively higher and higher temp. until the glass fractures. A. Winkelmann [24] and O. Schott introduce a number of assumptions into an argument which reduces to an empirical expression for what they call the *thermischer Widerstandskoefficient*—coeff. of **thermal endurance,** representing the power of glass to withstand the inequalities of temp. :

$$\text{Thermal endurance} = \frac{P}{aE}\sqrt{\frac{K}{cD}}$$

where $K$ denotes the thermal conductivity ; $c$, the sp. ht. ; $D$, the sp. gr. ; $E$, Young's modulus ; $\alpha$, the coeff. of linear expansion ; and $P$, the tensile strength of the glass. The values of the thermal endurance so calculated range from 3·51 to 13·52. The results often agree with observation, although some irregularities were noted. Glasses usually resist compressive forces better than tensile forces, and hence they will withstand rapid uniform heating better than quick uniform cooling. Glasses rich in alkali have a high coeff. of expansion, and therefore are more liable to break with abrupt temp. changes than glasses with a smaller expansion coeff.

The **refractive index** of glass ranges from 1·50 to 1·9626 for the densest flint glass. A. Baudrimont and J. Pelouze [25] said that the refractive index increases with the mol. wt. of the contained bases, thus lead glass has the highest index of refraction, next comes baryta-glass, then potash glass, and least of all, soda glass. J. von Fraunhofer found for crown glass and for medium and dense flint glasses :

| | *A*-line. | *C*-line. | *D*-line. | *E*-line. | *F*-line. | *G*-line. | *H*-line. |
|---|---|---|---|---|---|---|---|
| *Flint* (3·723) . . . | 1·628 | 1·630 | 1·635 | 1·642 | 1·648 | 1·660 | 1·671 |
| Flint (3·512) . . . | 1·602 | 1·604 | 1·609 | 1·615 | 1·620 | 1·631 | 1·640 |
| Crown (2·535) . . . | 1·526 | 1·527 | 1·530 | 1·533 | 1·536 | 1·542 | 1·547 |

Hundreds of other observations have been made—*e.g.* by M. Dutirou, H. Starke, H. du Bois, J. W. Gifford, F. E. Wright, T. Smith, F. Eckert, C. J. Peddle, P. J. van Kerkhoff, V. S. M. van der Willigen, R. J. Montgomery, etc. O. Schott gave for the index of refraction, $\mu$ for the $D$-line, the mean dispersion $\mu_C - \mu_F$ and the ratio, $\gamma$, of the mean dispersion divided by $\mu - 1$ :

| | Sp. gr. | $\mu$ | $\mu_C - \mu_F$ | $\gamma$ |
|---|---|---|---|---|
| Light phosphate crown glass . . . . | 2·58 | 1·5159 | 0·00737 | 70·0 |
| Crown glass . . . . . | — | 1·4650 | — | 65·7 |
| Borosilicate crown glass . . . . | 2·47 | 1·5100 | 0·00797 | 64·0 |
| Heavy baryta crown glass . . . . | 3·55 | 1·6112 | 0·01068 | 57·2 |
| Soft silicate crown glass . . . . | 2·55 | 1·5151 | 0·00910 | 56·6 |
| Extra light flint glass . . . . | 2·87 | 1·5398 | 0·01142 | 47·3 |
| Ordinary silicate flint glass . . . | 3·63 | 1·6202 | 0·01709 | 36·2 |
| Heavy silicate flint glass . . . . | 3·87 | 1·6489 | 0·01919 | 33·8 |
| Heaviest silicate flint . . . . . | 6·33 | 1·9626 | 0·04882 | 19·7 |

C. J. Peddle studied the refractive indices of the binary and ternary systems, $SiO_2$–$K_2O$–$Na_2O$ ; $SiO_2$–$CaO$–$Na_2O$ or $K_2O$ ; $SiO_2$–$BaO$–$K_2O$ or $Na_2O$ ; and $SiO_2$–$PbO$–$Na_2O$ or $K_2O$ ; and F. E. Wright, the refractive indices and dispersion of a variety of glasses. E. S. Larsen found that for all the albite-anorthite series of glasses the formulæ of Gladstone and Dale and of Lorentz and Lorenz give results which are sensibly additive ; E. W. Tillotson found the sp. refractivities calculated by either of the above-mentioned formulæ give results with the soda-lime glasses which are additive, so that if $a_1$, $a_2$, $a_3$, . . . denote the percentage amounts of the constituent oxides, and $y_1$, $y_2$, $y_3$, . . . the sp. refractivities of the oxides, $100K = a_1y_1 + a_2y_2 + a_3y_3 + \ldots$, where $y_1$ for $SiO_2$ is 0·1220 ; $y_2$ for $CaO$ is 0·1210 ; and $y_3$ for $Na_2O$ is 0·1302. Similar results were obtained for soda-baryta glasses, and for

the albite-anorthite series of glasses. J. R. Clarke and W. E. S. Turner found the replacement of soda by lime in the glasses of the type $2Na_2O:6SiO_2$ produces a linear change in the refractive index. R. J. Montgomery studied the refractive indices of the lead glasses. A. R. von Schrötter gave for the thallium lead glass of sp. gr. 4·18, $\mu=1·661$ for the *B*-line, 1·673 for the *D*-line, and 1·710 for the *H*-line. G. Muller also made observations on the refractive indices of thallium glasses. T. J. Pelouze, and W. E. S. Turner and co-workers studied the refractive indices of aluminous and boriferous glasses. E. Zschimmer found that the refractive indices of glassy boric oxide, 1·4620, and of fused silica, 1·4585, are raised by the dissolution of metallic oxides, but not proportionally with the mol. wt. For instance, $Li_2O$, ZnO, PbO, and BaO, each eq. to 40 per cent. BaO, in 100 parts of boric oxide raised the refractive index in the 3rd decimal respectively 77, 93, 114, and 248 units. The effect did not increase with conc., for the optical effect decreased with $Li_2O$ in $B_2O_3$, $Na_2O$ in $SiO_2$, and ZnO in $B_2O_3$ or alkali silicate glass, but it increased with PbO and BaO. In potassium-silicate glass—15 per cent. $K_2O$—the addition of boric oxide increased the refractive index to a maximum with 15 parts of $B_2O_3$ to 100 of glass, and therefrom decreased the refractive index. E. S. Larsen investigated the relation between the sp. gr. and refractive index of glass. H. Rubens measured the dispersion for the ultra-red rays; and H. T. Simon for the ultra-violet rays. The subject was also investigated by J. Hartmann, L. Mouton, S. P. Langley, H. Trommsdorff, H. Rubens, E. L. Nichols, O. Reinkober, C. Schäfer and M. Schubert, and K. Löwe. C. Pulfrich measured the effect of temp. up to about 100° on the index of refraction, and J. O. Reed worked at temp. up to 500°. F. Pockels studied the effect of elastic deformation on the optical properties of glass. The reflexion and elliptical polarization were examined by J. Jamin, P. Drude, Lord Rayleigh, G. C. Schmidt, O. Lummer and K. Sorge, M. Volke, H. Schulz, R. Kynast, and O. Hebecker. L. N. G. Filon, and F. C. Harris studied the effect of time and temp. on the photo-elastic constants of glass.

Glass which has been rapidly cooled is not optically homogeneous nor optically isotropic; the outer layers are cooled faster and shrink more than the interior. Hence, the interior is in a state of strain. In 1814, T. J. Seebeck, and D. Brewster showed that a piece of glass when irregularly heated exhibits double refraction like many uniaxial crystals, and that under press. the glass shows interference colours in polarized light. The colour patterns were called by T. J. Seebeck *die entoptischen Farbenfiguren;* and they have been called *Seebeck's colours*. According to E. G. Coker, when a strip of glass between crossed nicols is subjected to an increasing strain, it first shows a greyish-white colour which passes successively through the colour changes, lemon-yellow, reddish-purple, to blue; and if the strain increases, the scale of colours is repeated for approximately double the intensity of the stress. There is thus a well-defined colour scale corresponding to the torsional stress. For simple compression and tension, the relative retardation of the rays producing the colour effects is proportional to the intensity of the stress, and to the thickness of the material. E. Zschimmer found the strains could be introduced in large articles from their own weight.

The birefringence of strained glass was studied by J. Kerr, A. Q. Tool and C. G. Eichlin, H. du Bois, O. D. Tavern, O. Reeb, H. Ambronn, W. Köhler, A. Winkelmann, H. Boissier, F. Eckert, Lord Rayleigh, L. H. G. Filon, L. H. G. Filon and H. T. Jessop, F. Pockels, W. König, F. Twyman and co-workers, E. and M. Henriot, H. Schulz, G. Berndt, F. E. Neumann, F. Taffin, T. T. Smith and co-workers, P. S. Nutting, E. E. Wright, A. L. Kimball, S. Czapsky, etc. O. Schott found that the double refraction disappeared from strained ordinary and borosilicate crown glasses between 400° and 410°, and from flint glass between 350° and 360°. Glass is annealed in order to relieve these strains. E. Hagenbach examined samples of glass which had cracked without any apparent cause and found Seebeck's colours were present. He suggested testing glass for soundness by its appearance in polarized light, rejecting that which exhibits the strain-colours.

F. Vogel measured the **absorption of light** rays in the visible spectrum by different glasses and found for the coeff. of absorption, $k$, for two flint glasses and two crown glasses :

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| $\lambda$ . . . | 0·677 | 0·580 | 0·535 | 0·503 | 0·477 | 0·455 | 0·436$\mu$ |
| Flint (light) . | 0·0059 | 0·0102 | 0·0129 | 0·0138 | 0·0106 | 0·0214 | 0·337 |
| Flint (heavy) . | 0·0231 | 0·0188 | 0·0213 | 0·0246 | 0·0357 | 0·0411 | 0·0569 |
| Crown . . . | 0·0102 | 0·0137 | 0·0108 | 0·0137 | 0·0151 | 0·0196 | 0·0216 |
| Crown . . . | 0·0151 | 0·0201 | 0·0233 | 0·0254 | 0·0260 | 0·0261 | 0·0227 |

This shows that at the red end of the spectrum the light flint glasses are less absorbent than the crown glasses, but at the other end this condition is reversed. The absorption by the heavy flint glass exceeds that of other glasses as the wave-length diminishes ; and its absorption for the longer waves is not surpassed by the crown-glasses. The effect of temp. on the absorption of light by glasses was discussed by J. Königsberger and co-workers, W. Rieder, H. du Bois and G. J. Elias, G. B. Rizzo, R. A. Houston, A. Silvermann, J. Becquerel and F. Eckert, H. Rubens, G. Rosengarten, J. M. Eder and E. Valenta, F. Vogel, G. E. Grantharn, F. Eckert, W. W. Coblentz and W. B. Emerson, C. Schäfer, M. Schubert, F. Eckert, and A. W. Smith and C. Sheard investigated the transparency of various glasses for the ultra-red or heat rays ; according to W. W. Coblentz, the transparency for the ultra-red rays is very great up to 2$\mu$ ; and as with most silicon compounds, there are bands at 5·6$\mu$ and 6·25$\mu$. He also studied the ultra-red reflexion spectrum, The absorption of light in coloured glasses has been studied by R. Zsigmondy and C. Grebe, R. Zsigmondy, P. P. Fedotieff, J. Königsberger, P. P. Fedotieff and A. Lebedeff, J. W. Mellor, W. W. Coblentz and co-workers, K. S. Gibson, R. A. Houstoun, S. B. Nicholson and E. Pettit, R. C. Gibbs, E. P. Hyde and co-workers, M. Luckiesh, etc. F. Weidert studied the absorption spectra of glasses containing didymia. In general, the absorption increases as the temp. rises, though in some parts of the spectrum there may be a decrease. In some cases the absorption bands remain stationary ; in others, there is a shift towards the red. There is usually a complete recovery when the original temp. is restored. The absorption of ultra-violet light by glass has been investigated by E. Zschimmer, F. F. Martens, C. Fritsch, E. de Chardonnet, N. Schjerning, H. A. Krüss, G. Krüss, H. Pflüger, W. Rieder, J. Duclaux and P. Jeantet, F. Eckert, R. C. Williamson, F. Pflüger, and A. W. Smith and C. Sheard. The ultra-violet transmission spectrum of glasses has been investigated by W. R. Ham and co-workers, J. R. Clarke and W. E. S. Turner, L. Bell, H. P. Gage and W. C. Taylor, K. S. Gibson, E. Zschimmer, and H. T. McNicholas. W. Crookes studied the effect of the oxides of cerium, chromium, cobalt, nickel, copper, iron, manganese, neodymium, praseodymium, and uranium on the absorption of heat rays and ultra-violet rays, and on the transmission of luminous rays. H. J. Möller found dark brown, dark green, or red glass bottles protect best the contents from the chemical action of light. Obviously glasses which cut off the heat rays would be useful for railway carriage windows, etc., in sunny climes ; and goggles, and spectacle-lenses which cut off all but the luminous rays would prevent irritation. This subject has been discussed by W. W. Coblentz and co-workers, G. Alleman, W. P. Graham, M. Luckiesh, F. Eckert, C. Grebe, R. Zsigmondy, F. Schanz, F. E. Lamplough, E. L. Hettinger, K. W. Hausser and W. Vahle, J. van der Hoeve, A. L. Forster, etc. K. Köhler studied the transmission of light through frosted glass. E. P. Lewis and A. C. Hardy found that the **reflective power** of ordinary glass for radiation below $\lambda$=1860 was from 10–13 ; and for dense glass, 10 (rock salt, 8–9). M. Kahanowicz and A. Estrafalaces studied this subject. P. Zeeman and co-workers discussed the **Fizeau effect** in flint glass.

W. C. Röntgen observed that lead glasses absorb **X-rays** more than do the leadless glasses. A. Winkelmann and R. Straubel studied the subject and found that baryta glasses behaved like lead glasses, and that the presence of antimony oxide or zinc oxide diminishes the transparency. Of the glass-making compounds in

powder form, they found the most transparent were alumina, boric acid, and sodium nitrate and carbonate; the least transparent were lead oxide, red lead, antimony oxide, and barium nitrate; while zinc oxide, sand, and potassium carbonate and nitrate were of intermediate transparency. The order of transparency from greatest to least with glasses containing the rare earths, etc., were cerium, didymium, zirconium, and thorium. Glasses with zirconia behave like fluorite in transmitting the X-rays; the effect was weaker with glasses containing didymia and erbia. No effect was observed with glasses containing beryllium, uranium, cerium, or thorium. O. Schott found that transparency of glasess to X-rays follows the inverse order of at. wt. of the elements in the oxides; and found a glass containing 39·6 per cent. $SiO_2$; 30 of $B_2O_3$; 20 of $Al_2O_3$; 0·4 of $As_2O_5$; and 10 of $Na_2O$, to be very transparent to these rays. The absorption of X-rays by glass was investigated by R. Glocker, and C. and F. Lindemann; the reflection of X-rays by A. P. Compton; and the coloration of glass by X-rays, by A. Dauvillier.

The **fluorescence** of glass was discussed by E. Lommel, W. Spring, H. Geiger, J. B. Burke, E. L. Nichols and E. Merritt, G. M. Sägmüller, P. Lenard, P. Pringsheim, E. Wiedemann and G. C. Schmidt, R. C. Gibbs; the discoloration of glass by exposure to radiations of various kinds by M. Berthelot, B. Delachanel, J. C. M. Garnett, R. W. Lawson, L. Michel, H. Greinacher, G. T. Beilby, E. Rutherford, and P. Villard and F. Erkert; and the luminescence in **cathode rays** by E. Gehrke and O. Reichenheim, A. Schmauss, E. Wiedemann and G. C. Schmidt, E. Goldstein, and O. Reichenheim. The phosphorescence of potash glass when exposed to **radium radiations** was observed by G. T. Beilby; and when exposed to the rays from radio-tellurium, by H. Greinacher. E. Rutherford observed that radium emanation, decaying in a capillary tube of soda glass, formed a red-coloured area, probably due to the X-rays. C. Doelter and H. Sirk, A. Miethe, W. A. D. Rudge, S. C. Lind, F. Eckert, M. Berthelot, W. Crookes, S. Avery, and G. T. Beilby studied the coloration of glass by radium rays. Soda glass is coloured violet by a prolonged action, and when the glass is heated, like purple fluorspar, there is a pale violet thermoluminescence and the colour is discharged. E. Newberry and H. Lupton found that lead glass acquires a brown colour under the action of radium, and the colour is discharged by heat. Borosilicate glasses acquire a purple-brown colour under similar conditions. C. Doelter also examined the effect of radium rays on different kinds of glass. J. R. Clarke found that all the glasses he tried fluoresced in radium rays, but a fatigue effect was noted at about the same time as the maximum coloration was reached. He thought the $\alpha$-**rays** were the active agents. None of the glasses fluoresced with the **X-rays**; but soda-lime glass and a selenium glass fluoresced slightly in **ultra-violet light.** All the glasses exposed to radium radiations exhibited thermoluminescence with the disappearance of the coloration between 100° and 235°; and R. E. Nyswander investigated the thermophosphorescence produced by radium rays. H. Jackson considered the green phosphorescence of X-ray tubes depended on the presence of traces of manganese oxide; without this agent, the glow is faint blue. The coloration of glass by exposure to **sunlight** was observed by S. Avery, B. Delachanal, M. Faraday, R. A. Gortner, and W. Crookes; and by exposure to ultra-violet light, by F. Fischer, and J. B. Nathanson. J. R. Clarke found glasses containing selenium or cobalt oxide as bleaching agents were coloured brown by $\beta$-rays. A soda-lime glass was feebly affected only by the $\alpha$-rays. J. R. Clarke thought that the colorations are due to the formation of colloidal particles in the glass. The **triboluminescence** of glass was observed by F. Haukesbee [26] in 1705, G. de Razoumowsky in 1787, and T. Wedgwood in 1792. P. Heinrich said that Rupert's drops almost always emit light when they are ruptured.

H. F. Richards [27] studied the contact electricity of glass, quartz, fluorite, and steel when taken in pairs. F. Kohlrausch said that glasses easily attacked by water have bad **insulating properties** owing to the formation of a film of water on the surface acting in conjunction with alkali dissolved from the glass. Assuming that

the glasses at the outset all insulate well, and that they have been for some time in contact with water, rinsed with distilled water, and dried in the sun or in the oven, then decidedly bad glasses will be recognizable by their discharging a gold-leaf electroscope almost instantly when the percentage of saturation in the air is between 50 and 60, and in a short time (1 sec. or 2 secs.) when it is between 40 and 50. With glasses of medium quality, as well as with lead crystal and Jena thermometer glass, the corresponding percentages of saturation will be about 20 higher. The Thuringian glass made at Gehlberg insulates perfectly up to 40 per cent. of saturation, fairly well at 60 per cent., and discharges in a few seconds at 80 per cent. With Bohemian potash glass, which at least as regards quantity of alkali dissolved must be reckoned among good glasses, no traces of conduction appeared till the percentage was above 50 per cent.; and the insulation was still fairly good at 75 per cent. At the head of all stood the alkali-free Jena glass, which insulated perfectly at above 60 per cent., and well even at 80 per cent. of saturation. P. Woog examined the effect of the surface weathering of glass on its insulating qualities for high voltage currents.

H. Buff, and E. Warburg and F. Tegetmeier found that the **electric conductivity** of glass becomes appreciable at 200°. If sodium amalgam be separated from mercury by a glass partition in a containing vessel heated to 200°, and if an electric current be passed from the amalgam through the glass to the mercury, the glass is electrolyzed, sodium passes into the mercury, and a corresponding amount is lost by the amalgam without the glass losing its clearness. If the sodium amalgam be replaced by lithium amalgam, the glass becomes opaque on the lithium side, and the opacity travels through the glass, as lithium takes the place of the displaced sodium. The glass in which lithium has taken the place of sodium becomes very brittle. It is assumed that lithium—at. vol. 15·98—can pass along the tracks or mol. galleries left by the sodium atoms—at. vol. 16·04—but the potassium atoms—at. vol. 24—are too large to pass along the spaces left by the sodium. W. J. Sutton and A. Silvermann, K. Horovitz, M. von Pirani, H. Schönborn, H. Freundlich and P. Rona, G. Borelius, and C. A. Kraus and E. H. Darby also replaced sodium in glass by silver. The phenomena were confirmed by W. C. Roberts-Austen, who found that if copper or gold amalgam be used the glass is coloured by the copper or gold. The electrolysis of glass was also studied by A. Heydweiler and H. Kopfermann, H. Schiller, H. Schönborn, M. le Blanc and F. P. Kerschbaum, A. Günther-Schulze, J. Königsberger, E. Rasch and F. W. Hinrichsen, J. W. Rebbeck and J. B. Ferguson, and R. Lorenz. H. H. Poole showed that the electrical conductivity of glass is not entirely electrolytic; and K. Horovitz, and R. Ambronn found that not only does glass conduct electrolytically, but it also becomes polarized. The results obtained at different temp., $T°$ K., show that if $L_0$ and $\beta$ are constants depending on the composition of the glass, the conductivity, $L$, at $T°$, is $L=L_0e^{-\beta T^{-1}}$. $L_0$ is a linear function of the percentages of soda and lime in the glass. Observations on the electrical conductivity of glass were made by J. R. Clarke, A. Denizot, R. Ambronn, W. Dietrich, G. Foussereau, W. Thomson, J. Perry, A. A. Somerville, N. Rood, C. E. Philips, C. Barus, F. Haber and Z. Klemensiewicz, F. Baumeister, E. Bollé, A. Speransky, H. H. Poole, A. Günther-Schulze, etc. F. Farup and co-workers found that increasing the alumina and silica decreased the conductivity. T. and A. Gray and J. J. Dobbie found the sp. **electric resistance,** $R$, of glass increased with the percentage of lead oxide, and with the sp. gr.; and further, that the conductivity is doubled for every 9° rise of temp. It was further found that for soda-lime glass,

| | 55° | 72° | 93° | 116° | 149° |
|---|---|---|---|---|---|
| $R\times10^{10}$ . . . | 531·05 | 89·15 | 11·901 | 1·874 | 0·202 |

for potash-lead glass at 142°, $R\times10^{10}=1328·6$; and for soda-lead glass,

| | 73° | 83° | 104° | 120° | 140° |
|---|---|---|---|---|---|
| $R\times10^{10}$ . . . . | 215·13 | 144·64 | 20·82 | 4·93 | 1·89 |

L. L. Holladay represented the electrical resistance, $R$, of various glasses between

20° and 500° by $\log R = a \log T - bT^{-1} - c$, where $a$, $b$, and $c$ are constants dependent on the nature of the glass; and the temp. $T$ is represented in °K. F. W. Hinrichsen and E. Rasch, and E. Schönborn found the conductivity of glass followed the same rule. Different varieties of glass also showed a transition point ranging between 384° and 560°, analogous with those obtained with the thermal expansion. The effect of absorbed gases on the conductivity was measured by V. Bush and L. H. Connell. F. F. S. Bryson found pitting occurred in the glass in the vicinity of the sealed platinum electrode of an interrupter connected with an induction coil. This was attributed to the electrolysis of the glass lying between the wire and the surrounding liquid—sulphuric acid. F. Haber and Z. Klemensiewicz, H. Schiller, and W. S. Hughes measured the **potential difference** between glass and soln. in contact therewith. The variation is approximately the same as for the variation in the hydrogen electrode potential, and is approximately a linear function of the latter. K. von der Grinten studied the **cataphoresis** of powdered glass. A. V. Bleininger noted a **thermoelectric current** by sealing platinum wires in small blocks of different glasses ground flat, and heating a pair of blocks in contact with one another while the wires are connected with a millivoltmeter.

The permittivity, sp. inductive capacity, or **dielectric constant,** K, of glass was found by M. Romich and J. Nowak to be 7·5; N. N. Schiller gave 3·3–6·34; J. Hopkinson, 6·6–9·1; J. E. H. Gordon, 3·0–3·24; G. Quincke, 3·6–25·3; K. F. Löwe, 5·48–9·13; W. Donle, 6·88–7·76; and A. Winkelmann, 6·46–7·57. The last-named gave for leadless glass 7·11, and 7·44 for a glass with 45 per cent. of lead. H. Starke gave 5·48–9·13. The ratio $K/S$, where $S$ denotes the sp. gr., is 2·17–3·38. J. J. Thomson, E. Lecher, R. Blondlot, and K. F. Löwe found that the dielectric constant increases as the frequency diminishes. A. Gray and J. J. Dobbie found for the sp. inductive capacity of soda-lime glass at 11°, 6·26, and at 129°, 6·79; for soda-lead glass, 7·36 at 19°, and 8·44 at 130°; and for potash-lead glass, 6·76 at 19°. M. von Pirani, W. M. Thornton, H. F. Richards, E. Schott, C. F. Hill, A. Coehn and A. Curs, and F. L. Ekman made observations on the dielectric constants of glass. The former represented the relation between the dielectric constant, $K$, and the sp. gr. $S$ of flint glasses by $K = 6{\cdot}61 + 1{\cdot}2965(S - 2{\cdot}89)^2$; and the relation between the dielectric constant and the refractive index, $\mu$, for the $F$-line, by $K = 6{\cdot}61 + 95{\cdot}6(\mu - 1{\cdot}549)^2$. C. L. Addenbroke found these relations did not hold for flint glasses with $S = 4{\cdot}85$, and $K = 11{\cdot}2$; and $S = 6{\cdot}01$, and $K = 13{\cdot}0$. The ratio of $K$ to $\mu^2$ increased continually as the sp. gr. increased. The heaviest flint glass known has a sp. gr. 6·33 and has a composition very nearly $PbSiO_3$; it was therefore suggested that the heavy flint glasses may be solid soln. of silica in lead metasilicate. F. M. Jäger measured the dielectric constant for different wave-lengths. G. Quincke discussed the **puncture voltage** of glass; and the cleavage cracks of punctured glass. Different phases of the subject were examined by N. Hesehus, A. Günther-Schulze, K. W. Wagner, J. L. R. Hayden and C. P. Steinmetz, J. Mosciaki, B. Walter, J. Almy, F. Kohlrausch, J. Hopkinson, J. Currie, T. J. Baker. E. E. Schumacher examined the relation between the composition of a glass and its tendency to crack while conducting electricity. A. Wüllner and W. Wien found the increase in the internal vol. of spherical and cylindrical condensers produced by electrostriction is in general less than the value obtained from Young's modulus. They also examined the effect of press. on the dielectric constant. K. R. Brain studied the **piezoelectric effects** with glass. P. Drude, and K. F. Lowe measured the **absorption of electromagnetic radiation.** H. du Bois found **Verdet's constant,** $W_D$, ranged from 0·0161–0·0888 when the value for fluorite was 0·0091; and O. Junghaus, 0·0197–0·0856. The latter also measured the **electro-magnetic rotation** of the plane of polarization and found for Na-light, 1·827°–0·0421° for different glasses. H. du Bois, and O. D. Tavern studied **Kerr's effect**—*i.e.* the double refraction developed in an electric field—with various glasses; and J. Königsberger, the **magnetic susceptibility.**

F. Degen,[28] and M. Faraday noted that glass adsorbs water, and, according to

the latter, glass acquires a certain surface conductivity which renders it unsuited for electrostatic experiments. A. Fusinieri and A. Bellani, and M. Faraday also referred to the film of air which is adsorbed tenaciously on glass surfaces. P. Chappius found that 1·6752 sq. m. of glass surface between 0°–180° adsorbed 0·45 c.c. of hydrogen; 0·58 c.c. of air; 1·03 c.c. of sulphur dioxide; and 1·41 c.c. of ammonia—between 0° and 100°, 0·63 c.c. of ammonia was adsorbed. The amount of carbon dioxide was between that of air and of sulphur dioxide. H. Zwaardemaker found that pyridine is scarcely adsorbed by glass surfaces, though valerianic acid is retained by the glass. Observations on the adsorption of gases on glass surfaces were made by L. Chiozza, H. Kayser, F. Kohlrausch, F. Mylius, S. Dushmann, D. H. Bangham and F. P. Burt, I. Langmuir, R. G. Sherwood, G. von Elissafoff, W. Falta, K. Horovitz and F. Paneth, G. Quincke, P. Volkmann, J. E. Shrader, L. Joulin, A. Smith, F. Weber, E. W. R. Pfeiffer, N. R. Campbell, H. Krause, J. B. Hannay, W. Voigt, J. F. Bottomley, J. Gaspar, F. Melhorn, G. Melander, and D. Ulrey. R. Bunsen found that the amounts of water retained by 2·11 sq. m. at different temp. were:

| | 23° | 107° | 215° | 329° | 415° | 468° | 503° | |
|---|---|---|---|---|---|---|---|---|
| Water . . | 22·3 | 14·2 | 11·6 | 7·6 | 2·8 | 0·9 | 0·0 | mgrm. |

Hence, it requires a temp. approaching 500° to remove the adsorbed water from glass surfaces. R. Whytlaw-Gray found glass adsorbs and dissolves hydrogen chloride; and that it adsorbs niton. E. K. Carver, and R. E. Wilson and T. Fuwa studied the adsorption of toluene by glass surfaces; and M. H. Evans and H. J. George, the adsorption of sulphur dioxide, ammonia, nitrous oxide, and acetylene by powdered glass, and found no evidence that the surface layer of adsorbed gas is just one mol. thick—*vide* adsorption by carbon. I. Langmuir discussed the general problem of the adsorption of gases on glass surfaces. J. J. Manley investigated the films of gas on glass. G. C. Schmidt and F. Durau measured the adsorption of aniline dyes from soln. by glass powder. E. Warburg and T. Ihmori, and H. Krause showed that glass dried at 500° does not adsorb carbon dioxide appreciably, while in the presence of moisture much is adsorbed. P. Mülfart could not confirm this; but moist and dry carbon dioxide are adsorbed by glass. D. H. Bangham and F. P. Burt studied the adsorption of ammonia and carbon dioxide by glass. The **Pouillet effect** with glass (**1**. 9, 9) was examined by C. S. M. Pouillet,[29] H. L. F. Melsens, P. Chappius, C. Cantoni, T. Martini, and F. Meissner. P. Schützenberger said that a high-tension discharge will drive water vapour through glass, but neither F. Meyer nor M. Berthelot could confirm this. M. Pirani examined the behaviour of films of moisture on glass under the influence of streams of electrons. F. G. Keyes studied the errors in gas measurements due to the adsorption of the gas, say carbon dioxide, by glass.

Glasses, glazes, fused silicates, and slags can absorb gas and reject it with or without spitting during cooling. The phenomenon was noticed by H. St. C. Deville and L. Troost,[30] and J. B. Hannay. Again, I. L. Bell said that the slag from a blast furnace afforded evidence of being impregnated with gas, which during the cooling of the slag escapes in the form of miniature volcanoes on its surface, or bursts out into small jets of flame. If the glass of a vacuum tube used with hydrogen, argon, helium, and other gases be fused, it becomes clouded, and, under the microscope, is seen to be permeated to some depth from the inside surface by a multitude of minute spherical bubbles. Sometimes the melted glass appears to boil, and the bubbles can be seen and heard bursting. Observations were also made by R. S. Willows; and the Staff of the General Electric Co., J. E. Shrader, S. Brodetsky and B. Hodgson, and F. H. Newman studied the disappearance of gas in the electric discharge tube. Four explanations have been given. R. Pohl assumed that the bubbles are produced by a chemical action between the glass and the aluminium disintegrated from the electrodes; F. Soddy and T. D. Mackenzie said that the gas is evolved from the glass by chemical decomposition; and

A. A. C. Swinton said that the gas is driven mechanically into the glass by the cathode rays. When the glass is heated, the gas penetrates further and forms bubbles on cooling much in the same way that air bubbles are formed in ice. J. J. Thomson said that the gas passes into the glass by ordinary diffusion. G. A. Williams and J. B. Ferguson found that glass is impermeable to hydrogen, but some glasses are permeable to helium, and some are blackened when heated in hydrogen; and A. Piutti and co-workers, A. Lo Surdo, E. Cardoso, and C. C. van Voorhis examined the diffusion of hydrogen, helium, and neon through heated glass. G. A. Williams and J. B. Ferguson found one c.c. of pyrex glass, sp. gr. 2·25, dissolved 0·00835 c.c. of helium (at n.p. $\theta$) at 515° and press. 752–755 mm. B. Moore and J. W. Mellor also observed the dissolution of hydrocarbon gases in lead-silicate glass—about 14 c.c. of gas per 100 grms. of glass; and E. W. Washburn found that all varieties of glass dissolve gases, and the gas is thus liable to efferversce violently from the liquid glass if the press. be reduced. J. E. Harris and E. E. Schumacher studied the gases from glasses of different composition; the contained gases are principally carbon and sulphur dioxides, water, oxygen, and nitrogen. J. W. Ryde and R. Huddart analyzed the gases in the bubbles in glass. In agreement with these observations, M. Berthelot found that hot glasses are somewhat pervious to hydrogen, carbon monoxide, and oxygen gases, and C. Zenghelis reported that glasses are similarly permeable to iodine vap., but A. Stock and H. Heyemann were unable to confirm this observation. The subject was discussed by G. Quincke, H. H. Landolt, and B. Tollens. J. B. Firth observed no diffusion of bromine through a thin partition of glass in $9\frac{1}{2}$ years; but with iodine if the glass has been previously heated to 360° a small diffusion occurred. D. Ulrey observed no diffusion of atm. air through glass at temp. up to the softening point. M. Pirani found that the distillation of mercury in vacuo removed the film of air adsorbed by glass surfaces. K. von der Grinten showed that powdered glass adsorbs alkali from aq. soln., and the amount per sq. cm. of surface varies with the conc. of the soln., but reaches a maximum with $1{\cdot}6\times10^{14}$ mols. per sq. cm.

F. Kohlrausch [31] measured the hygroscopicity of powdered glass and found the percentage gain in wt. by different glasses varied from 2 to 18 per cent. The durability of glass exposed to moist air depends largely on its power of resisting attack by water. Dry glass, said R. Bunsen, resists attack by dry carbon dioxide. F. Mylius and F. Förster showed that the weathering of glass begins by the adsorption of water, then the water is absorbed, and hydrates are formed. The alkaline components are liberated, and the corresponding carbonates are produced. Lead glass is blackened when heated in an atm. of hydrogen sulphide, or hydrogen owing to the formation of lead sulphide. M. Faraday observed the blackening of flint glass in dwelling-houses owing to this cause; and a bottle of such glass was found by G. Bischof to be eroded and blackened by ammonium hydrosulphide. Ammonia vap. acting on the exposed surface of glass windows in the vicinity of stables and manure heaps is markedly corrosive. D. H. Bangham and F. P. Burt investigated the adsorption and desorption of carbon dioxide, sulphur dioxide, acetylene, and ammonia by glass. E. Mellor discussed the accelerating influence of lichen growths on the deterioration of glass.

E. Zschimmer studied the action of air and dry dust on glass kept in a room for a number of years. Silicates and borosilicates with up to 20 per cent. of $B_2O_3$ free from lead and alkali showed under the microscope (×80–120) a uniformly spread alteration of the whole surface, consisting either of minute drops or of a network of crystals, due to the slow separation of potash or soda from the silicate, and the subsequent formation of deliquescent potassium carbonate or crystalline sodium carbonate. Borate glasses absorb moisture without becoming damp, and simply swell on the surface, which is not visibly altered till the expansion becomes so great as to tear away the surface from the layers beneath when the whole surface becomes cracked and fissured. This cracking can be produced at an earlier stage

if the glass be heated to 170°. Similar borosilicates free from lead but containing alkali showed surface alterations only in the vicinity of specks of dust. The alterations consist in the deposition of minute drops of water, in the formation of crystals radiating from the speck, in a combination of both of these appearances, or, in the case of lead glasses, in a blackening near the speck, due to metallic lead or its sulphide. The nature of the dust (whether a hygroscopic body or an organic or sulphur-containing substance) is, of course, operative, as well as the composition of the glass, in determining the nature of the alteration of the surface. In lead-free silicates, the decomposition depends on the amount of alkali in the glass. With 10 per cent., dust-decomposition readily sets in, and with 20 per cent. or over, the separation of alkali sets up air-decomposition. In lead-containing silicates, the proportion of lead, as well as that of alkali, determines the ease with which decomposition occurs; but dust-decomposition will occur in silicates containing 20 per cent. or more of lead, even though free from alkali. The decomposition of borate glasses containing over 20 per cent. $B_2O_3$, and over 20 per cent. PbO occurs with the separation of the lead oxide not only on the outer surface, but in some of the layers below, producing an iridescence similar to that observed in labradorite and similar minerals. This iridescence is not removed by rubbing or polishing the surface, and is increased in intensity by heating the glass. The borosilicates are, on the whole, the least easily decomposable glasses; the alkalies seem to separate out less easily than from the silicates, and with a given alkali-content there is much less tendency to the appearance of hygroscopic moisture or of crystals on the surface than in the case of silicates. The phosphate glasses are all hygroscopic. The microscopic appearance is similar to that of the hygroscopic alkali silicates, though the crystals of phosphoric acid or of phosphate are easily recognizable. The dimming of optical glass owing to the formation of a film or deposit on the surface may give trouble. In order to enhance the desired optical qualities, the product may have a small margin of safety, and would not retain its polish and transparency under ordinary conditions of use. Optical glasses which are markedly unstable in the atm. are used only for combinations in which they can be cemented between two lenses or more durable glass. The method of testing optical glass for durability on exposure has been described by F. Mylius, W. Morey, J. W. French, F. Förster, A. V. Elsden, O. Roberts and H. S. Jones, E. Zschimmer, W. H. Withey, and F. R. von Bichowsky. W. D. Bancroft thought that mercury would wet glass if the adsorbed air were removed, and E. E. Schumacher found that this was true with some glasses, and with quartz.

A. L. Lavoisier, and C. W. Scheele were familiar with the fact that the glass vessels employed by the chemist are attacked by water (**1**. 2, 4), forming a soln. of alkali silicate, and flecks of silica or calcium silicate. The early chemists thought water could be transmuted into an earth by boiling it in glass vessels. H. Davy also proved that the alkali produced during the electrolysis of water is derived from the glass of the containing vessel (**1**. 2, 6). R. Weber, and F. Mylius observed that glass levels containing moist ether acquire an opaque coating on the inside owing to the action of water on the glass. The subject is of importance in certain analytical processes, as discussed by B. Reinitzer, G. Kreusler and O. Henzold, E. Bohlig, E. Hoyer, J. Kjeldhal, E. Jalowetz, K. Barelt and H. Schönewald, C. Liebermann, etc.; and mal-observations may occur if the fact be overlooked. Thus, the trace of alkali dissolved from glass was shown by M. Berthelot, and D. M. Kooij to act as a catalytic agent modifying the course of some chemical reactions. H. Moissan and F. Siemens found that silicon is slowly attacked by water at 100° in glass vessels through the traces of alkali dissolved from glass. J. S. Stas, and T. W. Richards emphasized the error introduced in at. wt. determinations by the use of glass vessels. R. Weber showed that microscopic objects preserved between glass plates might undergo change owing to the instability of the glass. C. Nicolardot, G. W. Morey, J. W. French, G. Bischof, J. N. von Fuchs, M. Faraday, J. B. A. Dumas, T. Griffiths, and D. Colladon cited experiments

confirming these observations. F. Mylius showed that much alkali but relatively little silica is extracted, and G. Bischof noted that moist glass powder reddens turmeric paper; red litmus is likewise coloured blue; phenolphthalein and hæmatoxyline are coloured red or purple; F. Mylius showed that a soln. of iodine and starch is coloured blue, and that the orange-yellow soln. of iodeosin in aq. ether is changed red—this reaction has been made quantitative—and similar remarks apply to R. F. von Walther's observation that a yellow soln. of alizarine becomes reddish-violet. Tests—quantitative and otherwise—were devised by R. Weber, F. Mylius, F. Mylius and F. Förster, F. Mylius and E. Groschuff, F. Haber and H. Schwencke, E. Baroni, E. W. Hagmaier, W. L. Baillie and F. E. Wilson, L. Kröber, W. L. Baillie, T. Kato, W. H. Withey, E. Zschimmer, W. E. S. Turner, A. E. Williams, etc. The Institute of Chemistry has prepared a specification for testing glass. G. W. Morey has discussed in a general way the effect of the composition of glass on its corrodibility; and E. Turner, and C. Barus, the action of steam on glass.

F. Mylius found that potash water-glass is more susceptible to attack than soda water-glass. F. Mylius and F. Förster found that the solubilities of potash and soda glasses diminish rapidly as the proportion of lime increases. F. Kohlrausch analyzed the material removed from glass by the solvent action of water. Numerous comparisons of the solvent action of water, etc., on glasses of different countries and different firms have been made. The general (of course erroneous) impression one gets is that each country, and indeed each firm, can produce a more resistant glass than any other country or firm. Observations on the solvent action of water on different glasses were made by R. Weber, F. Kohlrausch, F. Mylius and F. Förster, J. Pelouze, A. Daubrée, A. Vogel and C. Reischauer, H. C. Sorby, B. Tollens, A. E. Williams and S. E. Fox, O. Lecher, J. Wolf, J. Körner, L. Appert and L. Henrivaux, P. Nicolardot, H. von Schwarz, R. von Rieth, L. A. Palmer, D. E. Splitgerber, P. H. Walker, E. C. Sullivan, W. E. S. Turner and co-workers, R. Warington, R. Cowper, F. Cedivoda, and P. Nicolardot. C. J. Peddle studied the solubility of the binary and ternary glasses, $SiO_2$–$Na_2O$–$K_2O$, $SiO_2$–$CaO$–$Na_2O$ or $K_2O$; $SiO_2$–$BaO$–$Na_2O$ or $K_2O$; and $SiO_2$–$PbO$–$Na_2O$ or $K_2O$; G. Keppeler, baryta and strontia glasses; and G. Blumenthal, and W. E. S. Turner, the solubility of boric oxide frits. The above discussion may give a wrong idea of the relative solvent action of water on glass. With good glasses only minute portions of alkalies are removed after a prolonged action. If it were otherwise, the use of glass for domestic purposes would affect the composition and flavour of food-stuffs, and liquids with which it is brought in contact. Similarly, if window-glass under normal conditions were appreciably attacked by rain-water, or gases of the atmosphere, its use would be less satisfactory than it is to-day. P. Volkmann could detect no difference in the capillary rise of water in glass tubes made of different materials.

E. Pfeiffer showed that glass is attacked by water more vigorously when the temp. is raised, and F. Kohlrausch found that the solvent actions at 10·8°, 17·2°, and 23·6° are related as 1 : 2·7 : 7·4. Superheated water is an active corrosive agent as shown by the short life of the gauge glass tubes of steam-boilers working under high press. It is probably not steam, but liquid, which is the potent agent. This is shown by the corrosion above the water-line being in special tracks cut in the glass as the water condensed on the glass tube and trickled down. C. Barus found that liquid water attacks glass so rapidly at 185°, as to choke up the glass tubes in which it was confined by separation of hydrated silica. F. Förster made a number of observations on the resistance offered by different types of glass to water under a press. of steam at 183° in closed vessels. O. Schott and M. Herschkowitsch, and F. Krull investigated the effect with different kinds of glass when used in contact with hot water and steam up to 40 atm. press. F. W. Hodkin and W. E. S. Turner found soda-lime glasses are quickly attacked by steam and water at 2–25 atm. press. The action decreases as the proportion of lime is increased.

E. Turner studied the action of high press. steam on glass and silicates; and O. Schott and G. Linck showed that at 250° and 35 atm. press., a borosilicate glass absorbed 7 per cent. of water in 3 weeks. It is inferred that the absorption of water is not due to chemical combination, but rather imbibition by a gel. O. Schott and G. Linck found that powdered glasses adsorbed up to nearly 16 per cent. of water when heated with water in an autoclave for 30 days. The dehydration was not completed below 1000°.

When old soda-glass tubing, which has stood in the laboratory for some time, is heated, the outer surface may become exceedingly rough owing to the exfoliation and splintering, or to the development of innumerable spits—presumably by the evolution of absorbed water. Observations on this subject have been made by F. Mehlhorn, E. Priwoznik, and A. R. von Schrötter. O. Schott observed similar results with the thermometer tubes which had been immersed in boiling water for some days; he also found soda glasses are less affected than potash glasses. F. Förster found that water is always taken up when glass is acted on by liquid or steam, and hydrated products are formed—*vide* alkali silicates, hydrated water-glasses.

All kinds of glass are quickly corroded by hydrofluoric acid, forming silicon tetrafluoride, and fluosilicates of the alkalies, akaline earths, etc. H. Moissan found that thoroughly dried hydrogen fluoride attacks glass, but dried fluorine attacks it only slowly, and no action was observed at −187°. The etching of glass—H. F. Smith—and pottery glazes is effected by means of this acid. In the case of aluminous and plumbiferous glazes and glasses, the acid is mixed with some ammonium acetate to prevent the formation of a protective deposit of sparingly soluble fluorides on the parts to be attacked. According to J. B. A. Dumas, glass which has a low proportion of silica is attacked by boiling sulphuric acid; and glass which is easily devitrified is attacked by boiling hydrochloric or nitric acid, and by aqua regia. The acids dissolve out the alkalies, alkaline earths, and bases, while silica separates out. The acids attack powdered glass much more quickly than they do a plane or curved surface. C. Nicolardot, R. Warington, W. Tepohl, and A. Emmerling studied the action of dil. hydrochloric acid on glass. T. Griffiths found that boiling hydrochloric acid extracts potash only, not lead oxide, from glass. This statement is very doubtful in view of the action of that acid on lead silicate glasses, discussed by T. E. Thorpe and C. Simmonds, W. Jackson and E. M. Rich, and W. Thomason—*vide* lead-silicate glasses. H. Hess said that in distilling hydrochloric acid from a green glass retort, potassium chloride, ferric chloride, and silica were dissolved, and a crystalline sublimate was formed. K. Beck investigated the solubility of plumbiferous glasses in acetic acid—*vide* lead silicates. Glasses which resist attack by acetic acid were found by J. B. A. Dumas to be sometimes quickly attacked by sulphuric acid. R. Warington studied the action of tartaric acid on glass. F. Förster, M. Berthelot and L. P. St. Giles, E. P. Poste, E. Egger, P. H. Walker and F. W. Smither, F. Cedivoda, W. Tepohl, W. E. S. Turner and co-workers, etc., investigated the action of acids on glass. They found that for one and the same glass, the loss of weight at 100° was the same whether sulphuric, or nitric acid of normal, decinormal, or millinormal conc. be used. Conc. acids are less active than dil. acids; and all the dil. acids were less active than water. Hence, F. Förster concluded that the acid does not act directly on the glass, but merely modifies the action of water. The effects with superheated acids—at 160°–190°—were somewhat similar. F. Förster explains the action of acids on glass somewhat as follows: The first action involves the dissolution of alkali by the water. Under ordinary conditions the alkaline soln. so formed is more active than water—*vide infra*. The acid neutralizes the alkali and prevents it accelerating the attack, and the neutralization is effected more quickly with conc. than with dil. acids. The influence of the conc. is greatest when the alkali is being most quickly extracted, namely, at a high temp. The character of the action of water on glass is not altered by acids; the difference is merely due to the fact that the acid prevents

the accumulation of free alkali in the soln. The alkali is more completely washed out of the glass by acid soln. than it is by water alone. A few silicates—*e.g.* wollastonite, labradorite, and sodium metasilicate glass—are directly attacked by acids, and more quickly by conc. acids than by dil. acids; and dil. acids more quickly than by water. The glass $Na_2O.3SiO_2$ behaves towards acid soln. like ordinary glasses. The mechanism of the action of water on glass was discussed by F. R. von Bichowsky. The resistance of lead glasses to acids was found to be increased by long exposure to the acid. E. Siegwart found that flue gases containing sulphurous gases produce a white film of alkali sulphate on glass; and E. Priwozsnik observed a similar effect produced on the cylinders about the flame of coal gas. R. Cowper examined the action of aq. soln. of hydrogen sulphide. E. Frémy and L. Clémandot produced iridescent films on glass by the action of 10–12 per cent. of hydrochloric acid at 120°–150°. P. Jannasch decomposed various silicates by hydrochloric acid at high temp. and press. The effect of aq. soln. of carbon dioxide has been discussed in connection with the weathering of glass. C. Matignon and G. Marchal examined the corrosion of glass by water in the presence of carbon dioxide under 10 atm. press. during 10 years; L. Pfaundler, the action of liquid and compressed vap. of carbon dioxide. J. S. Stas found that glass containing lead or aluminium is more readily attacked by acids than is the case with potash-lime glasses which withstood the action best. J. W. Mellor found that a high content of boric oxide in lead glasses increases the solubility of the contained lead oxide in 0·25 per cent. hydrochloric acid, and conversely with alumina. Alumina helps to counteract the unfavourable effects produced by the boric oxide. F. Förster, and G. T. Beilby found that the vap. of sulphuric acid attacks glass, and this the more the higher the temp. The sulphuric acid contained in the products of combustion of coal and coal-gas attacks glass, giving it a white coating of alkali sulphates easily removed by washing with water. J. B. A. Dumas found that all kinds of glass are decomposed by hot conc. soln. of phosphoric acid; and the action of this acid was also investigated by K. Hüttner. Hypophosphorus attacks glass even more rapidly than phosphoric acid.

Glass is attacked by soln. of sodium or potassium hydroxide, and silica passes into soln. The attack is facilitated by raising the temp., or increasing the conc. At ordinary temp., the alkali-lye in glass bottles dissolves the glass and causes it to crack. F. Förster investigated the action of the alkali-lye on different kinds of glass. He found that no sharp line can be drawn between the attack by water and by dil. soln. of the alkalies. The alkali extracted by water from glass, so long as it remains near to the glass and is therefore only moderately diluted, strengthens the attack in two ways: (i) by swelling up the surface, and (ii) by dissolving silica—particularly at high temp. Very dil. soln., say millinormal, attack glass no more quickly than does water, but if the alkali soln. be more conc. the attack is quickened, and this the more with increasing conc. With lime-alkali glasses, the alkali silicate is dissolved, and the calcium silicate is left undissolved, so that the surface appears to be dulled. If the alkali-lye be more conc., the calcium silicate is also attacked, so that a 2*N*-NaOH soln. dissolves calcium silicate as a whole. No materially increased attack occurs by raising the conc. of the soln. The attack by conc. soln. of alkali hydroxides decreases by lowering the temp. The order of attack is soda-lye (most vigorous), potash-lye, ammonia soln., and baryta-water. Glasses do not usually differ so much in susceptibility to attack by alkali soln. as by water. W. E. S. Turner and co-workers found that after 3 hrs.' action of 2*N*-NaOH, the losses in mgrms. per sq. dcm., at different temp. were:

| | 20° | 40° | 60° | 80° | 90° | 100° |
|---|---|---|---|---|---|---|
| Loss . . | 0·0 | 1·7 | 4·1 | 18·9 | 31·7 | 74·2 |

The results vary with different glasses; F. Mylius and F. Förster found that with one glass the rate of attack was 1900 times faster at 80° than at 0°. They also examined the effect of magnesia on the resistance of glass to attack by alkaline soln. The action of alkalies on glass has been also studied by G. C. Schmidt and

F. Durau, W. E. S. Turner and co-workers, and P. H. Walker and F. W. Smithers ; of soln. of barium, strontium, and calcium hydroxides, by F. Jones ; and of baryta-water, by C. Bunge.

T. Griffiths, P. H. Walker and F. W. Smithers, P. Nicolardot, and A. Emmerling, found that aq. ammonia attacks many kinds of glass, and a flint-glass bottle containing a soln. of ammonium carbonate became so fragile that on shaking it pieces of glass were detached. B. Silliman found that a dry mixture of ammonium chloride and nitrate attacks glass when heated in contact therewith ; and R. F. Marchand observed a similar effect with dry ammonium sulphate or hydro-sulphate. P. Nicolardot, and F. Förster investigated the action of soln. of alkali carbonates on various glasses, and found that the attack is greater than with soln. of the alkali hydroxides. Sodium carbonate exerted a greater action than potassium carbonate. Alumina increases the resistance of glass to alkali carbonates. H. D. Richmond found a specimen of potassium carbonate containing less than 5 parts per million contained 120 parts of lead after being kept in a lead-glass bottle for 9 weeks. E. A. Coad-Pryor made some observations on this subject. A soln. of sodium sulphate did not have any marked effect ; but soln. of sodium phosphate have a marked action ; and aluminiferous glasses have a greater resistance than alumina-free glasses. W. E. S. Turner and T. E. Wilson examined the action of soln. of sodium phosphate. P. Nicolardot, and A. Emmerling studied the action of aq. soln. of ammonium chloride, etc., on glass. R. Cowper examined the action of ammonium sulphide soln. on glass ; A. Lachaud and C. Lepierre, the action of ammonium hydrosulphate ; and J. H. Smith, the action of sodium phosphate. E. C. Sullivan found coarsely powdered window glass became blue by contact with a soln. of cupric sulphate owing to the exchange of bases.

M. Berthelot studied the action of aq. soln. of alcohol, glycerol, and organic acids on glass ; R. Weber, and F. Mylius, the action of aq. ether ; and R. Weber, the action of aq. alcohol. In 1757, T. Tronchin, in his *De colica pictonum* (Genevæ, 1757), showed that many wines are able to dissolve lead from the glaze of earthenware vessels in which the wines were stored—*vide* lead. R. Warington, and A. Frank examined the effect of wines on glass ; R. L. Frink, the effect of beer ; A. Lesure, A. Dian, L. Kröber, the effect of pharmaceutical preparations ; and M. Guerbet, and A. W. Bitting, that of milk. K. Scheringa observed the adsorption of metal salts from drinking water by glass, and he found that lead is precipitated chemically on the glass. G. T. Beilby found that halos are formed about pieces of metal foil on glass when heated to a sufficiently high temp., in the presence of the products of combustion of coal gas and air. The halos are produced by the decomposition products of the glass itself.

F. Gelstharp studied the solubility of sodium sulphate, sodium chloride, and calcium and sodium sulphides in glasses ; A. D. Holdcroft, the solubility of zinc oxide in glazes ; and E. Greishammer, and R. Zsigmondy, the solubility of metal sulphides in glass. G. J. Knox found glass is reduced when heated with many metals.

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## § 38. Cement

The use of lime for making mortar has been traced back to very ancient times. There is a reference to mortar in *Deuteronomy* (**27**. 2), and the analyses of the mortar employed in the construction of the pyramid of Cheops, show that the early Egyptians must have possessed great skill in the arts of compounding lime-mortar. The Assyrians and Babylonians employed clay, or bitumen, or a kind of burnt gypsum as a mortar in building with bricks; and the early Greeks used lime as a kind of plaster to cover the walls of buildings constructed with unburnt bricks. About a century and a half before our era, Cato the Elder in his *De re rustica* has

several references to the preparation and use of lime-mortar; and Pliny, in his *Historia naturalis* (**36.** 55), in the first century of our era, referred to a number of public buildings in which lime-mortar was used in their construction. Vitruvius also, in his *De architectura* (**2.** 5), written near the beginning of our era, described the manufacture of lime-mortar for building purposes. A. F. Gori reported in his *Museum Etruscum exhibens insignia veterum Etruscorum monuments* (Florentiæ, 1743) that tombs and cisterns found near the ancient cities of Iguvium, Clusium, and Volterra were built or lined with a calcareous mortar. The writers in the Middle Ages seem to have done little more than follow Vitruvius' description of lime-mortar, but they also mentioned the use of volcanic tufa—santorine, pozzolane, and trass—in the production of mortars, and in some cases, the products had the property of setting hard while immersed in water.

The modern cement industry started in 1756, when J. Smeaton [1] was employed by Parliament to build a lighthouse on the partially submerged rocks at Eddystone in the English Channel. He required for the foundations a cement which would harden under water. The ordinary lime-mortars then in use completely failed to satisfy this condition. J. Smeaton obtained an argillaceous limestone which when calcined and mixed with the pumice-like pozzolana, of volcanic origin, produced a satisfactory mortar. The pozzolana was found in a few volcanic districts, notably in Italy, where it was used in making the famous old Roman cement, and further attempts were made to manufacture artificial Roman cements without using pozzolana. Most of these were made by burning argillaceous limestone. J. Parker, for example, in 1791 made a cement by calcining "certain stones or argillaceous productions," and it was later called by the misleading term *Roman cement*, but, later still, it was called *Parker's cement*. In 1818, M. St. Leger, and in 1822, J. Frost, also patented the manufacture of cement by burning siliceous limestones or marls. In M. St. Leger's case, the burning temp. was not very high, and the products were only hydraulic limes. J. Frost called his product *British cement*. In 1824, J. Aspdin patented an improved cement by heating together an intimate mixture of limestone and clay to a temp. sufficient to drive the carbon dioxide from the limestone. He called the product *Portland cement* from its resemblance to the building-stone of Portland. Although the temp. of burning in J. Aspdin's first process does not produce a cement like that now known as portland cement, this defect was very soon overcome, and the value of heating the raw materials to incipient fusion was discovered in 1825. Consequently, portland cement may be regarded as the finely pulverized product which results from the partial fusion of an intimate mixture of argillaceous and calcareous materials in certain proportions; and, when mixed with water, it sets to a hard stone-like mass. It is used largely in constructional work—sidewalks, houses, bridges, tunnels, etc.—as a substitute for stone. The strength and permanence of the cement depends largely upon the constituents formed in the cement during its preparation. Numerous patents for improvements in the methods of manufacture, etc., have been taken—*e.g.* by W. H. Hurry, T. R. Crampton, F. Ransome, F. W. S. Stokes, etc.

Portland cement is usually prepared by heating together limestone and clay; or blast-furnace slag and limestone; or any other combination of raw materials containing the right proportions of lime, alumina, and silica. The raw materials are crushed, mixed in the required proportions to give the necessary ratio $CaO : Al_2O_3 : SiO_2$ and ground to a fine powder. The mixture is burned in a rotary kiln 60–100 ft. long, and 5–8 ft. diameter, built of steel plates lined with firebricks; the cylinders are supported in a slightly inclined position on friction rollers, and slowly rotated. The raw materials are fed into the cylinder at one end, and discharged at the other as a partially fused mass in the form of granules varying in size from a pea to a large marble and called *cement clinker*. The fuel used is powdered bituminous coal blown by compressed air at the lower end of the cylinder so that the raw material passing down encounters a progressively increasing temp. The time of transit through the cylinder is about 1½ hrs. and the final temp. 1425°. In passing through the rotary kiln, the material is first dried, then the organic matter is destroyed and the carbon dioxide expelled, and finally there is a chemical reaction between

the lime, alumina, and silica to form the clinker. The clinker is ground to a fine powder to furnish the portland cement of commerce, and during the grinding a small proportion of gypsum may be added in order to regulate the time of setting of the cement when it is mixed with water.

R. K. Meade gave for the average composition of good grades of portland cement:

| $CaO$ | $Al_2O_3$ | $SiO_2$ | $Fe_2O_3$ | $MgO$ | $SO_3$ |
|---|---|---|---|---|---|
| 62·0 | 7·5 | 22·0 | 2·5 | 2·5 | 1·5 |

showing that more than 90 per cent. consists of the three oxides $CaO$, $Al_2O_3$, and $SiO_2$. The other oxides exert only a secondary influence, and a good portland cement has been made from these three oxides alone. G. A. Rankin and F. E. Wright have investigated the possible compounds of lime, alumina, and silica at high temperatures, and the results are summarized in the ternary diagram, Fig. 161; but since the relative proportions of the three oxides in good cements vary between comparatively narrow limits—60 to 64 per cent. $CaO$; 5 to 9 per cent. $Al_2O_3$; and 19 to 25 per cent. $SiO_2$—the practical problem is concerned with only a very restricted portion of the ternary field.

G. A. Rankin and F. E. Wright have shown microscopically that commercial portland cement clinker contains over 90 per cent. of a mixture of the three compounds, $2CaO.SiO_2$, $3CaO.SiO_2$, and $3CaO.Al_2O_3$, and it is therefore inferred that the cementing value of portland cement is largely due to one or more of these compounds. When a mixture of 64 per cent. of $CaO$ as carbonate, 8 per cent. of alumina, and 23·6 per cent. of silica is slowly heated, the principal changes which occur in different intervals of temperature during the formation of clinker are summarized by G. A. Rankin in Table XVIII. While free lime is present at 1450°,

TABLE XVIII.—THE TEMPERATURES OF FORMATION OF THE CONSTITUENTS OF PORTLAND CEMENT.

| Raw mix. | 1000°. | 1000°–1335°. | 1335°–1450°. | 1450°–1650°. |
|---|---|---|---|---|
| $CaCO_3$ . . . | $CaO$ | $CaO$ | $CaO$, Flux | $2CaO.SiO_2$ |
| $Al_2O_3$ . . . | $Al_2O_3$ | $5CaO.3Al_2O_3$ | $3CaO.Al_2O_3$ | $3CaO.SiO_2$ |
| $SiO_2$ . . . . | $SiO_2$ | $2CaO.Al_2O_3$ | $2CaO.SiO_2$ | $3CaO.Al_2O_3$ |
| | | $3CaO.Al_2O_3$ | $3CaO.SiO_2$ | |

it is entirely combined when the temperature reaches 1650°, and the cooled clinker has the composition indicated in the last column of the table. The small amounts of ferric oxide, magnesia, and alkalies always present under manufacturing conditions lead to the formation of a flux at a lower temperature than with pure materials, and this promotes the combination of lime with alumina and silica. Thus, G. A. Rankin has shown that the impurities were mainly $MgO$, $Fe_2O_3$, and alkalies. The second sample examined was commercial white portland cement; the third, a common grey variety. The three types of clinker are made up largely of the same constituents: tricalcium silicate, dicalcium silicate, and tricalcium aluminate, all compounds of the three major components of cement. If the clinker of the grey cement of Table XIX were perfectly burned it would contain about 36 per cent. of $3CaO.SiO_2$; 33 per cent. of $2CaO.SiO_2$; 21 per cent. of $3CaO.Al_2O_3$; and 10 per cent. of the minor constituents. If the raw materials be imperfectly ground, or inadequately fired, the chemical reactions will not be completed. The compound $3CaO.SiO_2$ is the last to form by the combination of lime with dicalcium silicate: $CaO+2CaO.SiO_2=3CaO.SiO_2$, and therefore if imperfectly burned the cement will contain free lime and more $2CaO.SiO_2$—according to the particular stage at which the reaction was arrested. The presence of free lime is detrimental, leading to the early disintegration of the cement, but increasing the proportion of *combined* lime increases the percentage of $3CaO.SiO_2$, and also

TABLE XIX.—THE COMPOSITION AND BURNING TEMPERATURE OF PORTLAND CEMENT.

| Percentage composition. | | | | Burning temp. | Constituents of cement clinker. |
|---|---|---|---|---|---|
| CaO. | $Al_2O_3$. | $SiO_2$. | Impurities. | | |
| 68·4 | 8·0 | 23·6 | 0 | 1650° | $2CaO.SiO_2$; $3CaO.SiO_2$; $3CaO.Al_2O_3$. |
| 66·2 | 6·4 | 25·0 | 2·4 | 1525° | $2CaO.SiO_2$; $3CaO.SiO_2$; $3CaO.Al_2O_3$, with a small amount of lime. |
| 63·2 | 7·7 | 22·4 | 6·7 | 1425° | $2CaO.SiO_2$; $3CaO.SiO_2$; $3CaO.Al_2O_3$, with small amounts of lime. $5CaO.3Al_2O_3$, and ferrites. |

the strength of the cement. This is the most important constituent of portland cement, and it is formed with the greatest difficulty; this constituent is the one which hardens and develops the greatest strength within a reasonable time.

In 1818, L. J. Vicat [2] also experimented on the cements made by calcining mixtures of lime and clay, and his *Recherches expérimentales sur les chaux de construction, les betons, et les mortiers ordinaires* (Paris, 1818), started in 1812, was an attempt (i) to find the relation between the quality of hydraulic lime and cement, and the chemical composition of the raw materials; (ii) to find the nature of the compounds formed during burning; and (iii) to find the changes which occur when cement is mixed with water and hardens. This work may be regarded as among the earliest of the attempts to found a "chemistry of cements." Other observations were reported by J. F. John, C. L. Treussart, B. Quist, S. Rinmann, R. A. Vogel, J. Ziegler, J. A. C. de la Faye, B. Faujas de la St. Fond, J. A. C. Chaptal, H. V. Collet-Descotils, C. F. Wiebeking, E. Candlot, B. F. Bélidor, P. Berthier, J. N. von Fuchs, H. Meyer and C. M. Kersten, F. Kuhlmann, J. Kreating, etc. E. Jordis and E. H. Kanter have compiled a bibliography dealing with work on the nature and properties of portland cement from the time of L. J. Vicat.

H. le Chatelier, and A. E. Törnebohm noted microscopically four different constituents in cement clinker. The two kinds which predominate have been called alite and celite. The former is the predominating constituent, the latter appears as a filling material or matrix between the grains of alite. This suggests that **alite** is the main product of the clinkering of cement, and that celite is the more fusible portion or flux which has solidified after the crystallization of the alite. In well-burnt cements the crystals of alite have sharp outlines, in poorly burnt cements the outlines are rounded and indefinite. O. Schmidt has prepared crystals of pure alite. The **celite** is usually a deeper colour than the alite, probably because the ferric oxide tends to accumulate in the flux. According to H. le Chatelier, celite acts on polarized light, and he gave it the imaginary formula: $3CaO.2(Al,Fe)_2O_3$. C. Richardson believed celite to be a solid soln. of dicalcium aluminate in dicalcium silicate. The crystals of alite belong to the rhombic system, and H. le Chatelier believed this constituent to be a calcareous *peridote*, or lime-olivine, $3CaO.SiO_2$, which on calcination crystallizes in the matrix of celite. C. Richardson claimed that alite is a solid soln. of tricalcium aluminate, $3CaO.Al_2O_3$, and tricalcium silicate, $3CaO.SiO_2$, because the analytical ratio Bases : Silica $=3:1$. The third constituent is called **belite,** and it resembles alite in some respects. It is usually dirty green in colour and striated. It has not been isolated. It is a secondary constituent and is found principally in cements poor in lime. This circumstance, and the fact that the crystals sometimes occur partially disintegrated, has led to its being considered to be calcium silicate, $2CaO.SiO_2$, *i.e.* calcium orthosilicate, $Ca_2SiO_4$. H. le Chatelier supposed it to crystallize in the cubic system, because he found it to have no action on polarized light. He regarded it as tricalcium aluminate, $3CaO.Al_2O_3$, or a solid soln. of this compound with dicalcium aluminate. The fourth constituent, **felite,** is also found in colourless rhombic crystals in blast

furnace slags which have partially disintegrated. H. le Chatelier found it to have a very energetic action on polarized light. This constituent has not been isolated, and it is considered by H. Kappen to be a solid soln. of dicalcium aluminate with the non-hydraulic form of dicalcium silicate, while belite contains the hydraulic form of this latter compound. Some magnesium silicate, $2MgO.SiO_2$, is probably also present in solid soln. in the dicalcium silicate.

When portland cement is mixed with water, a hard mass is formed by chemical reactions between the constituents of the cement and the water. In the first stage of setting, the cement mortar sets by passing from a plastic to a solid state —this requires a few hours; the cement then *hardens* by gradually increasing in strength—this may occupy years. G. A. Rankin added:

Taking the three constituents separately, tricalcium dioxydialuminate, $3CaO.Al_2O_3$, or $Ca_3O_2(AlO_2)_2$, when mixed with water sets and hardens very rapidly; the setting and hardening are due to the formation of an amorphous hydrate on the individual grains which are thus cemented together. The amorphous material sometimes crystallizes. Slabs made of this compound remain sound under water, but they develop little strength, they are rather soft and are appreciably soluble in water. Calcium orthosilicate, $2CaO.SiO_2$, or $Ca_2SiO_4$, slowly reacts with water, and only after many months does a moulded slab develop any marked strength; it is not appreciably soluble in water. The cementing material is a coating of an amorphous hydrate on the individual grains. Calcium hydroxide can be leached out from the hydrate until amorphous silica alone remains. Any crystals which develop are hydrated calcium hydroxide. The dicalcium silicate is more rapidly hydrated by water saturated with calcium aluminate, so that in portland cement the rate of hydration of the dicalcium silicate is faster than when alone. Tricalcium silicate, $3CaO.SiO_2$, or $Ca_3SiO_5$, sets and hardens rapidly. Slabs of this compound remain sound, and in a relatively short time develop a strength comparable with that of portland cement. The hydrated product behaves towards water just like hydrated dicalcium silicate. According to H. le Chatelier, *la réaction fondamentale*, which brings about the hardening, is the splitting up of a basic calcium silicate into hydrated calcium metasilicate and calcium hydroxide: $3CaO.SiO_2 + Aq. = 2Ca(OH)_2 + CaO.SiO_2.2\frac{1}{2}H_2O$. The beginning of the hydration and the formation of elongated crystals of the hydrated silicate, $CaSiO_3.2\frac{1}{2}H_2O$, is illustrated by Fig. 128, where the dimensions of the acicular crystals have been exaggerated by doubling their proportionate size. The rate of formation of the hydrated product is not affected by the presence of the other constituents of portland cement. The minor constituent, pentacalcium dioxytrialuminate, $5CaO.3Al_2O_3$, $Ca_5Al_6O_{14}$, or $Ca_5O_2(AlO_2)_6$, sets and hardens rapidly. Slabs of this cement when placed in water disintegrate rapidly partly owing to dissociation and partly owing to solubility. The compound in setting forms an amorphous material on the surface of individual grains, and this partially crystallizes. The crystals are probably hydrated tricalcium aluminate.

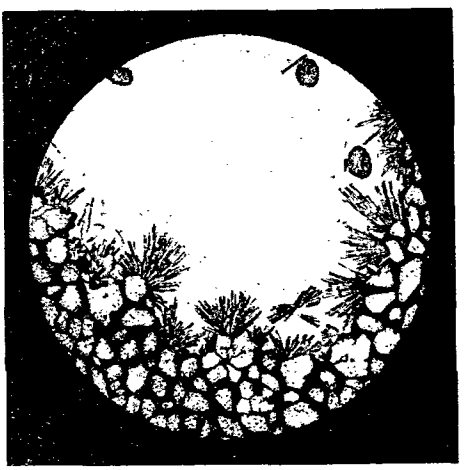


FIG. 128.—Formation of Acicular Crystals of Hydrated Calcium Metasilicate in the Hydration of Portland Cement.

G. A. Rankin describes the setting and hardening of portland cement as involving the formation of an amorphous hydrated material which subsequently partially crystallizes. "The initial setting is probably due to the hydration of $3CaO.Al_2O_3$; the hardness and cohesive strength at first are due to the cementing action of the amorphous material produced by the hydration of this aluminate and of the $3CaO.SiO_2$; and the gradual increase in strength is due to the further hydration of these two compounds together with the hydration of the $2CaO.SiO_2$. Of the three compounds which thus take part in the setting and hardening of portland cement, $3CaO.SiO_2$ appears the best cementing material; that is, this

compound is the only one of the three which when mixed with water will set and harden in a reasonable time to form a mass which in hardness and strength is comparable with portland cement. The compound $2CaO.SiO_2$ requires too long a time to set and harden in order to be in itself a valuable cementing material. The compound $3CaO.Al_2O_3$ while it sets and hardens rapidly, is rather soluble in water and is not particularly strong or durable. From this it would appear that tricalcium silicate is the essential constituent of portland cement; consequently, the higher its percentage the better, and that gelatinous silica is the most essential constituent of a cement mortar." The release of gelatinous silica in the action of water on tricalcium silicate is probably the reason why this compound is such a valuable cementing material; indeed, certain of the toughest sandstones are made up of grains of sand bonded together with gelatinous silica which was gradually deposited from soln. on to the grains of sand, and subsequently hardened.

P. H. Bates and A. A. Klein thus describe their observations of the different constituents during the setting of portland cement:

At early periods the constituents of portland cement of normal composition and manufacture, in order of their strength-conferring properties, are: Tricalcium silicate, tricalcium aluminate, and dicalcium silicate. At periods beyond 28 days the dicalcium silicate gains sufficient strength to place it almost on an equality with the tricalcium silicate. Tricalcium aluminate containing 10 per cent. plaster gains practically no strength after the first period at which it was tested; that is, 24 hours. Tricalcium silicate of the purity used in this investigation (90 per cent. $3CaO.SiO_2$ in one case and 95 per cent. in the other) has all the important properties of portland cement, especially those of the "rate of setting" and strength developed. Dicalcium silicate, such as used in this investigation, sets too slowly and attains strength too slowly to be of any commercial value when used alone. Tricalcium aluminate alone, as used in this investigation, sets too rapidly and attains too little strength to be of any commercial value as a hydraulic cementing material. Tricalcium aluminate, when used to replace about 19 per cent. of the dicalcium silicate (which is approximately the amount of aluminate present in portland cement) adds somewhat to the strength of the latter at the later periods. Tricalcium aluminate, when used to replace about 19 per cent. of tricalcium silicate, did not add to the strength of the latter, showing rather a slight tendency to decrease it. The addition of 3 per cent. of plaster gave higher early strengths but lower later ones. Tricalcium aluminate, when used to replace about 19 per cent. of a mixture of equal parts dicalcium and tricalcium silicate, increased the strength at 24 hours and 7 days, but decreased it at the later periods. It appears, therefore, that the composition of portland cement should be along lines which would not produce a great preponderance of either silicate. The ideal cement should possibly have an excess of the dicalcium silicate, which would give a not too dense hydrated material, gaining strength at later periods. A lesser amount of the tricalcium silicate would furnish the desired early strength and also overcome the excessive porosity of the dicalcium silicate. It is possible to make a cement that will have the properties of portland cement by grinding together the previously separately burned constituents in approximately the amounts in which they exist in portland cement. The function of tricalcium aluminate in the finished cement is somewhat problematical. A cement with less than one per cent. of alumina has all the properties of portland cement. Such a cement is, however, not a commercial possibility from the manufacturing standpoint, on account of the temperatures and amount of burning involved. To state, however, that the aluminate in the finished cement is of the nature of a diluent or inert material would be drawing a conclusion which, while justified by the present investigation, requires further confirmatory work. The actual products of the hydration are those noted by A. A. Klein and A. J. Phillips, excepting as noted before the case of the dicalcium silicate, when apparently during the hydration of this compound lime hydrate is formed.

The observations of A. A. Klein and A. J. Phillips are thus summarized by them:

The hydration of cements is thus brought about by the formation of amorphous hydrated tricalcium aluminate with or without amorphous alumina, the aluminate later crystallizing. At the same time sulphoaluminate crystals are formed, and low-burned or finely ground lime is hydrated. The formation of the above compounds begins within a short time after the cement is gauged. The next compound to react is tricalcium silicate. Its hydration may begin within 24 hours, and it is generally completed within 7 days. Between 7 and 28 days the amorphous aluminate commences to crystallize and beta-orthosilicate begins to hydrate. Although the latter is the chief constituent of the American portland cements, it is the least reactive compound. The early strength

(24 hours) of cements is probably due to the hydration of free lime and the aluminates. The increase in strength between 24 hours and 7 days depends upon the hydration of tri-calcium silicate, although the further hydration of aluminates may contribute somewhat. The increase between 7 and 28 days is due to the hydration of beta-calcium orthosilicate, but here are encountered opposing forces, in the hydration of any high-burned free lime present and in the crystallization of the aluminate. It is to this hydration that the falling off in strength between 7 and 28 days of very high-burned high-limed cements is due, whereas the decrease shown by the high alumina cements is due to the crystallization of the aluminate. Finally, the iron in the cement is resistive to hydration and does not form any definite crystalline hydration products, but occurs as a rust-like material.

These theories of the setting involve the crystallization of one or more constituents. A. Michaelis advocated a colloidal theory of setting in which the formation of a colloidal substance is the essential feature; and W. Rosenhain argued in favour of the colloidal theory in another form by assuming that the solid grains are initially surrounded by a liquid soln. of certain constituents which solidifies owing to the removal of water—by percolation or chemical action. This solidification may take place by crystallization, but if very thin it may congeal in an amorphous condition. These amorphous films or layers impart to the whole mass its great hardness and strength.

According to E. Martin,[3] if a mixture of a mol of silica and two mols of calcium carbonate be heated at 1200°, and the free lime removed with a soln. of sugar, the resulting silicate, $10CaO.5SiO_2$, or $(Ca_2SiO_4)_5$, is inactive as a cement. It is completely soluble in acetic acid; sodium carbonate removes 3 mols. of the silica from it. Cement silicate is obtained by heating a mixture of a mol of silica with 3 mols of calcium oxide at 1400°; it is never free from the inactive silicate, $5SiO_2.10CaO$, but its composition is deduced to be $5SiO_2.13CaO$. It is completely soluble in acetic acid, but is unaffected when boiled for a short time with sodium carbonate soln.; prolonged treatment with the cold soln. removes 2 mols. of the silica. When it sets there is liberated $3Ca(OH)_2$ with the formation at first of $5SiO_2.10CaO.2H_2O$, which gradually undergoes further hydrolysis. When setting takes place in presence of carbon dioxide a protective coating of calcium carbonate is formed. Prolonged heating of silicate cement at 1000° causes it to dissociate into $5SiO_2.10CaO$ and 3CaO. The silicate thus formed is not identical with the inactive silicate of the same composition, but is of a little value as a cement. A hydraulic cement of the composition $5SiO_2,8CaO$ was obtained by heating a mixture of hydrated silica (obtained from the acetate) with 2 mols. of $CaCO_3$ at 1200°.

The physical and chemical properties of portland cement, and the effect of various salts on the setting and endurance of the cement are described in special books on the subject.

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The so-called *ciment fondu, ciment noir*, or *ciment electrique* is made by fusing the raw materials in an electric furnace. Its composition approximates $SiO_2$, 10; $Al_2O_3$, 42; CaO, 42; $Fe_2O_3$, 46. The fused material is ground extremely fine, and magnetized. It is used in place of portland cement when quick-setting is specially desired.

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## § 39. Topaz

The τοπάζος of Theophrastus' Περὶ λίθων, and the *topazius* of Pliny's *Historia naturalis* (**37**. 42), referred to what is now called chrysolite, and their chrysolite refers to what is now called topaz; or, as A. B. de Boodt[1] expressed it, *topazius vulgaris erat chrysolithos veterum*. According to Pliny, the name topaz was adopted from that of an island in the Red Sea. The topaz was mentioned by J. de Laet, J. F. Henckel, J. G. Wallerius, A. Cronstedt, C. Linnæus, etc. The crystals were described by J. B. L. Romé de l'Isle, R. J. Haüy, J. A. Monteiro, A. Russell, and A. Lévy.

W. Hisinger and J. J. Berzelius applied the term *pyrophysalite*—from πῦρ, fire; and φυσαλίς, a bubble—to a coarse, opaque, yellowish-white, compact mass of topaz from Finbo, in allusion to its intumescence when heated before the blowpipe flame. C. A. S. Hofmann considered the first syllable to be redundant and called it *physalite*. A. G. Werner, A. Cronstedt, B. G. Sage, and J. B. L. Romé de l'Isle referred to a white schorl, or a schorl-like beryl which J. C. Delaméthérie called *leucolite*; D. L. G. Karsten, *Stangenstein*; M. H. Klaproth, *schorlite*; R. Kirwan, *shorlite*; and R. J. Haüy, *pycnite*—from πυκνός, dense, compact. The compact mineral with a columnar structure was

considered to be a distinct species because G. Forchhammer said that the mineral is monoclinic, while topaz is rhombic. G. Rose, and A. des Cloizeaux showed that the properties of the crystals are the same as those of topaz; and C. F. Rammelsberg showed that the two minerals have the same chemical composition.

Early attempts were made to find the chemical nature of topaz. J. H. Pott [2] reported that by calcination the crystals became matte, and brittle. A. S. Marggraf's analysis indicated that the dominant constituents were alumina and lime; but this was made ten years before the discovery of hydrofluoric acid. M. H. Klaproth, L. N. Vauquelin, J. C. Wiegleb, and J. T. Lowitz found that the chief constituents of topaz are silica and alumina; but M. H. Klaproth's analysis was about 7 per cent. low; he then showed that the missing component was fluorine, and L. N. Vauquelin found that the actual amount of fluorine in the mineral approaches 20 per cent. J. J. Berzelius, G. Forchhammer, H. St. C. Deville, and C. F. Rammelsberg approached the problem with improved methods, and since then many analyses have been made. C. F. Rammelsberg [3] assumed that topaz is an anhydrous silicate, and that the small amount of water indicated in many analyses is due to decomposition. He gave the formula $n Al_2SiO_5.AlSiF_{10}$. G. Städeler gave $Al_2SiO_4F_2$, and he regarded it as a compound of aluminium silicate, $SiO : O_2 : (AlO)_2$, and aluminyl fluosilicate, $SiF_2(AlO)_2$. H. Klemm used a mixture formula like that of C. F. Rammelsberg. P. Groth represented topaz as an isomorphous mixture of andalusite, $Al(AlO)SiO_4$, and the fluoride $Al(AlF_2)SiO_4$. F. W. Clarke and J. S. Diller represent the composition by $Al_3(SiO_4)_3(AlF_2)_3$ analogous with $Al_3(SiO_4)_3(AlO)_3$ for andalusite—both derivatives of aluminium orthosilicate $Al_4(SiO_4)_3$. S. L. Penfield and J. C. Minor assume the formula of topaz to be $SiO_4(AlF)_2$, or $Al{=}SiO_4{-}AlF_2$; like P. Jannasch and J. Locke, they consider that the hydroxyl can replace the fluorine isomorphously, and they write $SiO_4\{Al(F,OH)\}_2$. Topazes corresponding with the end-member, $SiO_4(AlF)_2$, are known, and Brazil furnishes a topaz with $F : OH = 3 : 1$ which is the highest hydroxyl derivative known. P. Erculisse regarded the topazes as salts of fluo-aluminosilicic acids. K. Daniel represented topaz as **dialuminyl difluosilicate :**



Topaz. Cyanite.

W. and D. Asch, postulating their hexites and pentites, assume a series with one terminal member, $(OH)_{12}Al_{12}Si_6O_{24}$, and by the successive replacement of hydroxyl by fluorine arrive at the other terminal member, $F_{12}Al_{12}Si_6O_{24}$. C. F. Rammelsberg observed that when topaz is heated to redness part of the fluorine escapes as silicon fluoride and part as aluminium fluoride; and W. and D. Asch affirm that twice as many fluorine atoms are united to the aluminium as are united to the silicon atoms, and added:

Weitere Untersuchungen müssten ergeben, dass das Verhältnis des als Fluorsilicum fortgehenden Fluors zu dem als Fluoraluminium sich abspaltenden = 1 : 2 ist.

Even if the premise be correct, so many secondary changes might obscure the issue that the " must " is too dogmatic. They also stated that only the fluorine atoms united to silicon, but not to aluminium, are easily replaced by hydroxyl radicles.

Topaz usually occurs along with tourmaline, mica, beryl, apatite, fluorite, and cassiterite in granite or gneiss, and especially in stanniferous pegmatites; [4] Brazilian topazes occur in decomposed material, which, according to O. A. Derby, was probably a mica schist. W. Cross also found it in cavities in rhyolite and other volcanic rocks. C. G. C. Bischof discussed the formation of topaz from kaolinite, and felspar by the action of alkali or aluminium fluorides. It is probable that gaseous emanations containing fluorine have played an important part in the genesis of topaz. A. Daubrée reported the synthesis of a substance allied to topaz

by heating alumina in a stream of silicon tetrafluoride, but H. St. C. Deville was unable to get a fluoriferous compound by this means. C. Friedel and E. Sarasin also said that they prepared a substance like topaz by heating a mixture of alumina, silica, water, and hydrofluosilicic acid at 500°. The only satisfactory synthesis is that by A. Reich, who heated a mixture of silica and aluminium fluoride at a bright red heat, and afterwards ignited the product in a stream of silicon tetrafluoride. The composition and crystallographic properties of the product agreed with those of topaz.

Topaz occurs usually in colourless, prismatic **crystals**; it also occurs in columnar masses, and coarse- or fine-grained masses. The colour may be white, straw-yellow, wine-yellow, grey, green, pale blue, or pale pink. The cause of the coloration is not known. L. Wöhler and K. von Kraatz-Koschlau assumed that the topaz from Villa Rica is coloured by chromium; W. Hermann found topaz coloured with iron oxide, but the results were indecisive with respect to chromic oxide; and C. F. Rammelsberg said that the topaz from Schnekenstein is coloured by a hydrocarbon. G. O. Wild and R. E. Liesegang also investigated the colour of the topaz. The crystals of topaz are sometimes red with enclosed microscopic crystals of rutile, ilmenite, or hæmatite. As shown by D. Brewster,[5] topaz contains liquid inclusions, *e.g.* water, liquid carbon dioxide, and possibly another kind of liquid. One liquid had a refractive index of 1·311 and a high coeff. of thermal expansion; it was called *brewsterlin*, *brewstolin*, and *brewsterlinite* by J. D. Dana. Another liquid had a refractive index 1·2946 and a coeff. of thermal expansion nearly like that of water; it was called *cryptolin* by J. D. Dana. These two liquids are immiscible. T. Erhard and A. Stelzner found the critical temp. of brewsterlinite to be near that of carbon dioxide. A. E. von Nordenskjöld observed in a Russian topaz a liquid which appeared to be a hydrocarbon like naphtha. There are besides crystals of several kinds of soluble salts within the fluid. This subject has been discussed by W. N. Hartley, A. A. Julien, H. Vogelsang, and H. Rosenbusch. No carbon dioxide is liberated in many of the reactions in which topaz has been formed in nature; and the presence of liquid carbon dioxide inclusions in the crystals shows that the liquid happened to be present when the crystals were formed. That a high temp. prevailed at the time of crystallization is evidenced by the fact that many of the cavities are only half filled with water. Both the water and the carbon dioxide are due to the condensation from enormously compressed vap. which, as W. N. Hartley expressed it, formed a kind of emulsion in the silicate soln. before crystallization occurred.

Topazes for use as gem-stones come from Russia, Brazil, Australia, etc. Colourless topaz, known also as *pingos d'agoa*—drops of water—are cut in the form of brilliants; the sp. gr. is near that of the diamond, but their birefringence and index of refraction are smaller than those of the diamond. The lustre and brilliancy of the topaz are much less than is the case with the diamond. Yellow corundum is also sold as a gem-stone, under the name *oriental topaz*. Many yellow stones sold as topaz—*golden topaz*, and *Spanish topaz*—are really quartz; and they are often heated to convert them into the more valuable pink topaz. Pink topaz is distinguished from pink tourmaline by the sp. gr. and dichroism. The violet-red topaz of Sanarka River is very rare. Bluish green and blue topaz are sold in the trade as beryl or aquamarine. The two minerals can be distinguished by their sp. gr.

According to N. von Kokscharoff,[6] the **crystals** of topaz belong to the rhombic system and have the axial ratios $a : b : c = 0{\cdot}528542 : 1 : 0{\cdot}476976$. Observations were made by A. des Cloizeaux, G. vom Rath, L. Grünhut, G. Rose, V. Goldschmidt, V. Rosicky, M. Hoshina, H. Bücking, D. Brewster, H. Laspeyres, P. Groth, A. Corsi, A. Breithaupt, P. von Jeremejeff, W. E. Hidden and H. S. Washington, etc. V. Goldschmidt and R. Schröder, and L. Cahn described some growths of topaz needles on garnet. The **cleavage** of the crystals parallel to (001) is perfect, but imperfect parallel to (101) and to (011). These directions, according to O. Mügge, correspond with the **percussion figure.** H. Baumhauer, M. Eichler, V. Rosicky, S. Ichikawa, and A. Pelikan studied the **corrosion figures.**

A. N. Alling, C. Hintze, A. des Cloizeaux, P. Groth, E. Bertrand, and W. Ramsay measured the **optic axial angles.** A. Mulheims found :

| | *a*- | *B*- | *C*- | *D*- | *E*- | *b*- | *F*-line |
|---|---|---|---|---|---|---|---|
| $2V$ . . | 65° 59′ | 65° 58½′ | 65° 58′ | 65° 41′ | 65° 12½′ | 65° 12′ | 64° 54½′ |

and F. Rudberg gave :

| | *E*- | *F*- | *G*- | *H*-line |
|---|---|---|---|---|
| $2V$ . . . | 56° 59′ | 56° 43′ | 55° 51′ | 55° 11′ |
| $2E$ . . . | 100° 55′ | 100° 32′ | 99° 0′ | 97° 50′ |

A. des Cloizeaux found that at 20°, $2E=119°$ and at 250°, $2E=123°$. P. Groth also found a small increase in the axial angles when the temp. is raised. S. L. Penfield and J. C. Minor measured the effect of the relative proportions of fluorine and combined water on the sp. gr. and on the optic axial angle. The results for Na-light are indicated in Table XX. The faces in the prismatic zone are often vertically

TABLE XX.—EFFECT OF COMPOSITION ON THE OPTIC AXIAL ANGLE OF TOPAZ.

| — | $2E$ | Sp. gr. | Per cent. F | Per cent. $H^2O$ |
|---|---|---|---|---|
| Thomas Range . . . | 125° 53′ | 3·565 | 20·37 | 0·19 |
| Nathrop, Colorado . . | 125° 51′ | 3·567 | 20·42 | 0·29 |
| Tenagari, Japan . . | 120° 59′ | 3·565 | 19·50 | 0·57 |
| Aduntschilon, Siberia . | 118° 46′ | 3·562 | 19·24 | 0·58 |
| San Lius, Mexico . . | 118° 17′ | 3·575 | 19·53 | 0·80 |
| Schneckstein, Saxony . | 114° 28′ | 3·555 | 18·50 | 0·93 |
| Stoneham, Maine . . | 113° 50′ | 3·560 | 18·56 | 0·98 |
| Minas Geraes, Brazil . . | 84° 28′ | 3·532 | 15·48 | 2·45 |

striated ; they often show vicinal planes ; and sometimes appear hemimorphic. F. Scharff made some general observations on the structure of the crystals of topaz. The **optical anomalies** were observed by D. Brewster, A. des Cloizeaux, and A. Mack ; and to explain them E. Mallard supposed the crystals of topaz to be pseudo-rhombic, really monoclinic. The optical anomalies are probably due to variations in the composition of different parts of a crystal resulting in variations in the density ; and producing molecular strains. H. Haga and F. M. Jäger, and J. Leonhardt examined the **X-radiograms** of topaz ; the last-named found that for the elementary parallelopiped, $a=4·6$ A., $b=8·78$ A., and $c=8·37$ A., in agreement with the axial ratios 0·5285 : 1 : 9540. There are four mols. in each elementary parallelopiped ; and it is assumed that there are no $SiO_4$-groups, but that $SiO_2$-groups are present. Each of the four molecules corresponds with $Al_2F_2O_2.SiO_2$. The **corrosion figures** were studied by H. Baumhauer, E. S. von Fedoroff, V. Goldschmidt, V. Rosicky, and A. P. Honess.

The observed **specific gravity** of topaz ranges from 3·40–3·65. A. H. Church found for white, flawless, Brazilian crystals, 3·571–3·597 ; for sky-blue crystals, 3·541 ; and for wine-yellow crystals, 3·539 before ignition, and 3·533 after ignition. I. I. Saslavsky studied the mol. vol. of topaz. The **hardness** of topaz is between that of quartz and that of corundum, and is 8 on Mohs' scale. A. Rosiwal measured the hardness of topaz ; and P. J. Holmquist, the abrasive hardness (quartz 1000), using carborundum of different grain-sizes as the abrasive. He gave for the (110)-face, and for the (001)-face, 813 ; and for the (001)-face, 633. W. Voigt found for the **modulus of elasticity**, $E_1$– 23,040, $E_2=28,900$, $E_3=26,520$, $E_4=26,700$, $E_5=28,920$, and $E_6=31,860$ kgrms. per sq. mm. ; for the **torsion modulus**, he found $T_{23}=11,040$, $T_{31}=13,530$, and $T_{12}=13,360$ kgrms. per sq. mm. ; and for the **compressibility** $\beta=0·60\times10^{-6}$. F. Auerbach gave for the elasticity modulus perpendicular to the base, 28,100–30,200 kgrms. per sq. mm. E. Riecke has made some observations on this subject. H. Fizeau found the coeff. of **thermal expansion** to be $\alpha=0·0_58325$

in the direction of the $a$-axis, $0{\cdot}0_58362$ in the direction of the $b$-axis, and $0{\cdot}0_54723$ in the direction of the $c$-axis. F. Pfaff gave $\alpha=0{\cdot}0_58325$ for the $a$-axis, $\alpha=0{\cdot}0_54723$ for the $b$-axis, and $\alpha=0{\cdot}0_58362$ for the $c$-axis; this makes the coeff. of cubical expansion 0·00002137. A. Offret made some observations on this subject. F. E. Naumann found the **specific heat** of topaz 0·2000–0·2037; J. Jolly, 0·1997–0·2004 between 10° and 100°; and G. Lindner found

| | 50° | 100° | 150° | 200° | 250° |
|---|---|---|---|---|---|
| Sp. ht. . . . | 0·2097 | 0·2151 | 0·2270 | 0·2357 | 0·2508 |

According to G. Forchhammer, and H. St. C. Deville, topaz, at a white-heat, loses the whole of its fluorine as silicon tetrafluoride; and, according to C. F. Rammelsberg, both silicon and aluminium fluorides are given off—*vide supra*. According to W. Vernadsky, topaz is transformed into sillimanite at a white heat. At a high temp., topaz melts and furnishes a glassy mass in which are crystals of sillimanite; these crystals are developed at a lower temp. if heated with a fluoride as a flux. The **indices of refraction** have been measured by A. des Cloizeaux, V. Rosicky, J. C. Heusser, A. Mülheims, P. Groth, F. Rudberg, A. N. Alling, etc. A. Mülheims gave for light of different wave-length:

| | *a*- | *B*- | *C*- | *D*- | *E*- | *b*- | *F*-line |
|---|---|---|---|---|---|---|---|
| $\alpha$ . . . | 1·60916 | 1·61000 | 1·61091 | 1·61327 | 1·61615 | 1·61680 | 1·61870 |
| $\beta$ . . . | 1·61187 | 1·61273 | 1·61365 | 1·61597 | 1·61882 | 1·61947 | 1·62134 |
| $\gamma$ . . . | 1·61838 | 1·61926 | 1·62019 | 1·62252 | 1·62542 | 1·62608 | 1·62792 |

S. L. Penfield and J. C. Minor studied the effect of fluorine and combined water on the index of refraction, for Na-light, and found for the Thomas Range topaz with 0·19 per cent. of water and 20·37 per cent. of fluorine, and the Minas Geraes topaz with 15·48 per cent. of fluorine and 2·45 per cent. of water (*vide* Table XX):

| | $\alpha$ | $\beta$ | $\gamma$ | $\gamma-\alpha$ |
|---|---|---|---|---|
| Thomas Range . . | 1·6072 | 1·6104 | 1·6176 | 0·0104 |
| Minas Geraes . . | 1·6294 | 1·6308 | 1·6375 | 0·0081 |

A. Offret measured the effect of temp. on the indices of refraction and found that raising the temp. from 0°–100° increased $\alpha$ by 0·00081, $\beta$ by 0·00090, and $\gamma$ by 0·00080 per 100°. The birefringence is low and, as just indicated $\gamma-\alpha$ decreases with increasing proportions of hydroxyl. A. Offret found for Na-light at 0°, $\gamma-\alpha=0{\cdot}00777$ per degree rise of temp. between 0° and 300°; similarly $\beta-\alpha=0{\cdot}00131$ per degree; and $\gamma-\beta=0{\cdot}00050$ per degree. Some crystals of topaz are markedly **pleochroic**; J. Grailich and V. von Lang, A. Kenngott, and L. Grünhut have made observations on this subject.

E. Engelhardt found that ultra-violet light induces a feeble **luminescence.** J. Schingaglia showed that yellow topaz gives red fluorescent light which is not always completely polarized. E. Newbery and H. Lupton found that colourless and yellow topaz did not exhibit any thermoluminescence either before or after exposure to radium rays. A yellow topaz became pink when heated, and regained its original colour, perhaps even a deeper yellow, by exposure to radium radiations; when reheated there was a slight thermoluminescence. C. Doelter found that **radium rays** coloured white topaz, orange, and wine-yellow topaz, a dark orange. He also found that topaz is less transparent than andalusite or cyanite to **X-rays**, and the introduction of fluorine is assumed to give increased opacity. The colour of topaz is intensified by X-rays; and a colourless topaz became yellow after 24 hrs.' exposure. Topaz is not affected by **cathode rays**, and it does not phosphoresce. Exposure to ultra-violet rays undoes the effects produced by radium rays. N. von Kokscharoff showed that a dark yellow Siberian topaz was almost completely bleached by exposure to light. W. Hermann found that Brazilian yellow topaz became pink when heated in oxygen; lilac, in nitrogen; and green, in sulphur vapour. A specimen heated in oxygen after treatment with radium was found by C. Doelter to be almost colourless, and lilac if heated in nitrogen. S. C. Lind and D. C. Bardwell also studied the action of radium rays on topaz.

The **pyroelectricity** of crystals of topaz was examined by R. J. Haüy, A. Erman, J. D. Forbes, W. G. Hankel, P. Riess and G. Rose, C. Friedel and P. and J. Curie, A. Mack, and J. Beckenkamp. Most crystals are pyroelectric in the direction of their vertical axes; and doubly terminated crystals become electrified at the two ends, and may therefore be twins. R. J. Haüy noted the extreme sensitiveness of topaz to develop electricity by friction. C. Friedel and P. and J. Curie observed that Brazilian topaz exhibits **piezoelectricity,** since it becomes electrified by pressure. C. Doelter found that the **electric conductivity** increases, or the **electric resistance** decreases, with rise of temp., and he assumed that the high temp. conductivity is electrolytic:

| | 800° | 980° | 1180° | 1280° | 1350° |
|---|---|---|---|---|---|
| Resistance . . | 190,000 | 116,000 | 10,050 | 3100 | 2000 ohms. |

W. Schmidt found the **dielectric constants** to be $e_a=6{\cdot}65$, $e_b=6{\cdot}70$, and $e_c=6{\cdot}30$. W. Voigt and S. Kinoshuto found the **magnetic susceptibility,** parallel to the $a$-axis, to be $-410\times10^{-7}$; to the $b$-axis, $-4{\cdot}20\times10^{-7}$; and to the $c$-axis, $-4{\cdot}20\times10^{-7}$. B. Bavink studied the magnetic properties of the crystals.

Topaz is only partially attacked by sulphuric acid. J. Lemberg [7] found that when topaz is heated with a soln. of sodium silicate for 174 hrs. between 200° and 210°, an alkali-alumino-silicate of a zeolitic character is formed. According to F. W. Clarke and J. S. Diller, topaz readily alters by hydration and by the action of percolating soln., and is transformed into muscovite. They add that the reported changes to steatite and lithomarge or kaolinite are probably mal-inferences. The alteration of topaz has been also discussed by A. Atterberg, K. J. V. Steenstrup, etc.

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## § 40. The Alkali Aluminium Silicates

A number of alkali-aluminium silicates have been prepared; but with most cases the only evidence of chemical combination is chemical analysis, and in some the formation of crystals which may or may not be isomorphous mixtures. Some of the processes have been discussed in connection with the synthesis of minerals. There is often a difficulty in the study of these ternary systems by the usual thermal methods because the vitreous products do not crystallize readily. R. Rieke,[1] and G. Flach studied the fusibility of mixtures of sodium and potassium oxides and clay. J. J. Berzelius, F. Fouqué and A. Michel-Lévy, S. J. Thugutt, G. Stein, J. Morozewicz, W. C. Brögger and H. Bäckström, W. Vernadsky, and P. G. Silber described products obtained by fusing together mixtures of silica, alumina, and sodium carbonate; and crystals corresponding with $Na_2O : Al_2O_3 : SiO_2 = 2 : 1 : 2$; $1 : 1 : 2$; and $3 : 3 : 6$; have been reported. T. J. Pelouze, and W. E. S. Turner and co-workers made a series of alkali-alumina glasses. J. J. Berzelius, and G. Stein obtained the $1 : 1 : 2$ potassium compound in a similar manner. P. Berthier, in his study of the fusibility of slags, worked with mixtures corresponding with the two alkali felspars $1 : 1 : 6$, and also with $3 : 5 : 33$. The $1 : 1 : 2$ compounds are discussed in connection with the nephelite family. A. Gorgeu claimed to have made the $1 : 1 : 1$ compound by fusing at a red heat an intimate mixture of kaolinite and potassium carbonate in a current of moist air. After drying in vacuo, the composition of the washed products corresponded with **potassium dialuminyl orthosilicate,** $K_2Al_2SiO_6$, or $K_2(AlO)_2SiO_4$. If the $2 : 1 : 2$ compound be not a mixture, then the product with the composition $Na_4Al_2Si_2O_9$ is presumably **sodium dialuminyl orthosilicate,** $Na_4(AlO)_2Si_2O_7$. This product was made by P. G. Silber by heating an intimate mixture of kaolinite and sodium carbonate for a long time, and leaching the soluble sodium carbonate and silicate from the mass. The product is decomposed by hydrochloric acid with the separation of gelatinous silicic acid; gaseous hydrogen chloride at 150° converts one-third of the sodium into soluble chloride; and digestion with conc. aq. soln. of silver nitrate at 130° rapidly converts it into canary-yellow **silver dialuminyl orthosilicate,** $Ag_4Al_2Si_2O_9$, or $Ag_4(AlO)_2Si_2O_7$.

Quite a number of alkali aluminium silicates have been prepared by hydrothermal processes. G. Friedel, for instance, obtained monoclinic, pseudocubic, doubly-refracting crystals with the composition $6Na_2O.3Al_2O_3.8SiO_2$, accompanying the hydronephelite formed by the action of a 9 per cent. soln. of sodium hydroxide on potash-mica at 500°. The sp. gr. was 2·660 at 12·5°; and the product was easily

decomposed by cold hydrochloric acid. H. St. C. Deville obtained a product with the composition $Na_2O.Al_2O_3.3SiO_2.3H_2O$ by the action of a very conc. soln. of sodium hydroxide on kaolinite, orthoclase, or bauxite; and F. Singer reported a similar product in small scaly crystals, but with the composition $Na_2O.Al_2O_3.3SiO_2.4H_2O$. H. St. C. Deville similarly obtained $K_2O.Al_2O_3.3SiO_2.3H_2O$; and S. J. Thugutt, $K_2O.Al_2O_3.3SiO_2.2H_2O$, by the action of an aq. soln. of potassium carbonate on nephelite, sodalite, kaolinite, and other silicates. J. Lemberg obtained $K_2O.Al_2O_3.4SiO_2.3H_2O$ by digesting zeolites, phillipsite, labradorite, analcite, or leucite with an aq. soln. of potassium carbonate; or by digesting aluminium hydroxide in a 10 per cent. soln. of potassium disilicate at 195°–200°. J. J. Berzelius mixed an aq. soln. of potassium aluminate with silicic acid, and H. St. C. Deville heated potassium aluminate and silicate at 200°, and obtained a crystalline powder of $K_2O.Al_2O_3.4SiO_2.4H_2O$. B. von Ammon reported $Na_2O.Al_2O_3.4SiO_2.3H_2O$, to be formed when a hot soln. of alum is allowed to stand in contact with crystallized sodium silicate—*vide infra*, leucite. F. Singer also obtained a product with the composition $Na_2O.Al_2O_3.4SiO_2.4H_2O$; and another with the composition $Na_2O.Al_2O_3.5SiO_2.5H_2O$. J. Lemberg obtained $K_2O.Al_2O_3.6SiO_2.6H_2O$ action of a soln. of sodium silicate and potassium chloride on albite; and obtained $Na_2O.Al_2O_3 : 6SiO_2 : 4H_2O$. The latter also reported the $Na_2O : Al_2O_3 : SiO : H_2O$, 1 : 1 : 7 : 5; 1 : 1 : 10 : 7; 1 : 1 : 12 : 6; 1 : 1 : and 1 : 1 : 20 : 8—*vide infra*, permutites.

K. von Haushofer treated a soln. of water-glass with potash-alum and obtai a precipitate approximately 1 : 1 : 12 : 40, but much free silicic acid was present. W. Heldt said that the precipitate after washing is free from alkali and approximates 0 : 2 : 15 : 10. B. von Ammon also said that if crystalline water-glass be added to an aq. soln. of aluminium sulphate a clear soln. is obtained until finally a precipitate begins to form. If a soln. of water-glass be treated with an excess of aluminium sulphate, the resulting precipitate contains $Al_2O_3.3SiO_2$, which after washing still retains about one per cent. of the alkali silicate. By digesting aluminium hydroxide with an aq. soln. of water-glass for 6 days at 100°, J. Lemberg obtained a precipitate approximating 1 : 1 : 5 : 0 after thorough drying. W. Heldt said that moist aluminium hydroxide removes no silica from a conc. soln. of water-glass. J. Lemberg digested aluminium hydroxide with a soln. of sodium silicate and sodium sulphide and obtained a precipitate with some of the sulphide; similarly also with soln. of sodium sulphate, carbonate, and chloride. There is nothing to show that these products were chemical individuals—*vide infra*, the sodalites.

U. Pratolongo studied the variation in the composition of the precipitates produced by mixing soln. of sodium aluminate and silicate of different conc. Working with a soln. containing 19·360 grms. of sodium silicate per litre, he found that when mixed with :

| Sodium aluminate Grms. per litre. | Percentage composition of precipitate. | | | |
|---|---|---|---|---|
| | $H_2O$. | $SiO_2$. | $Al_2O_3$. | $Na_2O$. |
| 42·318 | 79·25 | 41·63 | 26·56 | 31·81 |
| 21·309 | 84·25 | 43·30 | 25·71 | 30·99 |
| 8·524 | 93·30 | 45·52 | 24·06 | 30·42 |
| 4·261 | 94·05 | 51·80 | 20·14 | 28·06 |
| 2·131 | Gelatinization without precipitation | | | |

He also measured the variation in the solubility of one of the components according to the amount of solid present; and he found the variations in the amounts of potassium or ammonium chloride adsorbed by the solid with the relative proportion of solid phase present.

The three minerals eucryptite, nephelite, and kaliophilite form a group which can be called the **nephelite family.** The mineral **eucryptite**—from εὖ, well, and κρυπτός, hidden—forms with albite an apparently homogeneous substance which was once called *β-spodumene.* This latter term, by the way, is now applied to a variety of spodumene proper. G. J. Brush and E. S. Dana [2] showed that, under the microscope, *β-spodumene is made up of two minerals,* and, when treated with hydrochloric acid, it gives a residue of albite, and eucryptite passes into soln. with the *gelatinization of the silicic acid.* Eucryptite has a composition corresponding with **lithium aluminium orthosilicate,** $LiAlSiO_4$, or *lithium alumino-orthosilicate.* F. W. Clarke and J. S. Diller represent the constitution by the tripled formula $(AlSiO_4)_2 : Al.SiO_4Li_3$ — *vide* nephelite. P. Hautefeuille and A. Perrey synthesized this compound by fusing a mixture of kaolinite and lithium vanadate; and Z. Weyberg, by fusing a mixture of lithium sulphate and kaolinite. Hence, he regarded eucryptite as the lithium salt of what he called *kaolinic acid,* $HAlSiO_4$. The compound was also made by A. S. Ginsberg, F. M. Jäger and A. Simek, and R. Ballo and E. Dittler, by fusing the right proportions of the constituent silicates, Fig. 129, in a closed crucible at 1500°. This f.p. curve by R. Ballo and E. Dittler has two eutectics with an intervening maximum corresponding with the compound $Li_4SiO_4.Al_4(SiO_4)_3$, or $LiAlSiO_4$, melting at 1330°, which resembles eucryptite although the crystals were not sufficiently well-developed completely to establish the identity. A second compound, $3Li_4SiO_4.Al_4(SiO_4)_3$, or $Li_6Al_2(SiO_4)_3$, **lithium dialuminium orthosilicate,** decomposes at 1079°, *i.e.* below its m.p.—*cf. A,* Fig. 129. Only a portion of the ternary system $Li_2O$–$Al_2O_3$–$SiO_2$ was studied. R. Rieke studied the action of lithia on clay (*q.v.*).

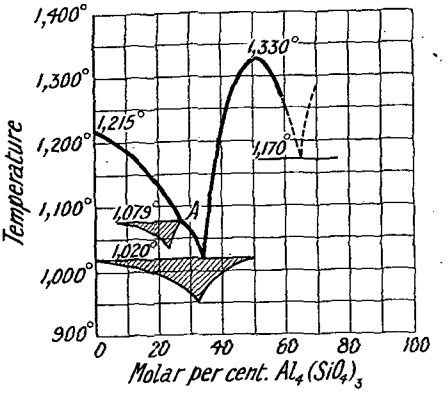



FIG. 129.—Freezing-point Curves of the Binary System: $Li_4SiO_4$–$Al_4(SiO_4)_3$.

In 1773, J. J. Ferber,[3] and in 1775, I. S. R. I. Eques a Born described some crystals of a mineral from Monte Somma, Vesuvius, which was called *sommite* by J. C. Delamétherie in 1797. R. J. Haüy applied to the same mineral the name *nepheline*—from νεφέλη, a cloud—in allusion to the cloudy appearance it assumes when placed in nitric acid. The name is sometimes altered to **nephelite.**

F. de Bellevue applied the term *pseudosommite* to some crystals from Capo di Bove which closely resembled those from Monte Somma, as shown by F. Zambonini; the term *pseudonepheline* was used for the same mineral. P. Carpi made a wrong analysis of this mineral. R. J. Haüy showed that all these substances belong to the same mineral species. According to A. Scacchi, pseudonepheline is represented by distorted crystals of sodalite. T. Monticelli and N. Covelli's *nephelina, davina* or *davyn*—named after H. Davy—and their *cavolinite*—named after F. Cavolini—were considered to be possibly *una sotto specie,* but A. Scacchi, H. Rauff, and E. Bertrand showed that they are different—*vide infra.* M. H. Klaproth applied the term *elæolite*—from ἔλαιον, oil—to a nephelite from Norway in allusion to its greasy lustre; A. G. Werner previously called this mineral *Fettstein,* and R. J. Haüy, *pierre de grasse.* C. Hartmann, and A. des Cloizeaux considered the mineral *phonite,* from Norway, to be a nephelite; W. C. Brögger showed that the *gabbronite* or *gabronite* of C. F. Schumacher is probably elæolite.

The first analyses of nephelite were made by L. N. Vauquelin,[4] A. Arfvedson, J. N. von Fuchs, C. G. Gmelin, M. H. Klaproth, and T. Scheerer. Numerous other analyses have since been made.[5] T. Scheerer [6] based a formula of the type $(Na,K)_8Al_8Si_9O_{34}$ on his analyses, while C. Bromeis advocated the simpler formula $NaAlSiO_4$. The latter formula may be regarded as representing that of an

idealized mineral. H. W. Foote and W. M. Bradley pointed out that the mol. ratio $Al_2O_3 : Na_2O$ is nearly 1 : 1, and the ratio $SiO_2 : Al_2O_3$ varies from about 2 to 2·21 : 1. There is often therefore an excess of silica above that required by the formula $NaAlSiO_4$. Synthetic nephelite is **sodium aluminium orthosilicate,** $NaAlSiO_4$, or *sodium alumino-orthosilicate,* which appears to have the same type of mol. as eucryptite, and kaliophilite; but the average of the best analyses corresponds more nearly with T. Scheerer's formula, which was also recommended by H. Rauff. C. F. Rammelsberg assumed that natural nephelite is a mixed mineral containing both the metasilicate, $KAlSi_2O_6$, and the orthosilicate, $NaAlSiO_4$. C. Doelter made nephelite by fusing together these two silicates. S. J. Thugutt, J. Morozewicz, S. Hillebrand, F. S. Starrabba, P. G. Tschermak, and W. Karandejeff also assumed that nephelite is a kind of additive compound or a solid soln. of two or more silicates. In order to account for the excess silica in the analyses indicated above, H. W. Foote and W. M. Bradley suggested that nephelite is a solid soln. of $RAlSiO_4$ and silica; while F. W. Clarke supposed the presence of potassium is due to admixed kaliophilite, and that the excess of silica in the natural mineral is due to the isomorphic replacement of $SiO_4$ by $Si_3O_8$ so as to form a salt isomeric with albite, $[NaAlSi_3O_8]_3$, which is admixed with the nephelite and kaliophilite. This view is favoured by W. T. Schaller, and N. L. Bowen. The *pseudonephelite* or *pseudosommite* of F. Zambonini, obtained from Cape di Bove, is an isomorphous mixture of nephelite and kaliophilite. J. Lemberg's transformation of nephelite into kaliophilite by heating it and a soln. of potassium silicate for 100 hrs. at 200°, shows the equivalency of nephelite and kaliophilite. Since (i) eucryptite and nephelite both readily alter into muscovite or paragonite, and conversely (ii), since C. and G. Friedel found that muscovite can be changed into nephelite by heating it in a soln. of alkali at 500°, F. W. Clarke argued that the constitutional formula of muscovite, paragonite, and nephelite must be of the same type; and "the formula of muscovite is the key to all the other formulæ in this group of silicates." He therefore writes:

| $Al_3(SiO_4)_3KH_2$ | $Al_3(SiO_4)_3NaH_2$ | $Al_3(SiO_4)_3Na_3$ | $Al_3(SiO_4)_3K_3$ | $Al_3(SiO_4)_3Li_3$ |
|---|---|---|---|---|
| Muscovite. | Paragonite. | Nephelite. | Kaliophilite. | Eucryptite. |

or graphically: nephelite, $(Al{\equiv}SiO_4)_2{=}Al{-}SiO_4{\equiv}Na_3$; and muscovite, $(Al{\equiv}SiO_4)_2{=}Al{-}SiO_4{\equiv}KH_2$. The tripled formulæ were supported by an experiment of P. G. Silber in which one-third the sodium of nephelite is replaced by silver when the nephelite is heated with a soln. of silver nitrate in a sealed tube. The resulting *silver nephelite* is interpreted to mean that only one of three sodium atoms in the mol. is replaced by silver; it may also mean that this represents the halting stage of a balanced reaction.

P. Hautefeuille [7] made hexagonal prisms of nephelite by fusing a mixture of sodium aluminate, silica, and an excess of sodium vanadate. J. J. Berzelius, and F. Fouqué and A. Michel-Lévy made hexagonal prisms of nephelite by fusing a mixture of silica, alumina, and sodium carbonate. They say that it is one of the minerals which very easily crystallize from fused magma. C. Doelter obtained the crystals in a similar way, and he also imitated the natural product by fusing a mixture of leucite, $KAlSi_2O_6$, and soda-nephelite, $NaAlSiO_4$. S. Meunier made it by fusing a mixture of silica, alumina, soda, and cryolite. A. Duboin obtained rhombic crystals by melting silica or potassium fluosilicate and alumina with an excess of potassium fluoride. R. Hoffmann made an amorphous silicate of the composition of nephelite by heating together a mixture of kaolinite and sodium carbonate at a temp. below the sintering point. A. Gorgeu, and P. G. Silber used a similar method. R. C. Wallace, and A. S. Ginsberg obtained nephelite by the direct fusion of the constituents. N. L. Bowen showed that there is a transition point at 1352°; above this temp. carnegieite is formed, and below, nephelite appears: Carnegieite$\rightleftharpoons$nephelite—*vide* anorthite. E. T. Wherry applied the at. vol. theory to the isomorphism of nephelite and kaliophilite; and he assumed

that K and $(Na+xSiO_2)$ are replaceable vol. for vol. Soda-lime-nephelites were made by C. Doelter and E. Hussak, N. L. Bowen, etc. Z. Weyberg made *baryta-nephelite*, and *strontia-nephelite* by fusing nephelite with baryta or strontia; and by fusing barium or strontium chloride with kaolinite. P. Eskola in his work on baryta-felspar observed no signs of the formation of a hexagonal baryta-nephelite, $BaAl_2Si_2O_8$. C. and G. Friedel converted muscovite into nephelite by heating a mixture of that mineral and a soln. of sodium hydroxide in a steel bomb at 500°. R. C. Wallace made a partial study of the ternary system $Na_2O$–$Al_2O_3$–$SiO_2$. W. Eitel heated mixtures of nephelite and calcium carbonate under press. of 100–115 kgrms. per sq. cm., so that no decomposition of the carbonate occurred. There is an eutectic at 1190°, Fig. 130, and there is formed cancrinite $3Ne.CaCO_3$, where Ne represents a mol. of nephelite. The compound melts at 1253°, and it has the refractive indices $\omega=1{\cdot}550$, and $\epsilon=1{\cdot}519$, which are higher than the values for cancrinite. For spurrite, *vide supra*.

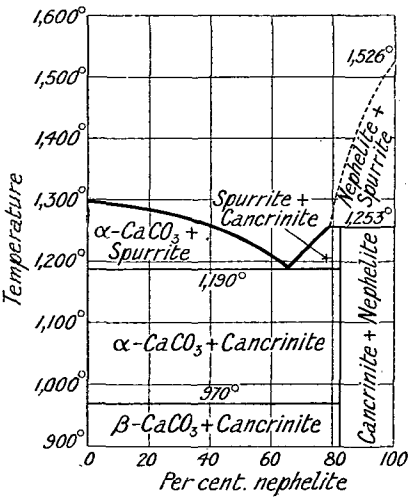



FIG. 130.—Binary System: Nephelite–Calcite.

B. Mierisch[8] described the mineral **kaliophilite**—from *kalium*, and φίλος, a friend—in allusion to the contained potassium. The mineral was obtained in bundles of slender, acicular, colourless, hexagonal crystals in the ejecta from Monte Somme, Vesuvius. E. Scacchi called it *facellite*—from φάκελος or φάκελλος, a bundle—hence it is sometimes called *phenacellite* or *phenacelite*. B. Mierisch, E. Scacchi, and N. Covelli analyzed the mineral. The composition corresponds with **potassium aluminium orthosilicate,** $KAlSiO_4$, or *potassium alumino-orthosilicate*, and in the opinion of F. W. Clarke and J. S. Diller, this formula should be tripled $Al_3(SiO_4)_3K_3$—*vide* nephelite. J. J. Berzelius, G. Stein, and C. Doelter synthesized the mineral by fusing together the constituent oxides or silicates; if an excess of potassium silicate be used, a glass is formed. S. J. Thugutt treated kaolinite with a 47 per cent. soln. of potassium hydroxide for 77 hrs. at 190°–210° and obtained kaliophilite; A. Gorgeu fused the kaolinite with potassium chloride, and Z. Weyberg found the reaction progresses quickly in the presence of a chromate, tungstate, vanadate, or sulphate. A. S. Ginsberg, A. Duboin, and G. Stein proceeded in a similar way. A. Duboin fused together potassium fluoride or fluosilicate, alumina, and silica. A. S. Ginsberg, G. Stein, and E. Bauer obtained kaliophilite by fusing the constituents. M. Schläpfer and P. Niggli heated alumina, potassium hydroxide, silica, and water in a bomb at 470°. C. and G. Friedel converted muscovite into kaliophilite by heating it with a soln. of potassium hydroxide in a steel bomb to 500°. J. Lemberg converted nephelite into amorphous kaliophilite by heating a mixture of nephelite and a soln. of potassium silicate for 100 hrs. at 200°.

The three minerals eucryptite, nephelite, and kaliophilite thus form a family of alkali alumino-orthosilicates which, said F. Zambonini,[9] are probably isomorphous. A. Sauer's *cryptotile* has the same empirical composition, but hydrogen takes the place of the alkali metal. The crystals may be colourless, or the colour may be white, with a yellowish-, greenish-, or bluish-grey tinge. Brown and red nephelites occur in nature. Eucryptite occurs in symmetrically-arranged, white, hexagonal **crystals** embedded in albite. The artificial crystals of P. Hautefeuille and A. Perrey were said to be rhombohedral; those of Z. Weyberg, rhombic or rhombohedral.

Z. Weyberg, indeed, said that this silicate is trimorphous. Nephelite furnishes stout hexagonal prisms or thick plates. P. Groth gave for the axial ratio of the hexagonal pyramidal crystals of nephelite $a : c = 1 : 0{\cdot}8383$; and N. von Kokscharoff, $1 : 0{\cdot}83893$. The crystals of nephelite were also examined by A. Breithaupt, A. and E. Scacchi, C. F. Rammelsberg, H. Baumhauer, G. Strüver, W. C. Brögger, N. B. Möller, P. T. Weibye, J. F. L. Hausmann, C. Klein, etc. For kaliophilite, N. Covelli gave the axial ratio $a : c = 1 : 0{\cdot}8388$. C. Doelter found the velocity of crystallization to be relatively high. The **corrosion figures** of nephelite with hydrofluoric and hydrochloric acids were studied by H. Baumhauer. F. Rinne found that the X-radiograms of nephelite agree with the corrosion figures in placing the mineral in the hexagonal pyramidal class. The **cleavage** of the crystals of the members of this group is distinct and parallel to the $(10\bar{1}0)$-face; and in nephelite, it is also imperfect parallel to the (0001)-face. F. Rinne, and H. Haga and F. M. Jäger studied the **X-radiogram** of nephelite. G. J. Brush and E. S. Dana gave for the **specific gravity** of crystals of eucryptite, 2·644–2·649. The crystals of nephelite prepared by F. Fouqué and A. Michel-Lévy had a sp. gr. 2·555; and those by N. L. Bowen, 2·619. A. Breithaupt gave 2·631–2·637 for the sp. gr. of nephelite; N. L. Bowen, 2·55–2·65; C. F. Rammelsberg, 2·600–2·6087; T. Scheerer, 2·60. For kaliophilite, B. Mierisch gave 2·602, but the observed numbers range from E. Scacchi's 2·4926–2·67; F. Zambonini found a pure transparent crystal had a sp. gr. 2·628; A. Breithaupt gave 2·631, and G. Stein, 2·6. The **hardness** of eucryptite, nephelite and kaliophilite is 5–6. G. Tammann gave 0·184 for the **specific heat** of elæolite crystals, and 0·192 for the glass. The **heat of solution** in a mixture of hydrofluoric and hydrochloric acids for the amorphous glass is 649 cals. per gram, and for the crystals 575 cals. per gram; or the **heat of crystallization** is 73 cals. per gram. A. S. Ginsberg gave 1307° for the **melting point** of eucryptite; R. Ballo and E. Dittler, 1330°. A. Brun gave 1120° for the m.p. of nephelite; R. Cusack, 1059°–1070°; A. L. Fletcher, 1109°–1120°; C. Doelter, 1110°–1195° for different samples; N. V. Kultascheff gave for artificial nephelite, 1007°; W. Guertler, 1055°; and R. C. Wallace, 1018°. F. M. Jäger and A. Simek gave 1388° for the m.p. of pseudo-eucryptite. R. Lorenz studied the relation between the m.p. and the transition temp. of eucryptite, kaliophilite, and nephelite. N. L. Bowen, and A. S. Ginsberg studied the fusion curve of mixtures of anorthite and nephelite. As indicated in connection with Fig. 130, the former showed that nephelite passes into carnegeite at 1352°. J. H. L. Vogt gave 73 cals. for the estimated latent **heat of fusion.** A. S. Ginsberg's, and R. Ballo and E. Dittler's preparations of eucryptite, and F. Fouqué and A. Michel-Lévy's crystals of artificial nephelite, were uniaxial and optically negative; so also was the kaliophilite of B. Mierisch. The **indices of refraction** of nephelite, according to A. des Cloizeaux, are $\omega = 1{\cdot}539$–$1{\cdot}542$, and $\epsilon = 1{\cdot}534$–$1{\cdot}537$; H. Rosenbusch, $\omega = 1{\cdot}5416$–$1{\cdot}5427$, and $\epsilon = 1{\cdot}5376$–$1{\cdot}5378$; S. L. Penfield, $\omega = 1{\cdot}5469$, $\epsilon = 1{\cdot}5422$; C. Hlawatsch, $\omega = 1{\cdot}539$, $\epsilon = 1{\cdot}536$; B. Jezek gave for *D*-light, $\omega = 1{\cdot}54886$–$1{\cdot}54912$, and $\epsilon = 1{\cdot}54327$–$1{\cdot}54382$; and F. S. Starrabba made some measurements. N. L. Bowen gave for artificial nephelite $\omega = 1{\cdot}537$ (1·541), $\epsilon = 1{\cdot}533$ (1·537), where the bracketed numbers refer to the natural mineral. The corresponding **birefringences**, $\omega - \epsilon$, range from 0·0040–0·0050 for the mineral, and 0·003 for the synthetic product. According to F. M. Jäger and A. Simek, when the artificial product is slowly cooled from a fused state, small, irregularly shaped crystals are obtained, for which measurements of the mean refractive index and the density gave $\mu_D = 1{\cdot}531$ and sp. gr. = 2·362 at 25°. These data indicate that the artificial silicate is not identical with the mineral eucryptite, and the synthetic product has been named *pseudo-eucryptite*. If the fusion is rapidly cooled by quenching, a pseudo-eucryptite glass is obtained, for which $\mu_D = 1{\cdot}541$. This glass is metastable with regard to the birefringent crystalline modification, and is rapidly converted into this on heating at 900°.

W. C. Brögger[10] emphasized the fact that nephelite is peculiarly subject to

change under natural influences, and C. R. van Hise and S. J. Thugutt have discussed its alteration into analcite, hydronephelite, kaolinite, muscovite, natrolite, sodalite, thomsonite, etc. G. J. Brush and E. S. Dana also noted that eucryptite readily changes into muscovite. The three nephelite minerals are decomposed by acids with the separation of gelatinous silica. J. W. Mellor found that 98·63 per cent. of coarsely ground nephelite and 99·62 per cent. of fine-grained nephelite were decomposed by an hour's treatment with hot sulphuric acid. Nephelite was shown by S. J. Thugutt to be decomposed by water after heating for about 100 hrs. in the vicinity of 200°, whereby natrolite, sodium aluminate, and a micaceous substance were formed; kaliophilite behaves in an analogous manner. He also studied the action of water on kaliophilite at 196°–233°. J. Lemberg, and S. J. Thugutt examined the effect of a prolonged digestion of nephelite with a soln. of potassium carbonate, sodium carbonate, magnesium sulphate, or calcium chloride. J. Lemberg obtained a substance resembling cancrinite, but with $SiO_3$ in place of $CO_3$, by digesting nephelite with a soln. of sodium silicate. F. Zambonini observed pseudomorphs of leucite after nephelite and of nephilite after leucite, and attributed the latter to the action of soln. of alkali silicate on the e at a high temp. S. J. Thugutt examined the action of potassium silicate soln.; and he found that the vapour of sodium chloride transformed nephelite into sodalite; and G. Strüver found that an aq. soln. of sodium chloride behaves similarly. S. J. Thugutt found that kaliophilite is partially changed into nephelite by digesting with a soln. of sodium chloride. Z. Weyburg found eucryptite to be stable in an alkaline soln. of lithium sulphate. F. W. Clarke and G. Steiger studied the action of ammonium chloride, and H. Schneiderhölm, the action of various salt soln. on nephelite. P. G. Silber examined the action of soln. of silver nitrate, and of hydrogen chloride, and concluded that one-third of the sodium behaved differently from the remainder. H. Lötz studied the action of air charged with sulphur dioxide on nephelite. Z. Weyberg found that when kaolinite is melted with lithium bromide, a product with the composition $7LiAlSiO_4.LiBr$, *lithium aluminium heptitabromo-orthosilicate*, is formed. S. J. Thugutt heated a mixture of kaliophilite, lithium chloride and carbonate, and water for 120 hrs. at 105°–200°, and obtained a *hydro-eucryptite*, or *hydrated lithium aluminium orthosilicate*, $LiAlSiO_4.H_2O$. G. Tammann and C. F. Grevemeyer found that magnesite did not react with nephelite at 100°; lime reacted slowly at 500°; and baryta, strongly at 275°–300°.

The white or dark grey mineral, *hydronephelite*, found by F. W. Clarke and J. S. Diller [11] at Lichfield, Maine, is an alteration product of sodalite. The analysis corresponds with $HN_2Al_3(SiO_4)_3.3H_2O$. It is apparently related with the mineral *ranite* (not *rauite*) from several islands in the Langsund fiord, Norway, described by S. R. Paijkull, and named after the old Norse sea-god Ran. According to W. C. Brögger, it includes part of what previously had been called *Spreustein*, by A. G. Werner; and K. Sonden's mineral *brevicite* should also be regarded as hydronephelite. C. F. Schumacher called a similar mineral *bergmannite*—named after T. Bergman; and A. Estner, *crocalite* or *krokalite*. S. J. Thugutt regarded hydronephelite as a mixture of natrolite and hydrargillite, and not as a *selbständiges* mineral species. The composition and nature of hydronephelite has been discussed by F. W. Clarke and J. S. Diller, S. J. Thugutt, A. Brun, J. E. Hibsch, J. Lemberg, C. von Eckenbrecher, F. Hundeshagen, R. A. A. Johnston, etc. Hydronephelite probably belongs to the hexagonal system, for it is uniaxial. The optical character is positive. The sp. gr. is 2·63, and the hardness 4–5; the sp. gr. of ranite is 2·48, and the hardness 5. W. W. Coblentz found the ultra-red transmission spectrum does not show that water of crystallization is present.

B. von Ammon [12] said that **hydrated sodium aluminium orthosilicate,** $NaAlSiO_4.1\frac{1}{2}H_2O$, separates as a white powder from a soln. of freshly precipitated aluminium hydroxide in a boiling conc. soln. of sodium hydroxide and silicate. J. Lemberg made it by heating aluminium hydroxide with sodium metasilicate;

and also by digesting alkali aluminium silicates, rich in silica, in conc. alkali-lye. Silica is removed and the residue has the composition indicated above. S. J. Thugutt heated kaolinite, sodium hydroxide, and water for about 100 hrs. at about 194° ; and the treatment was repeated. The product was regarded as *nephelite-hydrate*, $5NaAlSiO_4.2H_2O$ ; and, according to S. J. Thugutt, the product has little in common with hydronephelite. C. Friedel obtained rhombic crystals of $NaAlSiO_4.H_2O$ by the action of soda-lye on muscovite at 500°. A. E. Lagorio called the hydrate *lembergite*, and found the crystals are rhombic, but pseudo-hexagonal. C. Friedel gave 2·378 for the sp. gr. A. E. Lagorio said that the mean index of refraction of the rhombic crystals is 1·57 ; the optic axial angle 66° 45′ ; the double refraction is 0·003 ; and the optical character is positive. The optical properties change when the product is warmed. At a dull red heat all the water is expelled, but is reabsorbed when the substance has cooled. A soln. of potassium carbonate changes it into potash-natrolite ; and water changes it into natrolite. B. von Ammon said the product is soluble in hydrochloric acid. W. Heldt, and F. Singer made some observations on this hydrate—*vide infra*, permutite.

J. Lemberg[13] obtained a number of *hydrated kaliophilites*, or **hydrates potassium aluminium orthosilicate,** (i) by digesting kaolinite with a 37 per cent. soln. of potash-lye ; (ii) by treating various hydrated silicates—*e.g.* nosean hydrate, cancrinitic silicates, etc.—with a soln. of potassium carbonate ; (iii) by the action of a 64 per cent. soln. of potassium carbonate or silicate at 200° on nephelite ; and (iv) by the action of a soln. of potash-lye in leucite, or analcite in the presence of potassium chloride. The product of the last-named operation has the composition $KAlSiO_4.H_2O$ ; and, according to K. D. Glinka, this hydrate is formed when the potassium hydroxide soln. of aluminium silicate is neutralized with hydrochloric acid ; and when hydrargillite, halloysite, or calcined kaolinite, and silica are digested with potash-lye, the resulting soln., when neutralized with hydrochloric acid, furnishes the hydrate $KAlSiO_4.1\frac{1}{4}H_2O$.

J. Lemberg also claimed to have made tetrahedral crystals with the composition $NaAlSiO_4.NaOH.\frac{1}{2}H_2O$ (i) by digesting kaolinite with a 50 per cent. soln. of sodium hydroxide ; (ii) by treating kaliophilite with a mixed soln. of sodium silicate and hydroxide ; and (iii) by the action of sodium hydroxide on nephelite. Warm water removes the sodium hydroxide from the complex. He also obtained doubly refracting needles of the complex $6NaAlSiO_4.Na_2SiO_3.4H_2O$, by digesting at 200° kaolinite, kaliophilite, nephelite, analcite, leucite, or albite in sodium silicate melted in its water of crystallization. By digesting sodalite or nosean in an aq. soln. of sodium trisilicate at 200°, he obtained icositetrahedral crystals of the complex $NaAlSiO_4.Na_2Si_3O_7$.

Hydronephelite is possibly a member of a fairly well-defined group of hydrated aluminosilicates of the alkalies and alkaline earths, which are called **zeolites.** The term was first used by A. Cronstedt,[14] and was intended to emphasize their intumescence when heated rapidly as in the blowpipe flame—from ζέω, to boil ; and λίθος, a stone. For a time, the term was applied to other minerals—*e.g.* lapis lazuli, tourmaline, and gadolinite. T. Bergman showed that the zeolites are peculiar in being gelatinized by nitric acid, and this characteristic was emphasized by J. B. L. Romé de l'Isle. A. G. Werner subdivided the zeolites into those with granular, fibrous, radiating, and lamellar structures ; most of the minerals regarded by him in the zeolites are similarly regarded at the present time. A. Breithaupt accepted A. G. Werner's name, for, as he expressed it, *diese schöne natürliche Gruppe*. The zeolites are usually well crystallized ; they are fairly soft, and their sp. gr. is low. F. Mohs, indeed, proposed to call them *Kuphonspars*—from κοῦφος, light—in allusion to their low sp. gr. ; and G. A. Kenngott abbreviated the term to *kuphite*. The zeolites do not form a family of minerals with related crystalline forms, as in the case of the felspars. The family, indeed, includes a number of sub-groups widely diverse in form and composition. A. N. Winchell has based a theory of the composition of zeolites on the variation in composition by the replacement of Ca by Na or K, and the simultaneous replacement of Al

by Si. Table XXI contains a list of the more important members of the zeolite family. A. E. Fersman studied the zeolites of Russia; and T. H. Smith, those of Ardglen, New South Wales.

TABLE XXI.—THE MEMBERS OF THE ZEOLITE FAMILY.

| Zeolite. | Molecular ratio. | | | | R'' | Crystal system. |
|---|---|---|---|---|---|---|
| | R''O | $Al_2O_3$ | $SiO_2$ | $H_2O$ | | |
| Thomsonite | 1 | 1 | 2 | 2·5 | Ca, $Na_2$ | Rhombic |
| Gismondite | 1 | 1 | 2 | 4 | Ca, $Na_2$ | Monoclinic |
| Natrolite | 1 | 1 | 3 | 2 | $Na_2$ | Rhombic |
| Scolesite | 1 | 1 | 3 | 3 | Ca | Monoclinic |
| Levynite | 1 | 1 | 3 | 5 | Ca | Hexagonal |
| Analcite | 1 | 1 | 4 | 2 | $Na_2$ | Cubic |
| Eudomophite | 1 | 1 | 4 | 2 | $Na_2$ | Cubic |
| Laumonite | 1 | 1 | 4 | 4 | Ca | Monoclinic |
| Gmelinite | 1 | 1 | 4 | 6 | Ca, $Na_2$ | Trigonal |
| Chabazite | 1 | 1 | 4 | 6 | Ca, $Na_2$ | Trigonal |
| Faujasite | 1 | 1 | 5 | 10 | Ca, $Na_2$ | Cubic |
| Phillipsite | 1 | 1 | 5 | 5 | Ca, $K_2$ | Monoclinic |
| Epistilbite | 1 | 1 | 6 | 5 | Ca | Monoclinic |
| Heulandite | 1 | 1 | 6 | 5 | Ca | Monoclinic |
| Brewsterite | 1 | 1 | 6 | 5 | Sr, Ba, Ca | Monoclinic |
| Desmine | 1 | 1 | 6 | 5 | Ca | Monoclinic |
| Stilbite | 1 | 1 | 6 | 6 | Ca | Monoclinic |
| Harmotome | 1 | 1 | 5 | 6 | Ba, $K_2$ | Monoclinic |
| Mordenite | 1 | 1 | 10 | 7 | Ca, $K_2$, $Na_2$ | Monoclinic |
| Edingtonite | 1 | 2 | 3 | 3 | Ba, $K_2$ | Tetragonal |
| Prehnite | 2 | 1 | 3 | 1 | Ca | Rhombic |
| Hydronephelite | 3 | 3 | 3 | 3 | $Na_2$ H | Hexagonal |

The peculiar behaviour of the water in zeolites has attracted much attention. F. J. Malaguti and J. Durocher [15] showed that when laumonite loses its water, the mineral becomes opaque, but the water is restored on exposure to air, and the mineral again becomes transparent. A. Damour showed that the zeolites lose their water when exposed to a dry atm. or when heated; and regain the lost water on exposure to moist air. As a rule, it is assumed in silicate-chemistry that water which is lost at a low temp. is present as a kind of "water of crystallization," and water which is expelled only at a high temp. is "constitutional water." C. Hersch said that only the water which is expelled from zeolites above 250° is united to the aluminium atoms, and that which is driven off below this temp. is united to the silicon atoms. Hence, he supposed that the zeolites did not contain water of crystallization. W. Fresenius assumed that at each temp. there is a definite proportion of water retained by the zeolite; and that the expulsion and restoration are continuous functions of the temp. Consequently, zeolites tested do not contain constitutional water. Other observations were made by J. Lemberg, C. W. Cross, A. Streng, C. F. Rammelsberg, etc. These will be discussed in connection with the individual zeolites. P. Jannasch showed that the water in the zeolites is not merely hygroscopic water, and F. Rinne later on emphasized the fact that the dehydration curves of the zeolites do not show any abrupt changes such as would be expected if definite hydrates were involved. A. Hamberg also found that the proportion of contained water depended on the partial press. of the water vap. in the atm.; and G. Tammann, and E. Löwenstein observed that the vap. press. of the zeolites changes continuously with the proportion of contained water. F. Zambonini confirmed these observations, and showed that the absorptive power of the dehydrated zeolite depends on the temp. to which it has been heated, and also on the duration of the heating. Similar observations were made by U. Panichi, E. Baschieri, and J. Morozewicz. E. Sommerfeldt measured the heat of hydration

and inferred that the water of the zeolites is adsorbed, and not in a state of solid soln. C. Doelter, and G. Bodländer also regarded the water as being adsorbed. A. Beutel and K. Blaschke, and G. Stoklossa measured the speed of rehydration of the zeolites hydrated between definite ranges of temp., and obtained curves showing such a large number of definite hydrates that it would appear as if some other factor is involved. R. Rinne examined the effect of water on the optical properties, and showed that the crystals which have become opaque appear to be transparent if immersed in oil. He showed that important mol. changes accompany the loss of water; and assumed that the water forms a solid soln. with the silicate. G. Friedel, and E. Mallard likened the water in zeolites to the water in a sponge; F. Zambonini, and O. Bütschli assumed that the structure of the zeolites is mycelial like that of the hydrogels; and A. Johnsen supposed that the water and anhydrous silicate form two interpenetrating cubic lattices, that the water has a free passage in the network of silicate mols.; and that with the loss of water there is a disturbance of the crystalline structure and a reorientation to form the anhydride. F. Rinne said that there is no sharp line of demarcation between crystalloids and colloids and that the zeolites belong to an indefinite region between the two classes; accordingly he regarded the zeolites as crystalline substances in an *amikroskopisch Kolloid zustand*—not analogous to A. F. Rogers' *metacolloidal state*—represented by microcrystalline substances of colloidal origin. G. Friedel, and F. Grandjean showed that gases or vapours other than water can be taken up by dehydrated zeolites—*e.g.* ammonia, hydrogen sulphide, iodine, mercury, mercuric sulphide or chloride, benzene, ether, alcohol, etc.

One of the most interesting properties of the zeolites as well as of many other silicates is the mutability of the bases. H. S. Thompson[16] first established this fact by showing that when a soln. of ammonium sulphate is filtered through soil, the filtrate contains calcium sulphate, and an ammonium salt is retained. J. T. Way made an extensive series of experiments on this subject, and showed that the hydrated silicates in the soil were responsible for the phenomenon. The action was considered to be quite different from adsorption. The facts were subsequently confirmed by the work of H. Eichhorn, W. Henneberg and F. Stohmann, O. Küllenberg, F. Rautenberg, F. Brustlein, E. Peters, G. J. Mulder, C. J. Frankfortner and F. W. Jensen, and E. Heiden. The extensive researches of J. Lemberg, and S. J. Thugutt showed that the alkalies in these aluminosilicates can be largely replaced by alkaline earths, ammonium, thallium, silver, copper, manganese, nickel, ferrous-iron, lead, and other metals, when the silicate is digested with salts of those metals. Thus, 93 per cent. of the sodium in sodium-permutite is replaced by silver when immersed in a soln. of silver nitrate. Similarly also, F. Singer showed that the alumina of these aluminosilicates can be replaced by boric, vanadic, ferric, manganic, cobaltic, and chromic oxides; and I. D. Riedel found that the silicic acid can be replaced by boric, phosphoric, nitric, sulphuric, and other inorganic acids. The name **permutite**—from *permutare*, to change—is applied to an artificial zeolite or hydrated aluminosilicate whose bases are easily replaced by other metals and the products of the replacement can be easily restored to the primitive form. Thus, when sodium-permutite is introduced into a soln. of an ammonium salt, part of the sodium is replaced by an eq. quantity of ammonium; and the ratio $Na:NH_4$ for equilibrium, is determined by the temp. and conc. of the soln. An acid sodium silicate, described by T. P. Hilditch and co-workers, and sold under the trade-name *doucil*, belongs to this class. Methods of preparation have been described by A. Messerschmitt, P. Schuler, and many others.

G. J. Mulder first assumed that the law of mass action was applicable to the equilibrium conditions; consequently, added M. Dittrich, the exchanges are not adsorption phenomena, but purely chemical processes. J. Lemberg likewise concluded that in these purely chemical processes, mass plays the same *rôle* as it does in the theory of mass action, so that there is an incomplete exhaustion of the soln., and a mutual replacement of the bases. Consonant with A. W. Williamson's

well-known theory of dynamic equilibrium, J. M. van Bemmelen suggested the following *modus operandi* of the exchange :

If we assume with the physicists in explanation of electrolysis that in a dil. acid or salt soln. a few individual mols. are in a state of dissociation, it is conceivable that the potash of the mols. in soln. is fixed by the adsorbent, whereupon fresh dissociation and binding can take place until equilibrium is attained.

H. P. Armsby wrote on the application of the law of mass action to the phenomenon. Subsequent observations have shown that the primary action described by this law is obscured by secondary effects. R. Gans regarded the permutites and saline soln. as a single homogeneous phase, and he observed that the law of mass action is applicable to soln. of small conc.

In the reaction $Na\text{-}Pe+NH_4\rightleftharpoons NH_4\text{-}Pe+Na$ (when Pe stands for permutite), let $x$ denote the number of millimols transformed ; $m$, the number of grams of permutite ; $n$, the maximum number of milli eq. transformable per gram of permutite ; $g$, the number of millimols of $NH_4$ originally present in the soln. ; and $v$, the vol. of the soln. R. Gans (wrongly) assumed that the system is homogeneous, in which case the conc. of the different salts in equilibrium are $C_{NH_4Pe}=x/v$ ; $C_{NaPe}=(nm-x)/v$ ; $C_{NH_4Cl}=(g-x)/v$ ; and $C_{NaCl}=x/v$. From the law of mass action, therefore, $x^2=K(nm-x)(g-x)$. This agrees with observations only when the conc. of ammonium chloride is small, so that $x$ is negligibly small in comparison with $nm$, and then $x^2=Knm(g-x)$. An analogous expression is obtained by assuming that the partition law (2. 17, 11) is applicable to the permutite considered as a solid soln. of two permutites.

R. Gans prepared permutites, or colloidal hydrated aluminosilicates, with a composition $RO : Al_2O_3 : SiO_2=1 : 1 : 3\text{–}4$, by the action of a soln. of an alkali aluminate on silicic acid, but not by the interaction of an alkali silicate and aluminium hydroxide. Although the permutites are colloidal, R. Gans agreed that they are definite chemical compounds, and not adsorption products. R. Gans made artificial zeolite, or permutite, by fusing together a mixture of china clay, sodium carbonate and quartz, in the required proportions. The cold, vitreous, hard mass was pulverized, and the soluble sodium aluminate and silicate were removed by leaching with cold water. A mixture of 2·5–3 parts of china clay, 5–6 of alkali carbonate, and 1·5–2·4 of borax, treated in a similar way, gave a good result. The permutite so obtained should be granular or scaly, and with a high porosity. The composition approximates $Na_2O.Al_2O_3.2SiO_2.6H_2O$. F. Singer has given a large number of recipes for preparing permutites. The sodium-permutite so prepared can be converted into ammonium-permutite by treatment with a 10 per cent. soln. of ammonium chloride. By a similar method C. Massatsch, Y. K. Lee, T. P. Hilditch, and co-workers, etc., have prepared artificial zeolites or permutites.

A. Günther-Schulze found that the exchange of the base in sodium-permutite by silver is dependent on the ionic conc. of the silver in the soln. rather than on the total conc. of the silver salt. The silver and sodium are capable of diffusion in the solid permutite ; and from the fact that at 20° sodium-permutite has an electrical conductivity of $6{\cdot}53\times10^{-4}$ mhos, and silver permutite, $4{\cdot}48\times10^{-4}$, he calculated the diffusion constants of sodium and silver to be respectively $1{\cdot}30\times10^{-8}$ and $1{\cdot}90\times10^{-8}$ sq. cm. per sec. The porosity of permutite is 30 per cent. The same diffusion constant is obtained from the diffusion experiments when it is assumed that the active surface of permutite is 9 or 10 times as great as that of an equally large, non-porous mass. A. Günther-Schulze also measured the sp. resistance of 21 permutites at 18°, and found for Li-permutite, 1800 ohms ; $Na^{\cdot}$, 1780 ; $K^{\cdot}$, 1160 ; $Rb^{\cdot}$, 1400 ; $NH_4^{\cdot}$, 1700 ; $Mg^{\cdot\cdot}$, 8130 ; $Ca^{\cdot\cdot}$, 8330 ; $Sr^{\cdot\cdot}$, 8770 ; $Ba^{\cdot\cdot}$, 10,200 ; $Cu^{\cdot\cdot}$, >90,000 ; $Ag^{\cdot}$, 2220 ; $Zn^{\cdot\cdot}$, 11,700 ; $Cd^{\cdot\cdot}$, 16,200 ; $Pb^{\cdot\cdot}$, >150,000 ; $Mn^{\cdot\cdot}$, 11,200 ; $Ni^{\cdot\cdot}$, 5000 ; $Co^{\cdot\cdot}$, 5000 ; $Fe^{\cdot\cdot}$, 6600 ; $Fe^{\cdot\cdot\cdot}$, 320 ; $Al^{\cdot\cdot\cdot}$, 420 ; and $Cr^{\cdot\cdot\cdot}$, 730 ohms. The mean temp. coeff. is $R=R_{18}\{1+a(\theta-18)\}$, where $a=4{\cdot}1\times10^{-2}$. The electrical conductivities, he said, fall into three groups, those of the alkali metals, silver, and thallium, $50\text{–}90\times10^{-5}$ ; those of the alkaline earth metals, $9\text{–}11\times10^{-5}$ ; and the rest with very slight conductivities. The equilibrium

constants of the basic exchange of sodium-, potassium-, or ammonium-permutite with salts of copper, magnesium, zinc, nickel, cobalt, aluminium, barium, strontium, calcium, thallium, silver, manganese, chromium, lead, rubidium, and uranyl fall into similar groups as the conductivities, excepting that silver and thallium, in spite of the strong ionization of their permutites, are almost entirely removed from soln. while nickel and cobalt remain in soln. Usually, the higher the at. wt. of the metal, the more readily is it removed from soln. by the permutite—aluminium is exceptional. The subject was discussed by V. Rothmund and G. Kornfeld, and C. J. Frankforter and F. W. Jensen.

A. Günther-Schulze examined the relation between the water content of the permutite and the mobility of the cation as shown by the readiness with which the basic exchange occurs. The permutites of the alkali and alkaline-earth metals contain $5H_2O$, and it is generally considered that, of these, three are water of crystallization and two "water of constitution." With potassium-permutite, however, the water content varies continuously according to the temp. and vap. press., and no distinction was found between the first three and the last two mol. proportions. The increase in the mol. vol. of potassium-permutite at different stages of hydration is proportional to the number of mols. of water added. So long as the permutite is not completely dehydrated, it can again be fully hydrated, but after ignition it takes up only about $1{\cdot}25H_2O$. The permutites of the metals copper, silver, chromium, aluminium, formed by basic exchange from alkali metal permutites, contain from $6\text{–}8H_2O$; but when formed from ignited potassium permutite the water deficiency of this persists in the derived permutites. The mobility of the cation does not appear to be influenced by the water content. Ignited potassium-permutite comes to the same stage of equilibrium with a silver nitrate-potassium nitrate soln., for instance, as the fully hydrated permutite, but equilibrium is reached more slowly, because, through partial sintering during ignition, the high porosity of the permutite is lost. The ignited permutite is very similar in character, in fact, to natural zeolites.

According to A. Günther-Schulze, the laws governing the influence of two salts with the same anion on the ionization are true for solid permutite, in exactly the same way as for salts in soln. By the continual replacement of the cation of a strongly ionized permutite by that of a weakly ionized permutite, the mobility of the former is reduced, since the non-ionized, and therefore stationary, cation of the second permutite reduces the space available for the movement of the first cation. Permutite takes up a vol., determined by every type of cation in it, since each pure permutite has a different mol. vol., which depends on the ionic vol. of the base. The mol. vol. changes with base interchange proportionally with the amount of interchange as long as the amount of water of crystallization remains constant. This will also affect the space available for the migration of the cation. Most permutites contain $5H_2O$, but chromium permutite contains $13H_2O$. The mols of water enter into the interior of the molecule, which is thereby considerably loosened, so that the mobility of the chromium cation is very much increased, and in the case of pure chromium-permutite has a value of the same order as that of the chromium ion in aq. soln. In those cases where the base interchange brings about a very small electrolytic conductivity, the interchange is very slow, so that as much as ten days are required for complete reaction. A. Günther-Schulze, and R. Lorenz discussed the "atomic radii" of the cations in permutites.

G. Wiegener argued that the reaction between permutite and neutral salt soln. has all the characteristics of an adsorption process; cations are adsorbed from the salt soln. and equivalent cations are expelled from the hydrogel of aluminosilicic acid. He represented his results by the isothermal adsorption formula $x/m=kc^{1/s}$. D. J. Hissink suggested that the exchange of cations between the permutite and the soln. is not an adsorption process, but rather an absorption. V. Rothmund and G. Kornfeld showed that the resulting mixed permutite is to be regarded as a single solid phase; the composition of this solid soln. depends on the relative conc.

of the cations in the soln. They observed that with univalent cations the composition of the permutite is independent of the total conc. of the soln., but with bivalent cations, the total as well as the relative conc. must be considered. They showed that with silver permutite, and soln. of the nitrates of potassium, rubidium, lithium, ammonium, and thallium; and with sodium permutite and ammonium and thallium nitrates, if $C_1$ and $C_2$ represent the conc. of the two bases in soln., and $c_1$ and $c_2$ their respective conc. in the permutite in equilibrium with the soln., these four magnitudes have the empirical relation $(C_1/C_2)(c_1c_2)^n=K$, where $n$ is less than unity. The values of the constants $n$ and $K$ vary considerably. U. Pratolongo measured the equilibrium state when ammonium or potassium chloride is adsorbed from its soln. by permutite, (i) when the conc. of the salt soln. is increasing, and (ii) when decreasing. The systems are tervariant, for the solid phase behaves as if it had a variable conc. The systems also exhibited the phenomenon of chemical hysteresis or false equilibrium. F. W. Hisschemöller found *l'hystérèse chimique* can be removed by repeated transformations at the ordinary temp. The position of the real line of equilibrium is displaced by repeated transformations with warm soln. By keeping the permutite for some time in the dry state, the positions of both the false and true equilibria change, and the hysteresis diminishes but does not disappear. With a permutite which has been kept for some time, a single transformation with ammonium chloride results in the almost complete disappearance of the hysteresis. The position of the false and true equilibria is independent of the dilution and the size of the particles in the transformation of sodium permutite⇌ammonium permutite. The transformation sodium permutite ⇌calcium permutite also showed hysteresis, which was not suppressed by a single transformation.

The subject attracted the attention of J. von Liebig and agricultural chemists because it was obvious that these reversible exchanges must play an important *rôle* in the fertilization of soils. This phase of the subject was discussed by J. H. Aberson, H. P. Armsby, J. M. van Bemmelen, H. Brehm, F. Brustlein, E. Bussmann, P. Ehrenberg, H. Eichhorn, R. Gans, P. Gaubert, E. Heiden, W. Henneberg and F. Stohmann, D. J. Hissink, H. Kappen, O. Kellner, W. Knop, G. J. Mulder, E. Peters, W. Pillitz, U. Pratolongo, E. Ramann and co-workers, S. Rostworowsky and G. Wiegener, F. Ullik, etc. The subject also attracted the attention of mineralogists—F. H. Campbell, F. W. Clarke and G. Steiger, M. Dittrich, C. Doelter, I. Zoch, H. W. Foote and W. M. Bradley, J. Lemberg, H. Schneiderhöhn, S. J. Thugutt, etc. Various industrial applications have also stimulated the investigation of the various reactions involved. For instance, if water containing calcium or magnesium chloride percolates through a column of sodium-permutite, a soln. of sodium chloride free from calcium or magnesium is obtained, and calcium or magnesium permutites are formed. The original permutite is restored by percolating a conc. soln. of sodium chloride through the permutite, the calcium or magnesium is replaced by sodium. These facts are at the base of the permutite process for softening hard water. In working with say a water hardened with calcium sulphate, calcium permutite (insoluble) and sodium sulphate (soluble) are formed; during regeneration, with brine, permutite (insoluble) and calcium chloride (soluble) are formed. Obviously in these exchanges, balanced reactions are in question:

$$\underset{\text{Working}\rightarrow}{Na_2O.Al_2O_3.2SiO_2.2H_2O+CaCl_2\rightleftharpoons CaO.Al_2O_3.2SiO_2.2H_2O+2NaCl}\ \leftarrow\text{Regeneration.}$$

Again, if sodium or calcium-permutite be treated with a soln. of manganese salt, a manganese-permutite is produced; and if a soln. of potassium permanganate be used, the potassium-manganese-permutite which results is also covered with a finely divided higher manganese oxide. The product is used for removing iron from water and also for oxidizing organic matter and bacteria in water. Regeneration is effected by treatment with a soln. of potassium permanganate. The

purification of water by the removal of lime, etc., was discussed by R. Gans, W. M. Taylor, F. Beyschlag and R. Michael, H. Noll, H. Lührig and W. Becker, I. D. Riedel, P. Siedler, J. Don, A. Kolb, J. Bracht and G. Hausdorff, etc., and the filtration of molasses and sugar syrups by R. Gans, H. Claassen, and H. Rümpler.

J. Morozewicz prepared **sodium dialuminium triorthosilicate,** $Na_6Al_2(SiO_4)_3$, or *soda-garnet*, which he called *lagoriolite*—after A. Lagorio—by fusing at a dark red heat mixtures of silicic acid and hydrargillite, $Al(OH)_3$, with sodium and calcium sulphates and carbonates. The square plates are flattened cubes which are either isotropic or birefringent with twin lamellæ. Analyses gave the formula $3(Na_2,Ca)O,Al_2O_3,3SiO_2$ with $Na_2O : CaO = 3 : 2$; in one analysis, there was only a trace of calcium, and in all there were small quantities of sulphuric anhydride. This is a typical garnet formula, and lagoriolite forms a connecting link between the garnet and the nosean groups. The largest amount of alkali yet found in natural garnet is 4·22 per cent. in melanite from the phonolite of Oberschaffhausen—*vide* the garnets.

There is a small group of minerals whose members are assumed to be derivatives of nephelite with which they are commonly associated. These minerals include sodalite, haüyne, noselite or nosean, cancrinite, davyne, lapis-lazuli, and microsommite. The group can be called the **sodalite family.** In no case has the exact composition been established, and they have not the same interest to the chemist as to the mineralogist. The following formulæ representing the composition of the idealized minerals are most in favour—the first four were suggested by W. C. Brögger and H. Bäckström, and the last two by F. W. Clarke:

| | |
|---|---|
| Sodalite | Cubic, $Al_2(SiO_4)_3Na_4(AlCl)$ |
| Haüyne | Cubic, $Al_2(SiO_4)_3Na_2Ca(AlSO_4Na)$ |
| Nosean | Cubic, $Al_2(SiO_4)_3Na_4(AlSO_4Na)$ |
| Lazurite | Cubic, $Al_2(SiO_4)_3Na_4(AlS_3Na)$ |
| Cancrinite | Hexagonal, $Al_2(SiO_4)_3Na_4H(AlCO_3)$ |
| Microsommite (and davyne) | Hexagonal, $Al_2(SiO_4)_3(Na,K)_3Ca(AlSO_4Cl_2)$ |

C. F. Rammelsberg [17] regarded them as nephelites associated with more or less anorthite, $CaAl_2Si_2O_8$, and with NaCl, $Na_2SO_4$, $Na_2CO_3$, etc., as *Nebenmoleküls*; or, as J. Morozewicz expressed it, the alkali salts in the sodalite family *die Rolle des Kristallwassers spielen*. Somewhat similar explanations were given by V. Goldschmidt, J. Lemberg, G. Cesaro, C. and G. Friedel, H. Rauff, F. Zambonini, etc. K. Haushofer assumed that the chlorine of sodalite is directly associated with the aluminium; and A. Safarik suggested that in sodalite, the twelve hydrogen atoms of $(H_4SiO_4)_3$ are replaced by four sodium and three aluminium atoms, leaving one aluminium valency for a chlorine atom. Similar ideas were advocated by P. Groth, F. W. Clarke, W. C. Brögger and H. Bäckström, S. Hillebrand, etc. J. Jakob assumed that nephelite can take up chromophore groups like $Na_2S$, $Na_2S_2$, etc., and become coloured; similarly also with sodalite, nosean, haüyne, etc.

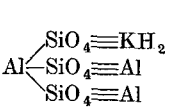
What was regarded as a blue variety of sodalite, occurring at Miask, Ural, was shown by G. Rose [18] to present a unique example of a silicate united with a carbonate; or a compound of nephelite and calcspar. He called it **cancrinite,** after Count Cancrin. A. Breithaupt, C. F. Rammelsberg, and A. des Cloizeaux regarded cancrinite as a variety of nephelite or davyne. H. Fischer, H. Rosenbusch, and F. Zirkel stated that it is not homogeneous and therefore as a mineral species *ist definitiv zu streichen*. J. D. Dana, L. Saemann and F. Pisani, H. Rauff, and A. E. Törnebohm, however, obtained homogeneous specimens, and proved that cancrinite is a definite mineral species. Analyses were made by G. Rose, G. Tschermak, A. Koch, G. Lindström, N. von Kokscharoff, M. R. Whitney, F. W. Clarke, H. Rauff, G. Strüver, J. Lemberg, P. von Pùzyrewsky, F. Zambonini, W. C. Brögger, L. Finckh, S. J. Thugutt, C. F. Rammelsberg, etc.

F. W. Clarke's formula for the idealized mineral is $Al_2(SiO_4)_3Na_4H(AlCO_3)$, or **sodium aluminium hydrocarbonatotriorthosilicate;** and P. Groth's $(Na_2,Ca)_4H_6(SiO_4)_9Al_3(NaCO_3)_2$—*vide supra*. Other suggestions have been made

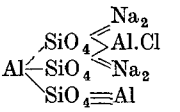
by C. F. Rammelsberg, S. J. Thugutt, J. Morozewicz, etc. A. Johnsen studied the *rôle* of the contained water. J. Lemberg made cancrinite (i) by heating under press. a mixture of alumina, sodium silicate, and a soln. of sodium carbonate; (ii) by the action of sodium carbonate, fused in its water of crystallization, on nephelite; and (iii) by heating to 215° a mixture of labradorite and a soln. of sodium carbonate. He also prepared cancrinitic substances by the action of a soln. of sodium carbonate or a mixture of soln. of sodium carbonate and hydroxide at 200° on kaolinite, analcite, leucite, vitrified orthoclase, nephelite, kaliophilite, sodalite, thomsonite, zoisite, prehnite, scolecite, paragonite. S. J. Thugutt also made similar observations on some of these mineral transformations. C. and G. Friedel obtained a cancrinite rich in potash by treating muscovite with a mixture of sodium hydroxide and carbonate at 500°. W. Eitel obtained lime-cancrinite by heating mixtures of calcium carbonate and nephelite (*q.v.*) under press. between 100 and 115 kgrms. per sq. cm., so that the carbonate was not decomposed. At lower press., say 65 kgrms. per sq. cm., no cancrinite was formed, and it is concluded that if in nature an alkali magma is heated in contact with a limestone above 1253°, at a press. above 65 kgrms. per sq. cm., cancrinite will be formed as a primary mineral of the igneous rock, but at lower press., anorthite or plagioclase will be formed. There is no evidence of the formation of cancrinite from nephelite at low temp. and press. The formation of cancrinite in nature has been discussed by G. Rose, C. F. Rammelsberg, G. von Rath, S. J. Thugutt, G. Strüver, J. Lemberg, W. C. Brögger, F. Zambonini, A. E. Törnebohm, B. J. Harrington, etc. For W. Eitel's observations, *vide supra*, nephelite.

Cancrinite usually occurs massive; prismatic crystals are rare. The colour is white, grey, yellow, green, blue, or reddish-brown. G. A. Kenngott noted a rose-red colour due to the presence of hæmatite; and S. J. Thugutt, a citron-yellow colour due to the presence of mosandrite or cainosite. W. C. Brögger found the crystals of cancrinite are hexagonal bipyramids with the axial ratio $a:c = 1:0{\cdot}44095$. The cleavage of the crystals is well-defined. The sp. gr. varies from 2·42–2·50; S. J. Thugutt gave 2·46. The hardness is 5–6. H. Rosenbusch gave for the indices of refraction $\omega = 1{\cdot}5244$, and $\epsilon = 1{\cdot}4955$; and for the birefringence $\omega - \epsilon = 0{\cdot}0289$; A. Michel-Lévy and A. Lacroix gave $\omega = 1{\cdot}522$, $\epsilon = 1{\cdot}499$, and $\omega - \epsilon$ by direct observation, 0·028. W. Eitel gave for the artificial mineral, $\omega = 1{\cdot}550$ and $\epsilon = 1{\cdot}519$. P. von Puzyrewsky, H. Rauff, and S. J. Thugutt found that when cancrinite is heated to redness, carbon dioxide is given off, and then water. H. Rauff, and F. Zambonini found the dehydration curve is continuous. E. Cohen, M. R. Whitney, and S. J. Thugutt also studied the action of heat on mineral. W. Eitel gave 1253° for the m.p. of cancrinite under press. S. J. Thugutt found that up to about 2·5 per cent. of moisture is adsorbed from the air by the powdered mineral. H. Rose, J. Lemberg, and J. Roth showed that boiling water extracts sodium carbonate from cancrinite; and F. W. Clarke showed that when moistened with cold water, phenolphthalein is reddened. S. J. Thugutt showed that when heated with water to 220°–231°, for 204 hrs., sodium aluminate is formed. A. Kaiser said that dil. acids attack cancrinite more rapidly than nephelite or davyne. According to J. Lemberg, an aq. soln. of potassium carbonate changed very little during 7 months at 100°, but at 210°–215°, the potassium and sodium were exchanged; and a soln. of sodium carbonate at 200° had no appreciable action. With a soln. of calcium chloride at 180°–190°, part of the sodium was replaced by calcium, water was absorbed, and some calcium carbonate was formed. An aq. soln. of sodium silicate at 100°, for 8 months, converted cancrinite into an analcite. An aq. soln. of ammonium chloride extracts sodium carbonate from cancrinite; and a soln. of magnesium sulphate acts similarly and forms a hydrated magnesium aluminosilicate. F. W. Clarke and G. Steiger heated cancrinite and ammonium chloride in sealed tubes at 350°, and found about 4·71 per cent. of ammonia was absorbed by the solid. The product obtained by the action of a soln. of calcium chloride at 180°–190° was

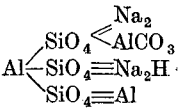
called *lime-cancrinite* by J. Lemberg. An analogous product was found by J. Lemberg among the products from Vesuvius. The composition was $10CaAl_2Si_2O_8.3CaCO_3$, which F. Zambonini regards as a solid soln. of $CaAl_2Si_2O_8$ and $Ca_2[Al_2Ca(CO_3)_2]$. It is here assumed that complex univalent groups like $AlCl_2'$, $AlSO_4'$, $AlCO_3'$, $AlSO_4Cl_2'$, and $AlSiO_3'$, and bivalent groups like $AlCl''$, $AlSO_4Na''$, $AlSNa''$, Al.S.S.Na'', and Al.S.S.S.Na'', play a part in building up the mols. W. C. Brögger and H. Bäckström emphasized the relationship between garnet and the first four minerals of this series, which they called *alkali garnets* on account of their formal relationship to ordinary (lime) garnet. F. W. Clarke also emphasized the relationship between nephelite and muscovite, and this series of minerals. These postulates, and the assumption that the formula of muscovite is $(AlSiO_4)_2 : Al.SiO_4KH_2$, led F. W. Clarke to the constitutional formulæ typified by those for sodalite and cancrinite which follow:



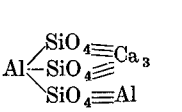
Muscovite.



Sodalite.



Cancrinite.



Garnet.

Similar formula apply to haüyne, noselite, and lazurite; while the composition of microsommite has to be represented as a mixture of two compounds each with a formula of this type. J. Lemberg[19] was able to prepare a substance with the $AlCO_3'$ of cancrinite replaced by $AlSiO_3'$ by the action of sodium silicate soln. on nephelite. S. J. Thugutt made a large number of products, like hydrated sodalites, by the action of sodium salts on hydrated nephelite. J. Lemberg, and S. J. Thugutt regarded sodalite as a mol. association of sodium chloride, because the salt is volatilized when sodalite is ignited; and it is argued that if the chlorine were directly united with aluminium, aluminium chloride would be volatilized; similarly, sodalite is hydrolyzed by water and sodium chloride separated. The arguments, of course, are not conclusive either one way or another. The hardness of these minerals is about $5\frac{1}{2}$. A. Brun gave 1450° for the m.p. of haüyne, and C. Doelter gave 1210°–1225° for haüyne, and 1140° for nosean. The index of refraction, by K. Zimanyi, F. Zambonini, and P. Gaubert, ranges from 1·4950 to 1·5060; and it increases with increasing proportions of lime. T. Liebisch found nosean gave only a feeble fluorescence in ultra-violet light, but blue haüyne gave a bright orange-yellow fluorescence. The phosphorescence was also marked. C. Doelter found that pale haüyne becomes intense blue or violet when exposed to radium rays. This colour is bleached by exposure to sunlight or to ultra-violet rays. G. vom Rath said that these minerals dissolve in hydrochloric or nitric acid with the separation of gelatinous silica, and the evolution of hydrogen sulphide. J. Lemberg found that a soln. of calcium chloride attacks haüyne more rapidly than it does sodalite; that when haüyne is heated 50 hrs. in molten sodium chloride it is converted into sodalite; and that when nosean hydrate is digested with a soln. of sodium silicate for 240 hrs. at 210°-215°, analcite is formed. C. R. van Hise discussed the natural transformations of nosean and haüyne.

T. Thomson[20] applied the term **sodalite** to a mineral which he obtained from Greenland, and which was named in allusion to the contained sodium. P. T. Weibye called a blue mineral from the islands in the Langesund fiord, Norway, *glauconite*—γλαυκός, sea-green—a name previously in use for a variety of scapolite (*q.v.*). W. C. Brögger and H. Bäckström showed that a similar mineral from Lake Baikal is sodalite. Analyses of sodalite were made by D. Borkowsky, C. F. Rammelsberg, etc. According to the above hypothesis, sodalite is **sodium aluminium chloro-triorthosilicate,** $Na_4Al_2(SiO_4)_3(AlCl)$. Sodalite has been prepared from nephelite, kaolinite, and muscovite, as well as from the simpler components. J. Lemberg made sodalite by fusing nephelite with sodium chloride; S. J. Thugutt, by heating natrolite with a soln. of sodium hydroxide and aluminium chloride at 195° in an

autoclave, and also by digesting kaolinite with sodium chloride and hydroxide at about 212°; Z. Weyburg, by fusing a mixture of silica, alumina, soda, and a large excess of sodium chloride; and C. and G. Friedel, by digesting muscovite with a soln. of sodium chloride and hydroxide at 500°; J. Morozewicz fused kaolinite with sodium carbonate and chloride, and obtained a substance resembling sodalite, $NaAlSiO_4.NaCl$; but when nephelite was used in place of kaolinite, a sodalite richer in sodium chloride was obtained, namely, $3Na_2Al_2Si_2O_8.2NaCl$.

C. F. Rammelsberg [21] analyzed a green sodalite from Monte Somma, but missed nearly 3 per cent. of molybdic oxide, which G. Freda showed was present. Hence F. Zambonini called it *molybdato-sodalite*. S. J. Thugutt prepared a large number of sodalites in which the sodium chloride of sodalite was replaced by other salts; but unlike the mineral, the artificial products were hydrated. Others have obtained anhydrous products by fusion processes. Over fifty such products have been obtained, but there is usually little or no evidence to show that chemical individuals are involved—rather the contrary in many cases. A. Gorgeu, S. J. Thugutt, and Z. Weyberg reported five *bromosodalites*; J. Lemberg, A. Gorgeu, and S. J. Thugutt, three *iodosodalites*; S. J. Thugutt, *chloratosodalite*, *bromatosodalite*, *iodatosodalite*, *perchloratosodalite*, *sulphitosodalite*, *selenitosodalite*, and *selenatosodalite*; J. Lemberg, S. J. Thugutt, and Z. Weyberg, five *chromatosodalites*; S. J. Thugutt, *molybdato-sodalite*, and *tungstatosodalite*; J. Lemberg, and S. J. Thugutt, two *nitratosodalites*; J. Lemberg, C. Bergemann, and S. J. Thugutt, three *phosphatosodalites*; S. J. Thugutt, *arsenitosodalite*, *arsenatosodalite*, *vanadatosodalite*, *hyposulphitosodalite*, and *sulphohydro-sulphosodalite*; J. Lemberg, *hydroxysodalite*, *metasilicatosodalite*, and *boratosodalite*; S. J. Thugutt, *formatosodalite*, *acetatosodalite*, and *oxalatosodalite*; J. Lemberg, *potash-sodalite*; S. J. Thugutt, *sulphatopotash-sodalite*, *molybdatopotash-sodalite*, and *phosphato-potash-sodalite*; K. Huemann, *sulphopotash-sodalite*; S. J. Thugutt, *lithia-sodalite*, *bromo-lithia-sodalite*, and *sulpholithia-sodalite*; J. Lemberg, S. J. Thugutt, and Z. Weyberg, three *calcium-sodalites*; Z. Weyberg, two *bromocalcium-sodalites*; and K. Heumann, and J. Szilasi, *sulpho-silver-sodalite*, *sulpho-lead-sodalite*, and *sulpho-tin-sodalite*; J. Lemberg, and S. J. Thugutt could not make *magnesia-sodalite*, and *strontia-sodalite*. The constitution has been discussed by J. Lemberg, S. J. Thugutt, P. G. Silber, W. and D. Asch, and R. Hoffmann. The *hackmannite* of L. H. Borgström[22]—named after V. Hackmann—occurs in cubic crystals at Lujaur-Urt, Lapland, can, according to W. C. Brögger and H. Bäckström, be regarded as sodalite contaminated with 6·23 per cent. of a white ultramarine compound, which gives off hydrogen sulphide when the mineral is treated with dil. hydrochloric acid; but, added S. J. Thugutt, nearly all sodalites give off some hydrogen sulphide when treated with acid. Hackmannite shows the evanescent pink coloration described below.

Sodalite crystallizes in the cubic system, and, by twinning, the crystals may form hexagonal prisms; the dodecahedron is a common form. Sodalite may also occur massive, and in nodules resembling chalcedony. The colour may be white, grey, green, yellow, red, or blue. The cause of the blue coloration is not certain; it disappears when the mineral is heated. As noted by the mineralogists, E. Vredenburg, T. L. Walker and A. L. Parsons, and J. Currie,[23] some red and rose-coloured sodalites keep their colour in darkness, but are bleached in daylight. W. C. Brögger and H. Bäckström studied the corrosion figures. The sp. gr. ranges from 2·14–2·40; and the hardness from 5–6. R. Cusack gave 1127°–1133° for the m.p.; A. Brun, 1250°–1310°; and A. L. Fletcher, 1177°–1183°. Sodium chloride is given off when sodalite is heated to a high temp. The index of refraction for Na-light, measured by L. H. Borgström, K. Feussner, P. Franco, F. Zambonini, and K. Zimanyi, ranges from 1·4827–1·4868. T. Liebisch found sodalite to be strongly fluorescent after exposure to the mercury arc-lamp; it phosphoresces in ultra-violet light only at the temp. of liquid air; and X-rays have no effect. F. Kreutz found that sodalite is coloured violet to peach-blue by exposure to cathode rays. F. W. Clarke noted that sodalite moistened with water has an alkaline reaction. G. Rose found that boiling water extracts sodium chloride from sodalite. Connected with this is J. Lemberg's observation that a soln. of silver nitrate colours sodalite brown. S. J. Thugutt examined the action of soln. of sodium and potassium carbonates, sodium and potassium chlorides, calcium chloride, etc., on sodalite; and J. Lemberg, the action of soln. of calcium chloride, magnesium sulphate, etc.—*vide supra*. H. Schneiderhölm investigated the action of various salt soln. on sodalite. F. W. Clarke and G. Steiger observed the action

of ammonium chloride vap. Sodalite is decomposed by acids with the separation of gelatinous silica—rapidly when heated, slowly when cold. The transformations of sodalite in nature have been studied by C. F. Rammelsberg, N. V. Ussing, C. R. van Hise, etc.

In 1803, C. G. Gismondi [24] described a blue or bluish-green mineral from Latium, and he called it *latialite:* T. C. Bruun-Neergaard called it **haüyne**—after R. J. Haüy—and J. D. Dana, *haüynite.* In 1612, M. Freher [25] mentioned a bluish mineral from Laacher-See, which C. W. Nose, and J. J. Nöggerath designated *sapphirin.* C. W. Nose also called it *spinellan;* M. H. Klaproth, *nosian*—after C. W. Nose; C. C. von Leonhard, *nosine;* and E. F. Glocker, **nosean.** L. N. Vauquelin [26] first analyzed haüyne, and a more complete analysis was made by C. G. Gmelin, who reported the alkalies as "potash." M. H. Klaproth also analyzed nosean. The relationship between nosean and haüyne was not suspected until J. J. Nöggerath published analyses of the two minerals in which special attention was paid to the alkali contents. As a result, it appeared as if the two minerals were closely related, and E. F. Glocker, J. F. L. Hausmann, W. H. Miller, A. des Cloizeaux, C. Hintze, C. Doelter, etc., regarded them as varieties of the same mineral species. G. Rose showed the crystallographic relationship of nosean and haüyne to sodalite; and M. R. Whitney represented them by analogous formulæ. Analyses of haüyne were reported by G. vom Rath,[27] J. Lemberg, C. F. Rammelsberg, L. Ricciardi, E. Casoria, A. Sauer, C. Doelter, N. Parravano, W. C. Brögger, and H. Bäckström, etc.; and analyses of nosean by C. Doelter, G. vom Rath, A. Sauer, etc. As indicated by the idealized formulæ—*vide supra*—haüyne may be regarded as nosean with part of the sodium replaced by calcium. Hence, *nosean* becomes **sodium aluminium sulphatotriorthosilicate,** $Al_2(SiO_4)_3Na_4(AlSO_4Na)$; and haüyne, **sodium calcium aluminium sulphatotriorthosilicate.**

L. A. Necker [28] applied the term *berzeline* to a mineral analyzed by C. G. Gmelin. It was described by G. A. Kenngott, W. Haidinger, and A. des Cloizeaux, and shown by G. vom Rath to be a white variety of haüyne. A mineral was discovered by F. von Ittner in the phonolitic rocks near Kaiserstuhl, Baden, and named *ittnerite* by C. G. Gmelin. It was co-related with nosean by E. F. Glocker, C. F. Rammelsberg, etc.; and analyzed by J. Lemberg, L. von Werveke, etc. Another mineral resembling ittnerite was found in the same locality by F. von Kobell, and named *scolopsite*—from σκόλοψ, a splinter—in reference to its fracture. It was examined by L. von Werveke, S. J. Thugutt, J. Lemberg, etc. H. Rosenbusch, H. Fischer, etc., allowed that both ittnerite and scolopsite are alteration products of haüyne and nosean.

Minute prismatic crystals of a mineral from Monte Somma, Vesuvius, were described by A. Scacchi [29] as belonging to the hexagonal system, with the axial ratio $a:c=1:0{\cdot}41834$. The mineral was called **microsommite;** A. P. Defrénoy called a similar mineral *acantoide.* Judging from the analyses by A. Scacchi, B. Mierisch, and H. Rauff, the composition varies considerably, but approximates very roughly to a mixture or solid soln. of sodalite and nosean minerals. Potassium takes the place of some sodium. F. W. Clarke gave $Al_2(SiO_4)_3Na_3Ca\{Al(SO_4)Cl_2\}$. J. Lemberg synthesized the mineral by acting on powdered nephelite at a red heat with calcium chloride and then with sodium chloride. The sp. gr. is 2·42–2·53, according to A. Scacchi; H. Rauff gave 2·444; and F. Zambonini, 2·60 at 15°. The hardness is 6. E. Bertrand said the crystals are optically positive. F. Zambonini gave for the indices of refraction for Na-light, $\epsilon=1{\cdot}5298$, and $\omega=1{\cdot}5218$; and for the birefringence, $\epsilon-\omega=0{\cdot}008$. G. Cesaro gave 0·007. C. Doelter found the colour of blue haüyne is darkened by exposure to radium rays, while ultra-violet light acts in the converse way. Hydrochloric acid decomposes it with the separation of gelatinous silica. F. Grandjean found that at 300°, microsommite absorbs vap. of ammonia, iodine, mercury, sulphur, etc.; and F. Zambonini said that the chlorine is thereby displaced by iodine, etc.

The mineral **davyne** discovered by T. Monticelli and N. Covelli at Monte Somma, Vesuvius, was analyzed by A. Scacchi, F. Zambonini, H. Rauff, and H. Traube. H. Rauff, and F. Zambonini could explain its composition only on the assumption that it is a mixture or solid soln. of other sodalitic minerals. The optical properties of the hexagonal crystals were examined by F. Zambonini, H. Traube, E. Bertrand, and H. Rauff. A. Breithaupt gave 2·429–2·53 for the sp. gr., and $6\frac{1}{4}$–7 for the hardness. H. Rauff showed that alkali chlorides are volatilized when the mineral is ignited; E. Kaiser, that carbon dioxide is evolved by the action of acids; F. Zambonini, that boiling water extracts chlorides; F. Grandjean, that at 250° iodine vap. is absorbed; S. J. Thugutt, and B. Mierisch

also studied the properties of the mineral. T. Monticelli and N. Covelli's *cavolinite* from Monte Somma is considered to be a variety of davyne, nephelite, or microsommite—A. Scacchi, and E. Bertrand favour the last hypothesis. L. J. Spencer described a related mineral from St. John's Island, Red Sea.

W. F. Hillebrand found a mineral at the Zuni Mine, Anvil Mt., Colorado, which he named **zunyite.** The analyses corresponded with $H_{18}Al_{16}Si_6(O,F_2,Cl_2)_{45}$, or, according to P. Groth, $Al_2\{Al(OH,F,Cl)_2\}_6(SiO)_3$ by analogy with dumortierite. The crystals belong to the cubic system, and W. C. Brögger and H. Bäckström suggested that it is related to the sodalite and garnet families; hence F. W. Clarke writes $Al:SiO_4.Al[\{Al(OH)_2\}_2AlF_2]_2$, with some fluorine replaced by chlorine.

J. Lemberg [30] obtained nosean by fusing nephelite or sodalite with sodium sulphate. J. Morozewicz prepared nosean crystals by fusing at 600°–700° a mixture of kaolinite, sodium carbonate, and sodium sulphate; and from the more complex mixture of calcium silicate, carbonate, and sulphate, and potassium and iron silicates, he obtained blue crystals of haüyne. Z. Weyberg obtained nosean by melting a mixture of sodium carbonate and sulphate, and kaolinite. J. Lemberg obtained very little haüyne by fusing anorthite with sodium sulphate.

C. and G. Friedel heated muscovite and a soln. of sodium hydroxide, sulphate and carbonate to 500° in an iron tube, and obtained a nosean with 1·78 per cent. of water. Hydrated noseans were made by J. Lemberg by the prolonged action of a soln. of sodium hydroxide and sulphate on kaolinite, analcime, leucite, orthoclase, sanidine, brevicite, albite, labradorite, nephelite, and lime-cancrinite. S. J. Thugutt made a number of experiments in this direction. The products, *nosean hydrate*, approximated $3–4(Na_2Al_2Si_2O_8).Na_2SO_4.3–4H_2O$.

The colour of nosean may be grey, blue, brown, or black; haüyne may be sky-blue, greenish-blue, asparagus-green, red, or yellow. In some cases the colour is produced by inclusions—*e.g.* green by ægirito, red by hæmatite, and black by ilmenite—in other cases the colour appears to be of the nature of ultramarine (*q.v.*) and may be due to the presence of a sulphide or rather colloidal sulphur vap., and blue haüyne is bleached in a stream of air. P. Gaubert [31] made some experiments on this subject. The crystals belong to the cubic system. Observations on the crystals were made by G. vom Rath, G. Strüver, C. F. Rammelsberg, A. Michel-Lévy and A. Lacroix, W. Bruhns, R. Brauns, and L. L. Hubbard. Twinning is well marked; and the cleavage is distinct. W. C. Brögger and H. Bäckström studied the corrosion figures. The sp. gr. ranges from 2·27 to 2·50; the hardness is 5·15. A. Brun gave 1450° for the m.p. of haüyne. The index of refraction given by K. Zimanyi, F. Zambonini, and P. Gaubert varies from 1·4890 to 1·5060. T. Liebisch studied the fluorescence and phosphorescence of the mineral; and C. Doelter, the coloration by radium rays. Sunlight and ultra-violet light bleach the coloured mineral. G. Rose found that boiling water extracts a sulphate from nosean and haüyne; and G. vom Rath showed that hydrochloric or nitric acid dissolves the mineral with the separation of silica, and in the case of hydrochloric acid, with the evolution of some hydrogen sulphide. H. Schneiderhölm, and J. Lemberg studied the action of salt soln. and sodium hydroxide on haüyne.

The intense blue-coloured stone, called **lapis-lazuli,** is more or less opaque, and it contains a number of impurities. The most prized stones have a deep blue colour and have but few impurities; in some cases the colour is pale blue passing into reddish-violet; and in other cases the colour is green. Lapis-lazuli is generally cut with a flat surface and employed as an ornamental stone in bijouterie; it is also used like agate for paper-weights, seals, knife-handles, etc.; and it has been used for inlaying and mosaics on the walls and ceilings of palaces, and the columns of churches. Formerly the blue pigment ultramarine was prepared from lapis-lazuli, but it is now made synthetically. It is used in the manufacture of paints, wallpapers, printing inks, mottled soaps, etc.; as a bleaching agent for neutralizing the yellow tint of paper, linen, cotton, whitewash, soap, starch, sugar, etc.; in making laundry blue; and in calico-printing. Commercial ultramarine is sometimes adulterated with gypsum, talc, kieselguhr, etc.

Lapis-lazuli or *azure-stone* was known to the ancient Greeks, even before the Mycenæan age, because beads and discs cut from the stone have been found in the ruins of ancient Troy. The description of the σάπφειρος, by Theophrastos (43, *c.* 320 B.C.) in his Περὶ λίθων, and of the *sapphiros* by Pliny, in his *Historia naturalis* (**37**. 8, 77 A.D.), apply to lapis-lazuli. The Greeks seem to have called it κύανος, a term now reserved for cyanite; but J. Beckmann [32] has shown that the *cyanus* of the ancients was probably a kind of mineral- or mountain-blue coloured with copper; and that their *cœruleum* may have been sometimes lapis-lazuli and sometimes copper ochre. He also showed that the sapphire of the *Bible*—*e.g. Job* (**28**. 6)—was probably lapis-lazuli, because there is an allusion to the inclusions of specks of gold, just as Pliny, in his *Historia naturalis* (**37**. 9, *c.* 77), said that the blue sapphire is interspersed with spangles of gold which sparkle like the stars in the blue sky—the specks of gold are grains of pyrites—*vide* J. Braun, and St. Epiphany. In the middle of the sixteenth century, G. Agricola called the stone *sapphirus*; and A. B. de Boodt, *lapis-lazuli*—from *lapis*, a stone, and *lazulus*, a Latinized form of the Persian term for blue. According to L. Salmasius, and J. Beckmann, *lazuardi* is the Persian word for lapis-lazuli and for a blue colour; the term was mutilated in the Arabian writings where it appears as *lazul* or *lazur*. The Spanish *azul*, blue, has the same origin. According to J. A. Fabricius, the term *lazurium* was used by M. Leontius in the sixth century; by L. A. Muratori in the eighth century; by T. Nonnius in the tenth century; and by M. Arethas in the eleventh century. About this time lapis-lazuli was confused with blue cupriferous ochres, for Constantinus Africanus and some subsequent writers refer to its medicinal qualities, and these are possessed not by lapis-lazuli, but by the copper ochres. Lapis-lazuli is called *pierre d'azure* and *outremer* in France—*e.g.* by A. des Cloizeaux—and *Lazurstein* in Germany—*e.g.* by J. G. Wallerius in 1747. The term *ultramarinum*—beyond the sea—is late Latin, and probably originated in Italy, being used for many articles brought to Europe from abroad; the Romans used the term *marinum* with a similar meaning. J. Beckmann could not find the name ultramarine in use for the lapis-lazuli before the fifteenth century. In 1502, C. Leonardus employed the term *azurrum ultramarinum*; and V. Biringucci, in 1540, clearly distinguished the real ultramarine *azurro oltramarino* from the cupriferous blue, which he called *azurro dell'Alemagna*. J. R. Spielmann, and G. Fallopius have made some remarks on this subject. For use as a pigment, lapis-lazuli was finely powdered, and the admixed impurities removed by washing. The process was described by A. B. de Boodt, F. Haudicquer de Blancourt, V. Biringucci, etc. The prepared pigment was called ultramarine. The process of preparation appears to have been somewhat as follows:

The finest selected lapis-lazuli was heated to dull redness, quenched in water, and ground to an impalpable powder. The powder was mixed with paste made of oil, resin, and wax. When the powder was mixed with the resinous paste, and kneaded in warm water, the blue particles floated on the water; the product was washed with an alkaline soln. to remove the resinous matters, and finally collected by settling. There is here a foreshadowing of the modern flotation process.

The mines in Badakshan, Afghanistan, are said to yield the finest quality of lapis-lazuli. They were mentioned by Marco Polo in 1271, and described by J. Wood. The stones from this locality have been conveyed *viâ* Bukhara into Russia, and also passed into the European markets through China and Persia. The places through which the stone has passed—Bukhara, China, and Persia—have been erroneously stated to be the localities where it is found. The mines west of Lake Baikal, Siberia, were described by N. Werssiloff—the colour of the product ranges from green to light and dark blue, and violet. According to M. Aracena, light blue lapis-lazuli occurs in the Andes of Ovalle, Chili. T. Monticelli and N. Covelli, L. Wiser, A. Scacchi, and G. vom Rath said that lapis-lazuli is found very rarely in the ejected masses from Monte Somma, Vesuvius. The occurrence of lapis-lazuli in the Albanian Hills was mentioned by G. Strüver,

F. de St. Fond, and L. de M. Spada. W. C. Brögger and H. Bäckström add that it probably is always formed as a result of contact metamorphism with limestone.

A. Cronstedt,[33] I. S. R. I. Eques a Born, and J. B. L. Romé de l'Isle regarded lapis-lazuli as a zeolite coloured blue by iron ; and L. A. Emmerling, as a peculiar kind of silica. R. J. Haüy was at first doubtful if lapis-lazuli should be regarded as a definite mineral, but he said *j'ai cru devoir, sur ce point, me conformer à l'usage*, and called it *lazulite ;* later, after the discovery of crystals of lapis-lazuli in Siberia, his doubts were removed. C. C. von Leonhard suggested that lapis-lazuli is altered haüyne ; A. Breithaupt classed it with sodalite, nosean, haüyne, and leucite under the generic term *alkalites ;* J. F. L. Hausmann regarded it as a variety of haüyne ; and A. des Cloizeaux, as a variety of haüyne mixed with other minerals. The fact that ultramarine gives off hydrogen sulphide when treated with acids soon led chemists to assume, as J. B. A. Dumas expressed it :

> La lapis est evidemment formée de deux substances distinctes. L'une fort abondante, et vraisemblablement incolorée, consiste essentiellement en silice, alumine, et soude. L'autre, plus rare et essentiellement colorée, se compose de soufre uni à quelque corps. . . .

N. von Nordenskjöld suggested that the colour of lapis-lazuli is due to the presence of a blue pigment, and the idea was developed by H. Fischer, F. Zirkel, and H. Vogelsang, who showed that lapis-lazuli is a heterogeneous aggregate containing a blue isotropic mineral and a number of colourless ones—calcspar, scapolite, felspar, and nephelite. The last-named added :

> The pigment of the heterogeneous aggregate called lapis-lazuli is a blue haüyne-like substance which is itself quite homogeneous and occurs of a higher degree of purity in lapis-lazuli than in haüyne or nosean.

W. C. Brögger and H. Bäckström reserved the name *lazurite* for the blue pigment in lapis-lazuli, a name previously employed by F. von Kobell, and C. F. Naumann as a synonym for lapis-lazuli ; and not to be confounded with lazulite, a name employed for a hydrated magnesium aluminium phosphate (**5**. 33, 23).

The lapis-lazuli was analyzed by M. H. Klaproth [34] in 1797 ; by F. Clément and J. B. Désormes, F. Varrentrapp, R. Hoffmann, C. G. Gmelin, C. F. Rammelsberg, F. Field, W. C. Brögger and H. Bäckström, J. Szilasi, etc. The variations in composition are wide, showing that mixtures are involved. The first of the following analyses is by W. C. Brögger and H. Bäckström, and the second by F. Varrentrapp. The first sample was powdered, and the blue pigment separated from the gangue by *J. Thoulet's solution* (an aq. soln. of potassium and mercuric iodides in the proportions 1·24 : 1).

| $SiO_2$ | $Al_2O_3$ | CaO | $Na_2O$ | $K_2O$ | SO | S | Cl |
|---|---|---|---|---|---|---|---|
| 32·52 | 27·61 | 6·47 | 19·45 | 0·28 | 10·46 | 2·71 | 0·47 |
| 45·50 | 31·76 | 3·50 | 9·09 | — | 5·89 | 0·95 | 0·42 |

The proportion of iron oxide varies from 0·1 to 4·2 per cent. W. C. Brögger and H. Bäckström showed that lazurite belongs to the sodalite family, in which the bivalent sulphate group (Al.$SO_4$.Na)″ of nosean is replaced by the bivalent sulphide group (Al.S.S.S.Na)″. He therefore writes the formula $Al_2(SiO_4)_3Na_4(AlS_3Na)$, making lazurite into **sodium aluminium trisulphotriorthosilicate**—*vide supra.* E. W. Büchner, and J. F. Plicque showed that carefully selected specimens of the blue pigmentary matter have proportions of silica, alumina, and soda similar to those in natrolite.

Lapis-lazuli occurs compact and massive, and also crystalline, in cubes, or more frequently, in dodecahedra. The crystals were described by A. Lévy, G. vom Rath, N. von Nordenskjöld, A. Dufrénoy, H. Fischer, etc. The colour may be azure-blue, violet-blue, or greenish-blue. The dodecahedral cleavage is imperfect ; and the fracture is uneven. The sp. gr. ranges from 2·38–2·45 ; and the hardness 5·0–5·5. It can be heated to an elevated temp. without losing its colour, but at a

white-heat, or in the blowpipe flame it intumesces, and melts to a white or yellow glass. T. L. Watson gave for the indices of refraction $\alpha=1{\cdot}604$, $\beta=1{\cdot}633$, and $\gamma=1{\cdot}642$; the optic axial angle, $2V$, is large, and the optical character is negative. According to G. Bergeron, Chilean lapis-lazuli phosphoresces when warmed by the flame of alcohol, but, added H. Fischer, the phenomenon does not recur when the stone is heated a second time. The powder is rapidly decolorized when treated with hydrochloric acid, and decomposed with the separation of gelatinous silica, and the evolution of hydrogen sulphide.

Attempts to make the esteemed ultramarine blue artificially must be very old. In 1700, F. Haudicquer de Blancourt[35] claimed to have made it, but J. B. A. Dumas added that *nous sommes d'ailleurs fort loin de croire qu' Haudicquer ait possédé ce précieux secret.* A. S. Marggraf made some trials in this direction in 1758. A blue substance was observed occasionally to present itself in the refuse of certain processes of chemical manufacture. J. W. Goethe noticed a blue vitreous substance in the lime-kilns at Palmero about 1787; and sometimes, when limestone or whiting is calcined in pottery kilns, blue patches are developed. H. Puchner observed the development of a blue colour during the calcination of humoidal calcareous sand. H. Fleissner and co-workers have discussed the formation of ultramarine blue in blast-furnace slags. In 1814, L. J. Tassart noticed a blue substance was formed in a kiln used for melting Glauber's salt; F. Kuhlmann also found that a blue substance was formed in the bricks of a sodium sulphate kiln which had been used for some time. L. N. Vauquelin showed that the composition of L. J. Tassart's blue substance was virtually the same as that of natural ultramarine; and added:

> It ought to be possible to imitate nature in the production of this precious colour; and I hope to make some experiments with this object in view.

F. Clément and J. B. Désormes' analysis of lapis-lazuli indicated the lines on which experiments to make artificial ultramarine should proceed. These observations stimulated the *Société d'Encouragement pour l'Industrie Nationale* in 1823, to offer a prize of 6000 francs for *un procédé propre à donner artificiellement et industriellement l'outremer* at a cost not exceeding 300 francs per kilogram. The prize was obtained by J. B. Guimet in 1828; and, about the same time, C. G. Gmelin independently devised a method of making the same product. The priority question—discussed by E. W. Büchner, J. L. Gay Lussac, J. C. Poggendorff, J. S. C. Schweigger, C. Leuchs, C. Schirges, H. Wichelhaus, J. F. L. Mérimée, A. Loir, and R. von Wagner—favours *incontestablement*: J. B. Guimet. J. Heintze has claimed that F. A. Köttig prepared artificial ultramarine at the Meissner Porzellanmanufactur, in 1828; and F. Varrentrapp made an analysis of the Meissen ultramarine.

In C. G. Gmelin's process for making ultramarine, a mixture of two parts of sulphur and one part of sodium carbonate, was fused in a Hessian crucible, and a mixture of sodium silicate and aluminate gradually added. The product was heated for an hour. In general, it may be said that ultramarine blue is formed whenever an aluminium silicate—say china clay—is calcined with sodium sulphide, or with some mixture which will form sodium sulphide in the course of the process of manufacture. Actual recipes are usually regarded as trade secrets, and rightly so. Three different grades of ultramarine blue are manufactured with different proportions of sulphur and silica. The following, by C. Fürstenau, illustrate three types of recipe:

| Grade. | China clay. | Soda ash. | Glauber's salt. | Carbon. | Sulphur. | Silica. |
|---|---|---|---|---|---|---|
| Pale . | 100 | 8 | 120 | 25 | 16 | — |
| Medium . | 100 | 100 | — | 4 | 50 | — |
| Dark . | 100 | 103 | — | 16 | 117 | 16 |

The varieties with a small proportion of sulphur and silica are usually paler, and more readily attacked by a soln. of alum than those with a high proportion

of these constituents. In the manufacturing process, an intimate mixture of the finely ground constituents is roasted in a muffle, shaft-kiln, or other suitable furnace. The cold product is washed ; ground to an impalpable powder ; levigated with water ; passed through a filter-press ; dried in a stove ; and sifted. Mixtures low in silica are usually green after the calcination—*ultramarine green.* This can be regarded as an intermediate product, for, when crushed and roasted again, it is converted into ultramarine blue which is washed, etc., as before.

Modifications of the process of manufacture have been described by C. P. Prückner,[36] P. J. Robiquet, J. de Tiremon, L. Elsner, C. Brunner, J. P. Dippel, C. Leuchs, G. E. Habich, C. Stölzel, J. G. Gentele, H. Ritter, G. E. Lichtenberger, C. Böttinger, J. Zeltner, A. Lehmann, R. Hoffmann, O. Ilgen, G. Guckellberger, L. E. Nottelle and M. J. Corblet, M. Sauvageot, L. Bock, F. Knapp, L. J. B. Bouillet, etc. Again, E. W. Büchner, and J. F. Plicque showed that by heating powdered natrolite in a stream of carbon disulphide, and then in a stream of sulphur dioxide, some clear blue patches are formed. F. Singer made ultramarine blue, and several analogous bodies by heating zeolites and related products with sulphides or oxysulphides of the alkalies or alkaline earths. Several wet methods have been described by F. Knapp, R. W. E. McIvor, etc. ; but the dry processes are used almost exclusively on a manufacturing scale. The general manufacture has been described by H. L. J. Rawlins, E. Röhrig, J. Wunder, J. Jordan, L. Bock, J. Pichot and P. Grangier, R. Hoffmann, K. Iwabuchi, G. Fürstenau, etc.

Analyses of samples of artificial ultramarine have been made by L. Elsner, C. Brunner, E. Breulin, H. Wilkens, H. Ritter, G. Scheffer, G. Guckelberger, A. Böckmann, J. F. Plicque, R. Lussy, R. de Forcrand, T. Morel, K. Heumann, E. Dollfus and F. Goppelsröder, J. Philipp, E. Guimet, B. Unger, C. Stölzel, etc. The extremes are 25·88–46·81 per cent. $SiO_2$ ; 23·71–38·89, $Al_2O_3$ ; 14·97–23·0, $Na_2O$ ; up to 1·65, $K_2O$ ; up to 3·24, $Fe_2O_3$ ; up to 1·11, CaO ; up to 3·47, $SO_3$ ; up to 1·0, Cl ; sulphur evolved as hydrogen sulphide by treatment with dil. acids, 1·32–2·38 ; sulphur unaffected by this treatment, 3·50–10·0 ; and total sulphur, 3·55–14·00. H. J. L. Rawlins', and E. J. Parry and J. H. Coste's analyses range from

| $SiO_2$ | $Al_2O_3$ | $Na_2O$ | S |
|---|---|---|---|
| 38·9–42·7 | 24·0–29·5 | 18·7–21·0 | 10·8–15·4 |

Omitting the oxygen and hydrogen, J. Jordan gave for white (R. Hoffmann), green and blue (J. Philipp), light blue, violet, and red (J. Wunder) ultramarines :

| | White. | Green. | Blue. | Blue. | Violet | Red. | Light Blue. |
|---|---|---|---|---|---|---|---|
| Si . . | 17·0 | 17·51 | 16·87 | 17·29 | 19·4 | 19·3 | 19·7 |
| Al . . | 16·6 | 15·81 | 15·39 | 12·55 | 13·1 | 13·3 | 13·1 |
| Na . . | 21·5 | 17·02 | 15·66 | 14·66 | 11·7 | 8·1 | 11·9 |
| S . . | 6·4 | 7·91 | 5·69 | 11·38 | 13·3 | 15·2 | 12·7 |

The similarity in the composition of different colours indicates that the actual colouring matter possibly represents but a small proportion of the total mass ; and P. Rohland suggested that a small proportion of the tinctorial agent is disseminated in a state of solid soln. in the colourless body.

The sodium of ultramarine blue can be completely replaced by silver and other univalent and bivalent radicles ; but the attempt to replace sodium by tervalent elements results in the decomposition of red, blue, or violet ultramarine. P. G. Silber found that when an aq. soln. of silver nitrate and ultramarine blue is heated for 15 hrs. in a sealed tube at 120°–140°, the sodium is replaced by silver, forming silver ultramarine. For reasons indicated below, it is assumed that in silver ultramarine one-third of the silver is bound to the sulphur. L. Braunschweiger studied the action of silver salts on ultramarine. According to J. Szilasi, J. Philipp, C. Unger, L. Bock, K. Heumann, C. Chabrié and F. Levallois, and R. de Forcrand and M. Ballin, if silver ultramarine be digested with the chlorides, or iodides of ammonium, potassium, lithium, calcium, barium, zinc, silver, cadmium, mercury (ous), lead, manganese, or iron (ous), the silver is replaced by the metal of the halide, and *ammonium* (blue), *silver* (grey), *potassium* (blue), *lithium* (blue), *calcium* (blue),

*barium* (yellowish-brown), *zinc* (violet), *cadmium* (orange-yellow), *mercurous* (bluish-grey), *lead* (brownish-yellow), *manganese* (grey), and *ferrous* (dark bluish-grey), *ultramarines* respectively are formed. Mercuric salts are reduced by ultramarine blue. R. de Forcrand heated silver ultramarine with various organic iodides and so obtained *ethyl, amyl, benzyl,* and *phenyl ultramarines.* These products give ordinary ultramarine blue when heated with sodium chloride, and they do not yield hydrogen sulphide with cold hydrochloric acid. C. Chabrié and F. Levallois could not make substitution products with ethylene, naphthalene, and triphenylmethyl radicles. E. Guimet, J. F. Plicque, and D. Morel replaced the sulphur of ordinary ultramarine by selenium and tellurium, forming respectively *selenium and tellurium ultramarines.* The former is red, the latter yellow. F. Knapp, J. Hofmann, and C. Nöllner obtained a light blue *boron ultramarine* by fusing a mixture of borax, boric acid, sodium or potassium sulphide, sulphate, or thiosulphate. Here boron takes the place of aluminium, and a polybasic boric acid takes the place of silica in ultramarine blue at 280°, and subsequently heating the product in a stream of chlorine and steam at 160°. C. Winkler said that germanium seems to be able to replace silicon in ultramarine; for, if a mixture of soda and sulphur is heated in a crucible used for roasting germanium sulphide, a blue colour is produced, although *germanium ultramarine* was not isolated.

E. Fischer obtained crystals of ultramarine from a works at Hannover. C. Grünzweig and R. Hoffmann, and H. Vogelsang showed that the crystals belong to the cubic system, and W. C. Brögger and H. Bäckström found them to be dodecahedra. Ultramarine blue, red, or violet, dried to constant weight in a desiccator, loses 1–3 per cent. of water when heated to 100°. When ultramarine white is heated in air or oxidizing agents it furnishes first green and finally blue ultramarine. P. Ebell stated that ultramarine will stay suspended in purified water for months when it is in a finely divided state. The settling was also studied by F. Schubert and L. Radlberger. P. Rohland said that ultramarine has hydraulic qualities like portland cement. J. Wunder investigated the absorption spectrum of green, blue, and violet ultramarines. Many properties of ultramarine are indicated in the next few paragraphs. C. Doelter found that ultramarine blue is only darkened slightly by exposure to radium rays; violet and white ultramarines are not changed. The effect with natural ultramarine is much more marked—*vide* haüyne. Ultramarine blue is decomposed by dil. acids, and R. Hoffmann found that about one-fourth of the contained sulphur is given off as hydrogen sulphide, and three-fourths remains in an ionized form among the products of decomposition; neither red nor violet ultramarine furnishes hydrogen sulphide when decomposed by dil. acids. The red product is decomposed by dil. acids more slowly than violet or blue. The action of acids has been studied by J. G. Gentele. F. Schubert, and L. Radlberger found that hydrogen sulphide is evolved when ultramarine is boiled with a 0·25 per cent. soln. of malic acid. B. von Szyszkowsky showed that carbon dioxide decomposes ultramarine suspended in water, and hydrogen sulphide is evolved; the action is retarded in the presence of neutral salts. According to J. Wunder, by treating ultramarine blue with hydrogen chloride at 170°–250°, about one-sixth the sodium is converted into soluble chloride, and with ultramarine violet, one-third of the sodium is converted into soluble chloride, and ultramarine red is formed. J. Zeltner, and R. Rickmann studied the action of hydrogen chloride. When ultramarine violet is treated with iodine and hydrochloric acid, J. Wunder found that half the sulphur behaves as if it were present as a thiosulphate. J. G. Gentele studied the action of ammonium chloride. L. Wunder found that sulphur monochloride in a sealed tube at 200°, converts ultramarine blue into ultramarine white; a soln. of phosphorus in carbon disulphide converts ultramarine blue into ultramarine violet; and the ultramarine blue is partially decomposed if mixed with phosphorus tri- or penta-chloride and heated in a sealed tube at 130°–180°.

If air be completely excluded during the ignition of the mixture employed in

the preparation of ultramarine blue, H. Ritter,[37] J. Philipp, C. Böttinger, and R. Hoffmann showed that the blue coloration is not produced, and that the resulting **white ultramarine** is converted into the blue product by heating it in a stream of oxygen, sulphur dioxide, or chlorine. J. Philipp found that when a little tin is added to the mixture employed in the preparation of ultramarine, the product is **green ultramarine ;** and a green product is sometimes formed in the preparation of the blue—*vide supra.* The green ultramarine is regarded as representing an intermediate stage in the formation of the blue, because green is converted into blue ultramarine by roasting it with sulphur. J. Philipp, however, concluded that sulphur is not taken up during the change from green to blue because the blue product is formed when green ultramarine is heated with water in sealed tubes at 100°—the water removes a little sodium from the green ultramarine. When the green product is heated in chlorine gas, it becomes bluish-violet, and when mixed with sodium sulphide and heated, it becomes grey. G. Scheffer found that if in the preparation of ultramarine blue, the temp. of calcination be higher than is normally required, and air has free access, **red ultramarine** is formed containing less soda and more alumina than ordinary ultramarine blue. According to E. W. Büchner, red ultramarine is formed when the blue product is heated to 300°–400° in oxygen or sulphur dioxide, and if the heating be prolonged, the red passes into **yellow ultramarine.** According to J. Zeltner, if chlorine be passed over the product obtained just before the blue is developed in the ordinary course of manufacture, at 410°, a green substance is first formed, and this then acquires a reddish-yellow colour. Yellow ultramarine changes to blue when heated in a stream of hydrogen or coal gas. If the red product be heated with sodium hydroxide all the chlorine is removed, and **violet ultramarine** is formed. This product goes into the red form when heated in the vap. of nitric acid or hydrochloric acid at 130°–150° ; and into the blue form when heated alone to about 520° (P. G. Silber) ; in hydrogen at 280°–290° (J. Wunder, and C. Grunzweig and R. Hoffmann) ; or when it is mixed with soda-lye and heated. T. Leykauf made violet ultramarine in 1859 by warming a mixture of moist calcium chloride and ultramarine blue, and in 1872, J. Wunder prepared it by lixiviating the product of the action of chlorine. Violet ultramarine is supposed to be a mixture of red and blue ultramarines.

Many guesses have been made to account for the colour of ultramarine blue and of lapis-lazuli or of lazurite. A. Schrauf,[38] H. Vogelsgang, R. Hoffmann, and many others are agreed that the colouring principles of natural and artificial ultramarine in a state of purity are *chemische identische Substanzen.* Most of the suggestions can be arranged in one of the three following groups, although the line of demarcation between the second and third is not always clear.

1. *The colour is produced by a colouring agent or chromophore.*—Before 1758, there was a general impression that the colour was produced by the presence of copper, but A. S. Marggraf showed that this assumption has no foundation, because the blue colour is present when copper is absent. He suggested that iron is the colouring agent. L. Elsner, K. Kressler, L. B. G. de Morveau, C. P. Prückner, and F. Varrentrapp believed that iron sulphide is the tinctorial agent, but here again, C. Brunner showed that quite as good a blue colour can be produced by using materials quite free from iron. C. Unger claimed that the colouring principle is a nitrogenous compound, but E. W. Büchner found ultramarine blues with no nitrogen. W. Stein suggested this principle is ammonium sulphide mixed with the ground mass in a state of *molekularer Vertheilung.* H. Ritter considered that there can be no question of a colouring principle *per se* because the whole of the ultramarine forms a chemical compound, as is evidenced by the fact that one form is colourless and may under certain conditions be transformed into a coloured form without the introduction of a new substance. The general similarity in the composition of different samples of ultramarine with very different tints supports the view that the actual colouring matter represents but a small fraction of the

whole; and P. Rohland called the colouring principle a *chromophore*—χρῶμα, *colour*; *and φέρειν, to bear*—*whose composition has not been elucidated, but which* he assumed to be uniformly distributed throughout the ground-mass in a state of solid soln.

C. G. Gmelin, and C. N. Nöllner assumed that the colouring principle is sulphur; and in a more modern guise, the hypothesis of E. Paterno and A. Mazzucchelli, Wo. Ostwald, H. H. Morgan, and J. Hoffmann assumed that the coloration is produced by a blue form of colloidal sulphur. The argument is based largely on analogy since many reactions are known in which colloidal sulphur is formed and a blue colour developed—*e.g.* molten potassium thiocyanate becomes blue at 400°, and the white colour returns at ordinary temp.; sodium chloride or sulphate becomes blue when roasted with sulphur; and alkali polysulphides form blue soln. with many boiling organic solvents, and the mixture becomes white again on cooling. Sulphur vapour is also blue. I. F. Keme found that consonant with the general observation that alkalies increase the dispersion of inorganic disperse systems, the fusion of blue ultramarine with alkalies transforms the colour to a deep red. This is taken to confirm the colloidal hypothesis. It has been urged *against this hypothesis that ultramarine blue withstands a red-heat fairly well*, even though the blue loses some of its brilliancy, and acquires a greenish tint. The objection is not serious when it is remembered that other colours are produced by colloids in solid soln. with another substance which acts as a protective or *stabilizing agent*. It is, however, necessary to assume that red, green, and violet colours can also be produced by the same colouring agent—presumably in a different state of subdivision. Wo. Ostwald made green and blue colloidal sulphur. The fact that the alkali ultramarines are alone blue does not favour the hypothesis that its colouring principle is colloidal sulphur. Indeed, L. Wunder states that three conditions must be fulfilled in order that ultramarine may be coloured blue: (i) an alkali must be present—if a mercurous ultramarine has only part of the alkali replaced by mercury, it becomes blue on calcination, but if all the alkali be replaced by mercury, it is colourless when calcined; (ii) a part of the sulphur must be directly united to a metal, for the blue ultramarines develop hydrogen sulphide when treated with dil. acids, while the red and violet ultramarines give sulphur dioxide, not hydrogen sulphide; and (iii) a part of the sulphur must be present in a lower state of oxidation, *for ultramarine blue becomes white when treated with* strong reducing agents, and the blue colour is restored by oxidizing agents.

2. *Ultramarine is a molecular compound or complex of a silicate and a sulphide.*—Another set of hypotheses attempts to explain the blue coloration by assuming the colour is a constitutive property, produced by definite mol. complexes. R. Hoffmann tried to establish the individuality or homogeneity of ultramarine blue by microscopic observations; but this test is incapable of distinguishing between chemical individuals and solid soln. Similarly, G. Guckelberger tried to show that ultramarine green is a single substance, and not a mixture of a blue and a yellow ultramarine, or ultramarine blue with adsorbed sodium sulphide. When a mixture of ultramarine blue and water is heated in a sealed tube between 200° and 300°, a colourless insoluble residue free from sulphur is formed, and sodium sulphide passes into soln.; when heated with mercuric oxide, the sulphur is likewise abstracted. Ultramarine is stable with alkalies, but is decomposed by dil. acids with the precipitation of sulphur, and the liberation of hydrogen sulphide. This behaviour supports the view that the colouring principle of ultramarine blue is a combined silicate and polysulphide of sodium and aluminium, *but against this hypothesis*, K. A. Hoffmann and W. Metzener find that, unlike polysulphides, and thiosulphates, ultramarine blue is not affected by conc. fuming sulphuric acid, or by a mixture of glacial acetic acid and acetic anhydride. R. Hoffmann's conclusion that the sulphur in ultramarine blue is present in a similar state of combination as it is in the polysulphide, $Na_2S_4$, cannot be right, since H. Erdmann showed that it does not yield silver sulphide when treated with silver nitrate, but is converted into silver

ultramarine in which sodium is replaced by silver. H. Erdmann suggested that the ultramarines are to be regarded as thiozonides containing the bivalent radicle $S_3$. In strict analogy with the ultramarines, H. Erdmann said that the sulphur dyes are transformed by powerful reducing agents into leuco-compounds corresponding with white ultramarines, and in both cases the white compounds are readily oxidized back to the original substance.

R. Hoffmann emphasized the idea that the cause of the colour may be due to the presence of definite sulphides contained in the ultramarine; he believes that the radicle is a kind of sulphonate, and that the various colours are produced by the addition, or subtraction, or substitution of oxygen, sulphur, sodium, etc., without destroying the combination of the silicate mol. which produces the colour. These changes, said he, occur in a similar manner to those in the side chains of organic compounds. R. Hoffmann thus distinguishes the silicate side from the sulphide of the ultramarine mol. without disturbing the combination as a whole. He added:

> The formation of green and blue ultramarines, and their behaviour towards various reagents confirm the view that the sodium added in the form of oxide must be more firmly united to the elements of clay than is the sulphide, and that it alone takes part in the further conversion of white to blue and green ultramarines. Consequently, it is possible to distinguish a silicate side from a sulphide side in the ultramarine mol. without in any way disturbing the combination of elements as a whole. . . . The formation of ultramarine by the ordinary method of preparation, and its chemical behaviour, are sufficiently explained by assuming the existence of a sodium silico-aluminate in which that part of the oxygen which is in closest combination with sodium can be replaced by sulphur—such silico-sulphonates behaving like free sodium monosulphonate from which higher sulphonates may be produced by combination with sulphur and loss of sodium, without the silico-sulphonate being decomposed.

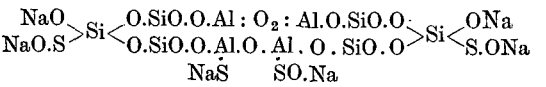
W. C. Brögger and H. Bäckström assume that white ultramarine has the composition $Al_2(SiO_4)_3Na_4\{Al(NaS)\}$; green ultramarine, $Al_2(SiO_4)_3Na_4\{Al(NaS_2)\}$; and blue ultramarine, $Al_2(SiO_4)_3Na_4\{Al(NaS_3)\}$. All these are derived from the parent silicate, $Al_2(SiO_4)_3Na_3$. It is further assumed that many artificial products are mixtures of these four typical compounds—*vide* lapis-lazuli. R. Hoffmann gave for the fundamental silicate $Na_2Al_2Si_3O_{10}$; for ultramarine blue, $Na_4Al_4Si_6O_{20}.Na_2S_4$; ultramarine red, $Na_2Al_4Si_6O_{19}.NaS_3O_3$; and for ultramarine yellow, $Na_2Al_4Si_6O_{19}.NaS_2.{}_5O_3$. As previously indicated, F. Singer prepared a number of ultramarine colours by substituting sodium sulphide for water in hydrated nephelite and it has therefore been argued that ultramarine is a mol. compound of nephelite with sodium polysulphide. Thus, white ultramarine has been represented as $6(NaAlSiO_4).2\text{–}4Na_2S$; green ultramarine, $6(NaAlSiO)_4.2\text{–}4NaS$; and blue ultramarine, $6(NaAlSiO_4).1\text{–}2NaS_2$. L. Bock regards the ultramarines as definite compounds based on $Al_2O_3.3SiO_2$. Starting with ultramarine green,

$$\begin{matrix}NaS\\NaO\end{matrix}\!\!>\!Al.O.SiO.O.Si(ONa)_2.O.SiO.O.Al\!<\!\begin{matrix}SNa\\ONa\end{matrix}$$

in the formation of ultramarine blue, the introduction of groups SONa′ is postulated; and in ultramarine violet, the groups $NaS_2O_3'$—*vide infra*. J. Jakob assumed that the chromophore groups are $Na_2S$, $Na_2S_2$, etc.

3. *Ultramarine is a compound containing labile chromophore radicles.*—The colour is regarded more or less as an accidental circumstance dependent on the nature of chromophore radicles associated with the fundamental alkali aluminosilicate. This means that ultramarine is a definite chemical individual with a specific structural formula. W. and D. Asch assume that the aluminosilicate is associated with the complex $S_2O_7''$, or $-O.SO_2.O.SO_2.O-$, which is prone to split off oxygen atoms, and take them up again, and to exchange all or part of the oxygen atoms for sulphur. In conformity with the views of O. N. Witt, M. Schütze, R. Nietzki, G. Krüss and co-workers, H. W. Vogel, E. Koch, etc., these complexes

are regarded as chromophores, and it is assumed that the simpler forms furnish yellow pigments, while with increasing mol. wt., the colour changes to orange, red, bluish-violet, violet, blue, bluish-green, and green ; and conversely. The nature of the base is assumed to be of importance, so that the effect produced by the one may be masked by the other. According to J. and L. Wunder, the facts are summarized in the formula :



corresponding with the empirical formula $Si_6Al_4Na_6S_4O_{22}$ for ultramarine blue. W. and D. Asch introduce an atom of oxygen between the aluminium atoms and sulphur, and use hexite and pentite rings for the silicate part of the mol. In the corresponding ultramarine violet, L. Wunder assumes that the SNa-group is hydrolyzed and replaced by OH, and that the univalent O : S.Na-group is transformed into the univalent radicle $NaS_2O_3$. This agrees with the empirical formula $Si_6Al_4Na_5HS_4O_{23}$ for ultramarine violet. When this product is transformed into ultramarine red, $Si_6Al_4Na_3H_3S_4O_{23}$, it is assumed that the two univalent S.O.Na-groups are hydrolyzed to S.OH. Hence, red ultramarine is considered to be an acid whose sodium salt is violet ultramarine. These formulæ agree with the hydration of ultramarine by water above 100°, and it is assumed that the four bivalent SiO-groups can be hydrated to bivalent $Si(OH)_2$. Dil. acids are supposed to attack the bivalent Al.SNa-group : $Al.SNa'' + 2HCl = AlCl'' + NaCl + H_2S$. Acids attack both side groups in accord with the equation: $SiONa(S.ONa) + 2HCl = SiONa(S.OH)'' + 2NaCl = SiO'' + H_2O + S + 2NaCl$, and in the decomposition of ultramarine blue by acids, three-fourths of the sulphur separates as milk of sulphur. The fact that when silver ultramarine is formed, one-third of the silver is bound to the sulphur is explained by assuming that there are three S.ONa-groups in the mol. of ultramarine, and only one is bound directly to the aluminium—each of the other two being united to a silicon atom. Tervalent elements are not able to replace sodium atoms because the mol. does not contain three sodium atoms united to the mol. in the same way. When ultramarine is reduced by a soln. of phosphorus in carbon tetrachloride in a sealed tube at 150°, washed with carbon disulphide, and dried, a flesh-coloured, almost white, substance is formed—*white ultramarine*—it is supposed that the phosphorus takes oxygen from the three SONa-groups, and that green ultramarine is formed by the deoxidation of one or two of these groups. Hydrogen chloride and steam between 170° and 250° are not strong enough to attack SONa-groups, but they react with the SNa-group, removing one-sixth of the sodium from the mol., $SNa' + H_2O + HCl \rightarrow H_2S + NaCl + OH'$. If an oxidizing agent is present at the same time, the SONa-group is simultaneously oxidized to a thiosulphate $NaS_2O_3$-group. The action of a soln. of iodine on violet ultramarine confirms these assumptions.

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## § 41. The Micas

The micas are a family of different, though probably related, minerals. They are all complex aluminium silicates or aluminosilicates. They are usually resolved into three sub-groups or families, whose members have more or less similar characteristics. They have a highly developed basal cleavage; they split into thin plates; and they crystallize in the monoclinic system. They may be classified thus:

| | | |
|---|---|---|
| Micas | Mica family . . . . . | Muscovite; biotite |
| | Clintonite family . . . . . | Clintonite |
| | Chlorite family . . . . . | Clinochlore |

The members of the *chlorite* family are sometimes called *hydromicas;* they are generally green in colour, and form scales and incrustations on the walls of cavities in dolomites and mica schists; or they may occur massive or earthy as alteration products of ferromagnesian silicates. The *clintonite* family, sometimes called the *brittle micas*, are usually more basic, chemically, than the micas proper. The cleavage laminæ are also brittle. The members of another group of micaceous minerals, classed as *vermiculites*, are usually regarded as alteration products of the true micas. Considering only the predominant basic constituents, the principal micas proper are:

| | | |
|---|---|---|
| Muscovite | Potash mica | $H_2KAl_3(SiO_4)_3$ |
| Paragonite | Soda mica | $H_2NaAl_3(SiO_4)_3$ |
| Lepidolite | Lithia mica | $(HO,F)_2(Li,K)_2Al_2Si_3O_9$ |
| Zinnwaldite | Lithium-iron mica | $(HO,F)_2(Li,K)_3FeAl_3Si_5O_6$ |
| Phlogopite | Magnesia mica | $(H,K,M,F)_3Mg_3Al(SiO_4)_3$ |
| Biotite | Magnesium-iron mica | $(H,K)_2(Mg,Fe)_2(Al,Fe)_2(SiO_4)_3$ |

The early observers included mica in the same class as gypsum, which can also be split into thin flakes. It was afterwards noticed that, unlike talc and gypsum, the cleavage plates of mica are highly elastic, and not pliable. Pliny, in his *Historia naturalis* (**36**. 45, 37. 73), has a description of a mineral *lapis specularis* which applies very well to mica. The scales of this mineral were strewn over the *circus maximus* at the celebration of games with the object of producing a sparkling whiteness. This shows that a mica schist furnished the material employed; and Pliny's *hammochryos*—from ἄμμος, sand; χρυσός, gold—was probably a sand containing golden-coloured scales of a biotitic mica. The Hindus appear to have used mica for decoration and other purposes, and they considered it to be endowed with extraordinary properties.[1] Mica has also been found in the graves of prehistoric American races, east of the Mississippi, in localities where the mineral does not occur.

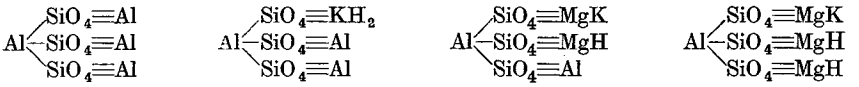
The term *mica* is not likely to have been derived from the Latin *mica*, a crumb, or grain, but rather from the Latin *micare*, signifying, like the German *Glimmer*, to shine. In mediæval times, scaly mica was called *cat-silver*, or *cat-gold*—Katzengold, or Katzensilber; *or des chats*, or *argent des chats*. Thus, G. Agricola [2] spoke of *Ammochrysos*, *Mica*, *Glimmer*, or *Katzensilber*. A. B. de Boodt, and J. G. Wallerius described several varieties. A. G. Werner, and A. Estner definitely adopted the term *Glimmer*, and described many varieties. No great progress could be made in the classification of the micas until they had been distinguished from one another by chemical analysis, and optical measurements.

The analyses of M. H. Klaproth [3] distinguished the magnesian and the alkali micas, and the analyses of C. G. Gmelin established the lithia-micas. H. Rose showed that fluorine is sometimes present, and that the mineral contains chemically combined water. J. Peschier studied some titaniferous micas. C. F. Rammelsberg collected a number of analyses; calculated the ratios K : Al : Si; and showed that the hydrogen of the contained water must be regarded as a univalent metal. C. F. Rammelsberg, H. Rose, and J. Roth regarded the alkali and magnesian micas as orthosilicates, and this view is generally accepted at the present day. G. Tschermak in his paper, *Die Glimmergruppe* (Wien, 1877–8), explained the composition of the micas by regarding them as isomorphous mixtures of three fundamental silicates: (i) $H_2KAl_3Si_3O_{12}$, corresponding with ordinary mica; (ii) $Mg_6Si_3O_{12}$, a hypothetical polymer of chrysolite; and (iii) $H_4Si_5O_{12}$, a hypothetical silicon hydroxide which may take the form $Si_5F_4O_{12}$. C. F. Rammelsberg, also, in his paper, *Ueber die chemische Natur der Glimmer* (Berlin, 1889), assumed that the micas must be associated with three silicates: $R_2SiO_3$, $R_4SiO_4$, and $R_6SiO_6$, associated in various proportions. Thus, muscovite was considered to be compounded of $R_4SiO_4$ and $Al_4Si_3O_{12}$. This mode of dealing with the problem cannot be considered a solution of the difficulty, for it can be applied to represent the composition of any conceivable silicate, however complex. W. and D. Asch apply their hexite hypothesis to the micas, postulating that they are compounded of three type micas. S. J. Thugutt, R. Brauns, J. W. Retgers, P. Groth, etc., have also discussed this subject. P. Erculisse, and J. Jakob applied the co-ordination theory to the micas, representing muscovite by $[Al(SiO_4)_3]Al_2KH_2$.

F. W. Clarke, in his *Theory of the Mica Group* (1889), argued that all the micas should be reducible to one general type formula; that the formulæ should express all known relations; and that hypothetical compounds should be as far as possible avoided. He used the normal salts $Al_4(SiO_4)_3$ and $Al_4(Si_3O_8)_3$ as theoretical starting points for the micas, vermiculites, chlorites, and margarite. Thus, in his memoir, *The Constitution of the Silicates* (Washington, 51, 1914), starting with normal aluminium orthosilicate, he obtains:

| | |
|---|---|
| Aluminium orthosilicate . . . . . | $Al_4(SiO_4)_3$ |
| Muscovite . . . . . | $Al_3(SiO_4)_3KH_2$ |
| Normal biotite . . . . . | $Al_2(SiO_4)_3Mg_2KH$ |
| Normal phlogopite . . . . . | $Al(SiO_4)_3Mg,KH_2$ |

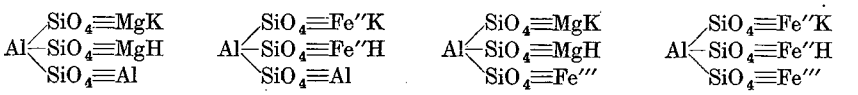
This makes the micas out to be *aluminotriorthosilicates*. Any further substitution of the same type would remove the linking atom of aluminium, and break up the fundamental nucleus $Al(SiO_4)_3$, as can be seen graphically:



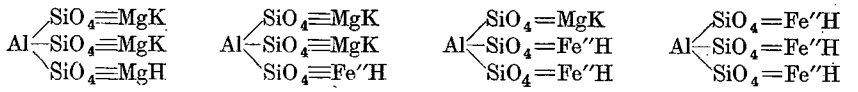

Aluminium orthosilicate. Muscovite. Normal biotite. Normal phlogopite.

J. Uhlig suggested that *cryptotile*, $H_3Al_3(SiO_4)_3$, found by A. Sauer as an alteration product of prismatine, is the terminal member of the series of alkali micas, $(AlSiO_4)_2Al(SiO_4H_3)$. F. W. Clarke added that while typical muscovites agree sharply with the formula, the composition may vary within limits: (i) Sodium may replace potassium until it merges into paragonite which has the corresponding formula, $(AlSiO_4)_2Al(SiO_4Na_2H)$; again, (ii) Some chromium may replace aluminium, furnishing the chromiferous mica called *fuchsite*. Usually, however, the proportion of chromium is small; (iii) Some ferric iron may replace the aluminium. This, too, is usually small but in a sericite mica analyzed by C. Senhofer, the formula approaches $Al_2Fe'SiO_4)_3KH_2$; (iv) The aluminium may be replaced by vanadium. In the idealized *roscoelite*, $AlV_2(SiO_4)_3KH_2$, there should be 33·6 per cent. $V_2O_3$, but not more than about 24 per cent. has been actually observed; (v) The presence of magnesium or ferrous iron is usually attributed to the admixture of some biotitic mica; and (vi) While normal muscovite has 45·3 per cent. $SiO_2$, the proportion may rise to about 59. G. Tschermak called these siliceous muscovites *phengites*—from φέγγος, glitter—and explained them by assuming that they are mixtures of muscovite with an acid silicate, $H_4Si_5O_{12}$; and F. W. Clarke assumed they are mixtures of muscovite with the *aluminotristrisilicates* $Al_3(Si_3O_8)_3KH_2$, built on the mica type of mol. Some of the lithia-micas are almost entirely the trisilicate, and other muscovite micas have from 0–50 per cent. of the trisilicate with ferric iron, chromium, or vanadium replacing more or less of the aluminium. The mica *euphyllite*, continued F. W. Clarke, has the univalent group $Al(OH)_2$, making $Al_3(SiO_4)_3KH.\{Al(OH)_2\}$. E. T. Wherry applied the at. vol. theory of isomorphism, and assumed that the passage from $H_4K_2(Mg,Fe)Al_4Si_7O_{24}$ to $H_4K_2Al_6Si_6O_{24}$ involves the double isomorphous replacement of (Al+Mg) and (Al+Si).

The *biotite* and *phlogopite* micas exhibit greater variability in composition than the muscovite micas. F. W. Clarke refers the biotite micas to the four types:




which when mixed in various proportions, with the substitutions previously indicated, can be made to simulate the composition of this group of minerals. Thus, F. W. Clarke showed that the *siderophyllite* of H. C. Lewis can be represented by the second of these formulæ; while the *haughtonite* of M. F. Heddle is a mixture of the first, second, and third. The phlogopite micas were represented in a similar manner, by admixtures of two or more minerals of the type:




F. Grünling described a sodium phlogopite containing no potassium; F. von Kobell's *aspidolite* may belong to the same class; and the *manganophyllite* of L. J. Igelstrom, G. Flink, and A. Hamberg with its 9–17 per cent. of MnO, seems to

be mixed with $Al(SiO_4)_3Mn_3KH_2$. G. Tschermak, K. Dalmer, etc., have also discussed this subject.

In cases where the oxygen is in excess of that required to convert all the silicon into $SiO_4$, and the excess is not due to defective analyses, it is assumed to be produced by alteration, or by replacement of univalent radicles by hydroxyl groups like $Al(OH)_2$, R″OH, etc. The function of titanic oxide in the analyses of the mica is not known, since it may replace silica as $TiO_2$; it may replace alumina as $Ti_2O_3$; or it may be present as inclusions of rutile. Fluorine is contained in many micas. It may be present as a monad group like $AlF_2$, or R″F. An average lepidolite, for instance, can be regarded as a 1 : 1 mixture of a trisilicate, $Al(Si_3O_8)_3K_3Li_3(AlF_2)_3$, and muscovite, $Al(SiO_4)_3Al_2HKLi$. H. Baumhauer, indeed, found inclusions of muscovite in lepidolite. Some potassium may be replaced by sodium; and some fluorine by the OH-radicle. Zinnwaldite is considered to be a mixture of the same trisilicate with ferrous biotite, $Al(SiO_4)_3(FeK)_2Al$. Cryophyllite is related to zinnwaldite, and its composition, though more complex, can be represented in a similar manner. Analogous remarks apply to the *irvingite* of S. Weidman, while the *polylithionite* of J. Lorenzen, and G. Flink and co-workers is considered by F. W. Clarke to be a trisilicate 1 : 5 mixture of $Al(Si_3O_8)_3(Na_2K)_3$ and $F_2 : Al.(Si_3O_3) : Li_3$.

The biaxial potash-mica appears to have been designated *vitrum muscoviticum* by J. G. Wallerius,[4] and, as previously stated, to have been found by A. B. de Boodt in Moscovia. It was called *muscovite* by J. D. Dana in 1850. It has also been called common mica, *potash-mica*, white mica, *biaxial mica*, and *oblique mica*; it was formerly called *muscovy glass*. When clear and transparent, it is sometimes called, in commerce, *water mica*.

Several varieties have been assigned special names. A. Delesse gave the name *damourite*—after A. Damour—to a variety previously designated *hydromica* by T. Thomson. Damourite was discussed by A. Knop, A. des Cloizeaux, J. D. Dana, C. F. Rammelsberg, D. Lovisato, E. Dittler, G. Tschermak, J. L. Igelström, and M. Bauer. The *gilbertite* of T. Thomson was found in the tin mines of St. Austell, Cornwall, and it was named after D. Gilbert; A. Frenzel also found the same mineral in the tin mines of Saxony and Bohemia. V. Dürrfield described a sample from Fichtelgebirge, Bavaria. Gilbertite was also described by A. Breithaupt, A. Frenzel, F. Sandberger, C. Peters, and J. H. Collins. J. F. L. Hausmann, and C. Hintze considered it to be related to china clay. T. Thomson described *talcite* from Wicklow, Ireland; and what he called *nacrite* from Maine—*vide* kaolin. R. P. Greg and W. G. Lettsom regarded gilbertite, talcite, and nacrite as varieties of *margarodite*. A. des Cloizeaux also discussed this mineral; and C. Hintze regarded it as an impure clay. The name talcite was applied by K. von Schafhäutl to a talc-like mica from Mt. Grenier, Zillerthal. The name margarodite was suggested by the lustre—*μαργαρίτες*, a pearl. J. P. Cooke obtained a variety of damourite from Sterling, Mass.; and he called it *sterlingite*. A greenish-black variety from Derby, Vermont, was called *adamsite*. It was analyzed by G. J. Brush, and likened to muscovite by G. Tschermak. T. D. Rand described a micaceous mineral from Greenland, which he called *iviglite*. Both G. Hagemann, and F. Johnstrup consider it to be a variety of gilbertite. F. Sandberger described a scaly mineral from Wittichen, Baden, which he called *lepidomorphite*—from *λεπίς*, a scale; and *μορφή*, form. P. Groth considered it to be a siliceous variety of muscovite. G. Starkl obtained a green mineral from the mica schist of Klein Pischingbachthel, Austria, and a sericite-like mass from Anna-Kapelle, Wiesmath, and Ofenbach, Frohsdorf, Austria. He called the former *pycnophyllite*, and the latter *leucophyllite*—from *πυκνός*, dense; *λευκός*, white; and *φύλλον*, a leaf.

C. List applied the term *sericite* to a talc-like mineral from Taunus—*σηρικός*, silky—because of its silky lustre. For a time, C. E. Stifft considered it to be a variety of talc; C. List, and A. Knop, a variety of damourite; and J. R. Blum, *nichts anderes als Kaliglimmer*. The relation of sericite to mica was emphasized by K. A. Lossen, F. Scharff, A. von Lasaulx, A. Wichmann, and H. Rosenbusch. H. Laspeyres showed that it is essentially identical with muscovite, and is originally derived from felspar. Occurrences and analyses of sericite were indicated by A. Pichler, A. E. Törnebohm, A. Rzehak, C. R. Credner, A. Wichmann, A. Hutchinson and W. C. Smith, C. W. von Gümbel, C. Schmidt, A. von Groddeck, B. Koto, A. F. Rogers, K. von Fritsch, etc. A greenish-white scaly mineral found by F. Sandberger as an alteration product of the oligoclase in the gneiss of Wildschapbachthal, Baden, was called *metasericite*.

F. von Kobell obtained a rounded, compact, light green mineral in the dolomite of Passecken, Salzburg, and he called it *onocsiné*—from *ὀνοκωαίς*, a swelling up—in allusion

to its behaviour before the blowpipe. G. Piolti described a sample from Variney, Italy. A. des Cloizeaux classed oncosine with halloysite, agalmatolite, etc.; J. D. Dana, with pinite; and G. Tschermak, with the compact muscovites. E. Cohen reported a compact muscovite from South Africa; and F. Sandberger obtained a variety he called *oncophyllite* as an alteration product of felspar. K. von Schafhäutl first designated a greenish mica containing calcium carbonate which he found in the chlorite schists of Zillerthal, *didrimite*, but later corrected the name to *didymite*—from δίδυμος, a twin. C. Hartmann showed that the calcium carbonate, *ohne Fehler*, is an admixed impurity of the mica. K. von Schafhäutl applied the term *amphilogite* to a mineral similar to didymite—from ἀμφίλογος, doubt—in allusion to his uncertainty as to whether the contained calcium carbonate was a mixture or an essential component. K. von Schafhäutl named chromiferous mica from Schwarzenstein, Zillerthal, *fuchsite*—after J. N. von Fuchs. Other chromiferous micas have been examined by A. C. Gill, A. Damour, H. Gorceix, G. T. Prior, etc. S. M. Losanitsch found an earthy aggregate of crystalline scales in the quartzite of Monte Avala, Belgrade. He called it *avalite*. It contains almost 15 per cent. chromic oxide. A. von Groddeck regarded it as a chromiferous mica related to sericite. A kind of *baryta-mica*—with 5 per cent. BaO—occurring near Kemmat, Tyrol, was named *ollacherite* by J. D. Dana—after J. Ollacher. It was described by G. A. Kenngott, C. F. Rammelsberg, and G. Tschermak.

K. von Schafhäutl [5] called the soda-mica which he found in the rock at Monte Campione, St. Gothard, **paragonite**—from παράγω, I mislead—in allusion to its resemblance to talc. G. A. Kenngott called it *pregrattite*—from Pregratten, Tyrol.

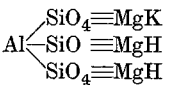
A compact variety of paragonite was identified in an antique ring or bracelet found in the neighbourhood of Turin. It was named *cossaite* after A. Cossa. It has been found in a number of other places. A kind of soda-potash-mica intermediate between muscovite and paragonite was named *euphyllite* by B. Silliman—from εὖ, well; φύλλον, a leaf. Specimens have been described and analyzed by J. L. Smith, G. J. Brush, F. R. Mallet, J. D. Dana, J. J. Crooke, etc. G. Tschermak seems to regard the mineral as a mixture of muscovite with paragonite and margarite.

I. S. R. I. Eques a Born [6] (1791) described what appeared to be a violet zeolite which occurred in white scales with a pearly lustre, and it was called *lilalite* in reference to its colour. A. Estner (1795) did not discuss it in connection with the micas. Soon afterwards, M. H. Klaproth analyzed the mineral, and named it **lepidolite**—from λεπίς, a scale—in allusion to the scaly structure. The same term was used by R. Kirwan. H. Credner showed that the mineral is related to mica. P. A. Wenz, and G. C. Gmelin showed that lithium is present; and G. C. Gmelin called it *Lithionglimmer—lithia mica*. W. Haidinger designated the lithium-iron mica from Zinnwald, **zinnwaldite,** and F. von Kobell included lepidolite and zinnwaldite as members of one class, *lithionite*.

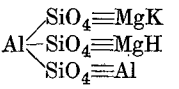
A hydrated lithia-mica occurring in minute scales and in slender six-sided prisms, sometimes bent, was described by G. J. Brush. It was named *cookeite* after J. P. Cooke, and obtained at Hebron and Paris, Maine. T. D. la Touche found it at Padar, Kashmir. It was analyzed by G. J. Brush, G. C. Hoffmann, and S. L. Penfield. F. W. Clarke represents the composition of cookeite by the formula $Al{\equiv}SiO_4-(AlOH)-SiO_4 \equiv\{Al(OH)_2\}HLi+H_2O$; and S. L. Penfield by $Li\{Al(OH)_2\}_3(SiO_3)_2$, *lithium trialuminium hexahydroxydimetasilicate*. The sp. gr. is 2·675; the hardness 2–3; and the double refraction positive. J. P. Cooke found a variety of lithia-mica in the granite of Cape Ann; and he called it *cryophillite*—from κρύος, ice; φύλλον, a leaf—in allusion to its easy fusibility and foliated structure. G. Tschermak classed it with zinnwaldite; P. Groth treated the two micas separately. J. Lorenzen applied the term *polylithionite* to a variety of zinnwaldite from Kangerdluarsuk, Greenland. The *Rubenglimmer* of A. Breithaupt was shown by G. Tschermak, P. Groth, and M. Bauer to be a kind of ferruginous zinnwaldite. F. Sandberger described a lithium-iron-mica from Erzgebirge, Fichtelgebirge, and Eibenstock, and named it *protolithionite* because he considered it to be the source of zinnwaldite. G. Tschermak, and P. Groth regarded it as a variety of zinnwaldite.

R. J. Haüy [7] allocated the crystals of mica first to the rhombic system, and later to the monoclinic system. Both J. B. Biot, and D. Brewster noticed that there are two kinds of mica—one being optically uniaxial, and the other biaxial. A. Breithaupt called the uniaxial micas *astrites*—from ἀστήρ, a star—and the biaxial micas *phengites*—from φέγγος, glitter. He designated the uniaxial biotite from

Vesuvius *astrites meroxenus*—from μέρος, a part; and ξένος, a guest—and the magnesia mica from Antwerp, New York, *phengites phlogopites*, or simply **phlogopite**—from φλόξ, flame; and ὤψ, appearance. J. F. L. Hausmann called the uniaxial mica **biotite** in honour of J. B. Biot. He also called the black uniaxial mica from Wermland, Sweden, **lepidomelane**—from λεπίς, a scale; and μέλας, black. Numerous analyses [8] of muscovite or potash-mica have been reported, and the inferences which have been drawn from these data as to the constitution of the muscovite have been indicated above. The idealized mineral can be regarded as **potassium dihydrotrialuminotriorthosilicate,** $KH_2Al_3(SiO_4)_3$. Analyses [9] have likewise been made of *paragonite* or soda-mica, and the idealized mineral can be regarded as **sodium dihydrotrialuminotriorthosilicate,** $NaH_2Al_3(SiO_4)_3$. The analyses [10] of lepidolite or lithia-mica show that it is more complex than muscovite or paragonite. As indicated above, the idealized mineral can be represented as a mixture of **potassium lithium hydrotrialuminotriorthosilicate,** $KLiHAl_3(SiO_4)_3$, and of **potassium lithium hexafluotetra-aluminotrimesosilicate,** $K_3Li_3(AlF_2)_3Al(Si_3O_8)_3$. The analyses [11] of zinnwaldite show that it is a complex lithium-iron-mica. It is considered to be a mixture of the trisilicate associated with lepidolite, and ferrous-biotite—*vide supra*. The analyses [12] of phlogopite or magnesia-mica, and of biotite or magnesium-iron-mica show that they are probably complex mixtures. Idealized biotite, on F. W. Clarke's system, is **potassium dimagnesium hydrodialuminotriorthosilicate,** and phlogopite, **potassium trimagnesium dihydroaluminotriorthosilicate,**



Phlogopite.



Biotite.

Similar remarks apply to lepidomelane. A. N. Winchell based a theory of the structure on the assumption that each crystal is an aggregate of a number of intergrown space-lattices which differ from each other in the sizes of their constituent atoms. P. Erculisse regards the micas as solid soln. of salts of two or three acids, $HAlSi_2O_6$, $H_3AlSiO_5$, and $H_2Al_2SiO_6$; and J. Jakob represented the magnesia-micas as complexes of

$$\left[Al(SiO_4)\right]^{Al_2}_{R'_3} \qquad \left[Al(SiO_5)_3\right]^{Al_2}_{R'_9} \qquad \left[Mg(SiO_4)_3\right]R''_5$$

Several varieties of biotite, phlogopite, and lepidomelane have been reported. J. D. Dana [13] called a black variety, almost free from magnesia, from Cape Ann, *annite*. J. P. Cooke showed that it is a lepidomelane. *Anomite*—*vide infra*—has been discussed by G. Tschermak, F. Becke, H. Rosenbusch, F. Malt, F. Eichstädt, etc. F. von Kobell applied the term *aspidolite*—from ἀσπίς, a shield—in allusion to the shape, to an olive-green mica from Zillerthal, Tyrol. P. Groth regarded it as an altered meroxene. A. Breithaupt applied the term *alurgite*—from ἀλουργός, purple—to a purple or red micaceous mineral occurring in the manganese ores of St. Marcel, Piedmont. It is also called *manganese-mica*. It may be the same as manganophyllite. W. T. Schaller considers that the *mariposite* of B. Silliman, and alurgite belong to a series of mixed crystals, and holds that the name mariposite should be abandoned. The minerals were analyzed by W. F. Hillebrand, and S. L. Penfield. Alurgite has the composition $6(H_2,K_2)O.2MgO.3Al_2O_3.12SiO_2$; and mariposite, $K_2O.4Al_2O_3.12SiO_2.3H_2O$. E. S. Larsen studied the optical properties of alurgite. A. Knop found the biotite from Schelingen, Kaiserstuhl, has over 7 per cent. of baryta, and he called it *baryto-biotite*. A. H. Dumont, and A. des Cloizeaux refer to a greenish-brown plicated mica occurring in the quartzite of Bastogne, Belgium, which was called *bastonite*. A. H. Chester described an alteration product of biotite from Franklin, New York, and called it *caswellite*. A. Renard considers it to be an altered phlogopite. J. P. Cooke refers to a mineral, *culsageeite*, from Culsagee, Franklin, North Carolina, which appears to be a hydrated alteration product of phlogopite. G. A. Koenig, and T. M. Chatard analyzed the mineral. F. W. Clarke also considers *dudleyite* from Dudleyville, Alabama, reported by F. A. Genth, to be a decomposition product of phlogopite; and also of margarite. He represents its composition by $CaH{\equiv}SiO_4{-}Al(OH){-}SiO_4 {\equiv}(AlOH)\{Al(OH)_2\}$. The chlorite-like mineral *euchlorite*—from εὖ, well; χλωρός, green—

obtained by C. U. Shepard from Chester, Mass., was shown by F. Pisani to be ordinary biotite. G. A. Kenngott described a *chloritähnliche Mineral* from Presburg, Hungary, which he named *eukamptite*—from $\epsilon\tilde{\upsilon}$, easy; $\kappa\acute{\alpha}\mu\psi\iota\varsigma$, bending. C. von Hauer, J. D. Dana, and G. Tschermak consider it to be a hydrated biotite. A. Leeds called a mica from East Nottingham, Penn., *hallite* after J. Hall. It was described by J. P. Cooke, and F. W. Clarke and E. A. Schneider. G. Tschermak regards it as an altered meroxene. M. F. Heddle called a highly ferruginous biotite from various Scottish localities *haughtonite*—after S. Haughton. R. T. Simmler, and G. A. Kenngott called a micaceous mineral from the Swiss Alps *helvetan*—from *Helvetia*, Switzerland. G. Tschermak regards it as an altered biotite. H. C. Lewis and A. Schrauf refer to hydrated biotites as *hydrobiotite*. F. W. Clarke represents hydrobiotite by the formula $Al{\equiv}SiO_4-Al{=}(SiO_4{\equiv}MgH)_2+3H_2O$. He likewise gives for *hydrophlogopite*, $Al{\equiv}(SiO_4{\equiv}MgH)_3+3H_2O$. G. J. Brush found a vermiculitic mica at Westchester, Penn., and named it *jefferisite*—after W. Jefferis. F. W. Clarke and E. A. Schneider, F. A. Genth, T. M. Chatard, and G. A. Koenig analyzed the mineral. G. Tschermak considers it to be a more or less altered phlogopite; and F. W. Clarke says that its composition is near that of hydrobiotite. F. W. Clarke and E. A. Schneider described a mineral which they called *kerrite* from Franklin, North Carolina; it approximates to hydrophlogopite. They called a vermiculitic mineral from Lenni, Delaware, *lennilite*—A. Schrauf regarded lennilite as a *parachlorite*; J. Eyreman analyzed lennilite. T. M. Chatard called a vermiculitic mineral from Franklin, North Carolina, *lucasite*—after H. S. Lucas. A manganiferous biotite from Pajaberg, Sweden, was named *manganophyllite* by L. J. Igelström—from $\phi\acute{\upsilon}\lambda\lambda o\nu$, a leaf. F. W. Clarke and E. A. Schneider called a vermiculitic mineral from Middletown, Delaware, *painterite*. F. A. Genth described a micaceous mineral from Unionville; he called it *pattersonite*. H. C. Lewis applied the term *philadelphite* to a vermiculitic mineral occurring near Philadelphia; and G. A. Koenig, *protovermiculite* to a micaceous mineral from Magnet Cove, Arkansas. F. W. Clarke and E. A. Schneider consider it to be a hydrated biotite. G. A. Koenig, and F. A. Genth have also discussed the mineral. F. W. Clarke says that the formula

$$\left.\begin{matrix}H_3{\equiv}SiO_4\\Al{\equiv}SiO_4\end{matrix}\right\rangle Al-SiO_4(MgOH)_3+3H_2O$$

fits the analysis of protovermiculite very well. A. Knop applied the term *pseudobiotite* to an altered biotite from Kaiserstuhl, Baden. A. Breithaupt described an olive-green or liver-brown mica from Brevik, Norway, and called it *pterolite*—from $\pi\tau\epsilon\rho\acute{o}\nu$, a feather—in allusion to the fan-shaped forms in which it occurs. A. Lacroix showed that the mineral is heterogeneous, and W. C. Brögger, that it is an alteration product of amphibole. F. von Kobell reported a micaceous mineral from Elba, which he named *pyrosclerite*—from $\pi\tilde{\upsilon}\rho$, fire; and $\sigma\kappa\lambda\eta\rho\acute{o}\varsigma$, hard (refractory). C. U. Shepard applied the term *rastolyte*—from $\acute{\rho}\tilde{\alpha}\sigma\tau o\varsigma$, very easy; $\lambda\acute{\upsilon}\omega$, dissolve—to a hydrated biotite from Monroe, N.Y. G. Tschermak regards it as a decomposed product of biotite. A. Breithaupt called a reddish uniaxial mica from Laacher See, *rubellan*. M. U. Hollrung considers it to be an altered biotite. H. C. Lewis described a biotite very rich in iron and poor in magnesia from Pike's Peak, Colorado, and called it *siderophyllite*—from $\sigma\acute{\iota}\delta\eta\rho o\varsigma$, iron; $\phi\acute{\upsilon}\lambda\lambda o\nu$, a leaf. N. S. Maskelyne and W. Flight described *vaalite* as a decomposition product of biotite at Du Toits Pan, South Africa. T. H. Webb applied the term *vermiculite*—*vermis*, a worm—to a micaceous mineral from Worcester, Mass., which was also described by T. Thomson, J. P. Cooke, A. Schrauf, and C. T. Jackson. F. W. Clarke and E. A. Schneider discussed the constitution of vermiculite. It is an altered phlogopite or biotite. E. E. Schmid applied the term *voigtite* to a kind of biotite from Ehrenberg near Ilmenau. G. Tschermak called it an altered biotite more or less hydrated. F. A. Genth described a micaceous mineral from North Carolina, as a decomposition product of biotite; and he named it *willcoxite*. F. W. Clarke regards this mineral as a kind of basic analogue of the mixed biotite—phlogopite type. H. Rosenbusch, and G. Lattermann have described a *titaniferous biotite* obtained from Katzenbuckel, and they called it *wodanite*—after the mythological Wodan.

Muscovite [14] is a pyrogenetic mineral which occurs as a primary constituent in deep-seated igneous rocks rich in alumina and potash, and poor in iron and magnesia. It is common in granites, syenites, and pegmatites. From its water-content muscovite was probably formed in these rocks under press. It does not occur as a primary constituent in recent lavas and their glassy magmas. Muscovite is common as an alteration product of many minerals—andalusite, cyanite, topaz, felspar, nephelite, spodumene, scapolite, etc. As a secondary mineral it is often called sericite. Paragonite is one of the rarer varieties; it occurs in crystalline schists, but does not occur as a pyrogenetic mineral. Lepidolite occurs in granite and pegmatite where it may form violet or lilac-coloured crystals

associated with muscovite. It sometimes occurs as a secondary product after muscovite, when it occurs as margins on the plates of muscovite. Cryophillite similarly occurs on plates of lepidolite. Phlogopite occurs chiefly in metamorphosed limestones and dolomites and serpentine; W. Cross found it in an igneous rock, and it appears in some igneous rocks rich in magnesia and poor in iron. Biotite occurs in many igneous rocks—granite, syenite, diorite, trachyte, andesite, basalt, etc. It is rare in rocks containing a small proportion of magnesia or potash. It separated early in the crystallization of rock magmas, and followed the metallic ores, apatite, and zircon. It is a common constituent of gneiss and schists, and is developed in some zones on contact metamorphism. Lepidomelane occurs in felspathic rocks low in magnesia and high in iron—*e.g.* some granites, syenites, etc. It is also found in metamorphic rocks.

The alleged syntheses of mica are not altogether free from objection, because the micaceous appearance of a product is not proof that a mica has been formed. Further, although some phlogopites are almost anhydrous; in general, water is an essential constituent of true micas, and therefore pyrogenetic processes which yield anhydrous products may furnish mica-like products, but not true micas. F. Fouqué and A. Michel-Lévy [15] heated powdered vitrefied granite with water under press. for a long time at red-heat, and obtained an artificial rock with scales of mica. C. Doelter reported the synthesis of scaly crystals of muscovite by heating andalusite with a soln. of potassium carbonate and fluoride at 250°. In nature, also, andalusite readily alters into muscovite. J. Lemberg did not get mica by heating andalusite with sodium silicate. S. J. Thugutt obtained potash-mica by heating to 196°–233° a mixture of potash nepheline and water—G. Friedel studied the reverse reaction. E. Baur and F. Becke made muscovite by heating in steel cylinders mixtures of silica, alumina, and a soln. of potassium hydroxide at 350°–450° for 12–16 hrs. C. Doelter also obtained micas by fusing various natural silicates—*e.g.* leucite—with potassium or sodium fluoride. When andalusite is fused with a mixture of potassium fluosilicate and aluminium fluoride, muscovite was formed; and when some lithium carbonate was present, a lithia-mica was produced. P. Hautefeuille and L. P. de St. Gilles found that biotite is formed by fusing a mixture of the constituents with potassium fluosilicate. K. Chrustschoff fused a mixture of the constituents of mica with the fluorides of sodium, aluminium, and magnesium, and also with potassium fluosilicate, and obtained crystals of biotite by slowly cooling the mass. J. Morozewicz mixed the constituents of rhyolite with one per cent. of tungstic oxide, and after prolonged fusion and slow cooling, obtained plates of biotite. C. Doelter obtained biotite (sodium) by fusing a mixture of hornblende, pyrope, augite, almandite, or grossularite with sodium and magnesium fluorides; by fusing leucite with magnesium fluoride; and by fusing a mixture corresponding with $KAlSiO_4$, $Mg_2SiO_4$, and sodium and magnesium fluorides. Glaucophane treated similarly also gave phlogopite. E. Mitscherlich, J. F. L. Hausmann, and G. Forchhammer found mica-plates in slags, crucible walls, and furnace masonry. J. H. L. Vogt found that some slags from a copper works contained phlogopite with the hydroxyl replaced by a monad radicle. G. V. Wilson observed the formation of mica by the action of molten glass on bricks.

Micas vary greatly in **colour.** Muscovite may be colourless, white, grey, yellow, brown, pale green to olive-green, violet and rarely rose-red. Some Bengal muscovites are dark red, and the colour deepens into ruby-red when in thick sheets. Amber-coloured muscovite is found only in the Nellore district, Madras. Paragonite may be tinged with yellow, grey, or green; lepidolite is white, grey, lilac, or rose-red; and zinnwaldite is coloured like lepidolite, but in addition it may be brown. Phlogopite is often brown or brownish-red, but it may be colourless, white, yellow, or green; biotite is usually green or brown to black, often pale yellow, and rarely white. Lepidomelane is black. Fuchsite, or chromiferous muscovite, is emerald-green. When in thin sections, the lighter-coloured micas may appear colourless. The colour is modified by inclusions. In some cases there are aggre-

gates of wavy lines of a lighter colour than the mica itself; or a sheaf of such lines may spread in one direction from an inclusion. The **lustre** of mica is often different on the cleavage planes from what it is on the other planes. The lustre may be vitreous, or pearly; and in some cases glassy, and dull.

J. B. Biot showed some **crystals** of biotite are uniaxial; but G. Rose found that the greenish-black crystals from Vesuvius belong to the monoclinic system, and this was verified by the measurements of W. Phillips. On the other hand, J. C. G. de Marignac said that the Vesuvian mica is hexagonal, while mica from Binnenthal is monoclinic. The hexagonal character of the crystals was accepted by G. A. Kenngott, N. von Kokscharoff, and F. Hessenberg. B. Silliman, however, remarked that the crystals of biotite are often biaxial, and that uniaxial biotite is anomalous. This was confirmed by W. P. Blake, H. W. Dove, H. de Sénarmont, J. Grailich, etc. F. Leydolt, F. von Kobell, F. Hessenberg, G. vom Rath, M. Bauer, H. Baumhauer, and others supported the view that some micas belong to the rhombic system. T. L. Walker said that probably all the micas except muscovite have hexagonal symmetry, and belong to the triclinic system. M. Royer also inferred from the growth of crystals of ammonium iodide on fresh cleavage faces of muscovite, that the mineral is of triclinic symmetry, and is built up of laminations twinned at 180° to one another so as to make the crystals pseudomonoclinic. A. des Cloizeaux proposed assigning all the micas to the rhombic system, but he later showed that some belong to the hexagonal system. C. Hintze showed that the effect of temp. on the axial angles of the crystals of mica does not support the view that the crystals are hexagonal, or rhombic. N. von Kokscharoff then proved that the facts best fit the assumption that all the micas are monoclinic. This conclusion was confirmed by the work of G. Tschermak, and M. Bauer, who showed that no mica has a higher symmetry than corresponds with this system. The biotites which have the optic axis in the plane of symmetry have been called *meroxenes*, and those with the optic axis perpendicular to the plane of symmetry have been called *anomites*—from ἄνομος, contrary to law. These two optical varieties of biotite have not been found to be associated with any particular composition or magma, for both varieties may be associated with the same rock.

Isolated crystals may be scattered through masses of rock, or groups of crystals may be present in curved, spherical, or radiating fan-like clusters. Mica occasionally occurs massive and cryptocrystalline. The size of the crystals varies from the cryptocrystalline forms to the crystals of muscovite from Nellore, India, which have been known to measure 10 ft. across their basal planes. Phlogopite crystals weighing 3000 lbs., and measuring 5 ft. by 9 ft., have been taken from Canadian mines. Such hypertropes are exceptional. Crystals from 6–12 ins. in diameter are common. Geometrically perfect crystals, free from distortion, etc., of a size suitable for accurate measurement, are comparatively scarce. The prism face *m* of the crystal, Fig. 131, is the (221)-face; *c* is the (110)-face; *b*, the (010)-face; and $\mu$, the (11$\bar{1}$)-face. The edge *cm* is sometimes replaced by facets of *o*, the (112)-face, and the angle $co=73° 1'$. Mica crystals—particularly those in the coarsely crystalline and softer rocks—may have been more or less distorted, crushed, and twisted. The so-called *step-crystals* are formed when the press. has acted across the crystals, so that the laminæ have slipped in layers of varying thickness to form a series of steps which have generally been cemented in their new position by thin films of calcite or other mineral. The crystals may also have been subjected to some kind of chemical action, as is evidenced by pitted or roughened surfaces. The crystals of the different micas are isomorphous with one another. As indicated above, it is possible that the crystals belong to the monoclinic system, but, owing to the basal angles measuring approximately 120°, there is in many cases a close approach to the hexagonal or rhombic symmetry. N. von Kokscharoff[16] gave for the

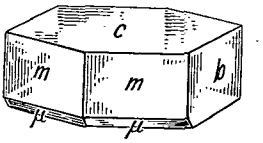



FIG. 131.—Muscovite.

axial ratios of muscovite, $a:b:c=0{\cdot}5774:1:1{\cdot}6456$; G. Tschermak gave $0{\cdot}5777:1:2{\cdot}1932$, and $\beta=95°\ 2'$; and A. des Cloizeaux, $0{\cdot}5777:1:1{\cdot}1583$, and $\beta=109°\ 25'$. N. von Kokscharoff gave for biotite $0{\cdot}57736:1:1{\cdot}64518$ and $\beta=90°$. The isomorphism of the micas is illustrated by the intergrowths of light-coloured muscovite with dark-coloured biotite, so that the latter encloses the former, and the cleavage of the one continues into that of the other. The symmetry planes often lie turned at an angle of 60° to one another. Lepidolite and muscovite behave similarly; and zonal intergrowths of biotite and pennine (a chloritic mineral) have been found. The frequent intergrowth of biotite and muscovite has suggested that the latter is an alteration product of the former. J. E. Pogue described the parallel growth of biotite and mica, and H. Baumhauer, of muscovite and lepidolite. Similar effects are produced simply by a crystal of dark-coloured muscovite enclosing a lighter crystal of muscovite; and in some cases the two crystals have a different shape. In more complex cases, the successive stages in the growth of the crystal conform more approximately to the symmetry of the central individual, for the growth of the crystal has proceeded nearly equally in different directions. This has produced a banded structure, forming the so-called *border mica*. These phenomena of *multiple crystallization* are probably produced by changes of press. and of the composition of the cooling magma, which have interrupted the processes of crystallization. When the normal conditions have been re-established, crystallization has begun anew, imparting a kind of *zonal structure* to the mica. R. Tronquoy discussed the zonal structure of mica. F. M. Jäger, and F. Rinne have studied the **X-radiogram** of muscovite, and biotite. The **twinning** of mica is shown in polarized light, when apparently well-formed crystals of mica are obviously composed of two or more individuals. The crystal forms, and the twinning of crystals of muscovite, lepidolite, and zinnwaldite were studied by G. Tschermak; those of muscovite by H. Baumhauer, P. I. Grishchinsky, and A. Johnsen; those of lepidolite, by W. T. Schaller; those of biotite and phlogopite, by N. von Kokscharoff, A. des Cloizeaux, G. Tschermak, G. vom Rath, H. Laspeyres, and S. Uroschewitsch. There is an irregular junction line, and the optic axial planes of the twins are inclined to one another at angles of about 60°. The common plane of twinning is in the prismatic zone (110) perpendicular to the basal plane *c* and parallel to the edge *cm*. This twinning plane may form the intergrowth face with both individuals in adjacent positions either with the front right prism edge or with the front left prism edge—Fig. 132. Twinning, however, does not usually proceed from twin faces—

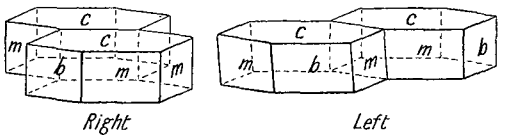



FIG. 132.—Juxtaposition Twins on the Front Prism Face—Right and Left.

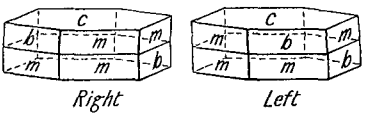



FIG. 133.—Superposition Twins on the Basal Plane—Right and Left.

*i.e.* horizontally, but rather from the basal plane, so that the two individuals are superimposed and in contact along a plane almost parallel to (110). Right and left twins then appear as in Fig. 133. The re-entrant angles $mm=162°\ 49'$ and $mb=179°\ 19'$. This twinning is common with zinnwaldite and is often evidenced by the matte appearance of the *m*-faces. Owing to the twinning, large crystals of mica appear as rude tapering prisms with irregular sides. Usually the crystals are tabular owing to the preponderance of the basal plane *c*; sometimes they have rounded edges; and rarely, the crystals are short and columnar in the direction of the vertical axes. In some cases, a number of small individuals of various shapes and sizes have intergrown symmetrically so as to form one large crystal. In some cases the large crystals are hollow as if the smaller crystals have grown about some mineral which has been subsequently removed. The **corrosion figures** have been studied by T. L. Walker, H. Baumhauer, etc.

The **cleavage** of mica parallel to the (001)-face or base of the prism is highly developed, and it causes the crystals to cleave readily into thin laminæ. There seems no other limit to the possible thinness of the plates than the mechanical possibility of splitting them. Plates $\frac{1}{1000}$th in. thick are easily obtained, and C. W. Jefferson and A. H. Dyer obtained plates 0·00003 in. thick, but of no great size. This thickness is about one-thirtieth of that of ordinary tissue paper. These sections of mica parallel to the (001)-face do not usually show any cleavage lines or fracture cracks; but in all other positions, numerous sharply defined parallel cleavage cracks are noticeable in the direction of the trace of the (001)-face. Other lines of parting may be developed in mica by percussion with a sharp-pointed instrument, or by press. **Pressure figures** can be developed by natural processes—say, by the crystallization of some foreign mineral within the mica crystals, or by an external press.—or they may be produced by pressing normally to a cleavage plate with a dull pointed instrument. The planes of fracture with a naturally developed press. figure divide the mica crystal into trigonal pieces. If the press. has been equally distributed, the cleavage plates may show a close network of intercrossing fine lines; and plates are said to be *ruled mica*. When the press. lines form in two directions the so-called *feather mica* may be produced. If the press. has been sufficient, these cleavage plates may split along such lines, forming small fragments of regular shape. This splitting spoils the commercial value of the mica. In some cases, the press. lines are developed in one direction so that the cleavage plates can be split into narrow strips commercially called *ribbon mica*. The fragments possess pseudo-crystalline faces, some of which are inclined about 67° to the basal cleavage plane. These faces are called **gliding planes.** The gliding planes and cleavage planes are quite distinct and do not coincide, although the twinning planes of mica crystals coincide with the gliding planes. A. Johnsen, and W. Wetzel studied the press. figures of mica. The **percussion figure,** developed by striking a cleavage plate of mica with a sharp, pointed instrument, may appear as a six-rayed star, or, if imperfectly developed, as a three-rayed star. The percussion figures were studied by H. Reusch, D. Rotman, M. Bauer, T. H. Holland, W. Wetzel, G. Tschermak, and A. Johnsen. The most prominent crack in the three-rayed star is approximately parallel to the (010)-face, and the other two, in biotite, are parallel to the $(\bar{1}10)$-face. The angle $\kappa$ of intersection of the rays is approximately 60°. T. L. Walker found that the inclination of the one crack to the principal one is 52° 53′–56° for muscovite; 59° for lepidolite; 60° for biotite; and 61°–63° 28′ for phlogopite. The principal crack in the percussion figure, being parallel to the (010)-face, serves to orient the mica when the outward form of the crystal is wanting. As shown by J. Grailich, and H. Reusch, one of the rays of the percussion figure is perpendicular or parallel to the optic axial plane, and it must therefore be the trace of the plane of symmetry. G. Tschermak called the micas in which the optic axial plane is perpendicular to the plane of symmetry, *micas of the first class*, or *macrodiagonal micas—e.g.* the alkali micas, and the rare varieties of biotite called *anomite*. Those micas in which the axial plane is parallel to the (010)-face were called *micas of the second class* or *brachydiagonal micas—e.g.* the ferro-magnesian micas, phlogopite, and zinnwaldite. T. H. Holland investigated the percussion figures and the natural press. figures due to the inclusion of crystals of a foreign substance. The angles of intersection of the rays approximate 30°, and one of the rays occupies the correct position of the principal ray of the artificially produced percussion figure. The natural figure, unlike the artificial, is formed by the intersection of rays at 60°. T. H. Holland also found that at 300°, the angle $\kappa$ of the rays of the percussion figures is always larger than the corresponding angle on mica at ordinary temp. Thus, the angle $\kappa$ at

| | | | | |
|---|---|---|---|---|
| Ordinary temp. . . . | 53° | 53° 30′ | 54° | 55° |
| 300° . . . . . | 56° | 56° | 57° | 57° 30′ |

This shows that muscovite possesses a higher degree of crystalline symmetry at

higher temp., and that the crystal, at the temp. at which natural figures are produced, might possess hexagonal rather than monoclinic symmetry. According to C. Hintze, the measurements of a Vesuvian biotite made the mineral appear hexagonal or rhombic, but in these systems the optic axis remains perpendicular to the base at all temp., whereas a change of over 30′ was observed at 178°, he inferred that the mineral was monoclinic.

When cleavage plates of some varieties of mica are examined by reflected or transmitted light, in certain directions, peculiar star-like light-rays appear. The phenomenon is called **asterism,** and it is also exhibited by other minerals—*e.g.* the sapphire, quartz, chrysotile, satin spar, etc. G. H. Volger suggested that in the case of the sapphire the asterism is produced by repeated lamellary twinning, and G. Tschermak, by minute interstices arranged parallel to the sides of the hexagonal prism. With mica the asterism may be produced by inclusions between the laminæ of numerous minute crystals whose axes are oriented at an angle approximately 60° to one another, and which were supposed by G. Rose to be mica, but were shown by G. Tschermak to be rutile. H. S. de Schmid found asterism was also produced in muscovite by regularly arranged hair-like tourmaline needles; he also said that the effect may be produced by very fine striations—*e.g.* polysynthetic twinning; minute fractures by a distortion of the crystals; inferior cohesion of laminæ; interstices; or fibres which go to compose the mineral itself. In some cases there is double asterism.

Most varieties of mica are biaxial with a measurable angle between the optic axes, but in some biotites the angle is so small that the crystals appear uniaxial. The **optic axial angle,** $2E$, of muscovite is large and varies greatly usually ranging from 50°–70°; that of phlogopite and biotite is small, ranging from 10°–17°. J. Grailich found the optic axial angle of muscovite increased as the sp. gr. increased. Thus:

| Sp. gr. | 2·602 | 2·714 | 2·755 | 2·782 | 2·790 | 2·796 |
|---|---|---|---|---|---|---|
| $2E$ | 65·2° | 69·7° | 70·5° | 71·2° | 72·3° | 72·0 |

The optic axial angle of muscovite was found by G. Tschermak to vary from 55°–69° 12′ with red glass; from 60° 12′–68° 54′ with Na-light; from 60° 6′–68° 30′ for green glass; and 67° 54′ for blue glass. R. Scharizer gave for the red ray $2E$=74° 50′, and for the Na-ray $2E$=73° 52′; B. Silliman found for different varieties of muscovite, $2E$=56° 20′–76°; H. de Sénarmont, $2E$=57°–73°; J. Grailich, $2E$=50° 12′–76° 12′; and M. Bauer, $2E$=61°–74° 36′. For paragonite, G. Tschermak gave $2E$=70°. For lepidolite, R. Scharizer gave $2E$=57° 13′–83° 16′ for red glass, and 57° 10′–84° for Na-light; M. Bauer gave $2E$=32°–36°, and 59° 24′; G. Tschermak, $2E$=77° 10′ for red light, 76° 51′ for Na-light, and 76° 34′ for green light; G. Rose, $2E$=51°–67°; and J. Grailich, 74°–76° 40′. For zinnwaldite, G. Tschermak gave $2E$=50° 36′ for red light, 50° 25′ for Na-light, and 50° 5′ for Tl-light. J. Lorenzen gave 67° 13′ for Li-light, 67° 19′ for Na-light, and 67° 51′ for Tl-light. For biotite G. Tschermak gave $2E$ from 6° 16′–12° 22′ for red glass, 6° 24′–12° 48′ for Na-light, 9° 24′–13° 18′ for Tl-light, and 8° 18′ for green glass. For phlogopite, G. Tschermak gave $2E$=14°–16° 17′; and for anomite, $2E$=12° 55′ for red glass, 12° 40′ for Na-light, and 12° 35′ for green glass. B. Silliman gave $2E$=7°–18°; J. Grailich, 0°–2° 40′; A. Lacroix, $2E$=15°–35°. The optic axial angle of phlogopite appears to increase as the proportion of contained iron increases. F. Kohlrausch gave for muscovite, $2V$=43° 48·8′ for Na-light; M. Bauer gave 40° 21°. A. des Cloizeaux measured the effect of temp. on the optic axial angle, and found for different samples $2E$=70° 4′ at 6·6°, and 68° 56′ at 155·8°; 69° 44′ at 6·6°, and 68° 5′ at 158° 8′; and

| | 6·6° | 71·5° | 105·5° | 125° | 146·5° | 170·8° |
|---|---|---|---|---|---|---|
| $2E$ | 76° 50′ | 76° 16′ | 75° 58′ | 75° 32′ | 75° 30′ | 75° 10′ |

showing that the optic axial angle becomes smaller with rise of temp. He also

found with red light for biotite at 17°, $2E=12°\,3'$, and 11° 5′ at 171°, 14° 3′ at 21·5°, and 13° 28′ at 181°; etc. T. L. Walker, H. C. Lewis, and K. Toborffy measured the optic axial angles of a number of micas. H. Baumhauer called the variety of lepidolite with a large optical angle *macrolepidolite*, and the variety with a small angle *microlepidolite*. A. Johnsen discussed the axial angles of meroxene. The **corrosion figures** of muscovite with hydrofluoric acid were studied by T. H. Holland, Z. Toborffy, H. Baumhauer, and F. J. Wiik; those of lepidolite, by F. J. Wiik; those of zinnwaldite, and biotite by H. Baumhauer, and F. J. Wiik. The crystallization of sodium chloride in definite positions on mica was studied by G. Kalb.

The **specific gravities** of most of the samples whose analyses have been indicated were also measured. In general, the sp. gr. of muscovite ranges from 2·76–3·00; paragonite, 2·8–2·9; lepidolite, 2·8–2·9; zinnwaldite, 2·82–3·20; phlogopite, 2·78–2·85; biotite, 2·7–3·1; and lepidomelane, 3·0–3·2. Micas are soft minerals; the **hardness** usually ranges from that of gypsum to that of calcite; they can be readily scratched by iron or steel, and, in some cases, by the finger-nail. The granitic micas are usually harder. The hardness ranges from 2–2½ with muscovite; 2½–4 with lepidolite; 2½–3 with paragonite, zinnwaldite, phlogopite, and biotite; and 3 with lepidomelane. A. Rosiwal made some observations on this subject. L. A. Coromilas found the maximum **elastic modulus** at 0° to be 22,133 kgrms. per sq. mm.; and the minimum value at 45° to be 15,543 kgrms. per sq. mm. L. H. Adams and co-workers found the **compressibility**, $\beta$, of phlogopite mica to be $2{\cdot}34+10^{-6}$ at 0 megabar press., $2{\cdot}27+10^{-6}$ at 2000 megabars, and $1{\cdot}99\times10^{-6}$ at 10,000 megabars; or $\beta=0{\cdot}0_5270-0{\cdot}0_{10}348(p-p_0)$. Although mica is such a soft mineral, the basal cleavage into smooth tough laminæ makes the grinding of mica to powder a difficult operation. The subject has been discussed by H. J. Hannover, J. Keeth, and A. Johnsen. E. Griffiths and G. W. C. Kaye gave 0·0010–0·0014 for the **thermal conductivity** of mica at 150° and under a press. of 120 lbs. per sq. in. H. C. Michell used scrap mica as a covering for steam pipes, boilers, etc. The effect is not due so much to the non-conductivity of the mica itself as to the numerous air-spaces in the lagging. F. Cirkel describes tests which show that with a bare steam-pipe, 75 per cent. of the loss of steam by condensation in the pipes can be saved by lagging the surfaces of the pipes, and 90 per cent. was saved by using a mica insulation; and also tests on the mica insulation of boilers which confirm these results. There is a saving of about 90 per cent. of the heat radiated from a bare boiler, and the efficiency is nearly twice as great as insulation by magnesia blocks. S. L. Brown measured the variation of the diathermancy of mica with temp.

P. Braesco found the expansion of mica to be regular up to 900°. J. Joly found the **specific heat** of muscovite to be 0·2049 between 12·4° and 100°; lepidolite, 0·2097; and biotite, 0·2057. According to C. Doelter, when muscovite is fused, it breaks up into leucite glass and a substance resembling nephelite; lepidolite behaves in a similar manner. J. Morozewicz said that he found sillimanite and corundum among the products of the fusion of mica. The change may be symbolized: $KH_2Al_3Si_3O_{12}=KAlSi_2O_6+Al_2SiO_5H_2O$. According to A. Brun, the dehydration of powdered mica commences in a vacuum at 98° and proceeds regularly; at 360°, one-quarter of the water is lost in the case of white micas, and four-ninths with black micas. Plates of mica were completely dehydrated when heated for half an hour at 830°, or for ten to twelve days at 510°–540°. The material suffered no change in its optical properties, but, owing to the liberation of gas between the lamellæ, the plates became opaque (this, however, could be avoided by heating in a vacuum under certain conditions). The quantity of hydrogen liberated depended on the rate of heating, less being obtained when the material is heated very slowly. The water was assumed to exist in the micas in a state of solid soln. According to C. Doelter, biotite does not yield leucite when fused, but breaks up into olivine and spinel. H. Bäckström obtained olivine, leucite, a little spinel, and a glass among the products obtained by fusing biotite. There is therefore no **melting**

**point** in the strict sense of the term. C. Doelter found samples of biotite which were molten between 1145° and 1240°; meroxene was molten between 1355° and 1370°; anomite, 1325°–1395°; lepidomelane, 1150°–1170°; and phlogopite, 1270°–1330°. G. Tammann and C. F. Grevemeyer found that mica forms a sparingly soluble potassium aluminosilicate when heated to 1000°. The fluxing of mica with clays and related materials has been examined by R. Rieke, R. T. Stull, and H. Ries. The **softening temperatures** of mixtures of muscovite and orthoclase were determined by A. S. Watts; and of mixtures of china clay and muscovite by R. Rieke.

The **index of refraction** varies considerably for each kind of mica. That of muscovite was found by M. Bauer, C. Viola, B. Hecht, R. Scharizer, etc. F. Kohlrausch gave for Na-light, $\alpha$=1·5609, $\beta$=1·5941, and $\gamma$=1·5997; A. Matthiessen, $\alpha$=1·5692, $\beta$=1·6049, and $\gamma$=1·6117; and C. Pulfrich, $\alpha$=1·5601, $\beta$=1·5936, and $\gamma$=1·5997. The last-named found for Li-light, $\alpha$=1·5666, $\beta$=1·5899, and $\gamma$=1·5943; and for Tl-light, $\alpha$=1·5635, $\beta$=1·5967, and $\gamma$=1·6005. R. Scharizer gave for lepidolite, $\beta$=1·5975 and $\gamma$=1·6047; but B. Hecht doubted if these values were accurate. A. Michel-Lévy and A. Lacroix gave for phlogopite, $\alpha$=1·562, $\beta$=1·606. H. Rosenbusch and E. A. Wülfing found the index of refraction of biotite increased with the iron content. G. Linck found $\alpha$=1·504, $\beta$=1·589, and $\gamma$=1·589. F. Kohlrausch, and K. Zimanyi obtained values for $\alpha$ ranging from 1·5412–1·586, and for $\gamma$, from 1·5745–1·6032. The **birefringence** is strong for all kinds of mica; that of muscovite is $\gamma-\alpha$=0·0392, $\gamma-\beta$=0·0061, and $\beta-\alpha$=0·0338; that of lepidolite is large and negative; and that of biotite $\gamma-\beta$ is almost zero; and $\gamma-\alpha$, increasing with the percentage of iron, attains to 0·06. Mica in general is optically negative. The optical properties of mica were also described by S. Tsuboi, F. W. Clark and W. F. Hunt, H. Backlund, A. Laitakari, etc. J. Chaudier found the electric birefringence of mica particles suspended in water to be 0·40, and the optical birefringence, 0·04. P. N. Ghosh investigated the laminar diffraction of mica; and C. F. Meyer and D. W. Bronk, the ultra-red spectrum.

The **pleochroism** of biotite is very strong especially with the deeper coloured varieties. This has been studied by K. Toborffy,[17] G. Tschermak, G. Flink, and A. Lacroix. Muscovite is not generally pleochroic, although M. Bauer found some varieties are pleochroic, and F. Cornu observed the phenomenon with the chromiferous muscovite, fuchsite. Brown micas, cordierite, and some other minerals have certain small circular spots when viewed in section. The spots are called **pleochroic haloes.** These haloes are invariably associated with a minute, centrally-placed crystal of zircon or apatite. The medium in which the halo occurs with biotite is pleochroic, but the pleochroic properties are intensified in the halo. The halo disappears when the mineral is heated, hence it was once thought to be produced by organic matter; but the haloes are really spherical, and it is doubtful if the diffusion of colouring matter would proceed at an equal rate across and along the cleavage of a mineral like mica. J. Joly showed that there is an exact correspondence between the radius of the halo and the distance which the $\alpha$-particles of radium would penetrate before the ionizing properties would disappear. The maximum diameter of the haloes is 0·05 mm.; the average 0·04 mm. Hence, J. Joly infers that the halo is produced by the radioactivity of a central radioactive substance. This is confirmed by O. Mügge, and G. Hövermann. M. Weber examined the effect of the pleochroic haloes of mica and cordierite on zircon.

W. W. Coblentz found that the **ultra-red transmission spectrum** of the micas showed no deep wide absorption bands at 3$\mu$, characteristic of hydroxyl groups. Muscovite gave a deep narrow band at 2·85$\mu$, and smaller bands at 1·9, 3·6, 5·6, 5·9, 6·3, and 7·1$\mu$; while biotite has small bands at 2·8, 5·9, 6·2, and 6·7$\mu$, and indications of bands at 5·6 and 7–8$\mu$. It has also one in the visible spectrum. Both micas have an opaque region from 9–11$\mu$, a transparent region at 12$\mu$, and again complete opacity. The spectrum energy curves were studied by E. F. Nichols and W. W. Coblentz, and G. W. Stewart. Metallic reflection bands were found

by H. Rubens and E. F. Nichols at 8·32, 9·38, 18·40, and 21·25$\mu$, so that the bands located by reflection and transmission do not coincide. W. W. Coblentz found reflection bands in the **ultra-red reflection spectrum** of muscovite at 9·2, 9·7, and 10·2$\mu$. H. Rosenthal also failed to observe a reflection band at 8·32. W. W. Coblentz found maxima with biotite at 9·3, 9·6, and 9·85$\mu$. The reflecting power of the micas is comparable with that of the silicates. The positions of the maxima are variable, presumably owing to variations in the composition of the mineral. P. Ites, and J. Königsberger studied the relation between the absorption of light and the colour of biotite. L. C. Martin, and S. L. Brown measured the transparency of biotite for the ultra-red rays. The **flame spectra** of micas were studied by W. Vernadsky and B. A. Lindener; and the grating spectrum by B. Davis and H. M. Terrill.

W. Vernadsky found muscovite and biotite to exhibit **triboluminescence.** C. Doelter found **radium radiations** have no action on muscovite, and they do not make biotite luminesce. C. Doelter also said that muscovite and biotite are not very transparent to **X-rays,** but thin layers 0·5 mm. thick are transparent; Singalese biotite was almost opaque; and a very ferruginous black biotite was opaque. The ratio of the transparency of phlogopite to that of tinfoil was as 1 : 20 when the ratio with the diamond is as 1 : 300 or as 1 : 425. Biotite is not radioactive when free from radioactive impurities.

J. Curie found the **electrical conductivity** increased with the temp. C. Doelter obtained a very small value for the conductivity at 1100°, but it increased in value beyond this temp. The conductivity at 1200° is small but measurable. Hence, mica is a good insulator at temp. below 1100°. W. H. Schultze found that sheets of mica split along the plane of cleavage resemble glass in improving in conductivity as the temp. rises, and also in a maximum conductivity being obtained at about 300°, after which further increase in the temp. causes a diminution in conductivity. Mica is a better insulator than glass. Measurements of the electrical conductivity were made by H. H. Poole, and E. Branly. A. L. Williams and J. C. McLennan, and K. R. Ramanathan measured the resistance of fused mixtures of mica and copper or iron. E. Wilson studied the magnetic susceptibility. E. and W. H. Wilson and T. Mitchell found the sp. resistance varied from $0{\cdot}44–133{\cdot}0\times10^{-12}$ ohms per cm. cube. The electrical resistance of mica has been studied by O. N. Rood. A. Klautzsch found the sp. resistance of a number of samples to vary from 700–1200 megohms—one sample had a sp. resistance of 380 megohms. The breakdown voltage of plates from 0·12–0·25 mm. in thickness varied from 10,000–18,000 volts.

E. Bouty found the **dielectric constant** to be 7·98–8·43; E. Mattenklodt, 7·1–7·7; H. Starke, 5·8–6·62; and A. Elsass, 5·66–5·97. The different micas have different values, particularly those with a varying proportion of water. E. Mattenklodt found the value to be independent of the field strength, and of the temp.—at least the temp. coeff. is less than 0·0000033. J. Curie obtained 8·0 for the dielectric constant of muscovite perpendicular to a cleavage surface. E. and W. H. Wilson and T. Mitchell measured the dielectric strength of different micas in terms of the difference of potential required to puncture a given specimen when surrounded by air; this constant is a function of the shape, relative size, distance apart, and nature of the electrodes. Some results for (1) Bengal ruby mica, (2) Canadian amber mica, and (3) Madras green spotted mica of different thicknesses, are shown in Fig. 134. They found that the specific inductive capacity of some samples of mica varied

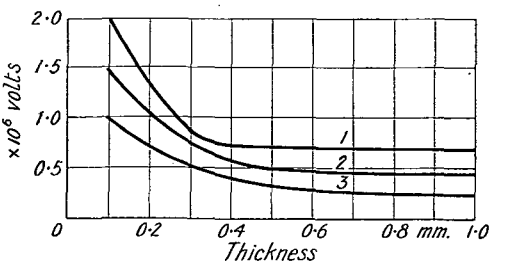



FIG. 134.—Dielectric Strength of Mica of Varying Thickness.

from 2·5–5·9 for thickness ranging from 1·22–5·0 mm. This subject has been further studied by J. Härdén, E. Schott, W. S. Flight, J. R. Weeks, H. H. Poole, H. J. MacLeod, D. W. Dye and L. W. Hartshorn, F. Grünewald, and C. W. Jefferson and A. H. Dyer. The deleterious effects of oil on the insulating properties of mica have been discussed by F. Droui. T. O. Maloney found that a piece of mica which withstood 16,000 volts alternating current resisted but 9000 volts after the surface had been lightly coated with paraffin oil; under similar conditions, the breakdown voltage of another sample changed from 8000 to 4000 volts. Mica is accordingly used for interposing between the segments of the commutators of dynamos. The amber-mica of Canada, and the lepidolite of India are used for this purpose; muscovite, with its higher dielectric strength, is not considered so good for the purpose on account of its greater hardness.

A. Brun [18] found that mica yields carbon dioxide, hydrocarbons, hydrogen, and nitrogen when heated—*vide supra*. I. Langmuir discussed the adsoprtion of gases on the surface of mica. According to A. Kenngott, moistened and powdered muscovite or biotite gives an alkaline reaction with litmus; after calcination, the reaction is feebler. With many biotites the reaction is very pronounced. E. W. Hoffmann made some faulty observations on the action of **water** on muscovite and biotite. A. Johnstone showed that the micas are hydrated by exposure to the action of pure carbonated waters for a year; muscovite appeared to be insoluble. T. Biéler-Chatelan found that 0·48 per cent. of potash was dissolved from muscovite by distilled water; 1·05 per cent. by peat water; 1·02 per cent. by a soln. of **calcium sulphate**; 1·55 per cent. by a soln. of **ammonium sulphate**; 1·76 per cent. by a soln. of **calcium hydroxide**; 2·24 per cent. by a soln. of **calcium monophosphate**; and 1·85 per cent. by a one per cent. soln. of **citric acid.** He also showed that the roots of some plants can assimilate the potassium from white mica in soils. E. C. Sullivan observed basic exchange occurs when muscovite and biotite are treated with a soln. of **cupric sulphate.** A. Johnstone found that biotite lost magnesia and iron when treated with **carbonic acid.** F. W. Clarke, and G. Steiger observed distinct evidence of dissolution when micas are treated with an aq. soln. of carbon dioxide; and C. Matignon and G. Marchal examined the corrosive action of water on mica in the presence of carbon dioxide under 10 atm. press. for 3 years. E. Reymond studied the action of **chlorine** and of **hydrogen chloride** on biotite and lepidolite. T. Biéler-Chatelan found that cold conc. **hydrochloric acid** contained 2·90 per cent. of potash after it had been allowed to stand in contact with muscovite. M. U. Hollrung, H. Lotz, and A. Breithaupt studied the action of hydrochloric acid on various types of biotite. F. Malt found that after a day's digestion with hydrochloric acid, doubly refracting plates of silicic acid were formed; and with 20 per cent. **hydrofluoric acid,** all the silica was removed and tabular crystals containing aluminium, ferric, and magnesium fluorides remained. W. B. Schmidt found that **sulphurous acid** dissolved some magnesia mica. J. W. Mellor found that an hour's treatment of fine- and coarse-grained mica of the respective average grain-size 0·087 and 0·040 mm., with **sulphuric acid** decomposed respectively 54·94 and 55·56 per cent. of muscovite; 67·94 and 70·02 per cent. of lepidolite; 71·07 and 92·50 per cent. of biotite; and 88·00 and 93·93 per cent. of phlogopite. H. Lotz studied the effect of air charged with **sulphur dioxide** on biotite and muscovite. C. and G. Friedel found that by treatment with aq. reagents—**potassium silicate, sodium hydroxide, sodium chloride,** and **sodium sulphate**—muscovite can be transformed into nephelite, sodalite, leucite, orthoclase, or anorthite. F. W. Clarke and G. Steiger studied the action of **ammonium chloride** on the magnesia micas.

Muscovite under ordinary conditions is not readily affected by atm. influences; witness, the felspar of granite may be completely kaolinized while the mica retains its pristine lustre. On the other hand, biotite, and phlogopite are readily transformed, the alkaline metals are replaced by hydrogen, and the products are hydrated, thus forming more or less indefinite substances called vermiculites and chlorites.

The weathering of biotite and phlogopite has been studied by G. Tschermak, J. D. Dana, C. F. Rammelsberg, G. A. Kenngott, E. Zschimmer, K. D. Glinka, F. Rinne, O. Dreibrodt, H. Rosenbusch, J. R. Blum, W. Haidinger, C. R. van Hise, G. W. Leighton, etc.

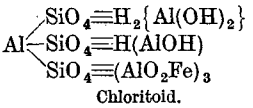
Crystals of a mineral from the Pini mine, Aue, Schneeberg, were described by C. A. S. Hofmann,[19] and M. H. Klaproth. It was named *pinite* by D. L. G. Karsten. The alteration products of a number of aluminosilicates correspond more or less closely in composition to muscovite, and they have been grouped as *pinites*. The pinites are considered to be a massive compact muscovite mixed with more or less clay, etc. Massive amorphous pinite with a compact texture is a part of the so-called *agalmatolite*—from *ἄγαλμα*, an image—from China. This name was applied by M. H. Klaproth ; [20] and C. A. G. Napione called it *pagodite*—from *pagoda*. The Chinese carve the soft stone into miniature pagodas, images, etc. Part of the Chinese agalmatolite is a compact pyrophyllite, and part is a steatite. L. J. Igelström found at Langban, Sweden, pseudomorphs of a pinite after iolite ; he named the mineral *cataspilite*—from *καταστιλάζειν*, to spot or stain—in allusion to its mode of occurrence. C. U. Shepard found a mineral which he named *dyssyntribite*—from *δύς*, bad ; and *συντρίβω*, to pulverize—at Diana, N.Y. T. S. Hunt made some observations on the minerals. J. L. Smith and G. J. Brush analyzed the mineral. Dyssyntribite resembled the mineral *gieseckite*, brought by Giesecke from Akulliardsuk and Kangerluarsuk, Greenland ; and named by T. Allan, who examined the crystals. It occurs associated with felspar. Observations on gieseckite were made by F. Stromeyer, L. W. Gilbert, C. C. von Leonhard, H. Rosenbusch, G. J. Brush, A. Breithaupt, F. Mohs, E. F. Glocker, C. H. Pfaff, J. R. Blum, C. G. C. Bischof, A. des Cloizeaux, W. Phillips, etc. A. E. Nordenskjöld reported a related mineral, which he named *gigantolite*, from the size of the crystals. It occurred in the gneissoid granite of Tammela, Finland. It was discussed by W. Haidinger, M. F. Heddle, A. Wichmann, F. J. Wiik, F. Zirkel, J. C. G. de Marignac, A. E. Nordenskjöld, J. R. Blum, and A. Lacroix. Gigantolite is derived from cordierite and resembles the mineral *iberite* obtained by L. F. Svanberg from Montalvan, Spain. Observations on the mineral were made by J. R. Blum, W. Haidinger, F. Zirkel, A. Wichmann, A. Lacroix, M. F. Heddle, F. J. Wiik, etc. A. F. Thoreld described a mineral which was found in the talcose schist at Kimsamo, Finland. It was called *gongylite*—from *γογγύλος*, round—and it is a kind of pinite. A. E. Nordenskjöld made some observations on this mineral. H. Laspeyres described a pinite-like substance in the felspar at Halle a. d. Saale ; he called it *hydrophylite*—from *ὑγρός*, moist ; *φίλος*, friend. F. Sandberger made some observations on a sample from Baden. F. A. Genth's *kerrite*—named after H. L. Kerr—is a decomposition product of chlorite from Macon, North Carolina. T. Thomson reported a pseudomorph after spodumene at Killeny Bay, Ireland. He called it *killenite*. It has been described by R. P. Greg and W. G. Lettsom, A. Julien, W. Galbraith, C. F. Rammelsberg, C. Dewey, etc. J. C. G. de Marignac obtained a pinite-like substance in the porphyritic felspathic rock at Mt. Viesena, Fleimsthel ; he called it *liebenerite*—after L. Liebener. Observations were made by W. Haidinger, J. Oellacher, G. A. Kenngott, C. von Hauer, A. des Cloizeaux, J. Lemberg, J. R. Blum, F. Zirkel, H. Rosenbusch, F. von Richthofen, J. Heinemann, etc. D. L. G. Karsten found an altered nephelite in the syenite of Fredriksvärn and Laurvik ; it was called *lythrodes*—from *λύθρον*, with blood and dust ; and *εἶδος*, appearance—and analyzed by J. F. John. J. F. L. Hausmann called it *wernerite*. The *maconite* of F. A. Genth is regarded as a variety of jeffersonite from Macon, North Carolina, and, like herrite, it is a decomposition product of chlorite. The *micarelle* of J. C. Freiesleben is a pinite found near Stolpen, Neustadt. A. Wichmann said that it is not a pseudomorph after iolite. Several different substances have been called micarell or micarelle—R. Kirwan, W. Haidinger, J. R. Blum, J. F. Hausmann, H. D. A. Ficinus, R. J. Haüy, A. Estner, A. des Cloizeaux, J. D. Dana, etc. A pinite-like mineral was found by C. M. Marx in the Oös Valley, Baden, and named *oosite*. It was also described by J. R. Blum, F. Sandberger, and W. Haidinger. A mineral resembling dyssyntribite was found by T. S. Hunt in several parts of Canada ; he called it *paraphite*. Another mineral from Saxony resembling dyssyntribite was called *pinitoid*, by A. Knop. It was further discussed by E. Cohen, C. W. von Gümbell, A. Hilger, and J. R. Blum. Reddish masses of a pinite-like substance occurring at Tunaberg, Sweden, were called by L. F. Svanberg *polyargite*—from *πολύς*, much ; *ἀργός*, sparkle. The mineral was investigated by L. Palmgren, A. des Cloizeaux, and A. Erdmann. According to A. des Cloizeaux, the name *pyrrholite* was applied to a mineral very similar to polyargite, and from the same locality. L. F. Svanberg also described a granular red mineral from Aker in Södermanland ; it was called *rossite*. G. Rose regarded it as an altered anorthite. F. W. Clarke gave it the formula $H(MgOH)_2 \equiv SiO_4 - Al = \{SiO_4 = (AlOH)H\}_2 + 2H_2O$. The mineral named *tererite* by E. Emmons is a pinite-like substance which has been likened to scapolite. T. S. Hunt's *wilsonite* from Bathurst, Canada, was considered to be a variety of gieseckite ; but E. J. Chapman found it closely resembled scapolite. Several alteration products of biotite are indicated in connection with the varieties of biotite.

*The uses of mica.*—H. A. Miers [21] described the use of fuschsite as a decorative

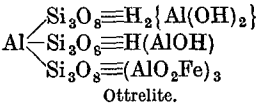
stone by the ancients; and M. Bauer, its use in making prehistoric implements in Guatemala. The most important use of mica is in the electrical industry as an insulator. It is one of the best of insulators because of its resistance to puncture, pre-resisting qualities, impermeability to moisture, toughness, elasticity, and flexibility; and its cleavage into thin sheets. It is largely used for insulating the segments of commutators, armature wires and bars, etc. Scrap mica is made into sheets, plates, and boards by means of a suitable bonding agent—say, shellac—and under the commercial name *micanite*, is used for making washers, etc., for insulating lamp-sockets, fuse-blocks, cut-out boxes, etc. Sheet mica is used for lanterns and windows where glass does not withstand the shocks and vibrations; for spectacles to protect the eyes of metal and stone workers from chips, etc. It is also used in place of glass where abrupt changes of temp. would be liable to crack glass—*e.g.* fire-screens, stove windows, lamp-chimneys, and some miners' lamps. Special sparking plugs for aeroplanes, etc., are built up from sheet mica. It is employed as a heat insulator in the lagging of steam-pipes, boilers, etc. It is used as a sounding-diaphragm in telephones, gramophones, etc. It is used as an absorbent for nitroglycerol; and as a heavy lubricant. Mica is used in making wall-paper pigments; and various ornamental purposes—a mixture of gum arabic and ground white mica makes the so-called *silver ink*; and it is employed for inlaying buttons, in making lustrous hair-powder, and in making the bronze-like colours which bear the name *brocades*, *crystal colours*, *mica-bronzes*, etc.; and in making frosted effects in decoration.

K. C. Fielder [22] described a mineral from the Urals as a *chlorite spar*, from its resemblance to chlorite; G. Rose, and A. Breithaupt called it **chloritoid**; E. F. Glocker, *barytophyllite*—from *βαρύς*, heavy; and *φύλλον*, a leaf; C. T. Jackson applied the term *masonite*—in honour of O. Mason—to a dark greyish-green mineral from Rhode Island, which M. R. Whitney, and G. A. Kenngott proved to be identical with chloritoid. A. E. Delesse named a mineral from St. Marcel, Zermatt, and Piedmont *sismondine*—in honour of A. Sismonda—and hence called *sismondite*. A. Brezina reported a mineral from St. Marcel which he called *strüverite*—named in honour of G. Strüver. G. Tschermak showed that strüverite and sismondite are identical; J. F. L. Hausmann, that sismondite is closely related to chloritoid; and F. von Kobell, that sismondite, masonite, and chloritoid are the same mineral species. T. Thomson described a mineral from Sterling, Mass., and called it *phyllite*; it had previously been called spangled mica slate by E. Hitchcock. A similar mineral from Newport, Rhode Island, was called *newportite* by C. U. Shepard. In 1821, C. C. von Leonhard mentioned a mineral brought from Ottrez, Ardennes; it was described by A. des Cloizeaux and A. Damour, and named *ottrelite*. This mineral was mentioned by R. J. Haüy. The resemblances between phyllite, ottrelite, and chloritoid were emphasized by T. S. Hunt, J. D. Dana, A. des Cloizeaux, G. Tschermak, and A. Lacroix. A manganiferous variety was called *salmite* by E. Prost; a variety from Venasque, Pyrenees, was called *venasquite*, by A. Damour; and a variety from Schmalenberg was called *brunsvigite*, by J. Fromme.

Attempts to devise formulæ from chemical analyses were made by C. F. Rammelsberg. C. Klemēnt gave $H_2(Fe,Mn,Mg)(Al,Fe)_2Si_2O_9$; and P. Groth gave $H_2(Fe,Mg)Al_2SiO_7$ for chloritoid, and $H_2(Fe,Mn)(Al,Fe)_2Si_2O_9$ for ottrelite. The subject was discussed by E. Manasse, and P. Niggli. G. Tschermak regarded the minerals as isomorphous mixtures of two silicates. F. W. Clarke co-relates the constitution of chloritoid to xanthophyllite and seybertite through the formulæ:



Chloritoid.



Ottrelite.

This makes idealized chloritoid a **ferrous pentaluminoxy-aluminotriortho-**

**silicate,** and idealized ottrelite a **ferrous pentaluminoxy-aluminotrimesotrisilicate.** The manganese oxide in ottrelite varies from 0–9 per cent. The colour of these minerals is dark grey, or greenish-black. The crystals of chloritoid occur in rosettes, or foliated masses. The tabular crystals of chloritoid rarely occur distinct; they are either monoclinic or triclinic; they have been investigated by G. Tschermak, F. Becke, H. von Foullon, A. Barrois, and A. des Cloizeaux. Ottrelite also furnishes either monoclinic or triclinic crystals, which have been studied by A. des Cloizeaux, A. Renard and C. L. J. X. de la Vallée-Poussin, H. Rosenbusch, and A. Lacroix. The basal cleavage is less perfect than is the case with the micas; the laminæ are brittle. Twinning is as common as with the micas; the crystals are oriented as though rotated 120° to one another. A zonal structure is sometimes developed; and inclusions are common. The optic axial angle of chloritoid is $2V=45°–55°$, according to A. Barrois, and $2E=65°–70°$, according to A. von Lasaulx. A. des Cloizeaux found for different samples of sismondite, $2H=64°\ 34'–74°\ 6'$ for red glass, and 57°–65° 38′ for green glass; and $2E=111°\ 50'–117°\ 48'$ for red glass, and 103° 40′–108° 44′ for green glass. The values for ottrelite vary considerably from sample to sample. The sp. gr. is 3·53–3·55; and the hardness 5–6. H. Rosenbusch found the index of refraction is high, about 1·78—A. Lacroix gave 1·78; A. C. Lane, 1·75; and A. Duparc and L. Mrazec, 1·77. The birefringence is feeble. A. Lacroix gave $\gamma-\alpha=0·015$. Chloritoid and ottrelite are optically positive. W. W. Coblentz found chloritoid to be rather opaque to the ultra-red rays; in the ultra-red transmission spectrum the water-bands 1·5$\mu$ and 3$\mu$ are absent; while there are small bands at 2·3$\mu$, 2·6$\mu$, 3·3$\mu$, 5$\mu$, 6$\mu$, and 6·3$\mu$. The pleochroism of chloritoid is strong, *a*=yellowish green; *b*, indigo-blue; *c*, olive-green. The pleochroism of ottrelite, said A. des Cloizeaux, is not so marked as with chloritoid. Finely powdered chloritoid is decomposed by sulphuric, nitric, and hydrochloric acids with the separation of gelatinous silica.

The term **chlorite** is a family name for a group of minerals closely related to the micas; they are more basic and more hydrated than the micas, and virtually free from alkalies. If alkalies are present, the chlorite is assumed to be mixed with some mica. The name—from χλωρός, green—emphasizes the green colour so common with these minerals. Pliny, in his *Historia naturalis* (**37**. 56), refers to the grass-green *chloritis*. A. G. Werner [23] applied the term *blattriger chlorite*, or *chlorites lamellosus*, to a hexagonal mineral from St. Gothard. D. L. G. Karsten, L. A. Emmerling, and A. Estner described several different kinds of lamellar chlorites. The minerals were analyzed by J. G. A. Höpfner, L. N. Vauquelin, and W. A. Lampadius. The minerals were regarded by R. J. Haüy, C. C. von Leonhard, and A. Cronstedt as *variétés de l'espèce talc*; but F. von Kobell showed that chlorite contains too much water for a talc. He further found that the chlorites then known were varieties of two species—one, *chlorite*, contained 25–27 per cent. of silica, and was typified by that from St. Gothard; and the other, *ripidolite*—from ῥιπίς, a fan; and λίθος, a stone, in allusion to its occurrence in fan-like aggregates—contained 30–33 per cent. of silica, and was typified by that from Achmatovsk. G. Rose unfortunately reversed these terms, and introduced some confusion in the nomenclature. J. D. Dana suggested keeping the term *chlorite* for the whole family; calling the original chlorite *prochlorite*—from πρό, before; dropping the equivocal term ripidolite, and using *clinochlore* in its place—κλίνειν, to incline—in allusion to the unequal inclination of two of the optic axes to the principal axis. The latter term had been applied by W. P. Blake to a chloritic mineral from Westchester, Penn., which W. J. Craw proved to be identical with the chlorite from Achmatovsk. This subject was discussed by N. von Kokscharoff, and F. Hessenberg. J. Orcel proposed to call the ferruginous prochlorites *ripodolites* when the ratio MgO : FeO is 3 or less, and the birefringence is 0·0001–0·005; and the magnesian prochlorites *grochauites* when the ratio MgO : FeO is about 10, and the birefringence is about 0·01.

The chlorites are hydrated magnesium or ferrous aluminosilicates or ferrisilicates. They resemble the micas crystallographically, and in their scaly or foliated habit.

Each member of the series exhibits some variation in composition. Hence, like the ferromagnesian micas, they are often regarded as isomorphous mixtures. In his memoir : *Die Chloritgruppe* (Wien, 1891), G. Tschermak [24] called those chlorites which ordinarily occur in distinct crystals or plates, *orthochlorites ;* and those which commonly occur in fine scales, or indistinctly fibrous forms, *leptochlorites*. According to K. Dalmer, the orthochlorites lose part of their water at 550°–570°, and part at bright redness ; while the leptochlorites lose part at 440°–500°, and part at 580°–600°. Hence he argued that the intrinsic nature of the two series is different. The following lists include most of the chlorites which have received a name ; but too much reliance must not be placed on the classification since too little is known about some of them. A list of unclassed chlorites is also appended. The summaries of the analyses represented by the formulæ are mainly due to G. Tschermak.

**Orthochlorites.**—The ordinary variety of *clinochlore*, $H_8(Mg,Fe)_5Al_2Si_3O_{18}$, is green or bluish-green, and it occurs in crystals, massive and foliated. Analyses were made by G. Tschermak,[25] V. Iskyul, and others. V. Iskyul examined the action of hydrochloric acid on the mineral. A. Hamberg obtained a sample from Pajsberg, Sweden, with 2·3 per cent. of *MnO ; he called it manganochlorite.* *P. von Jeffreinoff* [26] *named a variety of clino*-chlore from Zlatoust, Ural, *leuchtenbergite*—after N. von Leuchtenberg—which may be white, pale-green, or yellowish. Analyses were made by N. von Leuchtenberg, etc. The crystals were examined by G. A. Kenngott, F. C. Calkins, E. V. Shannon, and A. des Cloizeaux. V. Iskyul examined the action of hydrochloric acid on the mineral. N. von Koksharoff [27] named a variety of clinochlore from Ufaleisk, Ural, *kotschubeite*—after P. A. von Kochubei. Analyses were made by N. von Leuchtenberg, etc. A chlorite from the Pennine Alps was called *pennine—penninite*—by J. Fröbel and E. Schweizer.[28] L. A. Necker called it *hydrotalc*. The crystals were described by J. C. G. de Marignac ; the effect of temp. on the pleochroism, by O. Nagaoka ; and the action of hydrochloric acid, by V. Iskyul. Analyses were made by G. Tschermak, etc. A reddish chromiferous variety of penninite occurring near Miask, Ural, was called by N. von Nordenskjöld,[29] *kämmererite*—after A. Kämmerer. Analyses were made by R. Hermann, etc. F. Tucan represented the composition by $(Cr,Al)_2Si_4O_{22}Mg_6H_{10}$. A variety obtained by K. G. Fiedler, from Tenos, Greece, and by G. Rose from the Ural, was called *rhodochrome*—from *ῥόδον*, rose ; and *χρῶμα*, colour. V. Iskyul found it to be related to the metasilicates. A variety from Texas, etc., was called *chromochlorite* by R. Hermann, and *rhodophyllite*—from *ῥόδον*, rose ; and *φύλλον*, a leaf—by F. A. Genth. E. V. Shannon also described a chromiferous chlorite. F. Pearse found a green variety of kämmererite at Texas which he named *grastite*—from *γράστις*, grass. H. Vogelsang proposed the general term *viridite* for all the intermediate green compounds of secondary origin observed in rocks, and it may include different chlorites and serpentine. The viridites were discussed by E. Dathe, and H. Rosenbusch. G. A. Kenngott [30] described a compact massive form of penninite from Berg Zdjar, Moravia, which he named *pseudopite*—*ψεῦδος*, false ; *ophite*, serpentine—on account of its resemblance to serpentine. Analyses were made by G. A. Kenngott, L. van Werweke, H. Stadlinger, R. von Drasche, W. E. Gintl, E. Cohen, etc. Analogous substances were described by V. Wartha, and V. von Zepharovich, T. S. Hunt's *loganite* is very like pseudopite. A. G. Werner [31] described a *blue talc* or *mica chlorite* which was shown by T. Scheerer to be a bluish-green or green penninite like that he obtained from Taberg, Sweden, and called *tabergite*. A. des Cloizeaux studied the crystals, and G. Tschermak analyzed the mineral which he regarded as a mixture of phlogopite and clinochlore. V. Iskyul studied the action of hydrochloric acid on the mineral.

The *prochlorite*, $H_{40}(Fe,Mg)_{23}Al_{14}Si_{13}O_{90}$, of J. D. Dana,[32] and the chlorite of earlier observers was analyzed by A. J. Egger, etc. V. Iskyul studied the action of hydrochloric acid on prochlorite. G. H. O. Volger [33] described a prochlorite in slender vermiform crystals, hence the name *helminthe*—from *ἕλμιν*, a worm. M. Websky found crystals of a mineral which he called *grochauite* in cavities in the serpentine of Grochau, Silesia. It was studied by M. Bock ; and shown by G. Tschermak to be prochlorite. C. U. Shepard's *lepidochlorite*—from *λεπὶς*, a scale—is an impure chlorite from Mount Pisgah, Tennessee. A. Breithaupt's *lophoite*—from *λόφος*, a cock's comb—a name applied in allusion to the form of the crystal aggregates, is considered to be a chlorite ; a similar remark applies to his *onkoite* or *ongoite*—from *ὀγκόω*, swollen. G. W. von Gümbel's *phyllochlorite* is a ferruginous chlorite. Both *kerrite*, and *maconite* previously cited are sometimes classed with these chlorites. I. Lea described under the name *pattersonite* a micaceous chlorite from Unionville, Pennsylvania, which was analyzed by S. P. Sharples and F. A. Genth. According to M. F. Heddle, the *talc-chlorite* of J. C. G. de Marignac is a mixture of clinochlore and talc. The crystals were examined by A. des Cloizeaux.

E. V. Shannon and E. T. Wherry [34] class *colerainite* and *sheridanite* as *white chlorites.*

The former was reported by E. M. Poitevin and R. P. D. Graham in minute hexagonal crystals with the composition $4MgO.Al_2O_3.2SiO_2.5H_2O$; the sp. gr. was 2·44–2·51; the hardness, $2\frac{1}{2}$–3; the optical character was positive; and the refractive index 1·56. It occurs in the asbestos mines of Quebec. Sheridanite was found by J. E. Wolff in Sheridan Co., Wyoming, as a pale silvery-green talc-like mineral with a composition $H_6Mg_3Al_2Si_2O_{13}$. Very little water is expelled at 350°. The refractive indices are $\alpha=1·580$; $\beta=1·580$–$1·581$; and $\gamma=1·589$; the optical axial angle $2E=26°$–$50°$; and the optical character is positive. The mineral is slowly decomposed by boiling sulphuric acid, and with difficulty by hydrochloric acid.

C. U. Shepard [35] applied the term *corundophilite*, $H_{20}(Mg,Fe)_{11}Al_8Si_6O_{45}$—from $\phi\acute{\iota}\lambda o\varsigma$, a friend—to a chlorite occurring in the corundum of Asheville, North Carolina. J. P. Cooke showed it to be a variety of clinochlore. It was analyzed by F. Pisani, and E. V. Shannon. V. Iskyul studied the action of hydrochloric acid on the mineral. C. U. Shepard found a chlorite in the diaspore at Chester, Mass., which he called *amesite*. It was analyzed by E. V. Shannon, F. Pisani, G. Ponte, and G. Tschermak; and shown by G. A. Kenngott to be a chlorite. G. Tschermak represented its composition by the formula: $H_4(Mg,Fe)_2Al_2SiO_9$; E. V. Shannon, by $2(Fe,Mg)O.Al_2O_3.SiO_2.2H_2O$. The optical properties were studied by E. V. Shannon.

**Leptochlorites.**—G. Tschermak [36] found lamellar crystals of a chlorite associated with the arsenical pyrites and quartz of Penzance, Cornwall. He called it *daphnite*, $H_{56}Fe_{27}Al_{20}Si_{18}O_{121}$—from $\delta\alpha\phi\nu\acute{\iota}\varsigma$, the bay-berry—in allusion to the aggregation of the crystals. The crystals are probably monoclinic. E. Gueymard [37] referred to *mine de fer oxydé en grains agglutinés*, and P. Berthier to *un minerai de fer grains*, which he named *chamoisite* from the locality, Chamoson, Switzerland, where it occurred. B. Studer altered the name to *chamosite*. P. Berthier found that the iron ore at Hayanges, Moselle, contained calcium and ferrous carbonates and a silicate. The silicate was named *berthierine* by F. S. Beudant. J. J. N. Huot called the oolitic chlorites described by E. le Pouillon de Boblaye, *bavalite*, or *baralite*; and P. A. Dufrénoy proposed to designate all these related substances by the term *chamosite*. Analyses, etc., were made by E. Boricky, H. Loretz, C. Schmidt, J. Orcel, etc. These minerals were supposed to be mixed hydrogels of alumina, silica, and ferric oxide,[38] together with some impurities. G. Tschermak [39] described aggregates of lamellar crystals from Elbingerode, Harz, which he named *metachlorite*. Similar crystals had been previously noted by C. List, and G. Sillem. C. Klement described a chlorite from Vielsalm, Belgium, which G. Tschermak named *klementite*. A. von Lasaulx [40] reported a blue earthy mineral from the Pyrenees which he called *aerinite*. Its sp. gr. was 3·018, and hardness 3–4. A. des Cloizeaux showed it to be heterogeneous and not to be regarded as a definite mineral. Analyses were made by C. F. Rammelsberg, J. Macpherson, and J. Orcel. The last-named studied a mineral he also called aerinite from Casserras, Aragon; its composition was $1·5CaO.(Fe,Mg)O.2(Al,Fe)_2O_3.6SiO_2.7H_2O+3H_2O$; and he regarded it as a new type of leptochlorite. A. Breithaupt [41] described a compact aggregate of minute scales of a chlorite from Saafeld, Thuringia, which he named *thuringite*, $H_{18}Fe_8(Al,Fe)_8Si_6O_{41}$, and apparently the same mineral from Harper's Ferry, Virginia, was named by F. A. Genth *owenite*—after D. D. Owen. Analyses were reported by G. Tschermak, L. Slavikova and F. Slavik, J. L. Smith, P. Keyser, V. von Zepharovitch, S. L. Penfield and F. L. Sperry, H. Loretz, E. S. Larsen and G. Steiger, etc. The last-named found for the indices of refraction $\alpha=1·595$, $\beta=1·64$, and $\gamma=1·65$. C. Simmonds found that the reduction of thuringite is complete when heated to redness in hydrogen. F. Kretschmer [42] obtained a chloritic mineral, resembling thuringite, from Gobitschau, Moravia, and he called it *moravite*. Its composition approximated $H_4Fe_2(Al,Fe)_4Si_7O_{24}$. Its sp. gr. was 2·38, and hardness 3·5. It was decomposed by hydrochloric acid with the separation of gelatinous silica. According to L. Slavikova and F. Slavik, the refractive index is 1·615. J. Steinman [43] described a chloritic mineral from Pribram, Bohemia, which was named *cronstedtite*, $H_6(Fe,Mg)_3Fe_2Si_2O_{13}$—after A. Cronstedt. Crystals were examined by V. von Zepharovitch, N. S. Maskelyne, G. Tschermak, and A. des Cloizeaux; and analyses were made by J. Steinman, A. Damour, C. W. Hoadley, R. Köchlin, J. V. Janovsky, G. Tschermak, C. Vrba, F. Field, N. S. Maskelyne, etc. C. Simmonds found reduction is complete when the mineral is heated to redness in hydrogen. A. Breithaupt called a specimen *chloromelane*. The variety from Conghonas do Campo, Brazil, was called *sideroschisolite* by F. Wernekinck—from $\sigma\acute{\iota}\delta\eta\rho o\varsigma$, iron; $\sigma\chi\acute{\iota}\zeta\omega$, to split; and $\lambda\acute{\iota}\theta o\varsigma$, a stone. Analyses were made by J. F. L. Hausmann, and V. von Zepharovich. J. F. L. Hausmann showed that it is a variety of cronstedtite.

A chloritic mineral from Eura, Finland, was called *euralite* by F. J. Wiik,[44] and he suggested that it is related to delessite. E. Becker,[45] and M. Websky found a chloritic mineral occurring as a coating in druses or cavities in the granite near Striegau, Silesia, and it was named *striegovite*, $H_4(Fe,Mn)_2(Fe,Al)_2Si_2O_{11}$. K. T. Liebe [46] applied the term *diabantachronnyn*—from $\chi\rho\acute{\omega}\nu\nu\upsilon\mu\iota$, to colour—to a chloritic mineral occurring in the diabase of Voigtland and Frankenwand, and to which it imparts a green colour. G. A. Kenngott showed that the mineral is a chlorite. G. W. Hawes found a sample at Farmington Hills, Connecticut, and he called it *diabantite*, $H_{18}(Mg,Fe)_{12}Al_4Si_9O_{45}$. F. Sandberger [47] found dark olive-green scaly crystals of a soft ferruginous chlorite in a

mine at Weilburg, Nassau. The mineral was called *aphrosiderite*, $H_{10}(Fe,Mg)_6Al_4Si_4O_{25}$—from *ἀφρός*, foam; and *σίδηρος*, iron. The crystals were examined by G. A. Kenngott, H. Fischer, V. von Zepharovich, F. Slavik and V. Vesely, and E. A. Reuss. Analyses were made by F. Sandberger, F. Nies, M. Websky, G. Woitschache, L. Erlenmeyer, L. J. Igelström, etc. A. E. Delesse [48] found a fibrous chlorite with a scaly feathery texture as a coating or filling cavities of the porphyry at La Grève in the Vosges; he called it *chlorite ferrugineuse* or *iron-chlorite*, and C. F. Naumann called it *delessite*, $H_{10}(Mg,Fe)_4Al_4Si_4O_{23}$—after A. E. Delesse. E. Weiss used the name delessite for the varieties—*e.g.* the La Grève chlorite—containing more ferric oxide and less ferrous oxide, and *subdelessite* for those—*e.g.* the Friedrichroda chlorite—containing more ferrous oxide and less ferric oxide. Analyses of delessite were made by A. E. Delesse, N. I. Bezborodko, E. Weiss, and M. F. Heddle. C. W. von Gümbel called *das grün färbende Princip der Diabase* of Fichtelgebirge *chloropite*. It was considered to be a variety of delessite or diabantite. P. A. Dufrénoy regarded the chloritic mineral of A. E. Delesse, named *dumasite*, as a variety of delessite. A. Schrauf designated the group of delessitic minerals, *protochlorites*. G. Firtsch [49] named a basic aluminium and magnesium silicate from St. Michael, Styria, *rumpfite*, $H_{28}Mg_7Al_{16}Si_{10}O_{65}$—in honour of J. Rumpf. It is a chlorite rich in iron. Analyses were made by K. A. Redlich. G. Tschermak regards it as a relation of leuchtenbergite. The minerals *epiphanite*, *lennilite*, and *vaalite*, alteration products of biotite, are considered by G. Tschermak to be chlorites. A. Schrauf groups them as *parachlorites*.

**Unclassed chlorites.**—There are a few chlorites which were not classed by G. Tschermak. C. F. Rammelsberg and C. Zincken [50] found a chlorite in the serpentine at Harzberg which they named *epichlorite*. A sample from Voigtland was analyzed by K. T. Liebe. A chloritic mineral from Grängesberg, Sweden, was called *grängesite* by W. Hisinger.[51] The name is sometimes spelt *grengesite*. It was described by G. Suckow, A. Erdmann, A. Lacroix, and H. Heymann. E. T. Hardman found a black chlorite in cavities in the basalt of Carnmoney Hill, Belfast, and he called it *hullite*. M. F. Heddle found a similar mineral in the basalt of Kinkell, Fifeshire. H. Wurtz described a black chloritic mineral from a quarry near Charlestown, Mass. He called it *melanolite*—from *μέλας*, black; and *λίθος*, a stone. E. F. Glocker [52] described a chloritic mineral from various parts of Silesia which was called *stilpnomelane*—from *στιλπνός*, shining; and *μέλας*, black. The colour is black, greenish-black, yellowish-bronze, or greenish-bronze. C. U. Shepard called a yellowish variety *chalcodite*—from *χαλκός*, brass or bronze. Stilpnomelane and chalcodite have been described by H. Fischer, F. Sandberger, F. Roemer, V. von Zepharovich, J. W. Mallet, G. Gürich, W. C. Brögger, etc. Analyses were made by C. F. Rammelsberg, E. V. Shannon, A. F. Hallimond, K. Sarkany, L. J. Igelström, G. J. Brush, and F. A. Genth. F. F. Grout and G. A. Thiel gave for the sp. gr. 2·882; and for the indices of refraction of stilpnomelane $\alpha=1·546$, $\gamma=1·615$. They found the optic axial angle $2V$ was very small; A. F. Hallimond found for the sp. gr. 2·85; hardness 3 to 3½; $\omega=1·685$, and $\epsilon=1·595$; and a negative optical character. He gave for the composition $K_2O.3(R_2O_3,RO)6SiO_2+aq$. According to C. Simmonds, reduction is complete when stilpnomelane is heated to redness in hydrogen.

Some chloritic minerals have not been sufficiently investigated to decide if they really are chlorites. Thus, A. E. Reuss' earthy mineral [53] resembling glauconite, from Pribram, Bohemia, which was named *lillite*—named after M. von Lill—and examined by F. Babanek, J. A. Krenner, C. F. Rammelsberg, and A. H. Church. G. A. Koenig's *leidyite*—named after J. Leidy—was considered to be a zeolite; P. Groth classed it with the chlorites. The green *chrysopras earth* of M. H. Klaproth was named *schuchardtite* by A. Schrauf. D. L. G. Karsten called it *pimelite*—from *πιμελή*, fatness. It was examined by G. Starkl, and W. Baer. L. J. Igelström described a foliated green to black chloritic mineral from Grythytte, Sweden, which he called *ekmanite*—after G. Ekman. H. Hamberg, and J. Jakob investigated the optical properties of ekmanite. F. Zambonini represented it as a *ferrous manganese trimetasilicate*, $4RO.3SiO_2.3H_2O$. E. E. Schmid described a pale green mineral from cavities in the porphyritic rocks of Höllekopf, etc. It was called *steatargillite*. Its nature is doubtful. T. Thomson described a blue mineral from Baltimore, and called it *baltimorite*. It was examined by C. von Hauer, and R. Hermann. A leek-green soft chlorite from Kilpatrick Hills was called *prasilite*—from *πράσιος*, leek-green—by T. Thomson. An alteration product of serpentine from Krems, Bohemia, was described by A. Schrauf as *berlauite*. A chlorite occurring in small balls of irregularly arranged fibres was called *tolypite* by A. Uhlemann. G. Flink obtained a chloritic mineral from Narsasak, Greenland, which he called *spodiophyllite*; and A. Mallard, one from Noyant, France, which he called *bravaisite*. J. Samojloff found a lamellar variety of what looked like chlorite but whose chemical composition more nearly resembled clay or pyrophyllite. He called it *α-chloritite*. A. Lacroix obtained a chlorite from Segré, Maine-et-Loire, which he called *minguetite*, and which has a composition intermediate between lepidomelane and stilpnomelane.

**The constitution of the chlorites.**—C. F. Rammelsberg calculated a number of best representative formulæ from the analyses of various chlorites. The main diffi-

culties associated with work of this kind are due to the heterogeneous nature of the assumed mineral species; to the fact that some are isomorphous mixtures; and to the uncertainty as to the intrinsic or extrinsic nature of the water of hydration. Systems of formulation can therefore be easily carried beyond the range of known facts. The orthochlorites were supposed by G. Tschermak [54] to be isomorphous mixtures of different proportions of a magnesium silicate, $H_4Mg_3Si_2O_9$, having the same composition as serpentine, and magnesium aluminosilicate, $H_4Mg_2Al_2SiO_9$, which is represented by amesite. In order to explain the composition of the leptochlorites, G. Tschermak found it necessary to invent two other fundamental mols, $H_4Mg_2Al_2Si_2O_{11}$, represented by strigovite, and $H_2MgAl_2SiO_7$, represented by choritoid. By working in this manner, it would be possible to represent the composition of any aluminosilicate. Accordingly, the coincidence of calculated and observed results does not impart much confidence in the truth of the hypothesis; and the question might legitimately be raised whether the chlorites are of any interest to the chemist, however interesting they may be to the mineralogist. If serpentine be a component of the chlorites, and if serpentine on calcination breaks up into water, olivine, and enstatite (insoluble in acids), it follows that the calcination of the magnesian chlorites should furnish about 18 per cent. of enstatite. F. W. Clarke, and C. Doelter and E. Dittler found that actually no enstatite is formed; instead spinel is produced in quantities proportional to the excess of oxygen above that calculated for an orthosilicate. This, regarded as an *experimentum crucis*, makes it highly probable that serpentine mols. are not present in the chlorites, and, as F. W. Clarke puts it, G. Tschermak's hypothesis breaks down. V. Iskyul said that the existing theories as to the nature of the chlorites are based on too little experimental observations.

F. W. Clarke and E. A. Schneider based some formulæ representing the constitution of the chlorites on the action of hydrogen chloride on these silicates. R. Brauns, however, argued that the action was dependent on the degree of humidity of the gas employed, and he and A. Lindner questioned whether evidence on the constitution of the chlorites can be founded on these experiments. R. Brauns, V. Goldschmidt, P. Groth, and W. and D. Asch base formulæ for the chlorites on the assumption that the chlorites are isomorphous mixtures of idealized types or hypothetical components. P. Erculisse considered the chlorites to be solid soln. of the micas and spinel. B. Gossner represents clinochlore by

$$\left[SiO_2.2MgSiO_3\right]^{3AlO(OH)}_{3Mg(OH)_2}$$

and by replacements between $SiO_2$ and $AlO(OH)$, and between $AlO(OH)$ and $Mg(OH)_2$ he accounted for the composition of all the members of the chlorite family. W. Vernadsky, and V. Iskyul considered the chlorites to be salts of, or complex compounds with, the acids $Al_2Si_{2+m}O_{7+2m-n}(OH)_{2n}$. The composition of the chlorites has been discussed by E. S. von Fedoroff. In his later work, F. W. Clarke represented the chlorites as orthosilicates, or trisilicates which formed a series of idealized compounds parallel with those which he employed for the micas, and in which basic groups like $MgOH'$, $FeOH'$, $AlOH''$, $Al(OH)_2'$, $Fe(OH)_2'$, and $Fe(OH)''$ appear. Thus, he based formulæ for the chlorites on three types:

I. *The biotitic chlorites* are built on the biotite-chlorite type and are illustrated by his formulæ for rumpfite, cronstedtite, and melanolite.

$Al{\equiv}SiO_4{-}Al{<}^{SiO_4{\equiv}(MgOH)_2H}_{SiO_4{\equiv}(MgOH)_2H}$ Biotite-chlorite.

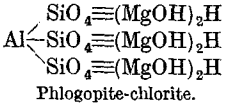
$Al{\equiv}SiO_4{-}Al{<}^{SiO_4{\equiv}(MgOH)_2H}_{SiO_4{\equiv}\{Al(OH)_2\}_3}$ Rumpfite.

$Fe{\equiv}SiO_4{-}Al{<}^{SiO_4{\equiv}(FeOH)_2\{Fe(OH)_2\}}_{SiO_4{\equiv}(FeOH)_2\{Fe(OH)_2\}}$ Cronstedtite.

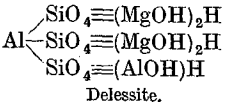
$Fe{\equiv}SiO_2{-}Al{<}^{SiO_4{\equiv}(FeOH)H_2}_{SiO_4{\equiv}(FeOH)H_2}$ Melanolite.

II. *The phlogopitic chlorites* are built on the phlogopite-chlorite type. The

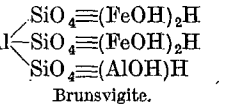
composition of an average pennite agrees with an isomorphous mixture of the biotitic and phlogopitic chlorites in the proportion 1 : 1, and clinochlore and leuchtenbergite,



Phlogopite-chlorite.

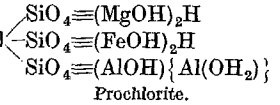


Delessite.

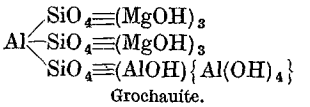


Brunsvigite.

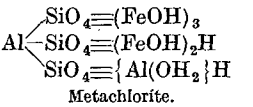
with the ratio 2 : 3 with one Al of the biotitic formula replaced by 3AlO. The formulæ given by F. W. Clarke for brunsvigite, delessite, prochlorite, grochauite, metachlorite, stilpnomelane, ekmannite, and corundophilite may be cited. In corundophilite the six R-atoms are made up from four Mg-atoms and two Fe″-atoms.



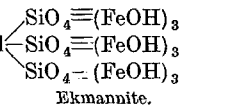
Prochlorite.



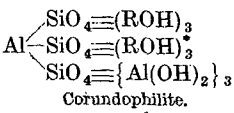
Grochauite.



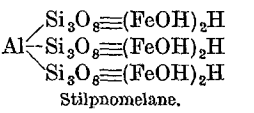
Metachlorite.



Ekmannite.



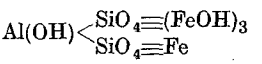
Corundophilite.



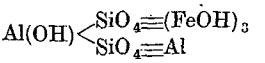
Stilpnomelane.

Stilpnomelane has the chlorite formula, but is a trisilicate instead of an orthosilicate. The composition of diabantite and thuringite can be imitated by assuming they are binary mixtures; and epichlorite, a mixture of stilpnomelane and the orthosilicate, $Al(SiO_4)_3(MgOH)_6H_3$.

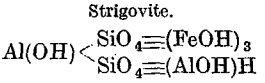
III. *The margaritic chlorites* are illustrated by strigovite, aphrosiderite, daphnite, and sheridanite.



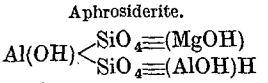
Strigovite.



Aphrosiderite.



Daphnite.



Sheridanite.

The hydrated character of the chlorites shows that they are not formed pyrogenetically. They are always of secondary origin, and almost all the ferromagnesian aluminosilicates may yield chlorites by hydrolytic reactions.[55] G. Friedel and F. Grandjean made chlorites artificially by the action of alkaline soln. on pyroxenes at 550°–570°.

The **colour** of the members of the chlorite group includes various shades of green, rarely brown; some are coloured violet, rose-red, and pink, particularly if chromium is present. Clinochlore occurs in tabular **crystals** flattened parallel to (001), and with a hexagonal outline; the crystals are sometimes prismatic. The crystals are monoclinic, and, according to G. Tschermak,[56] and N. von Kokscharoff, the axial ratios of crystals of clinochlore are $a : b : c = 0{\cdot}57735 : 1 : 2{\cdot}2771$, and $\beta = 89° 40'$. Clinochlore also occurs scaly, granular, or earthy. Penninite is trigonal in habit, but, as G. Tschermak, and E. Mallard have shown, the crystals are pseudotrigonal, and belong to the monoclinic system with axial ratios like those of clinochlore. According to J. P. Cooke, the axial ratio of the pseudotrigonal crystals is $a : c = 1 : 3{\cdot}4951$. Penninite also occurs in scaly or compact cryptocrystalline masses. The crystals are thick and tabular rhombohedra, and also tapering six-sided pyramids; the X-radiogram was studied by H. Haga and F. M. Jäger. Prochlorite occurs in monoclinic six-sided plates or prisms with the planes strongly furrowed. The crystals are often joined at their sides, and occur in fan-shaped, vermicular, or spheroidal groups. They also occur in foliated or granular masses.

Corundophilite occurs in monoclinic 6-sided or 12-sided plates or prisms. The crystals of the orthochlorites were studied by G. Tschermak, E. Mallard, A. Schrauf, C. F. Naumann, P. Groth, A. des Cloizeaux, F. Hessenberg, J. D. Dana, N. von Kokscharoff, R. Prendel, L. V. Pirsson, H. Laspeyres, and J. Grailich and V. von Lang.

The **twinning** is usually similar to that of the micas with the twinning plane perpendicular to (001) and in the zone (001) (110). In some cases, the composition plane is (001) with the planes of the optic axes intersecting at 60°; in other cases, (i) the twinned parts may lie in one plane adjacent to one another along two or three irregular planes, or (ii) they may form a trilling, or (iii) they may make one crystal with six sectors ⊛. The twinning may follow the so-called *penninite law*, with (001) for the twinning and composition plane. The two parts are in this case reversed, and corresponding faces differ in position 180°. Both modes of twinning may occur in one crystal. The apparent uniaxial character of penninite is explained by G. Tschermak and E. Mallard by assuming a highly developed multiple twinning of biaxial plates. The twinning was discussed by G. Tschermak, N. von Kokscharoff, G. A. Kenngott, and J. P. Cooke. The **cleavage** parallel to (001) is perfect furnishing flexible, tough, but not elastic laminæ. The **percussion figures** and the **pressure figures** are oriented as with the micas. The **corrosion figures** were studied by G. Tschermak, and F. J. Wiik. Those at the (001)-face of clinochlore are in part monoclinic, and in part triclinic; those on penninite are hexagonal or triangular, rarely monoclinic or triclinic; and those on corundopilite are monoclinic. The **optic axial angles** are variable even in the same crystal; and in some cases the crystals appear uniaxial. G. Tschermak gave for $2E=2°\ 30'$–$65°$ for clinochlore, and $2V=20°$–$51°\ 31'$; for penninite, $2E=0°$–$60°$; for prochlorite, $2E=0°$–$30°$; for corundophilite, $2E=8°\ 20'$, and $2V=46°\ 40'$; for leuchtenbergite, $2E=0°$–$29°$; for kotschubeyite, $2E=0°$–$36°$; and for kämmererite, $2E=0°$–$20°$. Observations have also been reported by A. des Cloizeaux, A. Michel-Lévy and A. Lacroix, and R. Prendel. According to A. des Cloizeaux, raising the temp. of clinochlore from 20°–205° raises $2E$ from 68°–75°; no change occurred with leuchtenbergite and penninite.

The **specific gravity** of clinochlore ranges from 2·65–2·78; of penninite, from 2·60–2·85; of prochlorite, from 2·78–2·96; and that of corundophilite is 2·90. The **hardness** of prochlorite is 1–2; and that of other varieties ranges from 2–2½. R. Ulrich gave 0·2046 for the **specific heat** of chlorite between 20° and 98°. K. Dalmer found that orthochlorites lose their water at 550°–570°; the leptochlorites commence to lose their water at 440°–450° and lose all at 580°–600°. C. Doelter found that when penninite is melted with magnesium fluoride, magnesia mica, olivine, and enstatite are formed. He also found that when slowly cooled, olivine, augite, and spinel are formed. Observations were also made by C. Doelter and E. Dittler. F. W. Clarke and E. A. Schneider found that when clinochlore is strongly ignited it furnishes a soluble and an insoluble portion, and the latter has the composition of a spinel. The **indices of refraction** are nearly the same as for mica; for clinochlore, A. Michel-Lévy and A. Lacroix, K. Zimanyi, and J. Königsberger gave $\alpha=1·585$–$1·586$, $\beta=1·586$–$1·588$, $\gamma=1·5955$–$1·596$; for penninite, A. des Cloizeaux, C. Pulfrich, A. Michel-Lévy and A. Lacroix, W. Haidinger, and K. Zimanyi gave $\alpha=1·575$–$1·5821$, $\gamma=1·576$–$1·5832$. The corresponding **birefringence** is low, ranging from $\gamma-\alpha=0·001$–$0·0101$. The **optical character** is usually positive, sometimes negative, and sometimes both in adjacent laminæ of the same crystal. E. S. Larsen studied this subject. The **pleochroism** of the crystals is well-marked; this subject was discussed by G. Tschermak, A. des Cloizeaux and J. C. G. de Marignac, G. A. Kenngott, J. P. Cooke, A. Bertin, and H. Rosenbusch. W. G. Hankel discussed the **pyroelectric properties** of the crystals.

G. A. Kenngott [57] observed that powdered and moistened chlorite has an alkaline reaction towards litmus. F. W. Clarke and G. Steiger found chlorites are partially decomposed by the vap. of ammonium chloride. C. Doelter and E. Dittler did not

obtain talc by the action of soln. of sodium carbonate and hydroxide. F. W. Clarke and E. A. Schneider found chlorites are decomposed when heated in a stream of hydrogen chloride; R. Brauns doubted if the gas was adequately dried. A. Lindner also made observations on this subject. The transformations of the chlorites in nature have been discussed by G. Tschermak, A. Funaro and L. Brussati, N. von Kokscharoff, etc. V. Iskyul studied solubility of the silica from the chlorites—prochlorite, corundophyllite, tabergite, rhodochrom, penninite, leuchtenbergite, and clinochlore. W. C. Smith and G. T. Prior described an ivy-green compact chlorite from Bernstein, Austria, which is sometimes erroneously called *precious serpentine*, and which is used for making vases and other small ornaments.


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## § 42. Alkali Aluminium Silicates (*continued*)

M. F. R. d'Andrada [1] found a white or yellowish-white mineral at Utö, Södermanland, Sweden, and he named it **spodumene**—from σποδός, ashes—in allusion to its colour before the blowpipe flame. R. J. Haüy called it *triphane*—from τριφάνη, appearing three-fold—in allusion to his idea that the crystals can be divided by three planes with equal ease. J. A. Arfvedson first demonstrated the presence of lithium in the mineral, and other analyses were made by F. Stromeyer, R. Hagen, H. V. Regnault, and T. Thomson.

A variety of spodumene from Stoney Point, Connecticut, was described by J. L. Smith, [2] and W. E. Hidden, and called *hiddenite*—after W. E. Hidden. The colour is yellowish-green to emerald-green, and the latter is used as a gem-stone. It shows rather more variety of colour than the emerald because of its pleochroism. Another variety from Pala, California, is a clear rose or lilac-colour; it was called *kunzite*—after G. F. Kunz—and is also used as a gem-stone. It was described by G. F. Kunz, C. Baskerville, W. T. Schaller, and R. O. E. Davis. K. Przibram and co-workers found that a sample of kunzite which was pleochroic from rose-red to colourless gave colours varying from blue to yellowish-green after exposure to Becquerel's rays. T. Tanaka considered that the spectrum of the luminescence of kunzites indicated the presence of manganese, iron, thallium, samarium, and ytterbium.

Analyses of spodumene were made by C. F. Rammelsberg, A. Julien, etc. No elements of the cerium-yttrium group were present; and magnesium, barium, strontium, chromium, iron, titanium, zirconium, thorium, and phosphorus were absent from the kunzite analyzed by W. T. Schaller, and R. O. E. Davis. According to A. Piutti, spodumene of Mines Graës is not radioactive, although kunzite contains some helium. The proportion of lithia in the early analyses was shown by C. Doelter to be too low owing to imperfections in the analytical methods. The later analyses are best represented by the formula $LiAl(SiO_3)_2$, so that spodumene may be regarded as **lithium aluminium dimetasilicate.** F. W. Clarke gave a complicated graphic formula for spodumene involving a sextupling of the simple empirical formula. The synthesis of a spodumene like the natural mineral has not yet been effected—*vide* leucite. R. Ballo and E. Dittler melted together lithium metasilicate and aluminium metasilicate, and obtained what has been called *γ-spodumene*, which has a smaller sp. gr. and index of refraction than spodumene itself. G. Stein, and F. M. Jäger and A. Simek also failed to synthesize the mineral, but they obtained the γ-spodumene. R. Ballo and E. Dittler's f.p. curve of mixtures of lithium and

aluminium metasilicates is shown in Fig. 135. Starting from the lithium end, solid soln. are formed as far as 30 mol. $Al_2(SiO_3)_3$, and beyond the eutectic point a maximum occurs at 965°, corresponding with the compound **lithium dialuminium pentametasilicate,** $2Li_2SiO_3.Al_2(SiO_3)_3$. There is then a second eutectic point at 920°, and the curve rises steeply to a maximum at 1275°, corresponding with **lithium aluminium tetrametasilicate,** $Li_2SiO_3.Al_2(SiO_3)_3$. The third eutectic point is at 1200°. Natural spodumene furnishes a similar product to synthetic spodumene when it is fused and slowly cooled. In the system $LiAlO_2$–$SiO_2$, R. Ballo and E. Dittler found lithium aluminium dimetasilicate, m.p. 1275°; lithium aluminium orthosilicate, m.p. 1330°; **lithium aluminium mesotrisilicate,** $LiAlSi_3O_8$, m.p. 1180°; and **lithium aluminium paratetrasilicate,** $LiAlSi_4O_{10}$, m.p. 1200°.

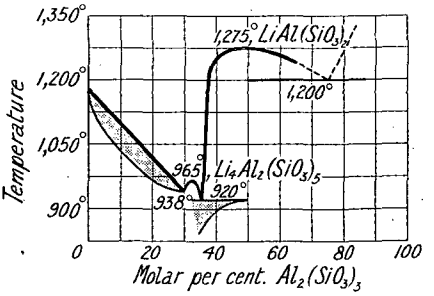



FIG. 135.—Freezing-point Curves of the Binary System: $Li_2SiO_3$–$Al_2(SiO_3)_3$.

Spodumene occurs in cleavable masses, and in prismatic crystals which are white and may be tinged green, grey, or yellow. There are also blue, rose, and lilac-coloured crystals—*e.g.* kunzite—and green crystals of hiddenite. F. A. Genth[3] found 0·18 per cent. of chromic oxide in green hiddenite. The crystals of spodumene usually appear as flattened prisms, and very large crystals have been reported. W. P. Blake mentioned crystals from the Black Hills, South Dakota, 36 ft. in length and 1–3 ft. in thickness; F. L. Hess, one 42 ft. in length and approximately 3 ft. by 6 ft. in cross-section; V. Ziegler, one 42 ft. long and 5 ft. 4 ins. maximum diameter, and it weighed 90 tons; and W. T. Schaller, one 47 ft. long. R. J. Haüy said the crystals are rectangular octahedra; and observations were made by J. D. Dana, R. Hermann, and A. des Cloizeaux. According to G. vom Rath, the crystals belong to the monoclinic system, and have axial ratios $a:b:c$ $=1·1283:1:0·62345$, and $\beta=69°\ 32\frac{1}{2}'$; and E. S. Dana gave $1·1283:1:0·6355$, and $\beta=69°\ 40'$. K. Endell and R. Rieke say that the crystals become isotropic at about 950°. The (110)-cleavage is well marked. The crystals sometimes have a lamellar structure, and can be separated or parted into thin plates parallel to the (100)-face. Twinning occurs on the (100)-plane. Corrosion figures produced by a natural solvent have been found by E. S. Dana on some crystals of hiddenite; and G. Greim obtained similar figures by etching with hydrofluoric acid. G. Greim also gave for the optic axial angle $2H=64°\ 47'$ for red light; $64°\ 58\frac{1}{2}'$ for Na-light; and $65°\ 4\frac{1}{2}'$ for blue light.

The sp. gr. of many of the natural spodumenes analyzed ranged from 3·1–3·2; their hardness varied from 6–7. F. M. Jäger and A. Simek determined the sp. gr. of a number of natural kunzites, and found 2·411 at 25° for the sp. gr. of synthetic spodumene. K. Endell and R. Rieke stated that the sp. gr. of spodumene is not affected by heating it to 920° and cooling rapidly, but at 980° it is diminished from 3·147–2·370. R. Ballo and E. Dittler called the mineral **α-spodumene,** and found that at about 1000° there is an irreversible transition temp. into **β-spodumene** whereby the sp. gr. falls from 3·17–2·41. Natural α-spodumene is slowly transformed to β-spodumene at temp. as low as 690°, and the change progresses with an increasing velocity as the temp. is raised. The term β-spodumene is no longer applied to the natural mixture of albite and eucryptite (*q.v.*). Fused spodumene rapidly cooled furnishes a colourless glass of sp. gr. 2·362. Synthetic **γ-spodumene** has a sp. gr. 2·3127; and kunzite which has been transformed into γ-spodumene by melting and recrystallizing by slow cooling has virtually the same sp. gr. 2·3130. The curve, Fig. 136, represents the average results of K. Endell and R. Rieke, and R. Ballo and E. Dittler on the sp. gr. of spodumene, which has

been heated to the temp. indicated and rapidly cooled. The slope of the curve at any temp. represents the speed of the transformation. F. Meissner believes that $\beta$- and $\gamma$-spodumene are the same and that the m.p. and refractive indices are the same. K. Endell and R. Rieke gave 1380° for the m.p. of spodumene; R. Ballo and E. Dittler, 1275° for the m.p. of $\gamma$-spodumene; and F. M. Jäger and A. Simek, 1400°. A. Brun gave 1010° for the m.p. of spodumene, but, as just indicated, this number is too low; J. Joly gave 1173°; and A. L. Fletcher, 1223°. F. M. Jäger and A. Simek measured the m.p. of a number of natural kunzites and found them to be higher than synthetic spodumene. Hence they inferred that the m.p. decreased as the sp. gr. increased. The observed difference in the m.p. of $\beta$-spodumene (1380°) and $\gamma$-spodumene (1290°) is attributed by F. Meissner to the low fusion and crystallization velocities. From his experiments on the action of soln. of the alkali salts on spodumene before and after fusion, J. Lemberg assumed that the melting is accompanied by the decomposition: $2(Li_2O.Al_2O_3.4SiO_2) = Li_2O.Al_2O_3.6SiO_2 + Li_2O.Al_2O_3.2SiO_2$. K. Schulz gave 0·2161 for the sp. ht. of spodumene. F. M. Jäger and A. Simek concluded that the natural kunzites, hiddenites, and spodumenes are metastable varieties ($\alpha$-spodumenes) of the compound, and that $\gamma$-spodumene is the stable form at all temp. below 1400°. The natural spodumenes cannot therefore be produced from dry magmas, and it is probable that their formation is due to so-called hydrothermal synthesis. R. Lorenz and W. Herz studied the relation between the m.p. and the transition temp. G. Tammann gave 714 cals. for the heat of soln. per gram in a mixture of hydrofluoric and hydrochloric acids.

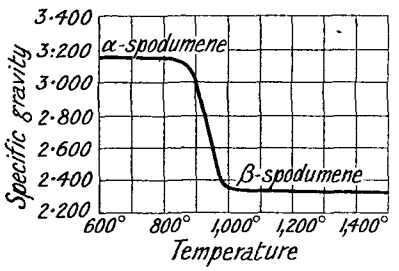



FIG. 136.—Effect of Temperature on the Specific Gravity of Spodumene.

A. Michel-Lévy and A. Lacroix gave for the indices of refraction of the mineral $\alpha$=1·660, $\beta$=1·666, and $\gamma$=1·676 for red light; while A. des Cloizeaux gave $\alpha$=1·651, $\beta$=1·669, and $\gamma$=1·677 for yellow light. L. Duparc and co-workers obtained:

| | White. | | | Green. | | | Rose-red. | | |
|---|---|---|---|---|---|---|---|---|---|
| | $\alpha$ | $\beta$ | $\gamma$ | $\alpha$ | $\beta$ | $\gamma$ | $\alpha$ | $\beta$ | $\gamma$ |
| Li-ray | 1·6567 | 1·6617 | 1·6719 | 1·6652 | 1·6682 | 1·6673 | 1·6567 | 1·6617 | 1·6722 |
| Na-ray | 1·6604 | 1·6648 | 1·6755 | 1·6682 | 1·6712 | 1·6815 | 1·6603 | 1·6653 | 1·6758 |
| Tl-ray | 1·6634 | 1·6680 | 1·6791 | 1·6717 | 1·6742 | 1·6837 | 1·6634 | 1·6681 | 1·6694 |

K. Endell and R. Rieke found the birefringence disappears after heating the mineral to 980°, or the very finely powdered mineral to 950°. They found the mean refractive index of spodumene is 1·66; and that of the glass, 1·519. R. Ballo and E. Dittler gave for $\alpha$-spodumene, 1·665; for $\beta$-spodumene, 1·527; for glassy spodumene, 1·519; for $\gamma$-spodumene (synthetic), 1·525; and for $\gamma$-spodumene from re-crystallized kunzite, 1·523. F. M. Jäger and A. Simek gave 1·521. The crystals are optically positive. E. S. Dana found the pleochroism to be strong particularly in the deep green varieties. As indicated above, A. Piutti [4] said that the mineral is not radioactive. C. Doelter found that by exposing kunzite to radium rays, it is coloured green; spodumene does not change; and hiddenite becomes bluish-green. He found that kunzite becomes colourless at 400°, and rose at 240°. Calcined kunzite becomes green when exposed to radium rays. The green colour changes to lilac when the mineral is heated to 200° in a stream of oxygen. C. Baskerville and G. F. Kunz found that kunzite has a red phosphorescent glow when exposed to radium rays; according to S. Meyer, the light is polarized. Spodumene and hiddenite do not phosphoresce under these conditions. F. H. Glew,

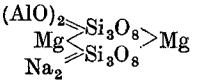
K. Przibram, and E. Newbery and H. Lupton also investigated the action of radium rays on kunzite. C. Doelter found that green kunzite is thermoluminescent at 40°; and kunzite is luminescent in X-rays, and in ultra-violet light. Thirty hours' exposure to X-rays produced a perceptible change in the colour of kunzite; hiddenite became greener. C. Doelter said that spodumene and hiddenite are almost transparent to the X-rays. Ultra-violet rays restore the original colour to green kunzite, but hiddenite is not changed. The subject was also studied by S. C. Lind and D. C. Bardwell.

G. A. Kenngott [5] found that powdered and moistened spodumene has an alkaline reaction both before and after calcination; but the powdered glass does not give the reaction. Spodumene is not attacked by the ordinary acids, although, as indicated above, it is attacked by hydrofluoric acid. J. Lemberg investigated the prolonged action of soln. of potassium and sodium carbonates, and potassium and sodium chlorides at 100°-230°, on both natural and glassy powdered spodumene. The lithium is displaced by potassium and sodium; and in some cases silica is removed as alkali silicate. The alteration of spodumene in nature was studied by A. A. Julien, C. R. van Hise, and G. J. Brush and E. S. Dana. Percolating soln. of sodium salts change it to eucryptite and albite. This mixture was once called *β-spodumene—vide* eucryptite. By the further action of potassium salts, the eucryptite is converted into muscovite. Thus, albite and muscovite appear as end-products of this reaction, and the mixture of albite and muscovite was called *cymatolite* by J. D. Dana; and *aglaite* by A. A. Julien. T. Thomson described an alteration product of spodumene from Killiney Bay, Ireland. This mineral is not unlike cymatolite. It was called *killinite*.

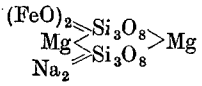
A. Damour [6] applied the term **jadeite** to a jade-like mineral from Eastern Asia. The colour is nearly white with a green tinge, leek-green, emerald-green, apple-green, or bluish-green. He also applied the term *chloromelanite*—from χλωρός, green; μέλας, black—to a dark green, almost black, variety—*vide* jade and nephrite. The analyses have been discussed under the last-named minerals. The results show that jadeite can be regarded as a *soda-spodumene*, $NaAl(SiO_3)_2$, **sodium aluminium dimetasilicate.** It is known only in a massive form with a crystalline or granular structure, and it may be obscurely fibrous. The crystals are monoclinic (or triclinic) with optical characters like the pyroxenes. The crystalline structure has been discussed by A. des Cloizeaux, E. Cohen, A. J. Krenner, and A. Arzruni. For Na-light, A. Michel-Lévy and A. Lacroix gave for the optic axial angle $2V=70°$; and A. J. Krenner, $2H=82°\ 48'$. A. Michel-Lévy and A. Lacroix found the birefringence $\gamma-\alpha=0{\cdot}029$. The sp. gr. is 3·30–3·35, and the hardness, 6–7. S. Weidmann referred to a pyroxene related to jadeite which he called *percivalite*. It is from the pegmatite deposits of Wisconsin; its composition indicates that it is a mixture of jadeite and acmite. H. S. Washington found a pea-green jade ornament near San Andrés de Tuxtla, Mexico, of date about 96 B.C.; its composition corresponded with a mixture of equal parts of jadeite and diopside, $NaMgCaAlSi_4O_{12}$. He called the mineral *tuxtlite*. The sp. gr. was 3·270; the hardness, 6·5; $\alpha=1{\cdot}666$, $\beta=1{\cdot}674$, and $\gamma=1{\cdot}688$; the birefringence, $\gamma-\alpha=0{\cdot}022$; the optical axial angle, 75°; and the optical character, negative. The minerals whose composition corresponded with solid soln. of textlite and albite were called *mayaite*—from the Maya nation.

J. F. L. Hausmann [7] described a green amphibole from Syra, one of the Cyclades Islands, but it has since been shown to be widely distributed. He called the mineral **glaucophane**—from γλαυκός, bluish-green; and φαίνεσθαι, to appear. G. Strüver called the mineral from Valle Grande di Lanzo, *gastaldite*—after B. Gastaldi. Analyses have been reported by C. Bodewig, O. Luedecke, F. Berwerth, A. von Lasaulx, E. Schluttig, G. Strüver, F. Zambonini, L. Milch, W. C. Blasdale, A. Johnsen, B. Koto, A. Liversidge, C. Barrois and A. Offret, H. S. Washington, U. Grubenmann, and H. B. Foullon. C. F. Rammelsberg regarded glaucophane as a complex mixture of $Na_2SiO_3$, $RSiO_3$, and $R_2'''(SiO_3)_3$; various other forms of

the mixture hypothesis were proposed by C. Doelter, L. Milch, U. Grubenmann, and C. W. Blasdale. Idealized glaucophane is represented as sodium aluminium dimetasilicate, $NaAl(SiO_3)_2$; and this is normally associated with ferromagnesian metasilicate, $(Fe,Mg)SiO_3$, and calcium metasilicate. F. W. Clarke regarded it as a trisilicate, analogous to crocidolite,



Glaucophane.



Crocidolite.

A. Osann reported a *lithium-glaucophane* which was named *holmquisite*—after P. J. Holmquist—in the iron ores of Utö, Sweden. It contains 2·13 per cent. $Li_2O$, so that part of the soda of glaucophane is replaced by lithia. The mineral is optically negative, with $2E=68°\ 56'$. Glaucophane is the amphibolic equivalent of the pyroxene, jadeite; and its composition was studied by B. Gossner.

Glaucophane occurs as the hornblendic constituent of some crystalline schists, mica schists, amphibolytes, gneiss, eclogytes, etc. B. Koto regarded it as a secondary product of the alteration of diallage. The subject has been discussed by H. Rosenbusch, L. Milch, G. F. Becker, K. Oebbeke, H. S. Washington, and J. P. Smith. Glaucophane has not been synthesized artificially. C. Doelter found that like other amphiboles, it furnishes a pyroxene when fused and crystallized. When heated along with magnesium, calcium, and sodium chlorides in a current of steam, C. Doelter obtained a product like glaucophane in some respects. The colour of glaucophane is azure-blue, lavender-blue, bluish-black, and grey. It commonly occurs massive, fibrous, columnar, or granular. The crystals are prismatic and monoclinic, closely resembling the amphiboles in form. The axial ratios are $a:b:c=0·53:1:0·29$, and $\beta=105°$. Observations were made by C. Bodewig, A. von Lasaulx, O. Luedecke, and G. Strüver. The cleavage parallel to (110) is complete. The optic axial angle for Na-light is $2E=85°\ 35'$; and, according to G. Strüver, $2V=43°\ 58'$. S. Kreutz gave $2E=72°\ 55'$ and $2V=42°\ 24'$ for red light, and $2E=72°\ 36'$ for green light. The sp. gr. ranges from 3·0–3·1, and the hardness 6. C. Doelter gave 1040°–1060° for the m.p. The mineral becomes brown when calcined. E. T. Allen and J. K. Clement discussed the nature of the water which is present to the extent of 1·78–2·57 per cent. in samples dried at 100°. E. Wallerant gave for the indices of refraction $\alpha=1·6212$, $\beta=1·6381$, and $\gamma=1·6390$; and S. Kreutz, $\alpha=1·630$, $\beta=1·646$, and $\gamma=1·648$. For the birefringence, $\gamma-\alpha=0·0178$, $\beta-\alpha=0·0169$, and $\gamma-\beta=0·0009$. The optical character is positive. The pleochroism is strongly marked. Observations were made by C. Bodewig, G. Strüver, A. von Lasaulx, A. Michel-Lévy, A. Stelzner, C. Barrois, F. Becke, B. Koto, J. W. Retgers, A. Wichmann, F. Becke and E. Schluttig. In general, *a* is yellowish-green to colourless; *b*, reddish-violet; and *c*, sky-blue to ultramarine-blue. K. Oebbeke noted the change which occurs after the mineral has been calcined. O. Mügge noted the formation of pleochroic halos when glaucophane is exposed to radium radiations. The mineral is scarcely affected by acids. L. Colomba described the alteration of glaucophane into chlorite, felspar, and hæmatite.

B. Faujas de St. Fond[8] mentioned the occurrence of pellucid crystals of a *zeolithe dure* on the Cyclopean Islands, Sicily; L. A. Emmerling, D. G. J. Lenz, and J. C. Delamétherie called it *zeolithe cubique*, and *zeolithe leucitique*; and R. J. Haüy called it *analcime*—from ἄναλκις, weak—in allusion to its feeble electrification when rubbed. D. de Gallitzin altered the name to **analcite.**

J. G. Werner called analcite *kubizite*, and also *analzim*; and A. Breithaupt, *kuboid*. The *picranalcime*—from πικρός, bitter—of G. Meneghini and E. Bechi, stated to contain about 10 per cent. of magnesia, proved, when analyzed by E. Bamberger, to be ordinary analcite. J. Esmark obtained a compact analcite from a number of islands on the Langesund fiord, Norway, and it was named *euthallite*—from εὖ, well; and θαλλός, a green twig

—in allusion to the colour. P. C. Weibye found rhombic crystals of a mineral on islands in the Langesund fiord, Norway, and he called it *eudnophite*—from εὐδνοφος, duskiness—in allusion to the cloudiness of the mineral. The crystals were examined by A. des Cloizeaux, E. Bertrand, and A. Lacroix. W. C. Brögger showed that the mineral is nothing but analcite with an unusually strong double refraction. T. Thomson found in the Kilpatrick Hills red vitreous crystals of a mineral approaching analcite in properties. It was named *cluthalite*—from Clutha, an old name for the Clyde Valley. It is considered to be an altered analcite. E. Bertrand examined its optical properties. F. Berwerth named a black-coloured rhombic mineral in a meteorite from Kodaikanal, Madras, *weinbergite*—after J. Weinberger—its composition corresponded with $9\{(Na,K)_2Al_2Si_2O_8\}.51(Mg,Ca,Fe)SiO_3$, or, more generalized, $Na_2O.6FeO.Al_2O_3.8SiO_2$; and it is assumed to be a mixture of $NaAlSiO_4+3FeSiO_3$. It is optically negative, has small axial angles, and a weak index of refraction and birefringence.

The first analyses of analcite were made by L. N. Vauquelin[9] in 1807, and H. Rose made more accurate ones in 1822. Many analyses of analcite have since been made. C. F. Rammelsberg[10] at first regarded the contained water as eq. to water of crystallization; later, he gave the formula $H_4Na_2Al_2Si_4O_{14}$. The formula usually accepted is $Na_2Al_2(SiO_3)_4.2H_2O$, or, as P. Groth puts it, *sodium aluminium dimetasilicate*, $NaAl(SiO_3)_2.H_2O$; but H. W. Foote and W. M. Bradley showed that in the published analyses, the ratio $Na_2O : Al_2O_3$ is nearly 1 : 1, and the ratio $H_2O : SiO_2$ is very close to 1 : 2; but there is no simple ratio between the alumina or soda and silica or water. G. Tschermak represented analcite as constituted of four alumino-silicates. J. Jakob represented it by the co-ordination theory:

$$[Al(SiO_4.SiO_2)_3]^{Al}_{(H_2O,Na)_3}$$

G. Friedel showed that over 100° there is a state of equilibrium between the vap. press. of the zeolites and the water vapour in the air; and for a given weight of mineral the vap. press. depends on the area of the exposed surface. He measured the dehydration curve of analcite—*vide infra*. F. W. Clarke and G. Steiger found:

| | 100° | 180° | 260° | 300° | 350° | Low redness |
|---|---|---|---|---|---|---|
| Loss of water | 0·13 | 0·75 | 2·44 | 1·28 | 1·76 | 2·03 per cent. |

They regarded the water as extrinsic and, from their experiments on the action of ammonium chloride vap. resulting in the formation of *ammonium aluminium dimetasilicate*, $(NH_4)Al(SiO_3)_2$, wrote the formula $Na_4Al_4Si_8O_{24}$, or:

$$Al{\equiv}Si_3O_8{-}Al\begin{matrix}<SiO_4>Na_2\\<SiO_4>Na_2\end{matrix}Al{-}SiO_4{\equiv}Al+4H_2O$$

R. Brauns regarded the part of the water as intrinsic or constitutional, and wrote the formula $Al:SiO_3.O.Si(OH)_2(ONa)$. C. Doelter, and E. T. Wherry consider that analcite is not a zeolite because it does not show the peculiar dehydration phenomena characteristic of zeolites. It is considered to be related with leucite. E. T. Wherry assumed that the mol. vol. of K and of $(Na+H_2O+x)$ are alike, and can replace one another isomorphously. From observations on the action of salt soln. on analcite, G. Tschermak, and C. Doelter regarded the mineral as a complex mixture or solid soln. of silicic acid and an anhydrous aluminosilicate, $Na_2Al_2Si_2O_8.H_4Si_2O_6$. H. W. Foote and W. M. Bradley also explained the variation in composition of analcite by assuming that a solid soln. of some other compound is present—presumably silicic acid, $H_2Si_2O_5$; $H_4Si_2O_6$; etc. Water in analcite does not behave like ordinary water of crystallization, and the vap. press. at a given temp. is not constant. This is taken to support this hypothesis. J. Lemberg inferred that the formula should be at least doubled. G. Stoklossa assumed that the water of analcite is chemically bound in the mol. There is a break in the dehydration curve of analcite dehydrated at different temp., and this is taken to correspond with the existence of a definite hydrate.

Analcite has been synthesized by hydrothermal processes, working under press. C. Doelter said the sphere of existence of analcite at high press. is from about 180°–500°. The reaction with nephelite is reversible; using simplified formulæ: $2NaAlSiO_4+H_2O \rightleftharpoons NaAlO_2+NaAl(SiO_3)_2.H_2O$; raising the temp. favours the system on the left, and conversely. Thus, he obtained analcite by heating nephelite with an aq. soln. of alkali carbonate in presence of free carbon dioxide at 200°; and with water and analcite at 400° he obtained some nephelite. If C. R. van Hise[11] is right in saying that there is a 5·49 per cent. increase in vol. when nephelite passes into analcite, a high press. is not suited for the conversion of nephelite into analcite. J. Lemberg, and S. J. Thugutt showed that when leucite is heated to 180°–195° along with a soln. of sodium chloride or carbonate, analcite is formed. The reaction is reversible. They also obtained analcite by the prolonged digestion of andesine or oligoclase with a soln. of sodium carbonate at 210°–220°. S. J. Thugutt found the reaction with andesine is not reversible. E. A. Stephenson obtained analcite by the action of soln. of sodium carbonate or hydrocarbonate on adularia at temp. ranging from 183°–233°. C. Doelter represents the conversion of albite into analcite as a reversible reaction: $NaAl(SiO_3)_2.H_2O+SiO_2 \rightleftharpoons H_2O+NaAlSi_3O_8$, when the left to right reaction requires a high temp.—over 420°, according to C. Doelter; over 520°, according to E. Baur. A. de Schulten made analcite by heating to 180°–190° a mixture of sodium silicate and hydroxide, and water in contact with aluminous glass; and by heating to 180° for 18 hrs. mixed soln. of sodium silicate and aluminate in proper proportions. C. Friedel and E. Sarasin prepared analcite by heating precipitated aluminium silicate, sodium silicate, and water in a sealed tube at 500°. E. Baur likewise made analcite crystals from a mixture of silica, sodium aluminate, aluminium hydroxide, and water in a steel tube at 350°–450°; and C. Doelter also formed analcite from mixtures of soln. of silica, alumina, and soda, or of silicic acid, aluminium chloride, and sodium carbonate at 100°–400°. J. Königsberger and W. J. Müller found that the formation of zeolites, in the absence of carbon dioxide in the system, $K_2O-Al_2O_3-SiO_2-H_2O$, commences below 100°, and may increase up to 400°, but probably their limit of stability, with the exception of analcite, is below 300°.

Analcite is readily formed as a secondary mineral, the product of the so-called *zeolitization*; and when formed with other zeolites, it is one of the first to appear. Alterations of leucite into analcite have been observed by A. Sauer,[12] F. Zambonini, J. E. Hibsch, H. S. Washington, S. J. Thugutt, W. H. Weed and L. V. Pirsson, J. F. Williams, E. Scacchi, E. Hussak, etc.; and W. C. Brögger noted the formation of analcite from elæolite and ægirite. Analcite may also be formed as a pyrogenic primary mineral in deep-seated rocks, where it was probably formed under press. Numerous observations have been reported in support of this statement.

Analcite may occur massive or granular; in composite groups of crystals, or in single crystals, usually in trapezohedra, or cubes, belonging to the cubic system. The cleavage is feebly cubic. Analcite may be colourless, white, or tinged grey, green, yellow, or red. The sp. gr. of many of the samples analyzed were determined, and the data range from about 2·15–2·35—thus, G. dal Piaz[13] gave 2·195; B. Popoff, 2·2145; E. Billows, 2·28; and E. Vaccari, 2·35. J. Königsberger and W. J. Müller gave 2·2 for the sp. gr. of the artificial crystals. G. Friedel found that the expulsion of water from analcite is attended by a contraction, thus:

| | | | | | |
|---|---|---|---|---|---|
| Water lost . . . | 0 | 3·60 | 6·29 | 8·02 per cent. |
| Sp. gr. . . . | 2·277 | 2·205 | 2·150 | 2·141 |
| Contraction . . . | 0 | 0·5 | 0·88 | 2·15 per cent. |

After a prolonged ignition, the sp. gr. rose to 2·437. The hardness of analcite is between 5 and 5½. G. Friedel found that when analcite is heated so that it loses water, it retains its original form and the refractive index is increased. At ordinary temp., the dehydrated mineral does not resorb water, but at about 100°,

it will absorb water from the air and return to its original composition. C. Doelter found melted analcite gives no crystalline products on cooling. F. Pfaff found the mean coeff. of linear expansion between 0° and 100° to be 0·0009261; A. Bartoli gave for the sp. ht., 0·226 between 23° and 100°, and 0·246 between 29° and 492°. G. Tammann gave for the heat of the formation 85·22 Cals. per mol, or 0·215 Cal. per gram. O. Mulert found the heat of soln. in dil. acid to be 0·5688 Cal. per gram. According to G. Friedel, if the dehydrated mineral be mixed with a few drops of water, combination occurs with great energy; heat is evolved, and at the same time much air is liberated; the resorption of water by analcite is attended by the evolution of 740 cals. per gram. A. des Cloizeaux gave for the index of refraction 1·4874 for the red ray; C. S. Ross and E. V. Shannon gave 1·486; and K. Zimanyi, 1·4861–1·4881 for the yellow ray. J. Königsberger and W. J. Müller found the refractive indices of artificial analcite are perceptibly higher than that of the natural.

Although the crystals belong to the cubic system and are isotropic, D. Brewster noticed that they are sometimes optically anomalous, and exhibit a weak double refraction. The phenomenon was studied by J. B. Biot, A. des Cloizeaux, A. de Schulten, E. Bertrand, A. von Lasaulx, C. Stadtländer, G. Friedel, A. Merian, A. Arzruni and S. Koch, R. Brauns, etc. A. Schrauf regards the crystals as pseudo-cubic and describes them as complex twins belonging to the rhombic system; and E. Mallard proposed a similar explanation. A. Ben-Suade explained the phenomenon as a result of internal strains, and obtained similar effects from solidified gelatine cast in moulds. C. Klein showed that when heated in an atm. of water vap. or placed in hot water, the anomalous crystals became isotropic, while with a dry heat, the birefringence was increased. Hence, he attributed the anomalous effect to the change in mol. arrangement which results from the loss of a little water. F. Rinne found that analcite which has been ignited is triclinic, and he calls the product *soda-leucite*, which is analogous with potash- or ordinary leucite in the same sense that monoclinic potash-felspar is analogous with triclinic soda-felspar. T. Liebisch and H. Rubens found the reflection spectrum in the ultra-red had a maximum over $10\mu$, and a minimum at $80\mu$. K. Brieger found a maximum corresponding with that of water. W. W. Coblentz found the ultra-red transmission spectrum of analcite has the water bands at $1{\cdot}5\mu$, $2\mu$, and $4{\cdot}7\mu$ quite obliterated. C. Doelter found that in a thin layer analcite is transparent to the X-rays, but in layers over 3 mm. it is almost opaque. J. Königsberger and W. J. Müller found 6·7 for the dielectric constant.

G. A. Kenngott,[14] and E. W. Hoffmann found that analcite moistened with water has an alkaline reaction. G. Steiger found analcite to be markedly soluble in water. According to G. Friedel, the water in the zeolites is not in chemical combination in the common sense of the word, and it can be replaced by various gases, and even by solids such as silica, without alteration in the crystalline form or optical properties of the minerals. Dehydrated analcite absorbs ammonia in large quantity with great energy and development of heat, the quantity absorbed being independent of the nature of the zeolite and proportional to the quantity of water previously expelled. When exposed to moist air, the ammonia is gradually expelled, and its place is taken by water. In the case of analcite the analogy is very close; the ammonia, like water, is not absorbed by the mineral if dehydrated below 100°, and it is not displaced by atm. moisture at the ordinary temp. J. Königsberger and W. J. Müller found that analcite dissolves in hydrochloric acid often leaving a skeleton of gelatinous silica. C. G. C. Bischof found that a soln. of calcium sulphate displaces some sodium from analcite. J. Lemberg studied the action of soln. of sodium and potassium carbonates; ammonium, potassium, and sodium chlorides; potassium hydroxide; and calcium chloride. In general, there is an interchange of bases; with sodium silicate a substance like cancrinite is formed with $SiO_3$ in place of $CO_3$. F. W. Clarke, and G. Steiger examined the action of ammonium chloride vap. in sealed tubes at about 350°, and, as indicated above, obtained ammonium-analcite. G. Steiger studied the action of soln.

silver nitrate, and obtained *silver-analcite*, or *silver aluminium dimetasilicate*, $AgAl(SiO_3)_2.H_2O$. H. C. McNeil studied the action of barium chloride on the mineral and obtained a *barium-analcite*.

J. J. Ferber,[15] I. S. R. I. Eques a Born, N. T. de Saussure, B. G. Sage, J. B. L. Romé de l'Isle and C. A. S. Hoffmann referred to *weisse Granaten*, *basaltes albus*, *grénats blancs*, or white garnet occurring at Vesuvius and Monte Somma. They said that it is a garnet which has been *altérés par une vapeur acide qui ayant dissout le fer a laissé les grénats dans un état de blancheur*. A. G. Werner distinguished the mineral from garnet, and called it **leucite**—from λευκός, white—in allusion to its colour. R. J. Haüy proposed *amphigène*—from ἄμφι, both; and γένος, kind—in allusion to the supposed existence of cleavage in two directions. M. H. Klaproth analyzed the mineral, and said:

> I was surprised in an unexpected manner by discovering a constituent part consisting of a substance whose existence, certainly, no one person would have conjectured within the limits of the mineral kingdom. . . . This constituent part of leucite is no other than potash, which, hitherto, has been thought exclusively to belong to the vegetable kingdom, and has, on this account, been called vegetable alkali.

M. H. Klaproth's analysis was quite good. A. von Awdejeff found soda to be also present; T. Richter detected traces of lithia; and J. L. Smith, traces of cæsia and rubidia. Many other analyses have been made.[16] C. Matignon [17] and others have described various deposits and the methods of working them as a source of potassium salts for agriculture, etc. C. F. Rammelsberg's summary [18] of the analyses corresponded with the formula $K_2O.Al_2O_3.2SiO_2$, or $KAlSi_2O_6$, *i.e.* **potassium aluminium dimetasilicate.** Up to about 6·5 per cent. of $Na_2O$ may also be present. This is not likely to be present as albite, and it is assumed that a *soda-leucite* is associated with potash-leucite. Soda-leucite does not occur in nature, but sodium aluminium dimetasilicate, $NaAl(SiO_3)_2$, has been made by J. Lemberg. He also replaced the potassium in leucite by beryllium. S. J. Thugutt infers that leucite is really a polymer, and is the potassium salt of a complex acid, $H_2Al_2(SiO_3)_2.nH_2O$. F. W. Clarke also believes that the ordinary formula should be quadrupled, making

$$Al{=}Si_3O_8{-}Al\begin{matrix}<SiO_4\\<Si_3O_8\end{matrix}\begin{matrix}>K_2\\>Al{-}SiO_4{=}Al\\>K_2\end{matrix}$$

analogous to sodalite (*q.v.*). G. Tschermak studied the silicic acid liberated when leucite is treated with hydrochloric acid at room temp., and he called the product *leucitic acid—vide supra*. His formula for leucite is therefore $KO.SiO.O.SiO_3.Al$. F. W. Clarke showed that although leucite and analcite are usually separated in mineralogical systems of classification, for one is placed with felspars and the other with zeolites, yet they are so similar in form, composition, and properties, that they cannot be adequately studied apart.

Leucite is a comparatively rare mineral; it is common in recent lavas; but it is not found in the older deep-seated rocks. This may be due to its easy alteration into other species, more probably due to the instability below the temp. 1170°, when it passes into orthoclase if silica be present: $KAl(SiO_3)_2+SiO_2=KAlSi_3O_8$—*vide* Fig. 154. It is formed in rock magmas only when the potassium is in excess of that required for the production of felspar; and A. E. Lagorio [19] found that in a leucite-tephrite magma, kept at red heat, leucite crystallizes out; and if the temp. be raised, the leucite dissolves, while if lowered, the mass becomes so viscous that crystallization ceases. This emphasizes the narrow range of temp. in the formation of leucite in rock magmas. A. Himmelbauer found leucite is formed when analcite is digested with a mixed soln. of potassium hydroxide and chloride—*vide infra*. F. Fouqué and A. Michel-Lévy showed that leucite can be formed by simply fusing together its constituent oxides, and also, along with other minerals, by fusing various rock magmas—*e.g.* a mixture of biotite and microcline; C. Doelter

obtained it when muscovite, lepidolite, or zinnwaldite are fused alone; and G. W. Morey and N. L. Bowen, by heating orthoclase (*q.v.*) above 1170°. Similar observations were made by K. Petrasch, K. Schmutz, G. Medanich, J. Lenarcic, and K. Bauer. P. Hautefeuille also fused a mixture of potassium aluminate and vanadate, and silica at 800°–900° for nearly a month, and obtained measurable crystals of leucite; similar crystals were obtained by fusing muscovite or a mixture of the constituent oxides along with potassium vanadate. S. Meunier made leucite by the action of silicon tetrachloride on aluminium turnings impregnated with alkali-lye; A. Duboin, by fusing a silicic acid or potassium fluosilicate and alumina in the presence of an excess of potasssium fluoride; and C. and G. Friedel, hydrothermally, by heating a mixture of muscovite, silica, and potash-lye in a steel tube at 500°.

F. Fouqué and A. Michel-Lévy suppose that a *lithia-leucite* is obtained of sp. gr. 2·41, by fusing a mixture of silica, alumina, and an excess of lithium vanadate or tungstate. It is not clear if this product is not after all a spodumene. Spodumene itself is trimorphous. According to C. Doelter, when potash-lithia mica is melted there is an isomorphous mixture of $KAl(SiO_3)_2$ and $LiAl(SiO_3)_2$ formed; and it is therefore assumed that spodumene can also crystallize in the form of leucite. Jadeite and glaucophane are probably related to a *soda-leucite*; and C. Doelter made soda-leucite by melting a mixture of andalusite and sodium fluoride. P. Hautefeuille and A. Perrey made crystals of what they regarded as *beryllia-leucite*, $KBe(SiO_3)_2$; and P. Hautefeuille, crystals of *ferric-leucite*, $KFe(SiO_3)_2$—*vide* silicates of beryllium and of iron.

Leucite occurs in pseudo-cubic crystals; in disseminated grains; and is rarely massive and granular. The colour is white, ash-grey, or smoke-grey. Leucite crystallizes in icositetrahedra which are so characteristic that this form has been called the *leucitohedron*. Fig. 137, by G. vom Rath.[20] In consequence, up to about 1870 the crystals were said to belong to the cubic system. About 50 years earlier, however, D. Brewster showed that the crystals are birefringent, and even biaxial in parts. These peculiarities were supposed to be the result of internal strains set up during crystallization as a result of cooling; and to be similar to the double refraction observed in chilled or compressed glass. J. B. Biot, A. des Cloizeaux, and F. Zirkel showed that the crystals are traversed by twin lamellæ parallel to the four faces (011), (0$\bar{1}$1), (101), and ($\bar{1}$01), of the dodecahedron; and the optical anomaly was accordingly attributed to the lamellar structure. If the dodecahedral face be a plane of symmetry, it cannot also be a twinning plane, and the crystals cannot therefore be cubic. G. vom Rath then showed that the angles between the faces are not those of the icositetrahedron which should be 48° 11½′; actually, the terminal faces, *o*, are inclined at an angle 49° 57′ and the lateral faces, *i*, 48° 37′. He therefore suggested that leucite belongs to the tetragonal system, and consists of a tetragonal bipyramid, *o*(112), and a ditetragonal bipyramid, *i*(211), twinned on the faces of the tetragonal bipyramid, (101). H. Baumhauer found the corrosion figures agreed with those of the tetragonal sytem. The subject was discussed by A. Scacchi, J. Hirschwald, A. des Cloizeaux, G. Tschermak, and P. Groth. If the crystals be tetragonal, they should be uniaxial; but although they are uniaxial in parts, they are biaxial in other parts. E. Mallard considered that the uniaxial parts are due to the overlapping of biaxial lamellæ; so that the crystals are really biaxial, and that their symmetry cannot be higher than that of the rhombic system. E. Mallard said that, optically, the crystals are monoclinic; and F. Fouqué and A. Michel-Lévy, triclinic. Later, A. Weisbach showed that the crystals are more probably rhombic (i) with twin lamellæ parallel to the dodecahedron faces (110) and (1$\bar{1}$0); (ii) referable to their rectangular axes in which the lateral axes are so nearly equal that angular measurements do not distinguish between tetragonal and rhombic symmetry; and

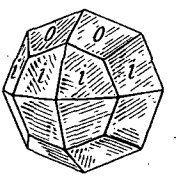


FIG. 137.—Icositetrahedral Leucite (the Leucitohedron).

(iii) traversed by so numerous and fine twin lamellæ that it is difficult to observe the biaxial figure of a homogeneous single crystal at any point in convergent light.

C. Klein showed that when the temp. of a section of leucite is heated to the beginning of redness, between crossed nicols, a dark shadow extends across the plate, and the leucite is then isotropic; H. Rosenbusch further showed that the twinning striations disappear on heating, and reappear in new positions on cooling. At the higher temp., therefore, leucite really belongs to the cubic system, and, on cooling, it probably breaks up into rhombic sections. S. L. Penfield, and O. Mügge gave 560° for the temp. of the enantiotropic change: $\alpha$-leucite$\rightleftharpoons\beta$-leucite. F. Rinne and R. Kolb said that at 684° the double refraction begins to diminish, and at 714° the crystals are isotropic. The transition is so sluggish that there appears an interval of 30° between the beginning and the end of the change. R. Lorenz and W. Herz studied the relation between the transition temp. and the m.p.

C. Doelter found the velocity of crystallization of leucite magma to be small, so that the velocity curve is flattened. L. Colomba investigated the influence of the cooling conditions on the transformation; and he found that a uniform press. of 6000 atm. has no appreciable influence. Skeleton forms of the crystals sometimes appear; and L. V. Pirsson has drawn a number of these representing various stages of growth. A selection is given in Fig. 138. The simplest forms have spurs attached to the four-fold cubic axes, *A*, Fig. 138; in *B*, these are thickened at the ends; and in *C*, the thickening has spread, and the icositetrahedron begins to appear. In the diagrams, the blackened areas represent the glassy base with inclusions. Spurs then appear along a two-fold axis as in *D*; and when these reach the margin, the form of the icositetrahedron is complete, *E*, and *F*, Fig. 138. Leucite may be free from inclusions, or inclusions of gas, glass, liquids, and minerals may occur. These minerals crystallized before the leucite, and they include augite, olivine, haüyne, nephelite, melanite, magnetite, picotite, and apatite. The inclusions may be arranged in clusters at the centre of the crystal; in one or more concentric zones; or in radial lines. The reason for the radial arrangement is indicated by L. V. Pirsson's study of the growth of the crystals. Some magma was first shut in, and afterwards separated into crystals. L. Colomba showed that crystals which have been formed in rapidly cooling rocks are apt to manifest anomalous characters, and a sectored structure. F. Zirkel, and H. Rosenbusch have made a special study of the inclusions.

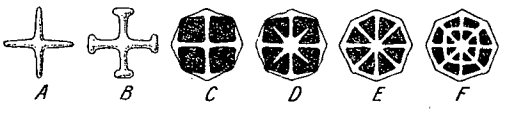


FIG. 138.—Skeleton Crystals of Leucite.

The sp. gr. of leucite ranges from 2·45–2·50—J. A. Douglas[21] gave 2·480 for the crystals, and 2·410 for the glass. V. Goldschmidt gave 2·464 for the crystals; C. F. Rammelsberg, 2·468–2·484; G. vom Rath, 2·479; L. Ricciardi, 2·480; and G. Tschermak, 2·469. The sp. gr. of many of the samples analyzed was also determined. The hardness is 5-6. J. Joly gave 0·1912 for the sp. ht., and G. Tammann, 0·178 for crystalline, and 0·175 for glassy leucite between 20° and 100°. The heat of soln. of crystalline leucite in 20 per cent. hydrofluoric acid is 507 cals. per gram, and of amorphous glassy leucite, 533 cals. per gram; hence the heat of crystallization is 26 cals. per gram. D. D. Jackson and J. J. Morgan found the vap. press. of the alkali vap. of leucite to be negligibly small below 1350°. According to O. Mulert, the heat of soln. in 20 per cent. hydrofluoric acid is 0·5187 Cal. per gram, or 226·8 Cals. per mol., and the heat of formation $K_2O+Al_2O_3+4SiO_2$ (amorphous)$\rightarrow K_2O.Al_2O_3.4SiO_2$ (crystalline)$+101{\cdot}8$ Cals. The mineral is said to be infusible in the ordinary blowpipe flame; G. Spezia fused it in a flame fed with oxygen. R. Cusack gave 1298° for the m.p.; A. L. Fletcher, 1348°; A. Brun, 1270°; and C. Doelter, 1275°–1315°.

The indices of refraction, according to A. des Cloizeaux,[22] are $\alpha=1{\cdot}508$, and $\gamma=1{\cdot}509$ for sodium light; K. Zimanyi obtained 1·5086. H. Rosenbusch, and

A. des Cloizeaux found very small crystals to be isotropic, and in thin sections, leucite is usually isotropic. F. Rinne and R. Kolb found the dispersion for $\alpha$-leucite at 21° from $A$ to $G$, 0·0142; and for $\beta$-leucite, at 750°, 0·0150. They gave for the indices of refraction of $\alpha$-leucite at 21°, and $\beta$-leucite at 750°:

| Line | $A$ | $B$ | $C$ | $D_2$ | $F$ | $G$ |
|---|---|---|---|---|---|---|
| $\alpha$-leucite | 1·5046 | 1·5054 | 1·5061 | 1·5088 | 1·5146 | 1·5188 |
| $\beta$-leucite | 1·4903 | 1·4912 | 1·4921 | 1·4947 | 1·5009 | 1·5053 |

The crystals are optically positive, but G. Tschermak found a specimen from Acquaacetosa to be optically negative. J. Schincaglia investigated the phosphorescence of leucite; C. Doelter found that it is not luminescent with radium rays; and that it is equal to muscovite in transparency to X-rays. W. Vernadsky did not find leucite triboluminescent.

G. A. Kenngott[23] found that the moistened powder of leucite has a stronger alkaline reaction than potash-felspar. J. Lemberg found that soln. of sodium chloride or carbonate transformed leucite into analcite. He investigated the action of soln. of sodium silicate in an autoclave at 190°–200°, and found the potassium was displaced by sodium, and analcite was formed. A. Himmelbauer showed that when analcite is digested with a mixed soln. of potassium hydroxide and chloride, leucite is formed. The reaction is reversible, $KAl(SiO_3)_2+NaCl+H_2O \rightleftharpoons H_2O+KCl+NaAl(SiO_3)_2$. Similar results were obtained by S. J. Thugutt, who said that the reaction progresses from left to right as well at ordinary temp. as it does at 200°; and in dil. soln. as in conc. soln. He also found that the complex is very stable; leucite is slightly soluble in a one per cent. soln. of potash-lye at about 200°; and it is not decomposed, but with a 30 per cent. soln. of alkali-lye, the leucite is decomposed, forming a substance resembling nephelite. H. Lotz found that a mixture of steam, air, carbon dioxide, and sulphur dioxide decomposes leucite. G. Tammann and C. F. Grevemeyer found that magnesia does not act on leucite at 1000°; lime acts slowly at 500°; and baryta acts strongly at 275°–350°. Several methods have been proposed for the extraction of potash from leucite—*e.g.* by C. Montemartini, G. A. Blanc, G. Rozzi, and J. W. Hinchley—*vide* **2**. 20, 4.

G. Steiger heated leucite with a soln. of thallium nitrate at 250°–290°, and obtained a substitution product—*thallium-leucite*. The natural transformation of leucite into analcite has been studied by A. Knop, C. F. Rammelsberg, A. Sauer, C. G. C. Bischof, and C. R. van Hise; into a zeolite, by E. Casoria, and J. Lemberg; into kaolinite, by E. Casorio, and C. R. van Hise; into orthoclase and muscovite, by J. F. Williams, E. Scacchi, G. F. Kunz, E. Hussak, C. R. van Hise, J. R. Blum, C. Bergemann, and A. Sauer; into calcium cancrinite, by G. Freda, F. Zambonini, A. Lacroix, C. Doelter, and J. Lemberg; into kaliophilite, by F. Zambonini, and G. vom Rath; and into a mixture of nephelite and sanidine—the so-called *pseudo-leucite*—by A. Sauer, T. T. Read and C. W. Knight, and J. Shand. F. Zambonini found pseudomorphs of nephelite after leucite and of leucite after nephelite (*q.v.*). The action of sodium hydroxide and various salt soln. on leucite was studied by H. Schneiderhölm.

O. B. Böggild[24] applied the term *ussingite*—after N. V. Ussing—to a reddish-violet-coloured, triclinic mineral from Kangerdluarsuk, Greenland. The analyses correspond with **sodium aluminium hydrotrimetasilicate,** $N_2HAl(SiO_3)_3$. Its sp. gr. is 2·495; and hardness 6–7. The indices of refraction are $\alpha=1·5037$, $\beta=1·5082$, and $\gamma=1·5454$; the birefringence is feeble. The axial angles are $2V=39°\ 4'$, and $2E=60°\ 34'$. It is optically positive, and is decomposed by hydrochloric acid with the separation of gelatinous silica.

In 1800, M. F. R. d'Andrada[25] described a mineral which he found at Utö, Södermanland, Sweden, and named it **petalite**—presumably from πέταλον, a leaf, in allusion to the cleavage. A few years later, E. T. Svedenstierna, and R. J. Haüy gave more detailed descriptions, and A. Arfvedson found lithia in the mineral; E. T. Svedenstierna called it *lithite;* and E. D. Clarke called it *berzelite.*

A. Breithaupt described a mineral from Elba, and called it *castor*—after Castor in heathen mythology. G. Rose showed that castor and petalite are similar, and A. des Cloizeaux showed that they have the same optical properties and cleavage. Analyses were made by A. Arfvedson, C. G. Gmelin, R. Hagen, C. F. Rammelsberg, A. Breithaupt, W. S. von Waltershausen, K. Sondén, F. W. Clarke, J. L. Smith and G. J. Brush, and P. von Jeremejeff. A. des Cloizeaux showed that petalite is in some respects like spodumene, and C. F. Rammelsberg assumed that the two minerals contained different proportions of the two silicates, $Li_2Si_2O_5$ and $Al_2(Si_2O_5)_3$. C. Doelter discussed the relation of petalite to spodumene, and he considered that the idealized mineral was best represented by the formula $Li_2Al_2Si_{10}O_{24}$; and P. Groth represented it by $LiAlSi_4O_{10}$, or $LiAl(Si_2O_5)_2$, that is, **lithium aluminium dimesosilicate.** R. Ballo and E. Dittler synthesized petalite by fusing lithium metaluminate and silica; and they found that it corresponds with a maximum at 1200° in the f.p. curve of the binary system, $LiAlO_2$–$SiO_2$.

Petalite commonly occurs in foliated masses, colourless, white, grey, or tinged yellow or green. Crystals are rare, and commonly tabular. A. Breithaupt noted that the crystals are monoclinic, and A. des Cloizeaux gave the axial ratios $a:b:c = 1{\cdot}1534:1:0{\cdot}7436$, and $\beta = 67° 34'$. The (001) cleavage is complete, the (201) good, and the $(\bar{9}05)$ is imperfect. A. des Cloizeaux found the optic axial angle $2H = 86° 24'$–$86° 27\frac{1}{2}'$ for the red ray; $86° 28'$–$86° 30\frac{1}{2}'$ for the yellow ray; and $86° 42'$–$86° 43'$ for the blue ray. The sp. gr. of petalite ranges from 2·4–2·5. R. Ballo and R. Dittler gave 2·290 for the sp. gr. of the glass; the hardness is over 6. P. E. W. Oeberg gave 0·236 for the sp. ht. A. Brun found the m.p. to be 1270°; and R. Ballo and E. Dittler gave 1370° for the m.p. of petalite from Elba. The last-named found that petalite between 1000° and 1100° becomes optically uniaxial; and at 1200°, optically isotropic. R. Lorenz and W. Herz studied the relation between the m.p. and the transition temp. A. des Cloizeaux found the refractive index $\beta = 1{\cdot}5078$, 1·5096, and 1·5180 respectively for the red, yellow, and blue-rays. A. Michel-Lévy and A. Lacroix gave $\alpha = 1{\cdot}504$, $\beta = 1{\cdot}510$, and $\gamma = 1{\cdot}516$; and the birefringence is strong $\gamma - \alpha = 0{\cdot}012$. A. des Cloizeaux found a rise of temp. up to 170° 8′ produced no appreciable change in the refractive index. R. Ballo and E. Dittler gave 1·4946 for the refractive index of glassy petalite. The optical character is positive. When gently heated, petalite exhibits a faint blue thermoluminescence. G. A. Kenngott found the moistened powdered mineral reacts alkaline, and if previously calcined, the alkalinity is less intense. Petalite is attacked by hydrofluoric acid, but not by other acids. The so-called *hydrocastorite* is a decomposition product of petalite or castor from Elba. It occurs in needle-like crystals of sp. gr. 2·16, and hardness 2. It was described and analyzed by G. Grattarola,[26] and F. Sansoni. The analyses agree roughly with F. W. Clarke's formula, $H.Si_2O_5.Al(OH)_2$, *aluminium dihydroxy-hydromesodisilicate. Vide* lepidolite for *lithium trialuminium hexahydroxydimeta-silicate.*

Different varieties of the zeolite now called **natrolite**—from *natron*, soda—were at first designated by an adjectival prefix. Thus, A. Cronstedt,[27] I. S. R. I. Eques a Born, A. G. Werner, and J. B. L. Romé de l'Isle, spoke of the *zeolites crystallisatus, prismaticus, capillaris*, &c. C. J. Selb designated a variety from Högau, *högauite*, and M. H. Klaproth *natrolite*. Natrolite was at first confused with the related minerals mesotype or mesolite, and scolecite (*q.v.*), and natrolite was for a time called by J. N. von Fuchs, and others, *soda-mesotype* or *soda-mesolite*, to distinguish it from lime-mesotype or scolecite.

Colourless acicular crystals of natrolite with up to 4 per cent. of lime were referred to by G. A. Kenngott and E. F. Glocker. The mineral from South Scotland was called *galacite* —from *γάλα*, milk—in allusion to the colour. A red sample from Glen Farg was called *fargite* by M. F. Heddle. The natrolite from Langesund fiord, Norway, was called *radiolite* by J. Esmark in allusion to its occurring in radiating masses; *bergmannite*, by C. F. Schumacher—after T. Bergman—or *Spreustein*, which T. Scheerer regarded as a paramorph after a unknown mineral which he called *palæo-natrolite*, but W. C. Brögger showed

that it is an impure natrolite derived from sodalite and cancrinite; and *brevicite*, by P. Ström. The last-named mineral was analyzed by K. Sondén. The *crocalite* of A. Estner is a red zeolite resembling bergmannite. The *savite* of G. Meneghini—named after P. Savi—found in the serpentine of Monte Caporciano, Italy, was shown by E. Mattirolo, A. des Cloizeaux, Q. Sella, and E. Artini to be identical with natrolite. The *iron-natrolite* of C. Bergemann, from the Brevik region, was supposed to have some alumina replaced by ferric oxide, but W. C. Brögger showed that the iron is derived from included ferruginous minerals. T. Thomson's *lehuntite*—named after C. Lehunt—is a natrolite from Antrim.

Numerous analyses of natrolite have been reported.[28] They can be summarized by the formula $Na_2Al_2Si_3O_{10}.2H_2O$, but a little lime is usually present—*vide* scolecite. The constitution of natrolite depends on what view is taken of the state of combination of the water—*i.e.* whether all or part is intrinsic or extrinsic. G. Friedel[29] investigated the dehydration curve, and found the loss very slow up to 250°, but at 280°, the water was rapidly given off, but no break was observed in the curve. F. Zambonini likewise found the curve at about 100° is almost horizontal, but at 300° almost vertical. The curve, however, continues without a break. His data are:

| | 110° | 205° | 240° | 264° | 278° | 297° | 324° |
|---|---|---|---|---|---|---|---|
| Water lost | 0·12 | 0·16 | 0·25 | 0·46 | 0·81 | 1·57 | 9·41 per cent. |

C. Hersch also made observations on this subject. A peculiarity is that, as first pointed out by A. Damour, the water is resorbed by dehydrated natrolite, but the crystal does not acquire its former transparency and firm texture. The resorbed water is lost at about 90°. F. Zambonini likened the water in the zeolites generally to that in hydrogels like silicic acid (*q.v.*). C. F. Rammelsberg assumed that the water is present as water of crystallization. G. Friedel, and F. Zambonini infer that the water is not an intrinsic part of the mol., and is eq. to neither the so-called constitutional water nor to the so-called water of crystallization. It is regarded as *zeolitic water*, which many consider to be either water in solid soln. (F. Rinne), or adsorbed water (C. Doelter). G. Friedel said that the zeolitic water is mechanically mixed occupying the space between the structural units of the crystal. The subject was investigated by A. Johnsen, and S. J. Thugutt. G. Stoklossa believed that the water is really combined in the mineral, and he considered that there are four hydrates represented by breaks in the rehydration curve of natrolite previously dehydrated at a temp. between 0° and 300°. Hence, he doubled the above formula, and wrote, $Na_4Al_4Si_6O_{20}.4H_2O_2$. S. J. Thugutt said that natrolite is to be regarded as a salt of aluminosilicic acid, $H_2Al_2O_{10}.nH_2O$, represented in the free state by pyrophillite and razumoffskyn. G. Tschermak assumed that natrolite is a complex containing an anhydrous silicate and silicic acid, $Na_2Al_2Si_2O_8.H_2SiO_4$; and in general he supposes the zeolites to be acid salts with part of the hydrogen replaced by sodium, calcium, aluminium, etc. C. Doelter extended this hypothesis and showed that the zeolites have a felspar or nephelite nucleus. E. Baschieri used a constitutional formula in harmony with G. Tschermak's views, $Na_2 : SiO_4 : (Al : SiO_4 : H_2)_2$. F. W. Clarke at first used a similar formula, but later when he found that natrolite is transformed into $Al_2(NH_4)_2Si_3O_{10}$ by the action of dry ammonium chloride in a sealed tube, and that the water is not intrinsic, he doubled the formula and wrote:

$$Al{\equiv}SiO_4{-}Al\begin{matrix}<SiO_4\\<SiO_4\end{matrix}\begin{matrix}>Na_2\\>Na_2\end{matrix}Al{-}Si_3O_8{\equiv}Al+4H_2O$$

The investigators named above regard natrolite as an orthosilicate. The formula $Na_2Al_2Si_3O_{10}.2H_2O$, used by C. F. Rammelsberg, and E. S. Dana, makes natrolite appear to be dihydrated *sodium dialuminium orthotrisilicate*. P. Groth considered natrolite to be a metasilicate, and wrote $Na_2Al(AlO)(SiO_3)_3.2H_2O$. G. F. H. Smith and co-workers gave $(Na,K)_2O.Al_2O_3.3SiO_2.2H_2O$.

C. Doelter[30] treated powdered natrolite with water sat. with carbon dioxide

in a sealed tube at 160°, and observed the re-crystallization of the mineral. S. J. Thugutt heated hydrated nephelite, sodium carbonate, and carbonated water in a sealed tube at 200°, and obtained prismatic crystals supposed to be natrolite; when potassium carbonate was used in place of sodium carbonate, *potash-natrolite* was formed. J. Lemberg also found that there is an exchange of potassium for sodium when a soln. of potassium carbonate is allowed to act on natrolite for a few months; the action is reversed by sodium carbonate. The formation of natrolite in nature has been investigated by J. E. Hibsch, A. Pelikan, A. Brun, C. N. Fenner, etc.

Natrolite is colourless, white, grey, yellow, or red. It is not commonly found massive, but it often occurs in masses of radiating fibres with a silky lustre, and also in slender prismatic crystals. J. N. von Fuchs and A. F. Gehlen [31] regarded the crystals as rhombic; G. Rose, as monoclinic; and later, G. Rose and P. Riess found them to be rhombic. W. C. Brögger gave for the axial ratios of the rhombic crystals $a:b:c=0{\cdot}97852:1:0{\cdot}35362$. Observations were also made by E. Artini, O. Luedecke, G. F. H. Smith and co-workers, S. Richarz, J. E. Hibsch, R. Görgey, G. Cesaro, A. Scheit, and G. B. Negri. S. J. Thugutt obtained what he regarded as a monoclinic form of natrolite which he called *epinatrolite* from Schömitz near Carlsbad. He found the action of silver nitrate (mixed with some potassium chromate) to be far more rapid than is the case with rhombic natrolite. It is also suggested that natrolite is derived from nephelite, and epinatrolite from haüyne. A. von Lasaulx, and W. C. Brögger also observed monoclinic forms with, according to the latter, the axial ratios $a:b:c=1{\cdot}0165:1:0{\cdot}35991$, and $\beta=89°\ 54'$; and S. Kreutz, $0{\cdot}97853:1:0{\cdot}35362$, and $\beta=90°$. The monoclinic form is isomorphous with scolecite. The relationships have been discussed by S. Kreutz, and G. Tschermak. Some of the rhombic crystals can be regarded as monoclinic twins. The twinning has been discussed by C. Stadtländer, V. von Lang, and O. Luedecke. The cleavage parallel to the (110)-face is perfect; and that parallel to the (010)-face is imperfect, perhaps only a plane of parting. The plane of the optic axes is parallel to the (010)-face; the optic axial angle is large. W. C. Brögger gave $2H_a=61°\ 29'$–$62°\ 25\frac{1}{2}'$ for Li-light; $61°\ 37'$–$62°\ 41'$ for Na-light; and $61°\ 46'$–$62°\ 50\frac{1}{2}'$ for Tl-light; $2H_0=118°\ 8'$–$121°\ 1'$ for Li-light; $118°\ 2'$–$120°\ 47'$ for Na-light; and $117°\ 53'$–$120°\ 24'$ for Tl-light; $2E=98°\ 7\frac{1}{2}'$ for Li-light, $98°\ 58'$ for Na-light, and $99°\ 34'$ for Tl-light; and for $2V$, $60°\ 51'$–$62°\ 16\frac{1}{2}'$ for Li-light; $61°\ \frac{1}{2}'$–$62°\ 29\frac{1}{2}'$ for Na-light; and $61°\ 13\frac{1}{2}'$–$62°\ 39\frac{1}{2}'$ for Tl-light. B. Mauritz gave $2V=60°$. Observations were also made by K. Zimanyi, E. Artini, and E. Palla. For red light, A. des Cloizeaux found that $2E$ changed from $98°\ 33'$ at 8·8° to $95°\ 0'$ at 105·5°; and with another sample, from $98°\ 58'$ at 15° to $90°\ 55'$ at 307·9°.

The sp. gr. of many of the samples analyzed were determined, and the results range from 2·2–2·5; the hardness is 5 or just about 5. J. Joly gave for the sp. ht., 0·23689–0·23819 between 11° and 100°. F. Rinne showed that when heated clear crystals of natrolite become turbid as the water is evolved, but they become clear again when dipped in oil. The optical properties of dehydrated natrolite correspond with that of a monoclinic substance which he called *metanatrolite*. No change in the geometrical form accompanies the mol. change. For the action of heat on the water-content of natrolite, *vide supra*. G. Tammann found that in an atm. with the vap. press. of water $p$ mm., the percentage loss of water from a sample of natrolite with 10·4 per cent. of water was:

| | | | | | |
|---|---|---|---|---|---|
| $p$ | 14·5 | 12·3 | 9·1 | 2·1 | 0·4 mm. |
| Loss | 0·21 | 0·25 | 0·39 | 0·61 | 0·79 per cent. |

O. Mulert found the heat of soln. in dil. hydrofluoric acid to be 0·5446 Cal. per gram; and the heat of formation, 95·76 Cals. The indices of refraction for Na-light by K. Zimanyi, A. des Cloizeaux, H. C. Backlund, B. Mauritz, W. C. Brögger, and A. Pelikan ranged from $\alpha=1{\cdot}47543$–$1{\cdot}47813$; $\beta=1{\cdot}47897$–$1{\cdot}48080$; and $\gamma=1{\cdot}48866$–$1{\cdot}49047$. S. G. Gordon gave $\alpha=1{\cdot}480$, $\beta=1{\cdot}482$, and $\gamma=1{\cdot}493$, with

$\gamma-\alpha=0{\cdot}013$—*vide* thomsonite and scolecite. The corresponding birefringence is $\gamma-\alpha=0{\cdot}0008$; $\gamma-\beta=0{\cdot}0004$; $\beta-\alpha=0{\cdot}0004$. O. B. Böggild found the double refraction of natrolite to be rather strong, almost 0·01; and the extinction parallel. J. Königsberger and W. J. Müller found the index of refraction and birefringence were not perceptibly changed by digesting natrolite in a 25 per cent. soln. of potassium chloride. The optical character of natrolite is positive. E. Engelhardt found the crystals exhibit a yellow fluorescence. W. W. Coblentz found the ultra-red transmission spectrum of natrolite showed the presence of water bands in their usual positions (**1.** 9, 10); and in the ultra-red reflection spectrum, there are maxima at $9{\cdot}05\mu$, $9{\cdot}5\mu$, and $10{\cdot}05\mu$ beyond which the reflecting power remains higher up to $12\mu$. G. W. Hankel examined the pyroelectric qualities of natrolite; and O. Weigel, the electrical conductivity.

Natrolite adsorbs moisture from the atm., and this the more the finer the state of subdivision of the powdered mineral. S. J. Thugutt[32] could find no relation between the newly adsorbed water and that already contained in the mineral. The amount adsorbed is a function of the grain-size or surface energy, the partial press. of the moisture in the atm., and the time of exposure. This subject was also investigated by W. F. Hillebrand. Powdered natrolite moistened with water was found by G. A. Kenngott to have an alkaline reaction; and A. Damour found that the soln. obtained by digesting dehydrated natrolite in water has an alkaline reaction. G. Steiger found that by digesting 0·5 grm. of natrolite in 50 c.c. of water at 21° for a month, 0·30 per cent. of alkali was dissolved by the water; 15·79 per cent. remained in the mineral. C. Doelter, and S. J. Thugutt made observations on this subject. J. Lemberg found that 8·37 per cent. of soda was removed from natrolite by 687 hrs.' digestion with water at 250°. C. H. A. Eichhorn found that a soln. of calcium chloride has but a slight action on natrolite. S. J. Thugutt studied the action of soln. of potassium and sodium carbonate, potassium and sodium chloride, and calcium chloride on natrolite, and found that part of one alkali is replaced by the other. A. Günther-Schulze found that 93 per cent. of the sodium can be replaced by silver when natrolite is immersed in a soln. of silver nitrate. The diffusion constant of the sodium is $1{\cdot}48\times10^{-10}$ sq. cm. per sec. K. Dalmer found that part of the sodium is replaced by ferrous iron when natrolite is digested with a soln. of ferrous sulphate. G. Steiger likewise found a replacement of sodium by silver or thallium occurs when natrolite is digested with a soln. of silver or thallium nitrate. F. W. Clarke and G. Steiger examined the effect of ammonium chloride on natrolite at 350°. When treated with acids, natrolite decomposes with the separation of gelatinous silica. V. P. Smirnoff studied the action of humic and crenic acids on natrolite. The effect of natural agents on natrolite has been discussed by J. R. Blum, C. R. van Hise, G. Sillem, G. Tschermak, C. Doelter, and S. J. Thugutt.


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## § 43. The Felspars

Felspar is a class name for a group of related minerals. They are the most important constituents of rocks ; indeed, F. W. Clarke [1] estimated that nearly 60 per cent. of the material contained in igneous rocks is felspar. A system of classifying rocks has been based on the particular type of felspar they contain. This important mineral species does not appear to have been particularly noticed by the earlier writers. G. Agricola probably alluded to felspar in saying *silex ex eoictu ferri facile ignis elicitur—ex cubis aliisque figuris intersectis constans ;* J. G. Wallerius referred to it as white, grey, and red *feltspat*, and *spatum pyrimachum ;* and A. Cronstedt, as *fältspat*, and *spatum scintillans*. The scholars are not certain if the " feld " is derived from *Fels*, a rock, as R. Kirwan, and M. H. Klaproth apparently assume in respectively calling the mineral *felspar*, and *Felsspath*, because

of its common occurrence in granite rocks; or from *Feld*, a field, in allusion to crystals being found scattered on the ground in some parts of the country. C. Hintze's view is that the *Feld* is the result of mutilating an old word in order to adapt it to the popular mind. The original word cannot now be traced. The term *Feldspar* is used in Germany, and *felspar* in England.

J. B. L. Romé de l'Isle mentioned seventeen varieties of felspar, but designated by special name only *pierre de Labrador*. G. Rose attempted a classification of the varieties known in 1823. The list has been extended and may now be taken to include the following idealized types. There are a number of varieties to some of these types. These may be arranged in two groups:—

I. *Trisilicates*.—The empirical composition of these felspars corresponds with $K_2O.Al_2O_3.6SiO_2$, or $KAlSi_3O_8$. It is, however, extremely rare to find a potash felspar without some accompanying soda, and conversely. Some lime is also usually present. These felspars include the artificially-prepared *lithia-felspar*, *rubidia-felspar*, and *cæsia-felspar*:

| | | |
|---|---|---|
| *Potash-felspar*, $KAlSi_3O_8$ | Monoclinic | ORTHOCLASE (Or) |
| | Triclinic | MICROCLINE |
| *Soda-felspar*, $NaAlSi_3O_8$ | Monoclinic | BARBIERITE |
| | Triclinic | ALBITE (Ab) |
| *Soda-potash-felspars* $(Na,K)AlSi_3O_8$ | Triclinic | ANORTHOCLASE |
| Or : Ab = 1 : 0—4 : 1 | Monoclinic | ADULARIA |
| 4 : 1—3 : 2 | Monoclinic | AMAZONITE |
| 3 : 2—1 : 1 | Monoclinic | PERTHITE |
| 1 : 1—1 : 4 | Monoclinic | LOXOCLASE |

II. *Disilicates*.—These are typified by anorthite, $CaO.Al_2O_3.2SiO_2$, or $CaAl_2Si_2O_8$; and possibly the artificially-prepared soda-anorthite, $Na_2Al_2Si_2O_8$:

| | | |
|---|---|---|
| *Soda-anorthite*, $Na_2Al_2Si_2O_8$ | Triclinic | CARNEGIEITE (Cg) |
| *Lime-felspar*, $CaAl_2Si_2O_8$ | Triclinic | ANORTHITE (An) |
| *Baryta-felspar*, $BaAl_2Si_2O_8$ | Monoclinic | CELSIAN |

*Mixed di- and trisilicates* are typified by a whole series of isomorphous mixtures of the alkali trisilicates, and alkaline earth disilicates.

| | | |
|---|---|---|
| *Lime-soda-felspars*, Ab : An = 6 : 1—3 : 1 | Triclinic | OLIGOCLASE |
| 3 : 1—1 : 1 | Triclinic | ANDESINE |
| 1 : 1—1 : 3 | Triclinic | LABRADORITE |
| 1 : 3—1 : 6 | Triclinic | BYTOWNITE |
| *Mixed-felspar*, Cg : Ab : An | Triclinic | ANEMOUSITE |
| *Baryta-potash-felspar*, $(K_2,Ba)Al_2Si_4O_8$ | Monoclinic | HYALOPHANE |

The classification here given for the soda-potash-felspars, and the soda-lime-felspars is due to G. Tschermak.[2] The subdivisions are quite arbitrary. Others for the soda-lime-felspars have been proposed by M. Schuster, and J. D. Dana. The artificial *lithia-felspar*, *rubidia-felspar*, *cæsia-felspar*, *strontia-felspar*, *magnesia-felspar*, *lead-felspar*, *zinc-felspar*, *potash-anorthite*, and *ferric-orthoclase*, which are mentioned below, are not included in the table.

Ordinary potash-felspar occurs in crystals or cleavable masses. The rectangular cleavage of some felspars suggested to R. J. Haüy [3] the name *orthose*—from *ὀρθος*, straight. A. Breithaupt, for a somewhat similar reason, called it *orthoclase*—from *ὀρθος*, straight; and *κλάω*, to break. A cleavable *glassy felspar* from Drachenfels was described by C. W. Nose, and called by J. J. Nöggerath *sanidine*—from *σανίς*, a tablet—in allusion to its usually occurring in tabular crystals. M. H Klaproth showed that sanidine is chemically the same as orthoclase. The *ice-spar* of A. G. Werner belongs to the same mineral species. G. Rose found that the mineral from Monte Soma which he called *ryacolite* or *rhyacolite*—from *ῥύαξ* (lava), stream; and *λίθος*, a stone—is glassy felspar mixed with some nephelite. E. Pini described a felspar from Adula which he called *adulaire*, and which is now called *adularia*, after A. G. Werner's suggestion. From L. A. Emmerling's and G. A. Kenngott's observations, Adula formerly included a more extensive area than it does to-day. Adularia is transparent, cleavable, and often has pearly opalescent reflections exhibiting a play of colours like labradorite. The so-called *moonstone*, *pierre de lune*, or

*Mondstein* is a variety of adularia, albite, or oligoclase. J. C. Delamétherie called it *hecatolite*—from ἑκάτη, the moon. A. Breithaupt found a mineral which he called *valenciánite* in a silver mine at Valenciana, Mexico. It was adularia. Other names seem to have been given to orthoclase or microcline more or less at random—*e.g.* A. Breithaupt's *paradoxite* from the tin mines at Marienberg is orthoclase with very little soda; according to the analyses of W. Schüler, the mineral paradoxite from Euba, Saxony, is a potash-felspar. A. Breithaupt's *cottaite*, from Carlsbad, Bohemia—named in honour of B. von Cotta—is greyish-white orthoclase; and his *muldan*, from Mulda, near Freiberg, was shown by C. F. Rammelsberg to be ordinary orthoclase. An orthoclase found by F. V. Hayden near Baltimore was called *necronite*—from νεκρός, a corpse—in allusion to its fœtid odour when struck. E. D. Clarke's *leelite* is a flesh-red orthoclase named after J. F. Lee; J. D. Dana's *chesterlite* from Chester Co., Penn., is a microcline. Other orthoclases are G. Jenzsch's *weissigite* from Weissig, near Dresden; I. Lea's *lennilite* from Lenni, Penn., and his *delanarite* from Lenni, which have a pearly lustre; and T. Thomson's *erythrite*—from ἐρυθρός, red. W. Phillips called a flesh-red felspar resembling perthite, *murchisonite*—in honour of R. I. Murchison. It was obtained at Dawlish and Exeter. N. von Nordenskjöld applied the term *lazur-felspar* to a felspar with the cleavage of orthoclase accompanying the lapis-lazuli of Lake Baikal. A. Breithaupt called the orthoclase from Hammond, New York, *loxoclase*—from λοξός, transverse; and κλάσις, fracture—in allusion to the peculiar cleavage parallel to the orthodiagonal section. J. L. Smith and G. J. Brush regarded it as a sanidine; and A. des Cloizeaux as a mixture of orthoclase and albite laminations. The so-called *sunstone*, *pierre de soleil*, or *Sonnenstein*, was shown by T. Scheerer, and A. des Cloizeaux to be an aventurine-orthoclase, associated with albite or oligoclase. J. C. Delamétherie called it *heliolite*—from ἥλιος, the sun. I. Lea's *cassinite* is an aventurine-felspar from Lenni, Penn. T. Thomson's *perthite*, from Perth, Canada, was shown by T. S. Hunt to be a soda-potash-felspar, and A. Breithaupt, G. A. Kenngott, and D. Gerhard showed that it consists of interlaminations of albite and orthoclase. Similar perthites were described by A. Streng, H. Credner, G. Tschermak, P. Mann, J. H. Kloos, G. Woitschach, etc. When the laminations are visible only microscopically, F. Beck called it *microperthite*; these minerals were examined by A. W. Stelzner. The name *microcline*—from μικρός, a little; and κλίνειν, to incline—was given by A. Breithaupt to felspars which have a slightly larger angle between the two cleavage planes than the 90° characteristic of orthoclase. G. Forchhammer applied the term *krablite* to a mineral from Krabla, or Krafla, Iceland, and G. Flink called it *kraflite*. G. Forchhammer called a pearly mineral from Baula, *baulite*. P. Schirlitz, F. A. Genth, H. Bäckström, etc., studied this mineral; and G. Flink regards it as a liparite rock containing orthoclase, quartz, etc. A. des Cloizeaux showed that while orthoclase is monoclinic, the microclines are triclinic. A. Breithaupt proposed the term *felsite* in place of felspar, and he suggested calling the non-microclinic felsite by the term *pegmatolite*. P. Mann, and C. T. Neubauer called perthite formed by the interlaminations of microcline and albite, *microcline-perthite*. W. C. Brögger investigated the *orthoclase-microperthite*, the *microcline-microperthite*, and microperthites of other felspars. These are often characterized by a marked schillerization. He assumes that the schiller is caused by laminations of the two felspars so extremely fine that they are not discernible by the microscope. He called these *cryptoperthites*. A. Breithaupt called the Amazon felsite *amazonite*. This is a bright, verdigris-green, microclinic felspar also called *amazon stone* or *pierre des amazones*. It occurs in Ural, and South America. A. des Cloizeaux, and N. von Kokscharoff assumed the existence of two amazonites, one corresponding to orthoclase, the other to microcline.

The *schorl blanc* of J. B. L. Romé de l'Isle [4] was probably soda-felspar, likewise also the *krummblätteriger Feldspath* of L. Hedenberg. It was called *albite*—from *albus*, white—by J. G. Gahn and J. J. Berzelius in 1815, and the mineral was analyzed by V. Eggertz in 1818. G. Rose regarded albite as an independent species; and A. Breithaupt proposed *tetartin* for the name of soda-felspar in allusion to the tetartohedral terminal faces. He also applied the term *pericline* to a variety from the Alps—from περικλίνης, steep—in allusion to "the marked inclination of the terminal faces to the first lateral." Pericline was analyzed by C. G. Gmelin. H. Thaulow, and W. Haidinger showed that pericline and albite are the same. The subject was also discussed by F. Münzing. A white lamellar albite from Chesterfield, Mass., was named *cleavelandite*—after P. Cleaveland—by H. J. Brooke. A blackish-green albite from Arendal was named by A. Breithaupt, *hyposclerite*—from ὑπό, under; and σκληρῶς, hard—in allusion to its softness. C. F. Rammelsberg said that 5 per cent. of pyroxene is present. T. Thomson applied the term *peristerite*—from περιστερά, pigeon—to a white albite from Villeneuve, Canada. The name refers to the fanciful resemblance of its iridescent colours to those on the neck of a pigeon. T. Scheerer called an albite from Snarum, Norway, *olafite*. The nature of this mineral was discussed by A. des Cloizeaux, A. Breithaupt, and C. H. Schneidhauer. O. L. Erdmann analyzed a Norwegian albite; C. F. Rammelsberg called it *sigtesite* (not *sigterite*) because it came from Sigtesö (not Sigterio) Island, Langesund fiord, and C. A. Tenne showed that it is a mixture of albite and eudialyte. H. S. Washington places sigtesite in the plagioclase series between andesite and oligoclase, but with soda-anorthite (carnegieite) in place of anorthite. A. Breithaupt called a mineral from Andreasberg, Harz, *zygadite*—from ζυγάδην, in pairs

or twinned—because it occurs in twinned crystals. A. des Cloizeaux, and J. A. Krenner and J. Loczka showed that it is identical with albite. F. von Kobell applied the term *tschermakite*—in honour of G. Tschermak—to an oligoclase albite from Bamle, Norway, etc. It was analyzed by G. W. Hawes, F. Pisani, and A. des Cloizeaux. Some varieties of moonstone and aventurine-felspar (*vide supra*) are albitic in composition. H. Rosenbusch called the triclinic potash-soda-felspar *anorthoclase ;* which A. Michel-Lévy and A. Lacroix translated *anorthose.* F. Zirkel said that it is better to use a term like *parorthoclase* signifying approximately rectangular than one like anorthoclase meaning not rectangular. H. Förstner called a variety *natromicrocline ;* and others, *microcline-oligoclase* and *microcline-albite ;* F. J. Wiik called the latter *microclase.*

Towards the end of the eighteenth and beginning of the nineteenth centuries, analyses of felspars were made by J. C. Wiegleb,[5] J. C. H. Heyer, B. F. Morell, J. F. Westrumb, V. Rose, L. N. Vauquelin, and M. H. Klaproth. The composition of potash-felspar was thus approximately determined. A very large number of analyses of orthoclase [6] have since been reported; and analyses of felspars are regularly made for industrial work. Similarly, many analyses of albite,[7] and of the potash-soda-felspars [8] have been made. A range of selected analyses is given in Tables XXII and XXIIA. G. Tschermak mentioned samples of sanidine

TABLE XXII.—ANALYSES OF FELSPARS WITH UP TO 5 PER CENT. SODA.

| —— | St. Gothard (R. Müller). | Schemnitz (C. Bischof). | Eifel (A. von Decken). | Silesia (J. Traube). | Schwarzbach (A. Beutell). | Mt. Amiata (J. F. Williams). | Baltimore (G. H. Williams). |
|---|---|---|---|---|---|---|---|
| $SiO_2$ . . | 65·24 | 64·00 | 65·84 | 65·49 | 65·61 | 64·20 | 65·41 |
| $Al_2O_3$ . . | 18·15 | 18·00 | 17·61 | 18·86 | 19·01 | 19·18 | 19·86 |
| $Fe_2O_3$ . . | — | 0·54 | 0·74 | 0·40 | — | 0·06 | — |
| MgO . . | — | 0·31 | 0·06 | — | — | 0·09 | — |
| CaO . . | 1·28 | 7·80 | 0·18 | 0·32 | 0·34 | 0·71 | 1·08 |
| $K_2O$ . . | 14·96 | 15·43 | 14·39 | 12·46 | 13·01 | 13·04 | 10·12 |
| $Na_2O$ . . | trace | 0·79 | 1·18 | 1·96 | 2·05 | 3·07 | 4·61 |
| $H_2O$ . . | — | 0·54 | — | 0·35 | 0·31 | 0·34 | — |

TABLE XXIIA.—ANALYSES OF FELSPARS WITH UP TO 7 PER CENT. POTASH.

| —— | N. Burgess (T. S. Hunt). | Lövö, Norway (T. Scheerer). | Pantelleria (F. Fouqué). | Maine (E. C. E. Lord). | S. Pietro (S. Bertolio). | Silesia (W. Lohmeyer). | Tyrol (G. Tschermak). |
|---|---|---|---|---|---|---|---|
| $SiO_2$ . . | 66·44 | 66·03 | 64·81 | 57·34 | 66·10 | 68·75 | 68·80 |
| $Al_2O_3$ . . | 18·35 | 19·17 | 20·65 | 20·79 | 18·20 | 18·79 | 19·30 |
| $Fe_2O_3$ . . | 1·00 | 0·31 | 0·95 | 2·88 | — | 0·55 | 0·10 |
| MgO . . | 0·24 | — | 0·09 | 0·16 | — | 0·04 | — |
| CaO . . | 0·67 | 0·20 | 2·01 | 4·27 | 0·1 | 0·51 | 0·40 |
| $K_2O$ . . | 6·37 | 6·96 | 3·84 | 4·17 | 3·5 | 1·21 | 0·50 |
| $Na_2O$ . . | 5·56 | 6·83 | 7·13 | 8·09 | 11·4 | 10·90 | 11·10 |
| $H_2O$ . . | 0·40 | 0·21 | — | 2·66 | — | — | — |

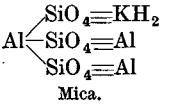
and adularia with up to 1·17 per cent. BaO. The analyses of the felspars were critically examined by C. F. Rammelsberg,[9] and the results show that those least contaminated with foreign materials agree well with the formula $R_2O.Al_2O_3.6SiO_2$, *i.e.* with $RAlSi_3O_8$.

Gaseous and liquid inclusions are not common with felspars; glass inclusions are present in felspars in some lavas, or glassy rocks. Mineral crystals of all kinds—hæmatite, chlorite, epidote, ilmenite, pyroxene, etc.—have been observed in felspars. The inclusions may be large or small, they may be sparsely distributed, or in multitudes. In some cases the inclusions are symmetrically arranged in concentric shells, or grouped either at the centre or margin of the crystal. In some cases the inclosed mineral separated primarily with the felspar, in other cases the minerals may have been formed by secondary processes—*e.g.* muscovite, china clay, etc. The felspar may have intergrown with quartz, nephelite, pyroxene, etc. Intergrowths of one kind of felspar with another are also common. Consequently, the analyses of a felspar may be that of a homogeneous material, a material with variable zones, or a material with inclusions of other minerals.

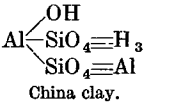
**The constitution of the alkali-felspars.**—M. L. Frankenstein regarded the felspars as isomorphous compounds of the aluminates $RO.Al_2O_3$ with different quantities of silica. Accordingly, P. Groth represented the alkali-felspar as a salt of trisilicic acid, $H_4Si_3O_8$, **potassium aluminium mesotrisilicate,** $KAlSi_3O_8$. In order to explain the ready transformation of these felspars into muscovite-mica, and into china clay, F. W. Clarke represents the structural formula of orthoclase as if it were **potassium trialuminium trimesotrisilicate.**



Felspar.

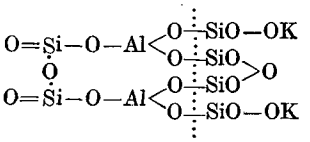


Mica.

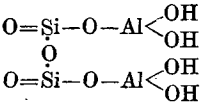


China clay.

This hypothesis is more satisfactory for the alteration of mica to china clay than it is for the alteration of felspar to mica, which involves a very drastic change in the acidic radicle, without altering the nature of the basic aluminium radicles. R. Scharizer's hypothesis overcomes this difficulty. He represents the orthoclase as if it were **potassium dialuminohexasilicate :**

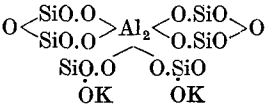


Felspar.

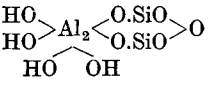


China clay.

This hypothesis fits the probable decomposition of china clay into free silica and free alumina better than the preceding one. J. W. Mellor and A. D. Holdcroft represented the changes in an equivalent manner :

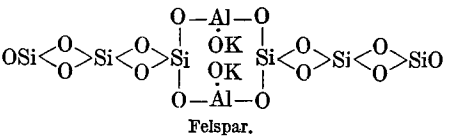


Felspar.

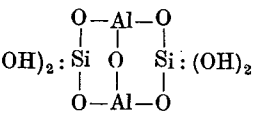


China clay.

W. Vernadsky gave the following formulæ for felspar and clay. The latter is slightly modified in the following scheme of his hypothesis : The ring corresponds with what W. Vernadsky calls the *Glimmerkern*, or mica nucleus :

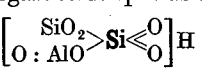


Felspar.



China clay.

W. and D. Asch's scheme is still more complex, with no gain in clarity of conception. P. Erculisse, M. E. Denaeyer, and J. Jakob also applied the co-ordination theory to the constitution of the felspars. The former said that formulæ of the type $KSiO_3.SiO.SiO_4Al$ must be wrong because of the difference in the behaviour of aluminium and potassium ; he regarded felspar as a salt of the monobasic acid :



M. E. Denaeyer regarded microcline as being formed from three components in solid soln. B. Gossner writes for *albite* $SiO_3Na_2[SiO_2,Al_2O_3]4SiO_2$, and his hypothesis is also based on a kind of co-ordination plan which offers no particular advantages —*vide infra*. P. Niggli represented albite by

$$\left[Al(SiO_4SiO_2SiO_2)_3\right]^{Al_2}_{Na_3}$$

and E. T. Wherry by $NaAl(Si_3O_8)$. Many other suggestions have been made and are indicated by reference in the discussion on the general formulæ for silicates. The impression obtained is that the arrangement of formulæ consistent with the valencies of the atoms is rather a test of man's ingenuity than a representation of the orientation of the atoms. F. Rinne has obtained **X-radiograms** of sanidine and albite, and his interpretation of the results for orthoclase and albite is shown in Fig. 139, where R represents an atom of potassium or sodium. This result indicates that the formula of felspar, $RAl(Si_3O_8)$, may have to be written $RAlSi(Si_2O_8)$ or $RAlSi(SiO_4)_2$.

A. Rivière said that the different kinds of felspar cannot be sharply distinguished from one another, but pass gradually one into the other. C. F. Rammelsberg also considered that the felspars should be regarded as an isomorphous family, and not as individual species. G. Rose expressed a similar view. He said that soda-felspar passes into potash-felspar by the simple substitution of potassium for sodium.

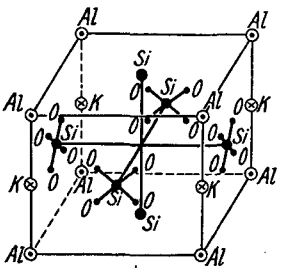



FIG. 139. — Stereochemical Scheme for the Molecules of Potash- and Soda-felspars.

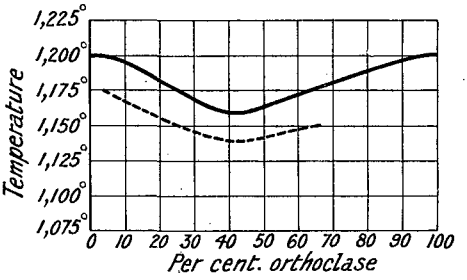



FIG. 140.—Fusion Curve of Binary Mixtures of Albite and Orthoclase.

H. Förstner described the native soda-orthoclases or anorthoclases, and their properties have been studied by F. Fouqué, C. Riva, and G. de Lorenzo and C. Riva. Homogeneous mixtures of the two felspars are found only in volcanic rocks; in other cases, according to W. C. Brögger, the mixture appears as cryptoperthite, or, according to F. Becke, as microperthite. J. H. L. Vogt, and J. A. Douglas have made some observations on the m.p. of orthoclase and albite. E. Dittler obtained a curve approaching that indicated in Fig. 140. The dotted line represents the beginning of the melting, and the continuous line, the temp. when all is melted. There is a minimum in the curve corresponding with 56–60 per cent. of albite or 44–40 per cent. of orthoclase. There is no sign of the formation of a definite compound of the two felspars.—*cf.* Fig. 157. J. H. L. Vogt assumed that the m.p. curve would represent type V (**1**. 10, 2), but E. Dittler's result, Fig. 140, corresponds with Type III. Felspars between the limits Or : Ab=72 : 28 and 12 : 88 give no evidence of the formation of mixed crystals.

The monoclinic alkali-felspars are common in the more siliceous plutonic rocks—for example, orthoclase, muscovite, and quartz are the minerals most conspicuous in granites. There is also a tendency for the plagioclase to appear in the less siliceous rocks like the gabbros and basalts, and for the felspars to approach anorthite as the proportion of silica in the rock decreases. W. Lindgren [10] reported orthoclase as a gangue mineral in metalliferous mineral veins; and R. A. Daly found albite and

orthoclase in sedimentary limestones and dolomite. It is inferred that the felspars are here of aq. origin, and in the calcareous muds, it is supposed to have been formed below 100°, probably below 70°. J. de Lapparent supposed that algæ are responsible for the formation of some small crystals of albite which he found associated with the remains of algæ and foraminifera. Orthoclase has not been reported in meteorites.

**The synthesis of the alkali-felspars.**—Attempts to prepare crystals of alkali-felspars by the simple fusion of a mixture of the constituents always furnish a glass. A. L. Day and E. T. Allen [11] suggested that the viscosity of the alkali-felspars impedes their crystallization in a practicable time. L. Appert and J. Henrivaux heated glass for a long time in an annealing kiln near the softening temp., and claimed to have made microlites of felspar. S. Meunier devitrified natural glasses, but, according to F. Fouqué and A. Michel-Lévy, no felspar was produced. S. Meunier also reported orthoclase to be formed by the action of silicon tetrachloride on aluminium and potassium hydroxides, but F. Fouqué and A. Michel-Lévy regard this as non-proven. A. Brun claimed to have crystallized orthoclase glass by the action of fluoriferous vap. If an *agent minéralizateur* be present, crystallization may occur. For example, J. Lenarcic found that albite may be recrystallized when fused with half its weight of magnetite; a mobile liquid is thus formed within which crystallization can readily occur. P. Hautefeuille heated a mixture of an alkaline sodium aluminosilicate and tungstic oxide to 900°–1000°, and obtained albite, and orthoclase was formed when potassium aluminosilicate was substituted for the sodium salt. A mixture of silica, alumina, and potassium tungstate also gave orthoclase; and a mixture of potassium aluminosilicate, and alkali phosphate and fluoride gave orthoclase and quartz. C. Doelter also obtained potassium-felspar by fusing a mixture corresponding with $KAlSiO_4$, and potassium fluoride and fluosilicate. A. L. Day and E. T. Allen heated a mixture of powdered albite glass and sodium tungstate. They found that the fragments of glass became crystalline without changing their form, indicating that the transformation occurred without dissolution of the material; on the other hand, R. C. Wallace observed that the crystallization at the zone of contact of the albite with the sodium tungstate is greatly accelerated, but the velocity of crystallization in the interior of the glass is not greatly affected. G. W. Morey and N. L. Bowen found that artificial crystals of orthoclase could be obtained by heating the glass and water vap. in a bomb. F. Fouqué and A. Michel-Lévy attempted to prepare artificial rocks containing orthoclase, but they succeeded only in producing plagioclase. K. Petrasch obtained albite in artificial rocks. K. Bauer obtained plagioclase by melting granite and Vesuvian lava; but both plagioclase and orthoclase were produced by melting a mixture of granite, sodium chloride, and potassium tungstate. J. Morozewicz heated various mixtures of the composition of trachyte rocks, and obtained no orthoclase, but he obtained an artificial liparite containing quartz, biotite, and sanidine when the liparite mixture and one per cent. of tungstic oxide was heated 14 days at 800°–1000°. J. F. L. Hausmann, C. M. Kersten, A. Gurlt, A. Breithaupt, G. vom Rath, C. J. Heine, F. Zincken, J. T. Prechtl, H. Avich, and C. F. Rammelsberg observed orthoclase crystals in blast furnace slags. G. V. Wilson observed the formation of felspar by the action of molten glass on bricks.

The alkali-felspars seem to be produced more easily by hydrothermal processes. C. Friedel and E. Sarasin produced quartz and orthoclase by heating gelatinous silica, precipitated alumina, potassium hydroxide, and a little water in a steel tube at dull redness; and a mixture with the composition of albite with an excess of sodium silicate furnished albite when treated in a similar way. K. von Chrustschoff also obtained quartz and orthoclase by heating a mixture of dialyzed silicic acid, alumina, and potassium hydroxide at 300° for several months. W. J. Müller and J. Königsberger obtained orthoclase by heating aluminium hydroxide with potash water-glass in the presence of carbon dioxide. C. and G. Friedel obtained orthoclase by heating muscovite, potassium silicate, and water at 500°. The

critical temp. of water is near 366°, so that it is probable that steam acts as a gaseous *agent minéralizateur*, discussed by P. Niggli. E. Baur heated variable amounts of water, amorphous silicic acid, and potassium or sodium aluminate in steel tubes for several hours at 520°. Orthoclase and albite were obtained only from soln. containing an excess of base. The results are summarized in Figs. 141 and 142. In his study of the binary system, $NaAlSiO_4$–$KAlSiO_4$, N. L. Bowen found that the sodium compound occurs in two enantiomorphous forms, nephelite and carnegieite, with an inversion point at 1248°. The higher temp. form, carnegeite, melts at 1526°. The potassium compound also shows two forms: kaliophilite, isomorphous with nephelite, and a rhombic form with twinning, like that of aragonite. The rhombic form is apparently stable at temp. above 1540°, and melts at about 1800°. The potassium compound has a eutectic with carnegieite at 1404°. With nephelite, it forms an unbroken series of solid soln. It is concluded, therefore, that $NaAlSiO_4$ and $KAlSiO_4$ are the fundamental mols. of natural nephelite. The presence of calcium and of excess of silica in the natural mineral is explained by the solid soln. of the albite, $NaAlSi_3O_8$, and anorthite, $CaAl_2Si_2O_8$, mols.

W. Vernadsky detected lithium, rubidium, and cæsium in many felspars, and

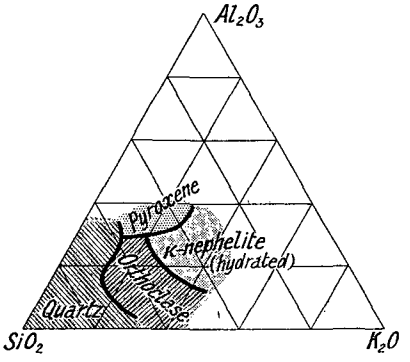



FIG. 141. — The Ternary System, $K_2O$–$Al_2O_3$–$SiO_2$, in the Hydrothermal Reaction at 520°.

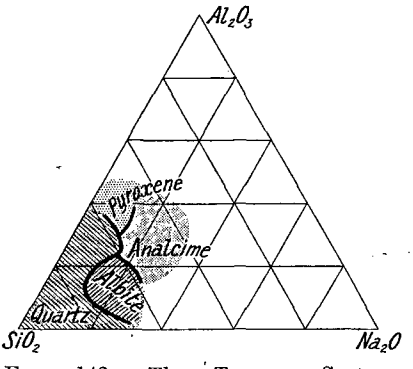



FIG. 142. — The Ternary System, $Na_2O$–$Al_2O_3$–$SiO_2$, in the Hydrothermal Reaction at 520°.

assumed that these elements were present as felspars in solid soln. He synthesized *rubidia-felspar*. P. Barbier found rubidium and lithium in 25 orthoclases and none in 19 microclines. Hence, he suggested the testing for the presence or absence of these elements as a chemical means of distinguishing microclines from orthoclases. W. Vernadsky and E. Revoutsky, however, showed that the test breaks down. Many microclines do contain these elements. H. Ramage confirmed this. W. H. Hillebrand found lithia in some microclines. A. de Gramont found rubidium, cæsium, gallium, and thallium in the microclines from Madagascar; W. Vernadsky also found thallium in some orthoclases. E. Dittler made some felspars which contained *lithia-felspar*, *rubidia-felspar*, and *cæsia-felspar*. The lithia-felspar, $LiAlSi_3O_8$, obtained by R. Ballo and E. Dittler by fusing a mixture of lithium metaluminate and silica in the right proportions melts at about 1250°—*vide lithium aluminium mesotrisilicate*. P. Hautefeuille and A. Perry heated a mixture of silica, ferric oxide, potassium vanadate, and nitrate at 700°, and obtained iron leucite, and *ferric-orthoclase* whose composition corresponds with $KFeSi_3O_8$.

**The physical properties of the alkali-felspars.**—The purer felspars are transparent and colourless. As T. Scheerer [12] indicated, the **colour** of many felspars is due to the presence of various inclusions which act as pigments; these may be microscopic or submicroscopic. The opacity of felspar crystals may arise from a multitude of inclusions. The yellowish, pink, and red tints usually come from iron oxides, although after calcination the red Swedish and Norwegian felspars

often have a whiter colour than the white Canadian felspars. The pinkish felspars are usually potash-felspars, though some albites have the same colour. Green colours are presumably derived from ferrous silicate inclusions, *e.g.* chlorite; but in some cases the cause of the colour is not known—*vide infra*, schillerization. The pearly bluish opalescence of Singalese moonstone may be due to the lamination of different felspars; to inclusions; or to decomposition; it is most conspicuous when turned towards the observer. A. des Cloizeaux attributed the green coloration to copper compounds, but E. Erdmann said the colour is more likely to be organic matter since the green felspar becomes white when calcined. Dark grey felspars owe their colour to innumerable dark-coloured inclusions or minute particles. These are common in the lime-felspars.

The **crystals** of the alkali-felspars were examined by J. B. L. Romé de l'Isle,[13] E. Pini, C. S. Weiss, G. Rose, A. T. Kupffer, J. D. Mackenzie, K. Schlossmacher, etc. The general results showed that the crystals belong to the monoclinic system; and N. von Kokscharoff gave for the axial ratios of orthoclase $a:b:c = 0{\cdot}6585:1:1:0{\cdot}5538$, and $\beta = 63° 56' 46''$. The crystals of plagioclase and anorthite belong to the triclinic system, and since most of these contain appreciable quantities of potassium in solid soln., it must be assumed that monoclinic orthoclase can form isomorphous mixtures with triclinic plagioclase, or that potash-felspar is dimorphous. In 1876, A. des Cloizeaux [14] showed that many potash-felspars are optically triclinic, and he grouped these under the name microcline. About the same time, on account of irregularities in angles and cleavages, E. Mallard, and A. Michel-Lévy suggested that if the cross-twinning and interpenetration of microcline be so minute as to be invisible under the microscope, the crystals would appear to be monoclinic and possess all the optical properties of orthoclase; otherwise expressed, ordinary orthoclase is extremely finely lamellated microcline. If this actually be the case, then orthoclase would be pseudo-monoclinic, but in reality it is triclinic; and the felspars, as a class, are all triclinic. This question has given rise to much duscission by A. Michel-Lévy and A. Lacroix, W. C. Brögger, P. Groth, R. Brauns, H. Förstner, F. Klockmann, F. Rinne, A. Beutell, J. Lehmann, F. Becke, J. H. L. Vogt, etc. H. A. Miers, J. D. Dana, H. Rosenbusch, C. Doelter, F. Zirkel, and G. Tschermak regard potash-felspar as dimorphous with monoclinic orthoclase and triclinic microcline. C. Hintze regards potash-felspar as exclusively triclinic with orthoclase as a pseudo-monoclinic form. According to F. Klockmann, if orthoclase be really triclinic, the axial ratios are $a:b:c = 0{\cdot}6495:1:0{\cdot}5546$, and $\alpha = 90° 7'$, $\beta = 115° 50'$, and $\gamma = 89° 55'$. According to E. Maekinen, alkali-felspars with 0–30 per cent. of orthoclase crystallize triclinic at the highest temp., and those with 30–100 per cent., monoclinic.

The crystals of albite were examined by G. Rose, G. vom Rath, M. Schuster, B. Krebs, etc. A. des Cloizeaux gave for the axial ratios of the triclinic crystals, $a:b:c = 0{\cdot}63347:1:0{\cdot}55771$, and $\alpha = 94° 3'$, $\beta = 116° 28\frac{5}{6}'$ and $\gamma = 88° 8\frac{2}{4}'$; S. von Glinka gave $0{\cdot}6330:1:0{\cdot}5573$, and $\alpha = 94° 5'$, $\beta = 116° 27'$, and $\gamma = 88° 7'$; B. Krebs, $0{\cdot}6352:1:0{\cdot}5584$, and $\alpha = 94° 14{\cdot}6'$, $\beta = 116° 35{\cdot}7'$, and $\gamma = 87° 46{\cdot}0'$; C. Melczer, $0{\cdot}635:1:0{\cdot}5578$, and $\alpha = 94° 6'$, $\beta = 116° 36\frac{1}{2}'$, and $\gamma = 87° 52'$; C. Dreyer and V. M. Goldschmidt, $0{\cdot}6376:1:0{\cdot}5592$, and $\alpha = 94° 15'$, $\beta = 116° 37'$, and $\gamma = 87° 41'$; and C. Viola, $0{\cdot}635:1:0{\cdot}657$, and $\alpha = 94° 15'$, $\beta = 116° 32'$, and $\gamma = 88° 5'$.

The monoclinic felspars with notable amounts of soda can be called *soda-orthoclases;* here the molar proportion of soda is less than that of the potash. When the molar proportion of soda exceeds that of the potash, the crystals are generally triclinic, and are *soda-microclines*, or anorthoclases. P. Barbier and co-workers' analyses of some potash-soda-felspars showed that although the soda was in excess of the potash, the crystals were monoclinic—in one case only 1·15 per cent. $K_2O$ was present. F. Angel described a monoclinic soda-sanidine. The monoclinic soda-felspar was called *barbierite* by W. T. Schaller. It therefore appears that soda-felspar and potash-felspar are dimorphous. The available evidence as to

whether the mixed alkali-felspars are simply isomorphous or isodimorphous is not conclusive. H. Baumhauer, and F. J. Wiik found the **corrosion figures** obtained by treating adularia with hydrofluoric acid are characteristic of the monoclinic system. H. Baumhauer also examined the effect with albite. J. Königsberger and W. J. Müller obtained corrosion figures with potash-felspar and water. A. E. Fersman found tourmaline and felspar grouped together at Mursinka, Ural.

As a rule, equidimensional crystals are found most frequently in potash-felspar in large prismatic crystals. The microscopic crystals of potash-felspar are usually tabular. In the idealized crystal, Fig. 143, the faces are $M(010)$, $P(001)$, $l(110)$, $x(101)$, $y(20\bar{1})$, $o(111)$, and $n(021)$; and the angles are $lM$, 59° 24′; $ll$, 61° 13′; $Px$, 50° 17′; $Py$, 80° 18′; and $Pn$, 44° 57′. These angles have been measured by N. von Kokscharoff, V. von Zepharovich, A. Hamberg, G. A. Kenngott, N. V. Ussing, A. Cathrein, A. des Cloizeaux, A. Lévy, M. von dem Borne, A. Becker, M. Websky, G. vom Rath, R. Brauns, M. Schuster, J. H. Kloos, F. A. Quenstedt, A. Beutell, F. Klockmann, G. Kalb, etc. F. Rinne, S. Kozu and K. Seto investigated the **X-radiogram** of sanidine; S. Kozu and co-workers, the X-radiograms of moonstone, and adularia—*vide infra*, Fig. 146; E. Schiebold, that of albite; and A. Hadding, those of the adularia, sanidine, albite, microcline, microperthite, and anorthoclase. For deductions from the X-radiograms of the alkali felspars, *vide* Fig. 139. The crystals show three distinct **habits**, (i) *the Baveno habit*, in which the crystal is elongated along the faces $PM$, Fig. 144; (ii) *the sanidine habit*, in which the crystals are tabular along $M$, Fig. 145; and (iii) *the adularia habit*, in which the prismatic crystals have rear hemidomes, Fig. 146.

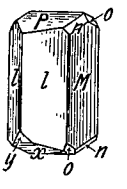



FIG. 143.—Idealized Orthoclase Crystal.

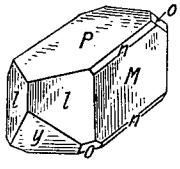



FIG. 144.—Baveno Habit.

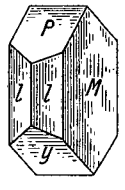



FIG. 145.—Sanidine Habit.

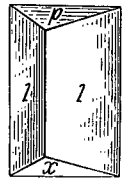



FIG. 146.—Adularia Habit.

The crystals of felspar are usually twinned, but sometimes not twinned. The twinning may be in one, two, or three directions. Sixteen different modes of twinning have been observed. Some are extremely rare; some may be chance groupings. F. Scharff has discussed *Die Bauweise des Feldspäths*. The three most common modes of **twinning** are named after particular localities where the first specimens which attracted notice were found—Carlsbad, Bohemia; Baveno, North Italy; and Manebach, Thuringia. The first two were named by F. A. Quenstedt, and the last one by J. R. Blum. The second kind was described by J. B. L. Romé de l'Isle, and all three were described by R. J. Haüy. The twinning of potash-felspar was also discussed by F. Mohs, C. F. Naumann, J. D. Mackenzie, G. vom Rath, J. F. L. Hausmann, A. Breithaupt, G. Cesaro, G. Rose, N. von Kokscharoff, E. A. H. Laspeyres, G. Tschermak, J. Hirschwald, L. Calderon, F. Klockmann, W. Müller, K. Haushofer, O. Mügge. (i) In *Carlsbad twinning*, Fig. 145, the face $M(010)$ is the plane of the twinning so that it truncates the obtuse edge of the vertical crystal. In the diagram, analogous faces are indicated by a letter with and without a dash. J. W. Goethe thus alluded to the Carlsbad twinning:

> The individuals in the doubled crystals are so interlocked that it is impossible to consider one without considering the other. A description of their form is not sufficient to bring it to the imagination, though they may be considered as two rhombic tables united to one another.

The crystals may be united as in Fig. 147, or that diagram reversed, thus forming right or left-handed twins. (ii) In *Baveno twinning* the crystals are attached to the rocks at one end, and at the free-end they show a very obtuse angle with a twin suture, Fig. 148. The two individuals are united by the $n(021)$ plane. (iii) In *Manebach twinning*, Fig. 149, two individuals are united by the $P(001)$ plane;

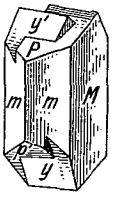



FIG. 147 — Carlsbad Twin.

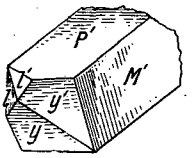



FIG. 148.—Baveno Twin.

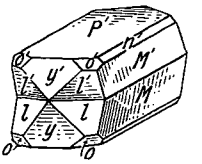



FIG. 149.—Manebach Twin.

and the base and the prism faces of the normal crystal form a prominent re-entrant angle. Sometimes Manebach and Baveno twinnings are combined in a single group.

The faces of the idealized crystal of albite, Fig. 150, are illustrated by $M(010)$, $P(001)$, $L(1\bar{1}0)$, $l(110)$, $x(10\bar{1})$, and $o(1\bar{1}\bar{1})$, and the angle $MP=86°\ 24'$; $Ml=60°\ 26'$; $lL=59°\ 14'$; $Pl=65°\ 17'$; $PL=69°\ 10'$; $Mo=66°\ 18'$; and $Px=52°\ 16'$. Measurements were made by A. des Cloizeaux, F. Klockmann, S. von Glinka, etc. F. Scharff has written *Ueber die Bauweise von Albite und Periklin.* The twinning of albite occurs according to the Carlsbad, Baveno, and Manebach plans, but less frequently than is the case with orthoclase. The so-called albite twinning is exceedingly common. (iv) In the *albite twinning*, Fig. 151, the two individuals are united by the $M(010)$ plane, and the faces $PP'$ at the exposed end make an angle of 7° 12′. (v) In *pericline twinning*, Fig. 152, the contact plane of the individuals

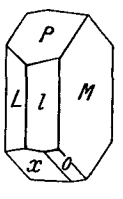



FIG. 150.— Idealized Albite Crystal.

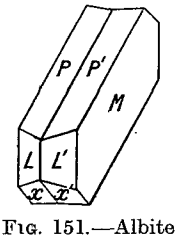



FIG. 151.—Albite Twin.

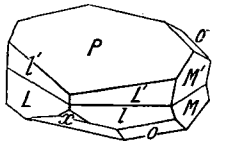


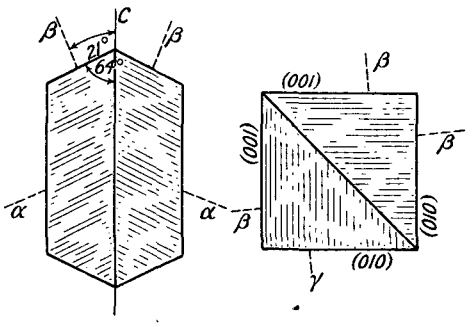

FIG. 152.—Pericline Twin.

is nearly along the plane $P$, not by reflection, but rather by rotation about the edge $Px$. The line of intersection of the faces $MM'$ is not parallel to the edge $PM$, but makes an appreciable angle with it. This angle depends on the composition of the felspar. For instance,

| Microcline. | Anorthite. | Labradorite. | Andesine. | Oligoclase. | Albite. |
|---|---|---|---|---|---|
| −80° | −18° | −9° | 0° | 1° | 13°-27° |

The pericline lamellæ are less common than the albite lamellæ; but both are abundant and very thin in microcline. The polysynthetic twinning of microcline according to the albite and pericline types is common. Fine striations by the albite twinning can often be observed on the basal face. The two kinds of twinning may give a double series of fine lamellæ nearly at right angles to one another, imparting a peculiar and characteristic grating structure when a basal section is examined in polarized light. Parallel growths of albite on orthoclase and orthoclase on albite are common; and the faces $MlL$ are approximately parallel. This

parallel intergrowth is readily seen in perthite; finer parallel intergrowths pass into microperthite or cryptoperthite; and finer still, into anorthoclase. G. Cesaro, G. Rose, G. vom Rath, C. F. Naumann have discussed the twinning of albite. Felspars usually show distinct **cleavage** which may be interrupted without extending to the full length of the crystal. The cleavage parallel to the (001)-face is generally more distinct than that parallel to the (010)-face. Some laval felspars do not show cleavage cracks. The cleavages of Carlsbad and Baveno twins are illustrated in Figs. 153 and 154. S. L. Penfield made some observations on the cleavage of albite; and J. Lehmann, on the contraction cracks in that mineral. Parting is sometimes distinct, and often parallel to the (100)-face, sometimes also parallel to a hemi-orthodome and inclined a little to the orthopinacoid producing a satin-like lustre or **schiller.** The pearly opalescence or schiller may be present when the parting is not distinct. The schiller has been discussed by F. E. Reusch, N. Fukuchi, Lord Rayleigh, A. des Cloizeaux, G. vom Rath, and W. Cross. W. C. Brögger assumes that schillerization is produced by extremely fine interlaminations of albite and orthoclase not discernible microscopically as in cryptoperthite. Moonstone also receives its name from this property. S. Kozu and co-workers showed that the double arrangement of spots in the X-radiogram disappear at 790°, and schillerization also disappears at this temp. Hence, it is inferred that this property is caused by a special arrangement of the space-lattices of two different kinds of solid soln.—*vide infra.* In some cases the schiller is due to the interference phenomena and reflections from minute inclusions arranged in definite positions in felspar crystals—*e.g.* labradorite. The sunstone and aventurine effects are produced by inclusions—hæmatite, or hydrated ferric oxide—which may be quite large. The **fracture** is uneven or conchoidal in directions other than those of the cleavage.




FIGS. 153 and 154.—Cleavages of Carlsbad and Baveno Twins of Orthoclase

In most cases, the plane of the optic axes of orthoclase is perpendicular to the (010)-face, and the normal is inclined 21° to the *c*-axis; in other cases, the plane of the optic axis is parallel to the (010)-face. With microcline, the plane of the optic axes is nearly perpendicular to the (010)-face. A. des Cloizeaux [15] found the optic axes of albite proper are always normal to a plane which cuts the angle (001)(010), and makes with (001) an angle of 101°–102°. A. des Cloizeaux found the **optic axial angles** of adularia to be $2V=69°\ 43'$, and $2E=121°\ 6'$. The angles are very variable with different specimens; and in some cases $2V$ is so small that the crystal is nearly uniaxial. The values observed for different samples of orthoclase by A. des Cloizeaux, E. Goens, T. Wolf, G. vom Rath, A. Mühlheims, K. Zimanyi, and F. Kohlrausch range from $2V=11°\ 51'$–$84°\ 26'$; and $2E=18°\ 14'$–$126°\ 22'$. For microcline, and Na-light, N. V. Ussing obtained $2H_a=87°\ 30'$; $2H_o=101°\ 7'$; and $2V=83°\ 41'$. For albite, A. des Cloizeaux's, and M. Schuster's values range from $2H_a=80°$–$88°\ 50'$; and $2H_o=102°$–$109°\ 26'$ for the red ray. C. Schmidt obtained $2H=83°\ 45'$ for the Li-ray; 84° for the Na-ray; and 84° 18′ for the Tl-ray. K. Zimanyi gave $2V=80°\ 58'$. H. Förstner made numerous observations on the values for anorthoclases, $2E$ ranged from 69° 26′–89° 48′ for Li-light; 68° 27′–88° 27′ for Na-light; and 67° 18′–86° 33′ for Tl-light. $2V$ ranged from 41° 52′–54° 40′ for Li-light; 41° 0′–53° 32′ for Na-light; and 40° 12′–52° 22′ for Tl-light. $2H_a$ ranged from 41° 39′–55° 9′ for Li-light; 40° 52′–54° 19′ for Na-light; and 40° 12′–53° 3′ for Tl-light. $2H_o$ ranged from 125° 14′–151° 33′

for Li-light; 126° 12′–152° 33′ for Na-light; and 127° 21′–154° 15′ for Tl-light. H. Fischer has made a special study of the optical properties of albite.

A. des Cloizeaux found that the effect of raising the *temperature* on the optic axes of microcline is insignificant, but the effect is very marked with orthoclase. The variability of the optic axial angle with temp. indicates an unstable mol. structure with respect to temp. The optic axial angle of sanidine from Laach, with red light, was found to be $2E=13°$ at 18°, and at 42° the crystals became uniaxial; at a higher temp., the optic axes separated out in the vertical plane, becoming parallel to the (010)-face instead of being perpendicular as at 18°. The different stages of this change are illustrated by the optic axial angles of crystals found in nature. In another sample

| Temp. | 43° | 60° | 100° | 150° | 190° | 250° | 302° | 342·5° |
|---|---|---|---|---|---|---|---|---|
| $2E$ | 6° | 18° | 30° | 40° | 46° | 53° | 60° | 64° |

S. Kozu and co-workers represented the relation between the optic axial angle and temp. and wave-length of light constant, and the relation between the optical axial angle and wave-length and temp. constant, by a series of curves. With albite, A. des Cloizeaux found an increase of 2·5° when the temp. rose from 21·5°–170·8°. H. Förstner found that while in some cases, raising the temp. from 20°–250° did not alter the value of $2E$, and on raising the temp. to 500° the value of $2E$ changed from 87° 46′–86° 31′, in other cases there was a change amounting to about 4°. There was usually a steady fall from 20°–250°, and subsequently a small increase. J. Beckenkamp made some observations on adularia; and F. Rinne, on albite. H. Bücking found that the effect of *pressure* was similar to that of temp.

The **specific gravity** has been determined of a large proportion of the samples of felspar which have been analyzed. The numbers for orthoclase range from H. Abich's [16] value 2·2467 for adularia to, for example, G. vom Rath's 2·619 for a sample of orthoclase from Bodenmais. L. Ahlers gave for theoretically pure orthoclase 2·536—2·438 at 4°. There is no appreciable difference in the values for the different varieties; and the best representative value for orthoclase is near 2·537. P. Hautefeuille's value for artificial orthoclase is 2·55 at 16°. Similarly for albite, the values range from G. vom Rath's 2·573 for a sample from Lagenburg, to F. L. Sperry's 2·633 for a sample from Haddam, Connecticut. L. Ahlers gave for theoretically pure albite 2·611–2·613 at 4°. The best representative value for albite is 2·613. P. Hautefeuille's value for artificial albite is 2·61 at 16°. The values for anorthoclase naturally depend on the relative proportions of Na : K, as well as on the composition generally. The observed values range from H. Förstner's 2·595 with a percentage (weight) ratio 7·99 : 2·53, to F. J. Wiik's 2·567 with the weight ratio 5·47 : 11·901; but comparable values for the Na : K ratio are not available since other variations in composition are involved. G. Tschermak, however, gave for adularia, approximately Or to $Or_4Ab$, 13–16 per cent. $K_2O$, the sp. gr. 2·56–2·57; amazonite, $Or_4Ab_2$ to $Or_3Ab_2$, 10–13 per cent. $K_2O$, 2·57–2·58; perthite, $Or_3Ab_2$ to OrAb, 7–10 per cent. $K_2O$, 2·58–2·60; loxoclase, OrAb to $OrAb_4$, 4–7 per cent. $K_2O$, 2·60–2·61; and albite, Ab to $Ab_4An$, 10–12 per cent. $Na_2O$, 2·62–2·64. C. St. C. Deville found that adularia crystals had a sp. gr. 2·561, and after fusion, 2·351; J. A. Douglas obtained respectively 2·575 and 2·370. This corresponds with an expansion of 8·65 per cent. J. W. Mellor obtained with commercial felspar respectively 2·611 and 2·467, or an expansion of about 6 per cent. The effect of the at. vol. of potassium and sodium on the limited isomorphism of albite and orthoclase was discussed by E. T. Wherry. The **hardness** of albite and of adularia on Moh's scale is about 6. F. Auerbach gave for the absolute hardness (**2**. 20, 7) of adularia, 253; or on a scale corundum 1000, 210; R. Frantz gave for the same scale, 392; F. Pfaff, 310; A. Rosiwal, 59; and T. A. Jaggar, 25. P. J. Holmquist found that the abrasive hardness of adularia is 316 for the (001)-face; 478 for the (010)-face; and 493 perpendicular to

(010)(001); he also measured the cutting hardness of adularia, microcline, sanidine, soda-orthoclase, and albite, using carborundum of grain-size 0·006–0·012 mm. on different faces of the crystals. The results are illustrated by Fig. 155.

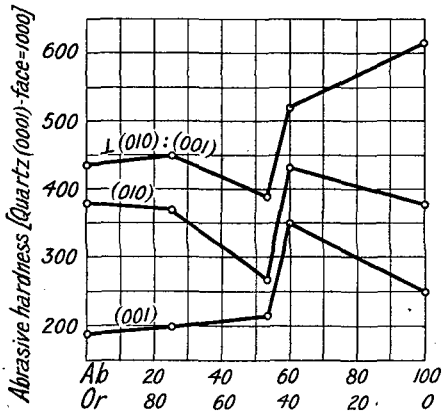



Fig. 155.—Cutting Hardness of the Albite-Orthoclase Felspars.

F. Auerbach gave for the **elastic modulus** of adularia, perpendicular to the base, 8460 kgrms. per sq. mm., and of sanidine, 8030 kgrms. per sq. mm. F. Rinne found 8120 kgrms. per sq. mm. for adularia, and 7710 for sanidine; and for the crushing strength of orthoclase (Hirschfeld), 1700 kgrms. per sq. cm. According to L. H. Adams and E. D. Williamson, the **compressibility**, $\beta$, of microcline, $Or_{91}Ab_9$, is $1{\cdot}92\times10^{-6}$ at 0 megabars, $1{\cdot}88\times10^{-6}$ at 2000 megabars, and $1{\cdot}68\times10^{-6}$ at 10,000 megabars, or $\beta=0{\cdot}0_51875-0{\cdot}0_{10}242(p-p_0)$; orthoclase and microperthite have nearly the same values for their compressibilities. E. Madelung and R. Fuchs gave $\beta=1{\cdot}74\times10^{-6}$ ($p=125$ atm.) for orthoclase, and adularia. P. W. Bridgman failed even at 30,000 kgms. press. per sq. cm. to make finely powdered felspar particles weld, owing possibly to films of air.

H. Kopp [17] gave for the coeff. of **cubical expansion** of orthoclase between 13° and 47°, 0·000026; and between 15° and 99°, 0·000017. F. Pfaff found the mean **linear expansion** coeff. of adularia to be 0·000015687 in a direction perpendicular to the *a*- and *c*-axes; 0·000000059 in the direction of the *b*-axis, and 0·000002914 in the direction of the *c*-axis. The coeff. of cubical expansion is then 0·00001794. H. Fizeau found for the axes of greatest mean and least dilatation of adularia 0·000019052, 0·000001507, and 0·000002030 respectively. The mean linear expansion is —0·000002030 to —0·0000020039; and J. Beckenkamp gave for the coeff. of linear expansion of adularia in the three directions 0·00001758, 0·0000019, and 0·0000063. E. S. von Federoff, E. Offret, and J. Joly also made observations on the thermal expansion of felspar. H. de Sénarmont found the **thermal conductivity** to be greatest in the direction of the symmetrical axes. E. Jannetaz found the sq. root of the ratio of the thermal conductivity in the direction of the symmetry axis (100), to the (001) axis in the direction (001) to be 0·951. F. E. Neumann found the **specific heat** of adularia to be 0·1861; of felspar from Lommitz, 0·1911; and of albite from Penig, 0·1961. H. Kopp gave 0·183 for orthoclase between 20° and 51°; and 0·190 for albite between 21° and 51°. P. E. W. Oeberg gave 0·1897 for orthoclase, and 0·1976 for albite between 15° and 100°. J. Joly gave for orthoclase 0·18865–0·18992 between 11° and 100°; between 0·18696 and 0·19219 for microcline; and between 0·19828 and 0·19846 for albite. R. Ulrich gave 0·1952 for orthoclase between 17° and 98°. K. Schulz found between 20° and 100° for amorphous (glass) adularia 0·1895, and crystalline, 0·1855; for amorphous microcline between 0·1881 and 0·1919, and crystalline, between 0·1845 and 0·1878. G. Tammann also gave for amorphous microcline 0·185 and for crystalline 0·197 between 20° and 100°. G. Lindner gave for adularia at 50°, 0·1835; at 100°, 0·1864; at 150°, 0·1956; and at 250°, 0·2140. A. Bartoli found the sp. ht. of orthoclase between 25° and 100° to be 0·204; between 28° and 309°, 0·226; and between 33° and 715°, 0·253. W. P. White gave for orthoclase crystals between 0° and 500°, 0·2247; and 0°–1100°, 0·2509; likewise for orthoclase glass 0·2297 at 0°–500°, and 0·2589 at 0°–1100°; for the true sp. ht. at 500° and 1100° he gave respectively 0·257 and 0·279 for orthoclase crystals, and 0·264 and 0·279 for the glass. A. Dannholm made measurements on this subject; and S. Kozu and

S. Saiki found abrupt changes in the linear expansion of adularia at 280°, 480°, 680°, 870°, and 950°.

Orthoclase has no sharp **melting point.** It melts slowly on a rising temp.; while its **rate of fusion** is small, its **rate of crystallization** must be extremely slow. A. L. Day and E. T. Allen [18] were unable to crystallize the cooling mass by slow cooling, by mechanical vibration and shock during cooling; by circulating air, carbon dioxide, or water vap. about the cooling mass; or by the action of an alternating current on the cooling mass. The difficulty in crystallization was attributed to the great viscosity of the molten glass. According to A. L. Day and E. T. Allen, the dry crystalline powder was heated and prodded from time to time with a stout platinum wire. At about 1000°, traces of sintering were observed; at 1075°, it had formed a solid cake which resisted the wire; at 1150°, the cake had softened sufficiently to yield to a continuous press.; and at 1300°, it had become a viscous liquid which would be drawn out into glassy opaque threads. Under the microscope, the opacity appeared to be due to fine included bubbles, the material being wholly vitreous. The term *melting point* thus appears somewhat of a misnomer, since the " point " is not a definite temp. but an interval of temp.—*softening temperature* is therefore a better term. This phenomenon is the normal kind of thing with complex aluminium silicates. S. Kozu and co-workers found that when examined by the X-radiogram method, a potash-felspar with about 23 per cent. of albite shows feeble indications of fusion at 1100°, and only at 1213° was fusion complete. The mineral was kept at the indicated temp. for 2 hrs. The liquidus therefore begins at 1213°, and the solidus at 1100° with a melting interval of 113°. In the particular case of orthoclase, G. W. Morey and N. L. Bowen showed that there is an incongruent m.p. at 1170°, incongruent because the liquid has a different composition from the solid owing to the formation of a new crystalline compound, namely, leucite, $KAlSi_2O_6$. Otherwise expressed, orthoclase decomposes at 1170°, forming leucite, $KAlSi_2O_6$, and a liquid. Its behaviour is best described on an equilibrium diagram with leucite (Lc) and silica as components. Orthoclase then appears as a binary compound of these components. If orthoclase be kept at 1200° for a week, the glassy mass contains leucite crystals and crystallites. The resolution of molten orthoclase into leucite was previously discussed by H. Bäckström, A. Lacroix, and C. Doelter. The speed of fusion depends on the size of grain; and J. W. Mellor and co-workers showed that there is a probability that the actual fusion temp. is lower with a fine powder than it is with coarser grains. This subject was discussed by W. Ostwald, F. W. Küster, R. C. Smith, P. Pawloff, M. T. Goldstein, P. P. von Weimarn, and C. Doelter. It is possible, as pointed out by G. Beilby, that the grinding renders the surfaces of the particles vitreous or amorphous—*vide* the sp. gr. of quartz. H. Leitmeier found that fine grains of adularia begin to melt at 1240°, coarse grains at 1300°; complete fusion occurred at 1350° with the fine grains and 1370° with the coarse grains. The high values here obtained were due to rapid heating; with slower heating, the m.p. appeared as 1145°. S. Kozu and co-workers also found evidence of a faster fusion with finely powdered felspar than is the case with the coarser-grained material. Accordingly, the reported values for the fusion temp. of orthoclase are somewhat discordant, and range from 1140° to 1300°. J. Joly obtained 1140° for the m.p. of sanidine; and 1175° for adular, microcline, and albite. R. Cusack gave

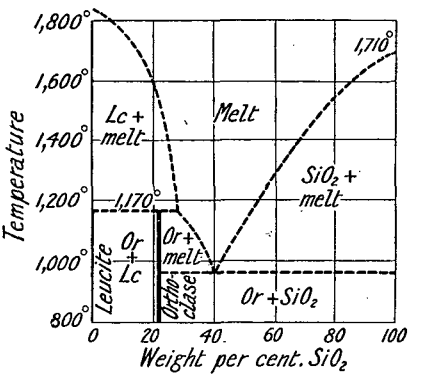



FIG. 156.—Equilibrium Curves of the Binary System: $KAlSi_2O_6$–$SiO_2$.

1169° for microcline, and 1172° for albite; A. L. Fletcher corrected these values to 1219° for microcline, 1214°–1218° for adularia, and 1222° for albite. J. H. L. Vogt gave 1300° for potash-felspar. H. A. Seger, and A. S. Watts made observations on the relation between the composition and fusibility of felspars. E. Dittler gave for soda-microcline, 1175°–1200°; soda-felspar, 1137°–1180°; crypto-perthite, 1130°–1140°; microcline, 1160°–1180°. C. Doelter gave for different samples of orthoclase, 1185°–1220°, and 1175°–1235°; for sanidine, 1145°–1175°; for microcline, 1150°–1160°, 1155°–1180°, and 1160°–1265°; and for albite, 1120°–1160°, 1130°–1170, and 1135°–1215°. A. Brun found 1250° for albite, 1300° for orthoclase, and 1290° for microcline. Y. Yamashita and M. Majima gave 1250° for the m.p. of an albite orthoclase. A. L. Day and E. T. Allen gave 1175°–1235° for orthoclase; 1220° for natural albite, and 1225° for artificial albite.

A. L. Day and co-workers found the m.p. near the albite end of mixtures of soda- and potash-felspars are difficult to determine on account of the high viscosity of the melting solids. E. Dittler believed that albite and orthoclase form a completed series of mixed crystals with a minimum m.p.; J. H. L. Vogt estimated that there is a eutectic between 1150° and 1160° with between 56 and 60 per cent. of albite and between 40 and 43 per cent. of orthoclase. He assumed that the eutectic mixture consisted of two kinds of felspar with the respective compositions $Or_{72}Ab_{28}$ and $Or_{12}Ab_{88}$. P. Tschirwinsky modified the equilibrium diagram to make it fit the facts a little better—*cf.* Fig. 140. The equilibrium is illustrated diagrammatically in Fig. 157. C. H. Warren estimated that orthoclase can carry up to about 10 per cent. of albite in solid soln., and that albite may take up similarly 8 per cent. of orthoclase. If a potash-felspar has more than about 10 per cent. of albite in solid soln., as the temp. falls, there will be a dissociation into two kinds of solid soln., and the so-called perthitic structure is considered to be a result of this dissociation. The perthitic structure thus occurs with potash-felspars carrying more than about 18 per cent. of albite. Similarly with soda-felspar carrying more than 8 per cent. of orthoclase. C. H. Warren also found evidence of an inversion point in potash-felspar above 575°; below this temp. α-potash-felspar is stable; above, β-potash-felspar. A. L. Day and co-workers found no signs of a break in the heating and cooling curves of felspar. This subject has been discussed by R. Herzenberg, and P. Tschirwinsky. H. Leitmeier observed a slight loss in weight which he attributed to the loss of alkali, when adularia (m.p. 1145°) or labradorite (m.p. 1245°) is kept about 10° below the m.p. for 500 hrs. The loss was of the order 0·2 per cent.

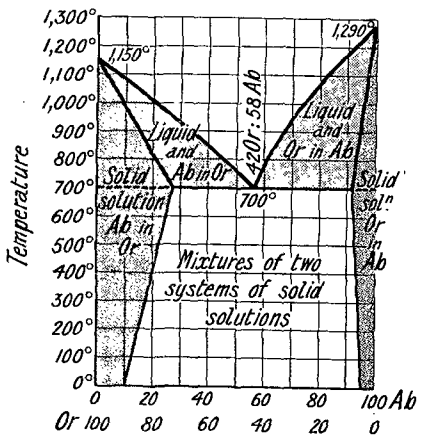



FIG. 157.—Freezing-point Curves of Mixtures of Albite and Orthoclase.

The **X-radiograms** of sanidine by F. Rinne, and of adularia, moonstone, etc., by S. Kozu and Y. Endo are normal and characteristic of one system of space-lattices, as L. Vegard and H. Schjedrup found to be characteristic of a simple lattice in which corresponding atoms replace one another at random, forming a homogeneous solid soln. The case is different with the potash-felspar moonstone containing about 23 per cent. of albite. S. Kozu and Y. Endo found that X-radiogram furnishes two systems of space-lattices representing the co-existence of two kinds of solid soln. The X-radiogram of adularia suffers no change when the temp. is raised from 25° to 1060° and suddenly quenched in mercury at room temp. This indicates that the crystal structure is stable throughout this range. On the other

hand, when the temp. of moonstone is raised, one of the two different systems of Laue-spots begins to decrease in intensity and to shift gradually towards the other, and the two systems merge into one. When the temp. is *slowly* reduced, the system of Laue-spots, stable at a high temp., begin to separate into two systems. Chillings in liquid air produce no appreciable difference to the results obtained by chilling in mercury at room temp. Fig. 158 shows portions of the X-radiograms of a potash-felspar heated to the temp. indicated above and rapidly chilled. Below 800°, the miscibility is incomplete, but at higher temp. albite and orthoclase are miscible in all proportions. If heated above 1115°, the spots gradually decrease in intensity, indicating that the space-lattices are gradually broken down into the disorderly arrangement of the amorphous state, and at 1190° the spots had almost all disappeared corresponding with almost complete fusion. A. Hadding did not find the differences in the X-radiograms to be sufficient for the identification of the different felspars.

The ceramic journals have an indefinitely large number of results of experiments on various mixtures of clay with felspar, felspathic rocks, and other fluxes. Mixtures of orthoclase and quartz were found by M. Simonis to give glassy mixtures

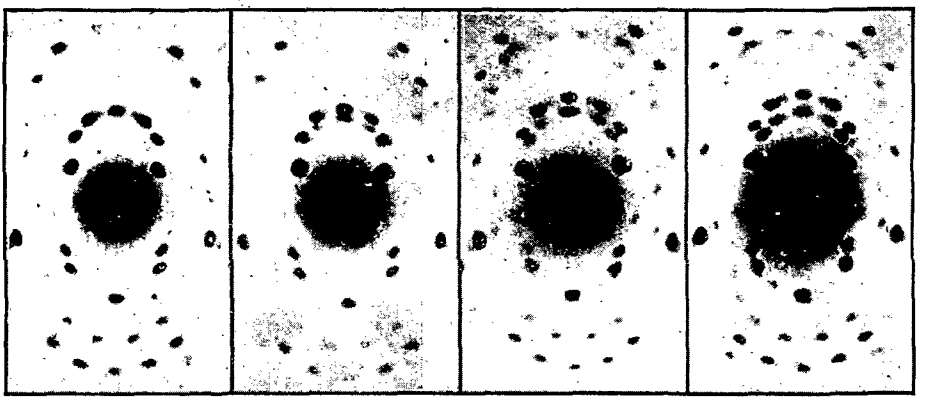


FIG. 158.—Effect of Heating and Chilling Or–Ab felspar with about 24 per cent. of Albite.

with no sign of a eutectic; A. S. Watts made analogous observations and obtained indications of a eutectic with 5 per cent. of felspar; J. W. Mellor likewise obtained indications of a eutectic with 25 per cent. of quartz. In both cases, however, the results measure some other quality but not eutectism. Pegmatite with about 25 per cent. of quartz and 75 per cent. of felspar has been thought to represent the eutectic, but there is no proof of this. A. Zöllner estimated that at 1400°–1450°, molten orthoclase can dissolve 60–70 per cent. of quartz. The fusion temp. of mixtures of china clay and felspar were measured by M. Simonis. A. Heath and J. W. Mellor made a rough estimate that at 1300°, molten orthoclase dissolves about 20 per cent. of clay to form a clear glass in a 3 days' heating, and A. Zöllner estimated that about 14 per cent. is dissolved at 1400°–1460° to form a clear glass. E. Berdel and many others have determined the shrinkage and porosity of slabs made of mixtures of felspar and clay. M. Simonis measured the softening temp. of ternary mixtures of felspar, quartz, and china clay, and the results are summarized in Fig. 159. W. S. Howat found that with binary mixtures of steatite melting at 1380°, and microcline melting at 1232°, there was a eutectic in the vicinity of 1160°.

A. L. Day and E. T. Allen found that felspars could be readily sublimed in the electric arc furnace—about 3700°. D. D. Jackson and J. J. Morgan found the **vapour pressure** of the alkali to be negligibly small below 1350°. N. V. Kultaschaff computed for the latent **heat of fusion** of orthoclase, 109·4 cals., and for albite,

48·5 cals. J. H. L. Vogt gave 100 cals. for potash-felspar. O. Mulert found the **heat of solution** of crystalline adularia in hydrofluoric acid to be 0·4686 Cal. per gram, or 261·5 Cals. per mol, and for glassy adularia, respectively 0·5684 and 317·3. Using some of G. Tammann's data, he accordingly calculated for the **heat of formation** of adularia, 131·2 Cals. per mol, or 0·235 Cal. per gram; and for microline, 104·2 Cals. per mol, or 0·187 Cal. per gram; similarly, for the **heat of crystallization** of adularia, he obtained 53·72 Cals. per mol, or 99·8 Cals. per gram; and for adularia and microcline, respectively 46·33 and 83·0 Cals. Hence, added C. Doelter, adularia and microcline are probably dimorphous forms of potash-felspar. G. Tammann gave 517 cals. for the heat of soln. of microline in a mixture of hydrochloric and hydrofluoric acids, 517 cals. per gram for the crystals, and 600 cals. per gram for the glass.

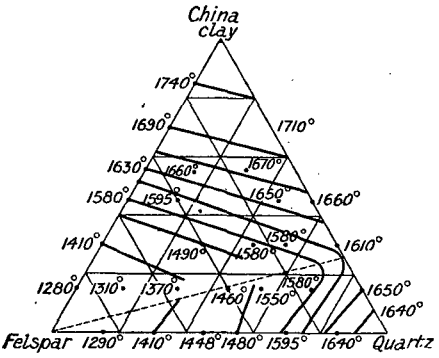



FIG. 159.—Softening Temperatures of Mixtures of Orthoclase, Quartz, and China Clay.

The **indices of refraction** of potash-felspar were measured by A. des Cloizeaux,[19] F. Kohlrausch, K. Zimanyi, A. Mühlheims, S. Tsuboi, H. Rosenbusch and E. A. Wulfing, N. V. Ussing, A. Michel-Lévy and A. Lacroix, E. Offret, H. Fischer, C. Viola, etc. A. des Cloizeaux obtained for sanidine $\alpha=1{\cdot}5170$, $\beta=1{\cdot}5239$, and $\gamma=1{\cdot}5240$ for red light, and $\alpha=1{\cdot}5265$, $\beta=1{\cdot}5355$, and $\gamma=1{\cdot}5356$ for blue light; and E. Offret, $\alpha=1{\cdot}520278$, $\beta=1{\cdot}524853$, and $\gamma=1{\cdot}524972$ for yellow light. The values for adularia range from $\alpha=1{\cdot}5181$–$1{\cdot}5195$, $\beta=1{\cdot}5223$–$1{\cdot}5237$, and $\gamma=1{\cdot}5243$–$1{\cdot}5260$ for yellow light; and for microcline, $\alpha=1{\cdot}5183$–$1{\cdot}5224$, $\beta=1{\cdot}5220$–$1{\cdot}5250$, and $\gamma=1{\cdot}5248$–$1{\cdot}5295$ for yellow light. For soda-potash-felspars, the values range from $\alpha=1{\cdot}5215$–$1{\cdot}5250$, $\beta=1{\cdot}5266$–$1{\cdot}5306$, and $\gamma=1{\cdot}5272$–$1{\cdot}5314$ for yellow light. For albite, $\alpha=1{\cdot}5282$–$1{\cdot}5320$, $\beta=1{\cdot}5321$–$1{\cdot}5340$, and $\gamma=1{\cdot}5386$–$1{\cdot}5400$. The best representative values are near $\alpha=1{\cdot}519$, $\beta=1{\cdot}524$, and $\gamma=1{\cdot}526$—mean $1{\cdot}532$—for orthoclase and microcline; and $\alpha=1{\cdot}525$, $\beta=1{\cdot}6306$, and $\gamma=1{\cdot}5314$—mean $1{\cdot}529$—for albite. W. T. Schaller found the index of refraction of barbierite to be lower than that of albite. A selection from E. Offret's observations on the effect of temp. and of light of different wave-length, $\lambda$, on the refractive index of sanidine, is given in

TABLE XXIII.—THE EFFECTS OF TEMPERATURE AND OF LIGHT OF DIFFERENT WAVE-LENGTH ON THE REFRACTIVE INDEX OF SANIDINE.

| | $\theta$ | Red. | | Yellow. | Green. | | Blue. |
|---|---|---|---|---|---|---|---|
| | | $\lambda_{Li}=0{\cdot}6706$ | $\lambda_{Cd}=0{\cdot}6437$ | $\lambda_{Na}=0{\cdot}5888$ | $\lambda_{Cd}=0{\cdot}5377$ | $\lambda_{Cd}=0{\cdot}5084$ | $\lambda_{Cd}=0{\cdot}4799$ |
| I. $\alpha$ | 0° | 1·517835 | 1·518632 | 1·520621 | 1·523045 | 1·524766 | 1·526774 |
| | 100° | 1·518063 | 1·518866 | 1·520869 | 1·523312 | 1·525056 | 1·527070 |
| | 200° | 1·518423 | 1·519232 | 1·521249 | 1·523712 | 1·525470 | 1·527498 |
| | 300° | 1·518888 | 1·519703 | 1·521737 | 1·524218 | 1·525989 | 1·528034 |
| II. $\beta$ | 0° | 1·522410 | 1·523213 | 1·525218 | 1·527660 | 1·529403 | 1·531416 |
| | 100° | 1·522560 | 1·523376 | 1·525410 | 1·527892 | 1·529664 | 1·531709 |
| | 200° | 1·522847 | 1·523672 | 1·525728 | 1·528237 | 1·530027 | 1·532096 |
| | 300° | 1·523246 | 1·524075 | 1·526143 | 1·528665 | 1·530465 | 1·532543 |
| III. $\gamma$ | 0° | 1·522503 | 1·523313 | 1·525332 | 1·527793 | 1·529549 | 1·531576 |
| | 100° | 1·522881 | 1·523702 | 1·525743 | 1·528235 | 1·530014 | 1·532066 |
| | 200° | 1·523407 | 1·524234 | 1·526293 | 1·528805 | 1·530598 | 1·532667 |
| | 300° | 1·524056 | 1·524886 | 1·526953 | 1·526953 | 1·529476 | 1·533354 |

Table XXIII. A. des Cloizeaux' value for the **birefringence**, $\gamma-\alpha$, of sanidine is 0·0070 for red light, and 0·0091 for blue light; and E. Offret's for yellow light is 0·004469. The values for adularia range from 0·0054–0·0070 for yellow light; for microcline from 0·0060–0·0071; for albite, 0·0080–0·0102; and for soda-potash-felspars, from 0·0057–0·0071 for yellow light. The best representative values are $\gamma-\alpha=0·007$ for microcline and orthoclase; and 0·0064 for albite. From E. Offret's observations, the indices of refraction of sanidine at 0° are $\gamma-\beta=0·00005$, $\beta-\alpha=0·00460$, and $\gamma-\alpha=0·00462$, and the corresponding changes per 100° rise of temp. are respectively +0·00021, −0·00006, and +0·00016. A. Ehringhaus studied this subject. Orthoclase, microcline, and anorthoclase are optically negative; albite is optically positive.

W. W. Coblentz found the curve of the **ultra-red transmission spectrum** of adularia shows bands at 2·0$\mu$, 3·2$\mu$, 3·9$\mu$, 4·8$\mu$, 5·6$\mu$, and 6·3$\mu$, and the bands of albite at 2·9$\mu$, 5·7$\mu$, and 6·3$\mu$ coincide with those of adularia. Orthoclase has silicate bands at 2·85$\mu$, 4·7$\mu$, 5·7$\mu$, and 6·28$\mu$. As in the case of the transmission spectra, the curves of the **ultra-red reflection spectra** of adularia and albite are very much alike The maxima with albite are at 8·7$\mu$, 9·7$\mu$, and 10$\mu$, and those with adularia are at 8·8$\mu$ and 9·8$\mu$—Fig. 160. With microcline, the reflection band from 9$\mu$–10$\mu$ is complex; there are sharp maxima at 8·85$\mu$ and 9·95$\mu$, with a probable band at 11$\mu$. W. W. Coblentz found the **reflecting power** of orthoclase for light of wave-length $\lambda=0·69$ is 39·4 per cent.; for $\lambda=0·95\mu$, 86·7 per cent.; for $\lambda=4·4\mu$, 38·2 per cent.; for $\lambda=8·8\mu$, 10·3–14·6 per cent.; and for $\lambda=24\mu$, 9·7 per cent.

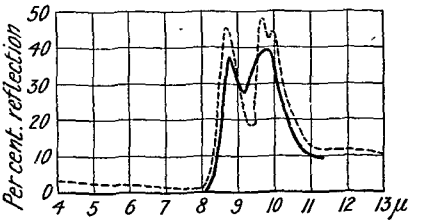



FIG. 160.—Ultra-red Reflection Spectra of Orthoclase, and Albite (dotted line).

K. Przibram studied the **phosphorescence** of orthoclase, and adularia when exposed to **radium rays.** D. Hofmann, G. de Razowmowsky, and W. Vernadsky noted the **tribo-luminescence** of felspar. K. Keilhack observed no luminescence with orthoclase. E. Engelhardt found orthoclase and microcline to have a feeble greyish-blue luminescence when exposed to **ultra-violet rays**. C. Doelter found that **radium radiations** gave a strong phosphorescence with orthoclase from Elba, but with other specimens the effect was feeble; no change in colour occurred. J. E. Burbank observed that **X-rays** make felspar phosphoresce; C. Doelter found adularia and albite are partially transparent to the X-rays.

C. Doelter [20] found the **electrical resistance** of adularia decreases with the rise of temp. The sp. electrical resistance, in ohms, on raising the temp. was:

| | 1000° | 1070° | 1200° | 1260° | 1300° | 1320° |
|---|---|---|---|---|---|---|
| Ohms | 13706 | 317·5 | 55·6 | 10·2 | 7·5 | 7·1 |

and on cooling the mineral:

| | 1300° | 1260° | 1200° | 1160° | 1100° | 1060° |
|---|---|---|---|---|---|---|
| Ohms | 7·4 | 8·1 | 9·4 | 10·9 | 13·3 | 15·0 |

There is no sign of a break in the curves at the softening temp. The sp. **electrical conductivity** of crystalline orthoclase is less than that of glassy orthoclase. The conductivity for glassy orthoclase has a break at 850°, and above 1000°, it gives a curve almost continuous.

| | 1100° | 1200° | 1240° | 1260° | 1300° | 1320° |
|---|---|---|---|---|---|---|
| Sp. elect. cond. | 0·04537 | 0·00411 | 0·01469 | 0·02182 | 0·02961 | 0·031133 |

Similarly, for albite:

| | 1523° | 1473° | 1418° | 1373° | 1313° | 1273° | 1213° |
|---|---|---|---|---|---|---|---|
| $R$ | 21·25 | 22·71 | 28·41 | 32·2 | 43·1 | 46·8 | 69·3 |

If the reciprocal of the temp. be plotted against log $R$, an approximately straight line is obtained, so that $\log R=\theta^{-1}+C$, where $C$ is constant. For the **electrical conductivity** of orthoclase C. Doelter gave 0·0000537 mho at 1100°; 0·00411 mho at 1200°; and 0·02961 mho at 1300°. J. Königsberger and K. Schilling gave 8500 ohms for the sp. resistance of orthoclase at 800°; and 800 ohms at 1000°. G. Tammann measured the electrode potential of orthoclase against the normal hydrogen electrode in soln. of various salts—zinc and silver sulphates, lead chloride, etc. G. W. Hankel found that orthoclase is **pyroelectric**; the face (010) is positively electrified, and the face (110) negatively electrified. He also found albite to be pyroelectric.

**The chemical properties of the alkali-felspars.**—According to A. des Cloizeaux,[21] when adularia is fused, it loses only about a thousandth part of its weight. E. Wolff examined the loss on ignition of felspars. A. L. Day and E. T. Allen found that when powdered felspars are exposed to the atm., moisture is adsorbed in quantities of the same order of magnitude as that usually quoted in mineral analyses; and that it requires a dull red heat—600°–800°—to expel all the moisture. M. W. Travers heated a felspar which contained about one per cent. of water, and obtained 0·214 per cent. of a mixture of hydrogen and carbon monoxide, and 1·201 per cent. of carbon dioxide. The two former gases are presumably formed by a reaction with the ferrous oxide, steam, and carbon dioxide: $2FeO+H_2O=Fe_2O_3+H_2$ and $2FeO+CO_2=Fe_2O_3+CO$. No hydrogen or carbon monoxide is produced when the mineral is treated with sulphuric acid.

G. A. Kenngott[22] found that when sanidine, adularia, or albite is moistened with **water** coloured with red litmus, the test-liquid is coloured blue. If felspar be ground in water for some hours the water becomes viscid, owing to the dissolution and hydrolysis of alkali silicate. In 1835, G. Forchhammer heated felspar with water in closed copper tubes to 150° and 222° (21 atm. press.), and found that much soluble potassium silicate (water-glass) was formed. Water hydrolyzes the mineral. S. J. Thugutt found that when 3·3153 grms. of a sample of typical orthoclase were exposed for 100 hrs. in contact with 500 c.c. of distilled water at 200°, the water on evaporation furnished a dry residue with 66·76 per. cent. of silica; 11·53 per cent. of potash; and 3·56 per cent. of soda. He also treated albite and obtained similar results. A. Daubrée also obtained 12·6 grms. of potash from 5 kgrms. of felspar. Confirmatory experiments were made by C. G. C. Bischof, W. P. Headden, K. Haushofer, A. Beyer, A. Pfaff, J. Königsberger and W. J. Müller, G. Steiger, D. Prianischnikoff, L. Splichal, J. W. Mellor, and M. Biéler-Chatelain. A. Pfaff worked with water at 8° under a press. of 160 atm. The effect of water on albite was examined by F. W. Clarke, G. Steiger, A. Bygden, etc. According to A. S. Cushman and P. Hubbard, and V. Lenher, the attack by water is more rapid when the mineral is finely ground. According to A. E. Tucker,[23] when powdered felspar is digested for 10 days at ordinary temp. with carbonated water, it is converted into a white powder resembling clay, and some micaceous-looking substance is simultaneously formed. Finely powdered felspar colours phenolphthalein almost immediately when wetted with water. A certain amount of the potassium of felspars is dissolved by water when the mineral is finely ground, and the amount dissolved is increased by addition of substances such as ammonium salts, lime, and gypsum. Complete dissolution of the potassium can be effected by means of an electrolytic method, both with and without addition of hydrofluoric acid. C. G. C. Bischof, W. B. and R. E. Rogers, E. C. Sullivan, C. Matignon and M. Marchal, A. Johnstone, F. Cornu, E. W. Hofmann, L. Splichal, and J. R. Müller have investigated the action of carbonated water, or **carbonic acid.** The last-named found:

| | $SiO_2$ | $Al_2O_3$ | CaO | $K_2O$ |
|---|---|---|---|---|
| Original felspar . . . . . | 65·24 | 18·15 | 1·28 | 14·96 |
| Extracted matter . . . . | 1·1552 | 1·1368 | — | 1·3527 |

The high proportion of potash which is extracted shows that the action is rather

a chemical process than one of mere dissolution. The attack by water was found by A. Brongniart and J. Malaguti, and by A. S. Cushman to be accelerated by passing an electric current through the water holding pulverulent felspar in suspension—*vide* kaolinite.

In general, the effect of acids on albite is less marked than is the case with orthoclase. G. Tschermak[24] obtained silicic acid, $H_2Si_3O_7$, by the action of hydrochloric acid on albite. The ordinary **acids** attack felspar rather slowly; the action is more rapid if the mineral be finely ground. The powdered mineral is rapidly decomposed by **hydrofluoric acid**; the action was studied by H. Baumhauer, and F. J. Wiik. J. H. Collins passed the vap. of hydrofluoric acid over felspar heated in a lead tube, and found the mineral to be rapidly converted into a hydrated aluminium silicate, soluble potassium fluoride, and silica. Dil. hydrofluoric acid acts in a similar manner. Orthoclase is more readily attacked than albite or oligoclase; and labradorite is attacked only in spots. The hydrated aluminium silicate had the same composition and appearance as china clay. E. Reymond studied the action of **chlorine** and of **hydrogen chloride** on adularia, and amazon stone. A. E. Tucker found that very dil. hydrofluoric, **hydrochloric, nitric, or sulphuric acid** decomposes powdered felspar in ten days, forming a white powder resembling china clay, and a scaly product micaceous in character. The solvent action of hot sulphuric acid on felspar was indicated by H. Rose. H. A. Seger, A. Sabeck, and W. Jackson and E. M. Rich found that about 2·24 per cent. of felspar was decomposed after an hour's treatment with conc. sulphuric acid; K. Langenbeck found 17·3 per cent. dissolved. J. W. Mellor showed that the amount dissolved depends on the grain-size of the felspar; with felspar of average diameter, 0·165, 0·082, and 0·032 mm., respectively, 0·34, 0·64, and 15·64 per cent. was decomposed by the acid treatment in a given time. If the felspar be weathered, a greater proportion is broken down. L. Splichal also treated orthoclase with **formic acid,** as well as with hydrochloric and sulphuric acid. W. B. Schmidt found aq. **sulphurous acid** extracted nearly three per cent. of soluble matters; and H. Lotz examined the effect of air charged with **sulphur dioxide** on sanidine and orthoclase. H. St. C. Deville found that boiling conc. soln. of **potassium hydroxide** decomposes felspar, forming a soluble alkali silicate, and an insoluble potassium aluminosilicate. The latter dissolves readily in acids. C. Doelter found that 15 per cent. soln. of **sodium hydroxide** removed 0·24 per cent. of $K_2O$ from adularia, and 2·20 per cent. from microcline at 200°. W. Flight found that after digesting adularia for 25 hrs. with soda-lye, the portion dissolved contained less alumina than the portion not dissolved; he also treated albite in a similar way. E. A. Stephenson studied the action of alkaline soln. on the felspars. G. Tammann and C. F. Grevemeyer found that **magnesia** does not act on orthoclase at 1000°; **lime** acts slowly at 500°; and **baryta** acts strongly at 275°–350°. A soln. of **sodium carbonate** dissolved some felspar after about 24½ hrs.' action at 100°. J. Lemberg treated orthoclase with soln. of the strong alkalies and transformed the mineral into zeolitic substances with an exchange of the basic element—thus andesine with sodium carbonate soln. forms analcite, and with **potassium chloride** soln., leucite. F. A. Genth also noted the alteration of potash- into soda-felspar by the substitution of bases. J. Splichal examined the effect of soln. of **barium and magnesium chlorides** on felspar; and F. W. Clarke and G. Steiger, the effect of **ammonium chloride** soln. on orthoclase, and on albite. J. Lemberg digested albite with a soln. of sodium silicate, and obtained a substance resembling cancrinite with $SiO_3$ in place of $CO_3$. H. Schneiderhölm studied the action of various salt soln. on felspars. G. André has investigated the action of soln. of different salts, and found that after grinding 10–20 grms. of felspar with 100 grms. of water and a gram of the given salt for 100 hrs. in an agate mortar, the amounts of potash indicated in Table XXIV were dissolved. The marked attack by ammonium sulphate is noteworthy. H. Streme, and E. C. Sullivan also examined the influence of a number of different substances on felspar. H. Leitmeier and H. Hellwig showed that felspar can slowly take up

TABLE XXIV.—ACTION OF SALT SOLUTIONS ON POTASH-FELSPAR.

| Solvent. | Grams of potash, $K_2O$, dissolved per | |
|---|---|---|
| | 100 grms. felspar. | 100 parts of $K_2O$ in the felspar. |
| Water alone | 0·139 | 0·22 |
| Sodium chloride | 0·37 | 3·25 |
| Calcium carbonate | 0·27 | 2·38 |
| Calcium orthophosphate | 0·22 | 1·96 |
| Calcium dihydrophosphate | 0·44 | 3·90 |
| Sodium nitrate | 0·36 | 3·21 |
| Ammonium sulphate | 0·84 | 7·38 |
| Calcium sulphate | 0·36 | 3·23 |

phosphoric acid from soln. of **ammonium phosphate.** H. Briegleb studied the action of **sodium phosphate** on felspar at a red heat.

F. A. Genth, J. de Lapparent, F. Grandjean, and H. Rosenbusch and E. A. Wülfing have shown that one felspar may pass into another, as when microcline or orthoclase changes into albite by the substitution of sodium for potassium. According to E. C. Sullivan, Table XXV represents the **metals** precipitated

TABLE XXV.—EFFECT OF SALT SOLUTIONS ON ORTHOCLASE.

| Solution. | Metal precipitated. | | Original content (Mgrm.-atoms). | Bases dissolved (Millimols). |
|---|---|---|---|---|
| | Grams. | Mgrm.-atoms. | | |
| Magnesium sulphate | 0·0099 | 0·40 | 1·98 | 0·47 |
| Calcium chloride | 0·0207 | 0·51 | 2·44 | 0·54 |
| Manganous sulphate | 0·0355 | 0·62 | 2·54 | 0·53 |
| Ferrous sulphate | 0·0365 | 0·65 | 2·10 | — |
| Ferric sulphate | 0·0648 | 1·16 | 1·21 | 1·41 |
| Nickelous sulphate | 0·0549 | 0·93 | 2·06 | 0·92 |
| Cupric chloride | 0·0716 | 1·13 | 1·98 | — |
| Cupric nitrate | 0·0625 | 0·98 | 1·99 | 0·85 |
| Cupric sulphate | 0·0729 | 1·03 | 1·98 | 0·85 |
| Zinc sulphate | 0·0611 | 0·93 | 3·05 | 0·99 |
| Strontium chloride | 0·0427 | 0·48 | 2·32 | 0·51 |
| Silver sulphate | 0·1027 | 0·94 | 0·98 | 1·01 |
| Barium chloride | 0·0982 | 0·71 | 2·04 | 0·78 |
| Auric chloride | 0·0563 | 0·27 | 1·36 | 1·21 |
| Lead nitrate | 0·2970 | 1·43 | 2·00 | 1·14 |

and bases dissolved when 25 grms. of orthoclase were treated with 50 c.c. of soln. The bases dissolved are usually in excess of the metal precipitated on account of the slight solvent action of water on the orthoclase. The acidic nature of the aq. soln. of auric chloride gave an excess of bases dissolved over metal precipitated. If the precipitate contains a basic salt the bases passing into the soln. throw out more than their eq. of metal. He also tried the effect of soln. of cupric sulphate on microcline and albite. V. P. Smirnoff studied the solvent action of **humic and crenic acids** on albite, and orthoclase.

The felspars are all highly susceptible to natural influences, and when exposed, they are readily attacked by the reagents which are so common in Nature's laboratory-water, water charged with carbon dioxide, acid waters formed by the oxidation of sulphides or issuing from volcanic vents, peat waters, alkaline waters, etc. The felspars are therefore highly alterable minerals, and they furnish numerous other minerals. The commonest end-products of the reaction between felspar and

natural agents are quartz and kaolinite—*vide supra*, clays—but other hydrated aluminium silicates are produced. Many zeolites, scapolites, epidote, zoisite, etc., may have been formed from felspar. According to A. Johnsen,[25] at ordinary temp. on the earth's surface, microcline is the most stable form of potash-felspar. The transformation of potash-felspar into muscovite has been discussed by H. Rössler, G. vom Rath, F. W. Clarke, C. G. C. Bischof, J. de Lapparent, etc.; into pinitoid, by A. Knop, E. Cohen, C. G. C. Bischof, A. Streng, C. W. von Gümbel, K. Dalmer, etc.; into analcime, by A. Phillips, T. Scheerer, etc.; and into kaolinite, by H. Stremme, G. L. Crasso, F. von Höchster, etc. Pseudomorphs after orthoclase have been described by A. Breithaupt, J. R. Blum, G. Tschermak, J. Roth, L. Hezner, etc. The alteration of albite into sericite and zoisite was discussed by A. Cathrein, C. Benedicks, etc. Some general observations on the transformation of potash- and soda-felspars were made by C. R. van Hise, C. G. C. Bischof, H. Rössler, M. Lublin, J. Roth, etc.

**The use of felspar.**—Felspar [26] is used in making some special types of pottery; but felspathic rocks like pegmatite and Cornish stone are perhaps as frequently employed as sources of felspar. These bring quartz and sometimes clay into the body along with the felspar. Felspar is also used in making certain types of pottery glazes, enamels for metals, opalescent glass, and artificial teeth. The higher grade potash felspars have been investigated with the idea of extracting their contained potash for making fertilizers, etc.—*vide* **2.** 20, 4.

P. G. Silber [27] obtained a canary-yellow **silver aluminium silicate**, $Ag_4Al_2Si_2O_9$, by heating the corresponding sodium aluminium silicate with silver nitrate. A number of silver derivatives has been obtained by the more or less complete displacement of the alkali or alkaline earth metal by silver. Thus, F. W. Clarke, and G. Steiger reported a *silver-chabasite*, $Ag_2Al_4(SiO_4)(Si_3O_8)_3 \cdot 4 \cdot 2H_2O$, to be formed by the action of silver nitrate on chabasite; G. Steiger similarly obtained *silver-analcite*, $AgAlSi_2O_6.H_2O$; *silver-natrolite*; *silver-thomsonite*, etc.—*vide index*. There are also the *silver-ultramarines* (*q.v.*) studied by K. Heumann,[28] R. de Forcrand and M. Ballin, J. Szilasi, C. Chabrié and F. Levallois.


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## § 44. The Alkaline Earth Aluminium Silicates

The calcium aluminium silicates have attracted much attention owing to the part they play in the formation of slags in metallurgical operations, in the manufacture of glasses and glazes, and in the formation of portland cement (*q.v.*). The calcium aluminium silicates in slags were studied by W. A. Lampadius,[1] P. Berthier, R. Kirwan, H. Abich, M. W. Iles, N. G. Sefström, J. Percy, and W. H. Miller, J. F. L. Hausmann, C. W. C. Fuchs, R. Akerman, P. Gredt, M. Theusner, etc. P. Berthier made some observations on slags containing $CaO : Al_2O_3 : SiO_2 = 6 : 2 : 3$; $3 : 1 : 3$; $3 : 1 : 9$; $1 : 1 : 22$; and $1 : 1 : 6$; both P. Berthier and N. G. Sefström made observations on $3 : 1 : 6$; $6 : 4 : 9$; and $3 : 2 : 6$; N. G. Sefström, on $3 : 2 : 9$; and C. Schnabel, on $9 : 1 : 10$. A. Gorgeu reported the $2 : 1 : 1$ silicate to be formed as a by-product when kaolinite is melted with 13–14 times its weight of calcium bromide. The anisotropic prisms, $Ca_2Al_2SiO_7$, may be **calcium dialuminometasilicate,** $(AlO.O.Ca)_2SiO_3$. O. Boudouard prepared the same compound. L. Bourgeois obtained $12 : 2 : 9$; $3 : 1 : 2$; $3 : 1 : 3$; and $6 : 4 : 9$; and W. Heldt, $8 : 2 : 15$, by fusion or sintering mixtures of the constituent oxides. C. F. Rammelsberg found crystals corresponding with $6Ca_3SiO_5.Al_2SiO_3$ mixed with calcium sulphide in the masonry of a soda-potash furnace. The greenish-yellow tetragonal bipyramids had the axial ratio $a : c = 1 : 0{\cdot}5832$, and sp. gr. 3·05. R. Akerman, O. Boudouard, and P. Gredt measured the heats of solidification and the temp. of formation of a number of calcium aluminium silicates, and L. Babu, H. E. Ashley, and H. M. Howe plotted the results on triangular diagrams.

R. Kirwan found that silica mixed with alumina and baryta or strontia fuses more readily than is the case with lime as the alkaline earth. P. Berthier also fused mixtures of $BaO : Al_2O_3 : SiO_2$ in the proportions $3 : 6 : 14$ and $3 : 4 : 12$. R. Rieke, and G. Flach studied the effect of the three alkaline earths on the fusibility of clay. E. Frémy and C. Feil obtained a product with the composition $4 : 5 : 10$ by the action of barium fluoride on a mixture of alumina and silica. F. Fouqué and A. Michel-Lévy obtained $BaO.Al_2O_3.2SiO_2$, $SrO.Al_2O_3.2SiO_2$, and $CaO.Al_2O_3.2SiO_2$ by the method indicated below for the synthesis of anorthite. Z. Weyberg obtained $4BaO.4Al_2O_3.7SiO_2$ in isotropic crystals by fusing a mixture of kaolinite and barium chloride.

T. J. Pelouze added calcium chloride to a soln. of alum and alkali silicate in an excess of alkali hydroxide, and obtained a mixed precipitate of lime, silica, and alumina. W. Heldt found that a mixture of precipitated calcium aluminate and water-glass soln. does not harden, but a similar mixture with the aluminate prepared by calcination does harden. C. and G. E. Tischler found crystals of $CaO.Al_2O_3.6SiO_2.6{\cdot}12H_2O$ in sand-lime bricks; the composition of stilbite is given as $CaAl_2Si_6O_{16}.5H_2O$. J. Lemberg heated aluminium hydroxide with calcium silicate and water to 180° and obtained six-sided plates of a calcium aluminium silicate. C. and G. Friedel heated mica with a soln. of calcium chloride and lime-water, and obtained crystals of anorthite (*q.v.*). J. Lemberg made a barium aluminium silicate by heating a mixture of kaolinite and barium silicate in water for 75 hrs. at 190°.

S. J. Thugutt prepared a product with the composition $CaAl_2Si_2O_8.2CaCl_2.20H_2O$, by the action of a soln. of calcium chloride on sodalite. A. Gorgeu melted garnet with calcium chloride and oxychloride, and also melted calcium chloride with kaolinite or a mixture of silica and alumina, and obtained a singly-refracting, crystalline product with the composition $Ca_6Al_6Si_3O_{21}.2CaCl_2$. Z. Weyberg obtained a similar product by the latter process; and prepared $Ca_{12}Al_{16}Si_5O_{36}.4CaBr_2$, by melting calcium bromide and kaolinite.

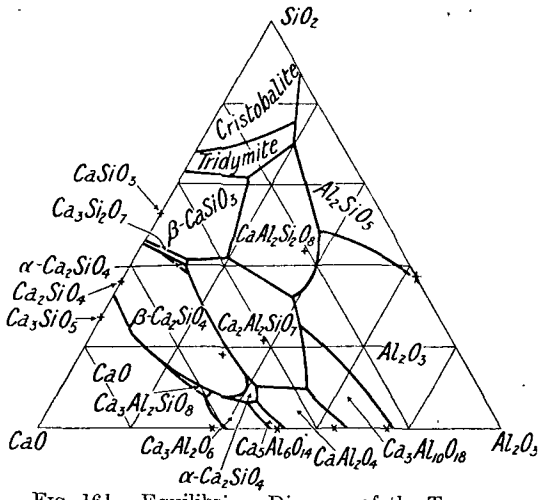



FIG. 161.—Equilibrium Diagram of the Ternary System: $CaO–Al_2O_3–SiO_2$.

Nature has provided an extraordinary number of calcium aluminium silicates—both hydrated and anhydrous. E. Selch [2] observed the effect of lime on clays; and R. Rieke, the softening temp. of mixtures of lime and china clay. Very few of these complex compounds are indicated on the diagram of the ternary system, Fig. 161, explored by G. A. Rankin and F. E. Wright for dry melts of the three oxides, $CaO–Al_2O_3–SiO_2$. This diagram shows well the strength and weakness of *P. Berthier's rule: Il paraît même que la fusibilité des silicates multiples est plus grande que la fusibilité moyenne des silicates composants.* The system was discussed by B. Neumann, and P. Niggli. A. L. Field and P. H. Royster discussed the viscosity of the molten ternary mixtures. Indeed, only three ternary compounds are indicated on this diagram, *anorthite*, $CaO.Al_2O_3.2SiO_2$; *velardenite*, $2CaO.Al_2O_3.SiO_2$; and **calcium dialuminatorthosilicate**, $Ca_3Al_2SiO_8$. The first two of these compounds are discussed later; the last one does not appear on the ternary diagram because it dissociates at its m.p. The absence of numerous anhydrous alumino-silicates from this diagram does not mean that such compounds do not exist. It is true that many break down at their m.p., but others, stable at this temp., are not formed under the conditions represented by Fig. 161. Other conditions, other diagrams. The isothermal m.p. of the ternary mixtures are indicated in Fig. 162. The binary compounds have been previously discussed. The compound calcium dialuminatorthosilicate,

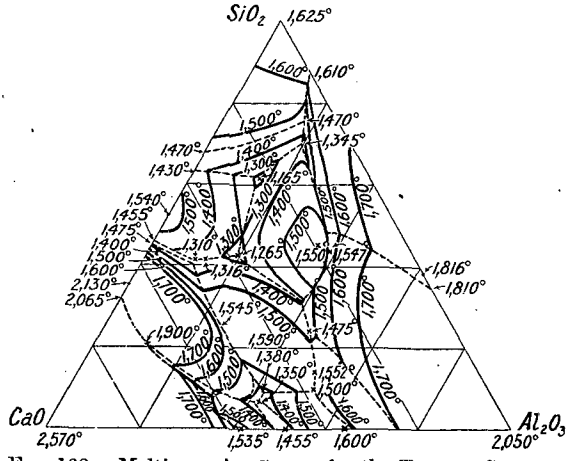



FIG. 162.—Melting-point Curves for the Ternary System: $CaO–Al_2O_3–SiO_2$.

$$O{=}Al{-}Ca{-}O\rangle Si\langle {}^{O.O}_{O.O}\rangle Ca$$
$$O{=}Al{-}Ca{-}O$$

dissociates at its mp., 1335° ± 5°, into calcium orthosilicate, $Ca_2SiO_4$, and calcium aluminate, $Ca(AlO_2)_2$; and hence it is best formed by crystallization from a glass of its own composition at a temp. below 1335°. According to G. A. Rankin and F. E. Wright, the preparation appears under the microscope dusty and so unsatisfactory that it is not possible to state definitely that it is homogeneous. The crystalline mass is usually crypto- to micro-crystalline and consists of overlapping fibres and grains. The larger grains show under high powers the ribbed structure common to crystal skeletons. The crystal system is possibly rhombic. The refractive indices are $\alpha_{Na}=1{\cdot}675 \pm 0{\cdot}005$, $\gamma_{Na}=1{\cdot}685 \pm 0{\cdot}005$. The birefringence is medium, $\gamma-\alpha$ being about 0·01. The optic axial angle is medium to fairly large. The optical character positive. The plane of the optic axes is apparently parallel with the positive elongation of the fibres. P. Niggli studied the ternary systems albite–anorthite–diopside; and anorthite–forsterite–silica.

The *matrix of corundum* from Carnatic, India, described in some detail by J. L. Bournon,[3] and afterwards called *indianite*, was recognized by A. Breithaupt to be a lime-felspar. Some crystals of lime felspar from Monte Somma, Vesuvius, were called by G. Rose *anorthite*—from *ἀνορθος*, oblique—in reference to the crystalline form.

T. Monticelli and N. Covelli called some crystals of lime-felspar from the same locality *christianite*—after Christian Frederick, Prince of Denmark; and others, *biotina*—after J. B. Biot. A. Breithaupt showed that the former, and H. J. Brooke that the latter, are simple anorthite. The *thiorsauite* of F. A. Genth, from Thiorsauite, Iceland, is also anorthite. N. von Nordenskjöld's *amphodelite*—from *ἀμφί*, double; and *ὀδελός*, spear, in allusion to the form of the crystals—is a reddish or peach-coloured variety from Lojo, Finland, and Tunaberg, Sweden. A. Breithaupt's *lepolite*—from *λέπος*, crust—is also an anorthite from Lojo and Orijärvi, Finland; it was studied by N. von Kokscharoff, who found the crystals were complex, but possessed angles like anorthite. H. J. Brooke's *latrobite*—after C. F. Latrobe—is a rose-red anorthite from Amitok Island, Labrador. N. von Nordenskjöld's *lindsayite* from Orijärvi, Finland, is an altered variety of lepidolite; it was investigated by R. Hermann, and F. J. Wiik. A. E. Nordenskjöld's *sundvikite*, from Nordsundvikite, Iceland, is also an altered anorthite. W. S. von Waltershausen named some glassy crystals from Trezza, Etna, and the Cyclopean Islands, *cyclopite*; A. Lacroix showed that they are anorthite. According to A. des Cloizeaux, some pinkish crystals from Arendal were called *tankite*; they were probably anorthite. T. Thomson's *huronite*, from Lake Huron, is an impure anorthite. B. J. Harrington confirmed this assumption, but T. L. Walker's analysis made the mineral resemble scapolite. Its index of refraction was 1·57–1·59. G. Tschermak proposed the term *microtine*—*μικρότης*, littleness—for the glassy plagioclase felspars analogous to the sanidine forms of orthoclase.

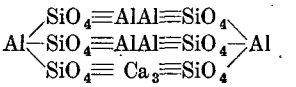
The *barsowite* of G. Rose, from Barsowsky, Ural, has the composition of anorthite when an allowance is made in the analyses of F. Varrentrapp, and K. M. Friederici for the corundum present as an impurity. The sp. gr. is 2·796. According to M. Bauer, the crystals are rhombic, and G. Rose, and P. Groth said that barsowite is dimorphous. J. Morozewicz doubted the existence of this mineral as a definite species; W. C. Brögger believed it to be a *selbständiges Mineral*, and he represented it and danburite by the formula $Ca_2R_4(SiO_4)_4$, where R represents an atom of boron in the case of danburite, and an atom of aluminium in the case of barsowite. F. L. Ransome and C. Palache regard barsowite, $Al : SiO_4.Al : SiO_4 : Ca$, as a product of the dehydration of lawsonite. J. Lemberg found that when barsowite is digested with a soln. of sodium silicate at 100° for 7 months, 50–70 per cent. of the calcium is displaced by sodium.

In 1824, J. J. Berzelius [4] recognized a new mineral in some specimens from Danviks-Zoll, and he called it *soda-spodumene*; and A. Breithaupt also found a variety of soda-lime-felspar which he named *oligoclase*; and afterwards showed its identity with J. J. Berzelius' mineral. Some *aventurine felspars*, and *sunstone* (*q.v.*) are oligoclase. H. Abich found a soda-lime-felspar at Marmato, Andes, and named it *andesine*. E. F. Glocker referred to a variety in the serpentine of Frankenstein as *saccharite* in allusion to its granular appearance, but A. Lasaulx showed that it is a mixture. A. G. Werner referred to the chatoyant *Labradorstein* brought by a Moravian missionary from St. Paul's Island, the coast of Labrador, about 1775. It was called *pierre de Labrador* by J. B. L. Romé de l'Isle; and *Labrador felspar* and *labrador* by G. Rose.

G. vom Rath showed that the lime-oligoclase or the *hafnefiordite* G. Forchhammer obtained from Hafnefiord, Iceland, is *labradorite*. The *silicite* and *mornite* of T. Thomson are from Antrim, Ireland, and are varieties of labradorite. The felspar from Carnatic, India, and named *carnatite* by A. des Cloizeaux, described by F. S. Beudant, is regarded by A. Breithaupt as labradorite. The term *saussurite*—from H. B. de Saussure—has been

given to some varieties of compact labradorite, although A. Cathrein showed that saussurite is a jade-like mineral containing zoisite and several felspars. This mineral was called *jade* by H. B. de Saussure; *Swiss jade*, by A. Höpfner; *lehmanite*, from Lake Lehman by J. C. Delamétherie; and *jade tenace* and *jade de Saussure*, by R. J. Haüy. It was discussed by T. S. Hunt, H. Traube, G. H. Williams, etc. A. Breithaupt's *radauite*, from Radau Valley, Harz, is a compact variety of labradorite. G. Tschermak applied the term *maskelynite*—in honour of N. S. Maskelyne—to an isotropic felspar found in some meteorites, and he suggested that it is a fused felspar. P. Groth considers it a particular species allied to leucite. The original *bytownite* by T. Thomson [5] was a greenish-white felspathic mineral from Bytown, Ottawa, Canada. It was analyzed by S. Tennant, and T. S. Hunt. F. Zirkel showed that this mineral is a mixture. G. Tschermak applied the term to felspars with a composition lying between that of labradorite and that of anorthite as indicated in the preceding table.

Numerous analyses of anorthite,[6] oligoclase,[7] andesine,[8] labradorite,[9] and bytownite [10] have been made. C. F. Rammelsberg [11] has shown that the many analyses of anorthite agree very well with the idealized formula $CaO.Al_2O_3.2SiO_2$, which has been interpreted in many different ways. G. Tschermak regarded it as a metasilicate because it furnished what he considered to be metasilicic acid when treated with hydrochloric acid. This idea gave him $Ca(O.Al : O_2 : SiO)_2$ or $Ca(O.SiO.O.AlO)_2$, and he preferred the latter. J. E. Reynolds' synthesis of what was thought to be anorthite by the action of oxygen and steam on $CaSi_2Al_2$, led him to the formula $Ca(O.SiO_2.AlO)_2$. F. W. Clarke gave $Ca(O.Si : O_3 : Al)_2$, or else



The triclinic soda-lime-felspars with oblique cleavages were grouped by A. Breithaupt as *plagioclase*-felspars—from πλάγιος, oblique; and κλάσις, fracture. The relations have been much discussed. J. F. C. Hessel, in his paper: *Ueber die Familie Feldspath* (1826), stated that labradorite is closely related with the other felspars, and it can be regarded as a mixture of albite and anorthite. W. S. von Waltershausen regarded the lime-soda-felspars as isomorphous mixtures of anorthite and the alkali-felspar. C. F. Rammelsberg, D. Gerhard, T. Scheerer, A. E. Delesse and T. S. Hunt, held similar views. The subject was taken up by G. Tschermak in his memoir: *Die Feldspathgruppe* (Wien, 1865). He showed that the *lime-soda-felspars are isomorphous mixtures of albite*, $NaAlSi_3O_8$, *and anorthite*, $CaAl_2Si_2O_8$. This is known as *Tschermak's theory of the isomorphism of the lime-soda-felspars*. This view was supported by A. Streng, who objected to the assumption that atoms of unequal valency like Na and Ca, or Al and Si, can replace one another isomorphously, and he represented albite and anorthite respectively by the doubled formulæ $Na_2Si_2.Al_2Si_4O_{16}$ and $Ca_2Al_2.AlSi_4O_{16}$; he also assumed that in the end-members there might be some $CaSi_2.Al_2Si_4O_{16}$ and $Na_4Al_2.AlSi_4O_{16}$. C. F. Rammelsberg, however, pointed out that this last assumption does not agree with the best analyses, and added that the isomorphism cannot be attributed to the number or to the equivalency of the constituent atoms. The subject was discussed by G. Tschermak, G. vom Rath, W. C. Brögger, A. Arzruni, J. W. Retgers, and F. Sandberger. The question has been raised whether some of the isomorphous mixtures of albite and anorthite represent definite compounds which can commingle isomorphously in various proportions; and discussed by A. des Cloizeaux and C. Friedel, F. Fouqué and A. Michel-Lévy, H. Bücking, A. Michel-Lévy and A. Lacroix, W. Tarassenko, F. Wallerant, E. S. von Federoff, T. Petersen, etc. As indicated below, the general physical and chemical properties of the isomorphous mixtures give no evidence of the formation of definite compounds of albite and anorthite. The isomorphism appears to be complete in the strictest sense of the term. As F. Fouqué expressed it:

La loi de Tschermak fournit un excellent moyen de controle et permet d'arriver à des déterminations très suffisantes. La simplicité, la bauté des conclusions ne doit pas faire oublier l'imperfection des prémisses.

E. T. Wherry has discussed the various hypotheses which have been proposed to explain the isomorphism of compounds of apparently dissimilar chemical type like the end-members of the plagioclase felspars $NaAlSi_3O_8$ and $CaAl_2Si_2O_8$. P. Groth emphasized the view that in isomorphous crystals, the elements concerned should be capable of playing an analogous *rôle* in the chemical mol., and that the space units of these elements should be characterized not only by like symmetry, but by nearly the same linear dimensions, and, consequently, nearly the same vol. He added:

> The isomorphism of two substances depends on the fact that the entrance of the atoms or groups of atoms which replace one another produces a similar change in the crystal structure of the compound from which they are in common derived. Since the extent of this change depends not only on the nature of the substituting atoms or groups of atoms, but also on that of the original substance, it follows that the differences which are to be observed in cases of isomorphous replacement by the same substitutions are different in different isomorphous series; and, in general, they must be smaller, the greater the number of atoms common to the isomorphous substances.

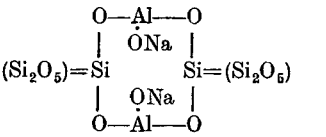
J. D. Dana cited cases to show that the mol. vol. of an isomorphous group of minerals have values approaching equality, and that the crystallographic relationship depends on mol. vol., and not on chemical composition—*vide* titanium dioxide. It has long been recognized that the mol. vol. of anorthite, $CaAl_2Si_2O_8$, and of albite, $NaAlSi_3O_8$, are the same, but this is not a sufficient criterion for explaining the isomorphism, even though G. T. Prior has shown that many substances with nearly the same mol. vol. and with apparently distinct types of formula are isomorphous. The identity of the mol. vol. shows that the isomorphism of the plagioclases is based on a 1 : 1 ratio of amounts indicated by the formulæ of the two end-members of the series.

Since the difference between albite and orthoclase consists merely in the replacement of one univalent element by another, it might be predicted that orthoclase would be isomorphous with anorthite. R. Freis showed that the potash-felspar can dissolve small quantities of lime-felspar; in nature, however, soda-felspar is always present as well. F. Gonnard assumes that if a monoclinic lime-felspar did occur it would be isomorphous with potash-felspar; and A. Schwantke assumed the existence of a compound $Ca_2Al_2Si_3O_{16}$ which is miscible with $K_2Al_2Si_6O_{16}$. E. Dittler, W. Wahl, and H. J. L. Vogt have made some observations on the system $KAlSi_3O_8$—$CaAl_2Si_2O_8$. E. Dittler obtained over-growths or zonal structures so long as the potash-felspar did not exceed 10–20 per cent., and with 70 per cent. of lime-felspar, the two components crystallized separately. If increasing proportions of soda-felspar be added, potash- and lime-felspars become more and more miscible. H. Alling suggested that potash- and soda-felspars are isomorphous, and he called the series *oranite*. There are no representatives of this series in nature, and the evidence adduced points only to the formation of limited non-isomorphous solid soln. Similarly, it might be anticipated that *carnegieite* would be isomorphous with anorthite since the only difference between the two silicates consists in the substitution of one bivalent atom by two univalent atoms. The evidence, however, shows that in *anemousite* only a very small proportion of carnegieite is present; and N. L. Bowen has shown that carnegieite holds only 5 per cent. of anorthite in solid soln., while anorthite holds only 2 per cent. of carnegieite.

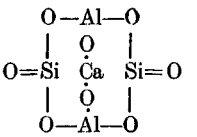
It is curious that in the felspars, ferric iron does not readily take the place of aluminium for when any ferric oxide has been incorporated with a native felspar, it has apparently separated as hæmatite inclusions. The artificial *ferric-felspar*, $KFeSi_3O_8$, reported by P. Hautefeuille and A. Perrey, is very unstable; and the gem orthoclase of Madagascar is almost unique. The fact that ferric oxide can replace alumina in garnet, tourmaline, etc.; and the general unstability of the ferrites as contrasted with the aluminates, led W. Vernadsky to suggest that the aluminium in garnet, etc., belongs to the basic radicle, but in felspars, to the acidic

radicle. E. T. Wherry arranges the hypotheses invented to explain these facts into three groups :

1. *Structural theories.*—Here it is assumed that the elements retain the same valence in the solid and liquid states, and that the isomorphism of the basic radicles is always valence for valence ; but widely dissimilar acidic radicles may be isomorphous. W. Vernadsky assumes that the felspars have a group of atoms which he called the mica nucleus. He considered alumina to be part of the acidic radicle, but the formula to be otherwise different (*vide supra*, orthoclase) :



Albite.



Anorthite.

F. W. Clarke, as indicated above, also has the quadrivalent radicle $Si_3O_8$ in albite, and $SiO_4$ in anorthite. The ring formulæ of W. and D. Asch belong to this type. B. Gossner writes $SiO_3Na_2[SiO_2.Al_2O_3]4SiO_2$ for albite, and $SiO_3Ca[SiO_2.Al_2O_3]$ for anorthite, where the $4SiO_2$ of albite is missing from anorthite. These explanations cannot be called *hypothèses louches*, for they do not look two ways at once. In straining after similarity with the basic radicle, diversity with the acidic radicle is ignored. No attempt is made to account for the other peculiarities indicated above.

2. *Arithmetical relations.*—Here the simple integral relationship between the constituents or their properties is used to explain isomorphism. The valence-volume theory of W. Barlow and W. J. Pope (**1**. 5, 18) is based on the chance relation that quadrivalent carbon occupies approximately four times the vol. of univalent hydrogen. The total valence of albite and anorthite is 32, and the groups NaSi and CaAl of valency 5 are supposed to be mutually replaceable. Other silicates have total valencies of 32, but are not isomorphous with albite or anorthite. R. B. Sosman argued that the oxides of ordinary silicates tend to unite in simple numerical proportions regardless of structural relations, so as to form molecular compounds. This would double the above formula for albite. I. Langmuir's hypothesis (**4**. 27, 4) assumes that elements are radicles possessing a like electronic structure, are isomorphously eq. though chemically dissimilar. Albite and anorthite alike possess 64 electrons, and hence they should be isomorphous. *Au contraire*, calcium is isoteric with potassium but not with sodium, meaning that anorthite should be more fully isomorphous with orthoclase than with albite—which is not in agreement with facts. Hence, continued E. T. Wherry :

> This group of hypotheses does not furnish any adequate explanation of the complexity of isomorphous relationships. If carried to their logical extreme they would predict numerous cases of isomorphism which do not occur. They require that in the plagioclases, one univalent, one bivalent, or one trivalent radicle should be replaceable by another corresponding valence—lithium or potassium for sodium, strontium or barium for calcium, or ferric iron or chromium for aluminium, yet not one of these actually occurs.

3. *Atomic isomorphism.*—Isomorphism is assumed to occur only between mutually similar atoms or groups of atoms irrespective of the valence exhibited by the same atoms or groups of atoms in soln. This is illustrated by the case of calcite, $CaCO_3$, and soda-nitre, $NaNO_3$, which are closely isomorphous, while $CaCO_3$ and $Na_2CO_3$ or $CaCO_3$, and $Ca(NO_3)_2$ are not isomorphous. The structural hypothesis would indicate that $Ca{=}O_2{=}C{=}O$ should be isomorphous with $Na_2{=}O_2{=}C{=}O$, but not with $Na{-}O{-}N{\equiv}O_2$. P. Groth applied the idea to the plagioclases, and the hypothesis was developed by H. S. Washington. Here, albite becomes $(NaSi)(AlSi_2O_8)$, and anorthite, $(CaAl)(AlSi_2O_8)$, where the (NaSi)-group and the (CaAl)-group are quinquevalent. This renders it unnecessary to assume iso-

morphism between widely dissimilar acidic radicles; it does not account for the failure of one atom to replace another of the same valence; and it splits up the atomic grouping without any vindicatory evidence.

P. Niggli, and J. Jakob applied the co-ordination theory and wrote the formula of anorthite in several different ways, among others, they gave

$$\left[Al(SiO_4SiO_2AlO_2)_3\right]^{Al_3}_{Ca_3} \qquad \left[Al(SiO_4SiO_2SiO_2)\right]^{Al_2}_{Na_3}$$

Anorthite. Albite.

P. Erculisse did not favour formulæ of the type $AlSiO_4.SiO.O.Si(OH)_2.SiO_4Al$, but regarded the plagioclases as solid soln. of the acids $H_3AlSiO_5$ and $H_2Al_2SiO_6$.

$$\left[\begin{matrix}O:Al.O\\ HO\end{matrix}\!\!>\!\!Si\!\!<\!\!\begin{matrix}O\\ O\end{matrix}\right]H_2 \qquad \left[\begin{matrix}O:Al.O\\ O:Al.O\end{matrix}\!\!>\!\!Si\!\!<\!\!\begin{matrix}O\\ O\end{matrix}\right]H_2$$

$H_3AlSiO_5$ $H_2Al_2SiO_6$

Assuming atomic isomorphism between Ca and Na, and Al and Si, M. E. Denaeyer, and P. Erculisse also used the co-ordination theory in this connection. P. A. von Bonsdorff argued that while alumina usually acts as a base, it can also act as an acid, and take the place of silica mol. for mol. The idea was developed by T. Scheerer, and D. A. Brauns, but opposed by V. Wartha. E. T. Wherry argued that the non-replaceability of aluminium by ferric iron in these felspars requires the aluminium to be definitely associated with the alkali or alkaline earth metal; and the co-ordination plan requires the aluminium atom to be dominant and in a central position. He therefore postulated the formulæ $[Na\mathbf{Al}(Si_3O_8)]$ for albite and $[Ca\mathbf{Al}(AlSi_2O_8)]$ for anorthite; or, omitting the square brackets, $Na\mathbf{Al}(Si_3O_8)$ and $Ca\mathbf{Al}(AlSi_2O_8)$ respectively.

W. Barlow and W. J. Pope assume that isomorphism depends on the replacement of atoms of similar sizes as well as on like valency. F. Zambonini, and E. T. Wherry agree in attributing the isomorphism of albite and anorthite to a close agreement in the at. vol. of the vicariant elements, but the former also considers that equality of the sum of the valencies of the replacing elements is essential. E. T. Wherry considers the valence relations are negligible. R. W. G. Wyckoff believes that sufficient data are not available to settle the question. F. Rinne's interpretation of the X-radiograms of anorthite and oligoclase is indicated in Fig. 163. Comparing this diagram with Fig. 138, it follows that the chemical mol. of albite is $NaAl[\mathbf{Si}(SiO_4)_2]$, and that of anorthite $CaAl[\mathbf{Al}(SiO_4)_2]$; or, in words, **calcium aluminium aluminodiorthosilicate.**

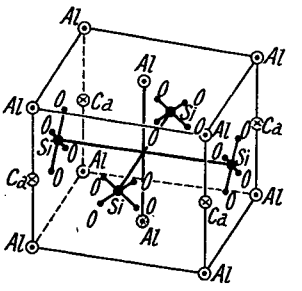



FIG. 163.—Stereochemical Scheme of Anorthite.

The modern theories of crystal structure show that atomic isomorphism should be the rule whenever the atoms concerned are so nearly equal in vol. as to fit into the geometrical arrangement. W. L. Bragg showed that sodium normally occupies a vol. slightly greater than calcium, and silicon a little less than aluminium; on the other hand, potassium occupies a decidedly larger vol. than sodium or calcium, so that potassium nitrate cannot be expected to be isomorphous with calcite, nor orthoclase with anorthite. In the case of carnegieite with its two sodium atoms for one calcium atom in anorthite, the larger vol. required by the two sodium atoms should make isomorphism even less possible.

The plagioclase felspars of the less siliceous rocks have a tendency to approach the anorthite end-member as the proportion of silica decreases. C. H. Warren [12] found anorthite as a contact mineral of limestone. Anorthite and the plagioclases have been observed in meteorites.

Anorthite is the felspar which is most easily obtained pyrogenetically, and its crystallization tendency is comparatively great. A. L. Day and co-workers [13] readily obtained it in a crystalline form by simply fusing a mixture of the constituent oxides. F. Fouqué and A. Michel-Lévy, A. S. Ginsberg, and A. Brun also obtained anorthite directly from its components. G. A. Rankin's diagram, Fig. 161, shows the range of stability of anorthite in the ternary system, $CaO$–$Al_2O_3$–$SiO_2$. J. H. L. Vogt observed it in various slags; S. Meunier found it in the masonry of a gas-furnace at Vaugirard; A. Mallard, in the ashes from a colliery; and C. Vélain, in the glass produced during the burning of a corn mill. J. Morozewicz obtained felspars ranging from labradorite to nearly pure anorthite in his experiments on magmas. S. Meunier fused a mixture of silica, lime, and aluminium fluoride, and obtained sillimanite, tridymite, and anorthite. Anorthite is also produced when many complex silicates are fused. Thus, A. des Cloizeaux obtained anorthite by fusing together garnet and vesuvianite; and C. Doelter and E. Hussak obtained similar results; and K. Petrasch obtained it by fusing a mixture of granite and andesite. C. Doelter obtained anorthite in the products obtained by fusing epidote, axinite, chabazite, heulandite, laumontite, and scolecite; and also by melting calcspar with basalt. C. Medanich obtained it by fusing a mixture of granite and sodium phosphate, boric oxide, and tin chloride; and K. Bauer, by fusing a mixture of diorite with sodium, potassium, or calcium fluoride. C. and G. Friedel made anorthite by the hydrothermal process, namely, by heating a mixture of lime, calcium chloride, muscovite, and a little water in a steel tube at 500°; J. E. Reynolds, by the action of steam on his silicalcyanide; and M. Schläpfer, by heating a mixture of the constituents of anorthite, calcium chloride, and water in a bomb at 470°. W. Eitel obtained anorthite (plagioclase) by heating nephelite (*q.v.*) and calcium carbonate at press. below 65 kgrms. per sq. cm.

F. Fouqué and A. Michel-Lévy made felspars analogous to anorthite, oligoclase, and labradorite with strontium, barium, or lead in place of calcium. Mixtures of silica, alumina, sodium carbonate, and the proper oxide were heated at temp. a little below the fusion point. This gave *strontia-felspar*, *baryta-felspar* (celsian), and *lead-felspar*. Plagiofelspars containing potassium in place of sodium were made by E. Dittler; and also hyalophane as a solid soln. of orthoclase and celsian. F. von Kobell suggested that in *tschermakite* the magnesia replaces lime in felspar in the form of *magnesia-felspar*; but a subsequent examination by G. W. Hawes, F. Pisani, and A. des Cloizeaux showed that there is much less magnesia present than F. von Kobell supposed. H. Schulze and A. Stelzner found what they regarded as *zinc-anorthite* in the walls of a zinc furnace. C. Doelter did not succeed in making *ferric anorthite*.

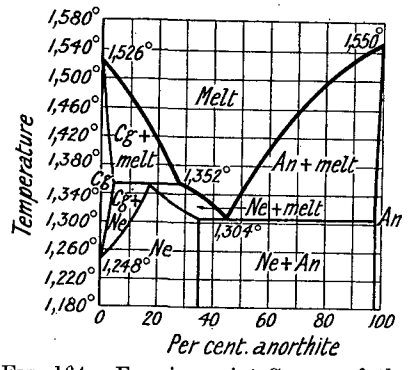



FIG. 164.—Freezing-point Curves of the Binary System: $Na_2Al_2Si_2O_8$–$CaAl_2Si_2O_8$.

It is possible that Z. Weyberg made *potash-anorthite* in his synthetic experiments on kaliophilite. J. Lemberg did not succeed in making *soda-anorthite*, but S. J. Thugutt's product, obtained by rapidly cooling fused nephelite hydrate, was probably this compound. The triclinic nephelite reported by E. Esch from the Etinde volcano, West Africa, was probably soda-anorthite. H. S. Washington and F. E. Wright found soda-anorthite, *i.e.* carnegieite, to be a constituent of a felspar from the island of Lenosa, near Tunis, and they synthesized the mineral by heating to 1080°, the glass obtained by fusing a mixture of the constituents. N. L. Bowen charted the equilibrium diagram of the binary system, $Na_2Al_2Si_2O_8$ (soda nephelite or carnegieite) and $CaAl_2Si_2O_8$ (anorthite),

and found that the sodium compound is stable in nephelite below 1248°, as carnegieite is above that inversion temp.—Fig. 164. The eutectic occurs at 1304° with 45 per cent. of anorthite; and mixed crystals range from nephelite (Ne) to $Ne_{65}An_{35}$; and the maximum amount of anorthite taken up by carnegieite (Cg) is $Cg_{95}An_5$.

O. Andersen has studied the binary and ternary systems with anorthite, forsterite, and silica as components. The curves, Figs. 165–168, of the system,

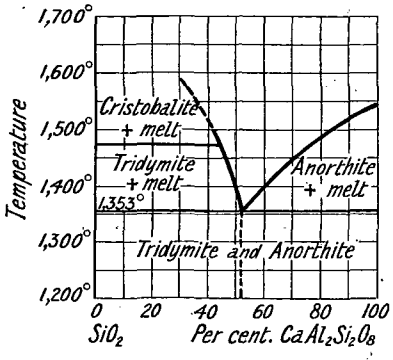



FIG. 165.—Freezing-point Curves of the Binary System: Anorthite–Silica.

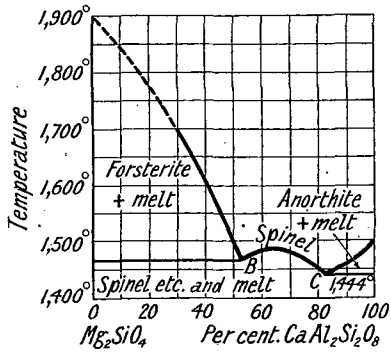



FIG. 166.—Freezing-point Curves of the Binary System: Anorthite–Forsterite.

Anorthite–Silica, show that no higher silicate is stable under the experimental conditions; and the f.p. curves, Fig. 166, of the system, anorthite–forsterite, show that the curve *BC* has not the maximum shown on the liquidus curves of ordinary two-component systems by a binary compound, since spinel, $Mg(AlO_2)_2$, cannot be considered a binary compound of the components $Mg_2SiO_4$ and $CaAl_2Si_2O_8$. The ternary system, Fig. 167, shows no combinations of the components $CaAl_2Si_2O_8$,

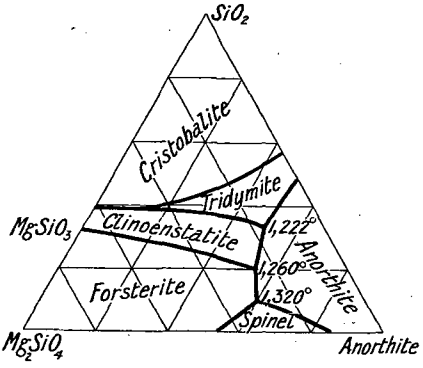



FIG. 167.—Ternary System: Forsterite–Anorthite–Silica.

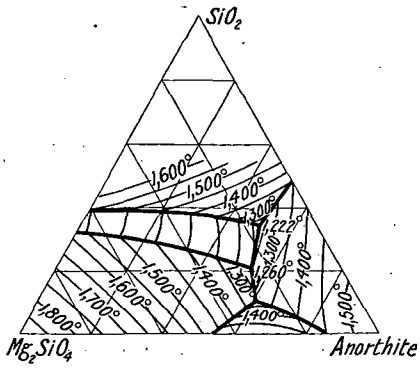



FIG. 168.—Isothermal Freezing Curves of the Ternary System: Anorthite–Forsterite–Silica.

$Mg_2SiO_4$, and $SiO_2$. The spinel field is not a ternary compound of the components of the system, but represents the products obtained by the breaking down of the anorthite. It would appear as a compound in the quaternary system $MgO–CaO–Al_2O_3–SiO_2$. Magnesium metasilicate is unstable at the m.p. The isothermal curves of the system are shown in Fig. 168. P. Lebedeff studied mixtures of anorthite and wollastonite. N. L. Bowen's curves for the binary systems: anorthite–diopside and albite–diopside, are illustrated in the diagrams respectively,

Figs. 165 and 170. The isothermal lines for the ternary system : albite–anorthite–diopside, are shown in Fig. 171. Following similar lines to those employed

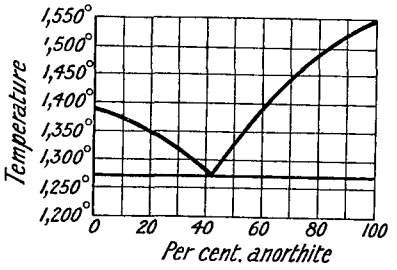



FIG. 169.—Freezing-point Curves of the System : Diopside–Anorthite.

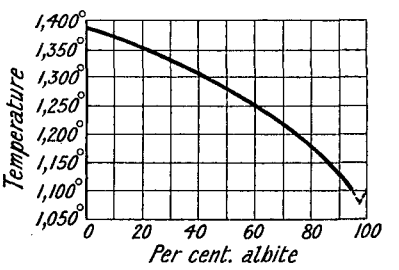



FIG. 170.—Freezing-point Curves of the System : Diopside–Albite.

for anorthite, P. Hautefeuille[14] F. Fouqué and A. Michel-Lévy, A. L. Day and E. T. Allen, K. Bauer, K. Petrasch, and G. Medanisch synthesized oligoclase ; F. Fouqué and A. Michel-Lévy, A. L. Day and E. T. Allen, and J. Morozewicz synthesized *andesine ;* and F. Fouqué and A. Michel-Lévy, A. L. Day and E. T. Allen, J. Morozewicz, S. Meunier, and K. Petrasch synthesized labradorite and bytownite. Labradorite has been reported by K. Hausmann in blast-furnace slags, and by F. Sansoni, in the masonry of a kiln at Naples. S. J. Thugutt obtained a *hydrated chloro-anorthite,* $9CaAl_2Si_2O_8.2CaCl_2.20H_2O$, by the action of calcium chloride on sodalite.

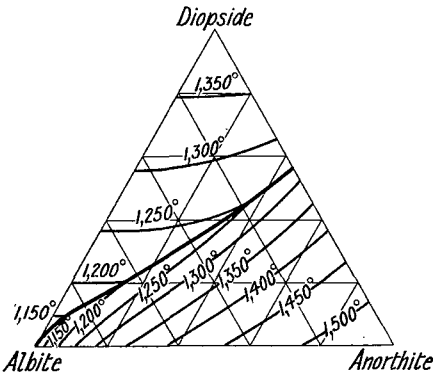



FIG. 171.—Freezing-point Curves of the System : Diopside–Albite–Anorthite.

**The physical properties of the lime-felspars.**—Many of the general properties of the alkali-felspars are also characteristic of the lime-felspars. The remarks on colour, the effect of impurities on the colour, and the schillerization also apply to anorthite and the plagioclases. Sunstone and aventurine felspars are also found among these felspars. Labradorite is of a dull smoke-grey **colour,** but when it is observed at a particular angle, the surface lights up with brilliant play of colours—blue, green, red, bronze, etc.—and the mineral is accordingly cut and polished for jewellery and small ornamental objects. The effect is attributed to the presence of a large number of minute scales and needles of included minerals.

The **crystals** have been studied by G. Rose,[15] J. D. Mackenzie, F. Rinne, J. Kratzert, A. des Cloizeaux, G. vom Rath, etc.—*vide supra,* the isomorphism of albite and anorthite. The general results show that the crystals belong to the triclinic system. A. des Cloizeaux, and N. von Kokscharoff gave for anorthite, $a : b : c = 0{\cdot}63473 : 1 : 0{\cdot}55007$, and $\alpha = 93° 13\frac{1}{3}'$, $\beta = 115° 55\frac{1}{2}'$, and $\gamma = 91° 11\frac{2}{3}'$. J. Beckenkamp gave $0{\cdot}63473 : 1 : 0{\cdot}55007$, and $\alpha = 93° 13\frac{1}{2}'$, $\beta = 115° 55\frac{1}{2}'$, and $\gamma = 91° 11\frac{3}{4}'$ ; and J. Kratzert, $0{\cdot}63523 : 1 : 0{\cdot}55048$, and $\alpha = 93° 95'$, $\beta = 115° 52{\cdot}6'$, and $\gamma = 91° 16{\cdot}4'$. P. Groth and E. Schmidt gave for labradorite, $a : b : c = 0{\cdot}6377 : 1 : (0{\cdot}5)$, and $\alpha = 93° 31'$, $\beta = 116° 3'$, and $\gamma = 89° 54\frac{1}{2}'$ ; G. vom Rath gave for andesine, $a : b : c = 0{\cdot}63556 : 1 : 0{\cdot}55204$, and $\alpha = 93° 22\frac{3}{4}'$, $\beta = 116° 28\frac{1}{2}'$, and $\gamma = 89° 58\frac{5}{6}'$ ; and for oligoclase, $a : b : c = 0{\cdot}63206 : 1 : 0{\cdot}55239$, and $\alpha = 93° 4\frac{1}{8}'$, $\beta = 116° 22\frac{1}{2}'$, and $\gamma = 90° 4\frac{1}{2}'$. According to J. P. Iddings, the data in Table XXVI may be taken as representative values. E. Schmidt, and E. A. Wülfing gave for plagio-

TABLE XXVI.—CRYSTALLOGRAPHIC CHARACTERS OF THE PLAGIOCLASES.

| —— | $a:b:c$ | $\alpha$ | $\beta$ | $\gamma$ |
|---|---|---|---|---|
| Anorthite . . . . | 0·6347 : 1 : 0·5501 | 93° 13′ | 115° 55′ | 91° 12′ |
| Labradorite . . . | 0·6377 : 1 : 0·5547 | 93° 31′ | 116° 3′ | 89° 54½′ |
| Andesine . . . . | 0·6357 : 1 : 0·5521 | 93° 23′ | 116° 29′ | 89° 59′ |
| Oligoclase . . . . | 0·6321 : 1 : 0·5524 | 93° 4′ | 116° 23′ | 90° 5′ |
| Albite . . . . | 0·6335 : 1 : 0·5577 | 93° 3′ | 116° 29′ | 88° 9′ |

clase with 0, 50, and 100 per cent. anorthite, $\alpha$=94° 31′, 93° 27′, and 93° 05′ respectively; $\beta$=116° 38′, 116° 10′, and 115° 54′ respectively; and $\gamma$=87° 01′, 90° 06′, and 91° 34′ respectively. The idealized crystal of anorthite, Fig. 173, has the faces $A$(100), $B$(010), $C$(001), and $M$(1$\bar{1}$0), $m$(110), $m'$(111), $e$(021), $t$(201), $x$(101), and $y$(201); and the angles $BC$, 85° 50′; $Bm$, 58° 4′; $mM$, 59° 29′; $Cm$, 65° 53′; $Cm$, 69° 20′; $CA$, 63° 57′; $Cx$, 51° 26′; $Cy$, 81° 14′; and 42° 38′. The change in the angle $BC$, Fig. 173, with temp. is illustrated by Fig. 172. The crystallographic and optical properties of anorthite were studied by J. Kratzert. E. Kittl, and E. Dittler have studied the **velocity of crystallization** of anorthite and labradorite. The habit of crystals of the plagioclase-felspars resembles that

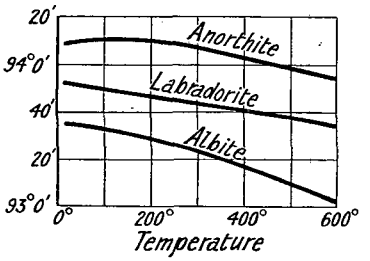



FIG. 172.—Effect of Temperature on the Angles of Plagioclase.

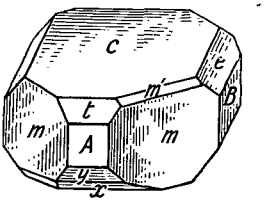



FIG. 173.—Idealized Crystal of Anorthite.

of the alkali-felspars, but in megascopic crystals it is oftener tabular; and in microscopic forms, oftener prismatic. F. Rinne obtained **X-radiograms** of anorthite and oligoclase. For the deduction from these results, *vide* Figs. 139 and 163. A. Hadding investigated the X-radiograms of labradorite, and anorthite. Sections of the crystals of soda-lime-felspars often exhibit a concentric zonal structure with different zones exhibiting different optical orientations. Usually the innermost zone is the most calcareous; the sodiferous and calciferous alternate with one another. **Twinning** occurs, according to the Carlsbad, Manebach, Baveno, albite, and pericline laws cited in connection with the alkali-felspars. G. A. Rankin and F. E. Wright found the polysynthetic twinning of artificial anorthite to be very characteristic. When the albite twinning of the plagioclases is repeated many times the alternate lamellæ with their reversed optical orientation appear in thin sections between crossed nicols, in striped bands alternately light and dark. The bands may taper out or end abruptly at any place. They are clearest and sharpest-edged when the section is perpendicular to the (010)-plane of twinning. E. Herrmann has written *Ueber Zwillingsverwachsungen gestein bildender Plagioklase;* and the subject was studied by A. Köhler, C. W. Carstens, etc. For the **cleavage** and fracture, see alkali-felspars. The cleavage of oligoclase was investigated by S. L. Penfield.

The **optic axial angles** of anorthite were studied by M. Schuster, who found $2H_0$=114° 10′ for the red ray and 114° 47′ for the green ray. F. Fouqué found $2V$ ranging from 77° 18′–77° 55′; and $2E$=147°; J. Kratzert gave $2V$=102° 28′

for anorthite, for labradorite and bytownite he found $2V=76°\ 10'–79°\ 40'$; for andesine, $2V=87°–88\frac{1}{4}°$; and for oligoclase, $2V=71°–89°$. F. Becke and M. Goldschlag obtained for andesine, $2V=90°–98°$; for labradorite and bytownite, for the red ray $2H_a=84°\ 29'–89°\ 10'$; and $84°\ 23'–87°\ 49'$ for the blue ray. A. des Cloizeaux gave for andesine, $68°\ 58'–103°$ for $2H_a$ with the red ray, and $2H_c=84°\ 31'–125°\ 18'$ for the blue ray. He also gave for oligoclase, $2H_a=56°\ 30'–101°\ 36'$ for the red ray, and $2H_c=89°\ 10'–105°\ 24'$ for the blue ray. Other observations were made by E. S. von Federoff, F. Becke, H. Gylling, F. J. Wiik, D. Orueta, etc. The following data show the effect of different molar percentages of anorthite on the optic axial angle $2V$ of the plagioclase crystal:

| | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| Anorthite . | 0·5 | 13 | 20 | 25 | 37 | 52 | 56 | 63 | 75 | 100 |
| $2V$ . . | 78° | 85° | 94° | 99° | 90° | 75° | 75° | 82° | 94° | 103·5° |

The effects of variations of temp. on the optic axial angle were investigated by J. Beckenkamp, F. Rinne, B. Hecht, and L. Fletcher; and the mixed crystals, by E. Köstermann and co-workers.

G. Tschermak[16] computed the values indicated in Table XXVII for the **specific**

TABLE XXVII.—SPECIFIC GRAVITY AND COMPOSITION OF THE PLAGIOCLASES.

| $Ab_n : An_m$ | | Sp. gr. | Composition. | | | |
|---|---|---|---|---|---|---|
| | | | $SiO_2$ | $Al_2O_3$ | CaO | $Na_2O$ |
| Albite . | 1 : 0 | 2·624 | 68·7 | 19·5 | 0 | 11·8 |
| | 12 : 1 | 2·635 | 66·6 | 20·9 | 1·6 | 10·9 |
| | 8 : 1 | 2·640 | 65·7 | 21·5 | 2·4 | 10·4 |
| | 6 : 1 | 2·645 | 64·9 | 22·1 | 3·0 | 10·0 |
| Oligoclase . | 4 : 1 | 2·652 | 63·3 | 23·1 | 4·2 | 9·4 |
| | 3 : 1 | 2·659 | 62·0 | 24·0 | 5·3 | 8·7 |
| | 2 : 1 | 2·671 | 59·9 | 25·4 | 7·0 | 7·7 |
| Andesine . | 3 : 2 | 2·680 | 58·1 | 26·6 | 8·4 | 6·9 |
| | 4 : 3 | 2·684 | 57·4 | 27·1 | 8·9 | 6·6 |
| | 1 : 1 | 2·694 | 55·6 | 28·3 | 10·4 | 5·7 |
| Labradorite | 3 : 4 | 2·703 | 53·7 | 29·6 | 11·8 | 4·9 |
| | 2 : 3 | 2·708 | 53·0 | 30·1 | 12·3 | 4·6 |
| | 1 : 2 | 2·716 | 51·4 | 31·2 | 13·7 | 3·8 |
| | 1 : 3 | 2·728 | 49·3 | 32·6 | 15·3 | 2·8 |
| Bytownite . | 1 : 4 | 2·735 | 48·0 | 33·4 | 16·3 | 2·3 |
| | 1 : 6 | 2·742 | 46·6 | 34·4 | 17·4 | 1·6 |
| | 1 : 8 | 2·747 | 45·9 | 34·9 | 18·0 | 0·2 |
| Anorthite . | 0 : 1 | 2·758 | 43·2 | 36·7 | 20·1 | 0 |

**gravity** of plagioclases of different composition. Sp. gr. determinations were made on many of the samples which have been analyzed, and on those whose optical properties have been measured. V. Goldschmidt has collected data on this subject. The observed values for anorthite with very low alkalies range from G. vom Rath's 2·668 to his 2·812; for bytownite, from T. Wada's 2·62 to G. H. Williams' 2·74; for labradorite, from G. vom Rath's 2·608 to his 2·814; for andesine, from C. von Hauer's 2·36 to H. Abich's 2·7328; and for oligoclase, from A. E. Delesse's 2·586 to M. F. Heddle's 2·834. Errors due to inclusions, cavities, etc., no doubt affect the extremes of these results. L. Ahlers gave for the sp. gr. of theoretically pure anorthite, 2·752–2·754 at 4°. J. A. Douglas found the sp. gr. of natural crystals of anorthite to be 2·750, and for the cold glass, after fusion, 2·665, corresponding

with 3·18 per cent. expansion. A. L. Day and E. T. Allen found for the sp. gr. of artificial plagioclases—crystals and glass :

| | An | $Ab_1An_5$ | $Ab_1An_3$ | $Ab_1An$ | $Ab_2An$ | $Ab_3An$ | Ab |
|---|---|---|---|---|---|---|---|
| Crystals | 2·765 | 2·733 | 2·710 | 2·679 | 2·660 | 2·649 | 2·605 |
| Glass | 2·700 | 2·648 | 2·591 | 2·535 | 2·483 | 2·458 | 2·383 |

The sp. gr. of artificial preparations are often low, owing to the presence of minute sealed gas pores. A. L. Day and E. T. Allen observed no differences in the sp. gr. of glasses cooled at different rates. The **hardness** of anorthite is 6 or a little over ; that of labradorite and of andesine, 5–6 ; and that of oligoclase, about 6. P. J. Holmquist measured the cutting hardness of albite, oligoclase, labradorite, and anorthite using carborundum of grain-size 0·006–0·012 mm. on different faces of the crystals. The results are illustrated by Fig. 174, where the dotted lines show the probable course of the curves freed from errors of experiment. L. H. Admas and E. D. Williamson found the **compressibility** of oligoclase, $Ab_{78}An_{22}$, to be $\beta=1{\cdot}74\times10^{-6}$ at 0 megabars press. ; $1{\cdot}71\times10^{-6}$ at 2000 megabars; and $1{\cdot}58\times10^{-6}$ at 10,000 megabars; or $\beta=0{\cdot}0_51712-0{\cdot}0_{10}166(p-p_0)$; labradorite, $Ab_{48}An_{52}$, had a value $\beta=1{\cdot}74\times10^{-6}$ at 0 megabars press. ; $1{\cdot}71\times10^{-6}$ at 2000 megabars; and $1{\cdot}58\times10^{-6}$ at 10,000 megabars ; or $\beta=0{\cdot}0_51508-0{\cdot}0_{10}218)p-p_0)$; for anorthite, $\beta=1{\cdot}1\times10^{-6}$ at 2000–10,000 megabars press. ; for andesine, $Ab_2An$, $\beta=1{\cdot}63\times10^{-6}$ at 2000 megabars, and $\beta=1{\cdot}49\times10^{-6}$ megabars ; and for $Ab_1An_2$, $\beta=1{\cdot}37\times10^{-6}$ at 2000 megabars, and $1{\cdot}30\times10^{-6}$ at 10,000 megabars.

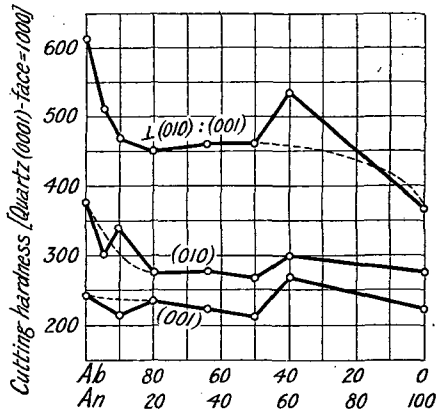



FIG. 174.—Cutting Hardness of the Albite-Anorthite Felspars.

J. Beckenkamp found the linear coeff. of **thermal expansion** of anorthite in the three principal directions to be 0·00001758, 0·00000854, and —0·000032. Some observations were made by E. S. von Federoff. P. E. W. Oeberg gave for the **specific heat** of anorthite, 0·1937 ; F. E. Neumann gave for labradorite, 0·1926 ; J. Joly, 0·19317–0·19351 between 12° and 100°. J. Joly also gave for oligoclase, 0·19967–0·20600, and R. Ulrich 0·2048 between 18° and 98°. A. Brun gave for the **melting point** of anorthite, 1490°–1520° ; J. H. L. Vogt, 1220° ; C. Doelter, 1150°–1220° and 1250°–1350° ; E. Dittler gave 1240°. G. A. Rankin gave 1550° ± 2° for the m.p. of artificial crystals of anorthite. Y. Yamashita and M. Majima gave for the m.p. of anorthite 1528°–1533° ; andesine, 1333° ; and oligoclase-andesine, 1232°. A. Brun gave for the m.p. of oligoclase, 1260° ; J. Joly gave 1220° ; A. L. Fletcher, 1270° ; C. Doelter, 1130°–1175° ; and later, 1170°–1250°. A. Brun gave for andesine, 1280°, and C. Doelter, 1180°–1280°. C. Doelter gave for labradorite, 1210°–1300° ; J. Joly, 1230° ; A. L. Fletcher, 1273°–1285°. E. Dittler gave for artificial labradorite, 1370° ; A. L. Day and R. B. Sosman, 1477° ; and A. L. Day and E. T. Allen, 1463°. For artificial oligoclase, A. L. Day and R. B. Sosman gave 1345°, and A. L. Day and E. T. Allen, 1340° ; while for artificial andesine, A. L. Day and R. B. Sosman gave 1375°, and A. L. Day and E. T. Allen, 1419° ; the last-named also found for the series :

| | An | $Ab_1An_5$ | $Ab_1An_2$ | $Ab_1An$ | $Ab_2An$ | $Ab_3An$ |
|---|---|---|---|---|---|---|
| M.p. | 1532° | 1500° | 1463° | 1419° | 1367° | 1340° |

N. L. Bowen's freezing curves for the plagioclases are shown in Fig. 175, and he gives 1550° for the m.p. of anorthite. The remarks as to the effect of the size of grain

and speed of heating on the m.p. indicated in connection with the alkali-felspars are applicable here—with this difference, unlike orthoclase, anorthite has a congruent m.p. in which the liquid has the same composition as the crystals. A. L. Day and E. T. Allen found a sharply defined m.p. C. Doelter found that the fusion temp. really stretches over an interval:

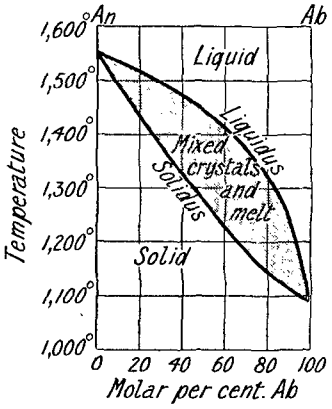



FIG. 175.—Freezing Curve of the Plagioclases.

| | $Ab,An_5$ | $Ab,An_2$ | Ab,An |
|---|---|---|---|
| M.p. . | 1465°–1521° | 1372°–1490° | 1287°–1450° |
| | $Ab_2An$ | | $Ab_3An$ |
| M.p. . . . . | 1205°–1394° | | 1175°–1362° |

H. Lietmeier observed that a sample of labradorite from Kieff, when very slowly heated had a m.p. 1245°–1250°, but was not then completely fused. A. L. Day and E. T. Allen found that microscopic crystals of a homogeneous compound, when slowly heated can persist 150° or more above the temp. at which fusion begins, since the viscosity or rigidity of the amorphous melt is of the same order as that of the crystals. The absorbed heat of fusion is distributed over this interval. They state that powdered crystalline plagioclase felspars, which are free from inclusions and from glass, even when very fine, do not sinter until melting begins; powdered glasses of like composition sinter readily at relatively low temp. (700°–900°) depending primarily upon the degree of comminution. J. H. L. Vogt estimated the total **heat of fusion** from −273° to be 503 cals., and the latent heat of fusion to be 100 cals.

The **indices of refraction** of the plagioclases have been measured by A. Michel-Lévy and A. Lacroix,[17] F. Fouqué, E. Offret, C. Viola, M. Schuster, A. N. Winchell, O. Grosspietsch, C. Riva, F. Becke, H. Rosenbusch and E. A. Wülfing, H. Tertsch, G. Linck, A. des Cloizeaux, E. S. von Federoff, F. Klein, W. Luczizky, E. Mallard, F. Pockels, G. Wulff, etc. The general results show that for anorthite the values of $\alpha$ range between 1·5740 and 1·5757; $\beta$, from 1·5810–1·5837; and $\gamma$, from 1·5860–1·5884. Bytownite, $\alpha$, from 1·5597–1·5617; $\beta$, from 1·5628–1·5647; and $\gamma$, from 1·5677–1·5689. Labradorite, $\alpha$, from 1·5540–1·5167; $\beta$, from 1·5570–1·5647; and $\gamma$, from 1·5620–1·5689. Andesine, $\alpha$, from 1·5490–1·5548; $\beta$, from 1·5530–1·5578; and $\gamma$, from 1·5560–1·5625. Oligoclase, $\alpha$, from 1·5337–1·5389; $\beta$, from 1·5376–1·5431; and $\gamma$, from 1·5420–1·5469. G. A. Rankin and F. E. Wright gave for artificial anorthite, $\alpha$=1·576, $\beta$=1·585, and $\gamma$=1·589. J. Kratzert gave for anorthite, $\alpha$=1·575, $\beta$=1·583, and $\gamma$=1·588. F. Becke and M. Goldschlag measured the indices for some andesines. J. P. Iddings' diagram showing the indices of refraction of the lime-soda-felspars between albite and anorthite is given in Fig. 176. The data are derived from the following observations:

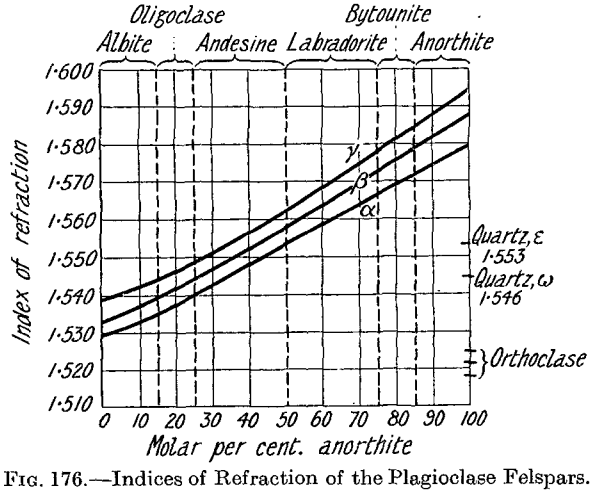



FIG. 176.—Indices of Refraction of the Plagioclase Felspars.

| | $Ab_{100}An$ | $Ab_{87}An_{22}$ | $Ab_{78}An_{22}$ | $Ab_{60}An_{40}$ | $Ab_9An_{91}$ |
|---|---|---|---|---|---|
| $\alpha$ . . | 1·5291 | 1·5337 | 1·5389 | 1·5490 | 1·5752 |
| $\beta$ . . | 1·5332 | 1·5376 | 1·5430 | 1·5530 | 1·5833 |
| $\gamma$ . . | 1·5390 | 1·5429 | 1·5466 | 1·5560 | 1·5884 |

E. Offret studied the effect of *temperature* on the refractive indices of oligoclase, and a selection from his results is given in Table XXVIII. S. Tsuboi studied the

TABLE XXVIII.—THE EFFECT OF TEMPERATURE ON THE REFRACTIVE INDICES OF THE PLAGIOCLASES.

| — | | Red. | | Yellow. | Green. | | Blue. |
|---|---|---|---|---|---|---|---|
| | | $\lambda_{Li}=0·6706$ | $\lambda_{Cd}=0·6437$ | $\lambda_{Na}=0·588.$ | $\lambda_{Cd}=0·5377$ | $\lambda_{Cd}=0·5084$ | $\lambda_{Cd}=0·4799$ |
| $\alpha$ | 0° | 1·536265 | 1·537095 | 1·539163 | 1·541683 | 1·543483 | 1·545560 |
| | 100° | 1·536547 | 1·537384 | 1·539470 | 1·542014 | 1·543830 | 1·545925 |
| | 200° | 1·536930 | 1·537773 | 1·539870 | 1·542428 | 1·544256 | 1·546362 |
| | 300° | 1·537378 | 1·538231 | 1·540336 | 1·542903 | 1·544736 | 1·546849 |
| $\beta$ | 0° | 1·540382 | 1·541257 | 1·543420 | 1·546021 | 1·547856 | 1·549950 |
| | 100° | 1·540770 | 1·541649 | 1·543822 | 1·546435 | 1·548280 | 1·550384 |
| | 200° | 1·541227 | 1·542114 | 1·544305 | 1·546940 | 1·548801 | 1·550923 |
| | 300° | 1·541723 | 1·542620 | 1·544838 | 1·547494 | 1·549378 | 1·551525 |
| $\gamma$ | 0° | 1·544052 | 1·544944 | 1·547141 | 1·549774 | 1·551624 | 1·553729 |
| | 100° | 1·544450 | 1·545340 | 1·547533 | 1·550162 | 1·552010 | 1·554111 |
| | 200° | 1·544911 | 1·545805 | 1·548005 | 1·550649 | 1·552506 | 1·554617 |
| | 300° | 1·545408 | 1·546302 | 1·548529 | 1·551200 | 1·553077 | 1·555212 |

optical dispersion of the plagioclase felspars. The **birefringence** of anorthite ranges from 0·0120–0·0132; labradorite, from 0·0069–0·0089; andesine, from 0·0070–0·0077; and oligoclase, from 0·0080–0·0092. E. Offret found the birefringence at 0°, $\gamma-\beta=0·00393$, changed $-0·00004$ for 100°; $\beta-\alpha=0·00414$, changed $+0·00011$ for 100°; and $\gamma-\alpha=0·00879$, changed $+0·00007$ for 100°. The **optical character** of andesine with 37 molar per cent. anorthite is neutral, and that of the other plagioclases depends on the composition. Expressing the proportion of anorthite in molar percentages:

| Anorthite . | 0·5 | 13 | 20 | 25 | 37 | 52 | 56 | 63 | 75 | 100 |
|---|---|---|---|---|---|---|---|---|---|---|
| Optical char. . | + | + | − | − | 0 | + | + | + | − | − |

The plagioclase felspars are very similar but vary continuously in composition from albite to anorthite. Methods for distinguishing between the different plagioclases based on differences in their optical characters—*e.g.* in the orientation of their axes, and in the planes of optical symmetry relatively to their crystal structures—have been developed by M. Schuster, A. Michel-Lévy, E. S. von Fedoroff, and W. W. Nikitin, L. Duparc and M. Reinhard, E. D. Stratanowitsch, H. Sigg and co-workers, M. Berek, R. Sabot, and M. A. Ouroussoff.

A. de Gramont[18] examined the **spectra** of anorthite, labradorite, and oligoclase. W. W. Coblentz found oligoclase has no marked absorption bands in the **ultra-red transmission spectrum**; but there is a depression in the transmission curve at 3·3$\mu$. W. Vernadsky found anorthite to exhibit a feeble **triboluminescence.** E. Engelhardt observed a pale blue luminescence with anorthite exposed to **ultra-violet light**; and K. Keilhack found anorthite to be luminescent when exposed to **X-rays.** C. Doelter's measurements of the **electric resistance** of labradorite are summarized in Fig. 177.

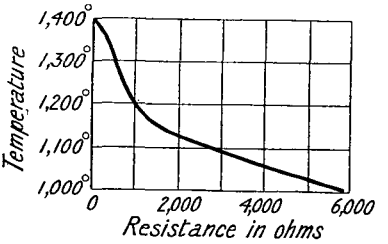



FIG. 177.—Electrical Resistance of Labradorite.

**The chemical properties of the plagioclases.**—C. Doelter[19] digested anorthite in **water** at 80°, and after 30 days found that small quantities of silica and lime were dissolved, but only a trace of alumina. G. A. Bender worked with water at 90° and obtained crystals which were too small to investigate quantitatively, but which were thought to be chabasite. F. W. Clarke found that oligoclase moistened with water gave an alkaline reaction with phenolphthalein. G. Steiger found water has a slight solvent action on oligoclase. J. R. Müller investigated the action of carbonated water on oligoclase and found it to be more soluble than orthoclase. A. Johnstone also examined the action of carbonated water on oligoclase and labradorite. C. Doelter found that carbonated water in a sealed tube at 200° for 14 days converted anorthite into products with the optical properties of heulandite and chabasite. J. Splichal concluded from his experiments on the action of **carbonic acid** on anorthite, that lime and alkalies are extracted and a kaolinitic product is formed. E. Reymond studied the action of **chlorine** and of **hydrogen chloride** on labradorite. Anorthite is soluble in **acids.** As a rule, anorthite is decomposed by acids with the separation of gelatinous silica, and the less the proportion of anorthite in a given plagioclase, the less readily is it attacked by acids. H. S. Washington obtained a polysilicic acid, $H_5AlSi_2O_8$, by the action of acids on anorthite. J. Splichal found that **acetic, chloric, and perchloric acids** partially dissolve anorthite. He found great differences in the character of the silica gels with variations in the nature and conc. of the acids. Forty-five per cent. **formic acid** gives a gelatinous silica. J. Splichal found that with **hydrochloric acid** of sp. gr. 1·19, oligoclase is partly dissolved, and from the results inferred that the plagioclases are solid soln. and not mechanical mixtures. P. Jannasch showed that labradorite is attacked with difficulty by hydrochloric acid. W. Tarassenko studied the action of hydrochloric acid on labradorite. W. B. Schmidt found that **sulphurous acid** attacks oligoclase and labradorite more than does carbonic acid. H. Lotz examined the action of air charged with **sulphur dioxide** on labradorite. J. Lemberg found that a soln. of **sodium carbonate** converted anorthite into a *mixture of calcium carbonate and a cancrinite-like substance.* C. Doelter digested anorthite with a 10 per cent. soln. of sodium carbonate for four weeks at 180°, and found 3·1 per cent. of silica, 5·26 per cent. of alumina, and 12·1 per cent. of lime were dissolved. J. Splichal obtained rather different results, for only traces of lime passed into soln. J. Lemberg also studied the action of soln. of sodium carbonate on oligoclase. J. Lemberg observed that a soln. of **potassium carbonate** converted anorthite into a zeolitic substance—a kind of *potash-anorthite,* $K_2Al_2Si_2O_8$. A soln. of **sodium silicate** furnishes acicular crystals of a calcium sodium aluminosilicate. He also examined the effect of soln. of potassium and sodium carbonates and of **potassium and sodium chlorides** on labradorite—crystals and glass. C. Doelter and E. Hussak, and J. Lenarcic examined the effect of molten fluxes on labradorite. F. W. Clarke and G. Steiger examined the action of **ammonium chloride** on heated oligoclase, and found that the dried residue contained 0·32 per cent. of ammonia. Washing with water afterwards removed 0·96 per cent. CaO, and 2·71 per cent. $Na_2O$. V. P. Smirnoff examined the action of **humic and crenic acids** on anorthite, and oligoclase.

The remarks on the effects of natural agents on alkali-felspars (*q.v.*) apply also to the lime-felspars; the products from the latter usually have a higher proportion of lime and magnesia. C. R. van Hise[20] discussed the change of anorthite into prehnite, zoisite, meionite, scolesite, laumonite, gismondite, and thomsonite; C. F. Rammelsberg, the change into amphodelite; A. E. Nordenskjöld, the change into sundvikite; A. des Cloizeaux, the alteration to polyargite, and tankite; and R. Hermann, and J. Roth, the change into lindsayite.

H. Sjögren[21] found a mineral in the manganese mines of Jakobsberg, Sweden; its composition corresponded with the barium analogue of anorthite, *baryta-felspar;* and he called it **celsian**—in honour of A. Celsius. W. S. von Waltershausen had previously obtained a complex baryta-potash-felspar from the same locality,

and he called it **hyalophane**—from ὑαλέος, glass-like; and φαίνω, appearance. Analyses of hyalophane were made by G. A. Kenngott, T. Petersen, L. J. Igelström, C. F. Rammelsberg, F. Sandberger, J. C. Heusser, etc. G. Tschermak showed that hyalophane can be regarded as a mixture of baryta-anorthite, orthoclase, and albite. E. Tacconi shows that the mineral *paracelsian* which he found near Candoglia, Italy, is really an impure celsian. Baryta-felspar has also been described by A. Knop, F. A. Genth, S. L. Penfield and E. S. Sperry, and L. J. Igelström. A. des Cloizeaux described a triclinic form which he regarded as a *barium-plagioclase*. A Mitscherlich, and H. S. Washington also mentioned finding up to about 1·10 per cent. of baryta and 0·30 per cent. of strontia in a number of orthoclase felspars. As indicated with anorthite, F. Fouqué and A. Michel-Lévy synthesized both baryta-felspar, and strontia-felspar. E. Dittler also made *baryta-felspar*, $BaAl_2Si_2O_8$. P. Eskola found that the baryta or strontia-felspar could be crystallized by fusion with molten barium or strontium vanadate, at 1400° for about 12 hrs., and washing the soluble matters from the cold mass. The crystals of baryta-felspar are mostly Carlsbad twins, and the apparent rhombic characters observed by F. Fouqué and A. Michel-Lévy, and E. Dittler are misleading because the crystals are monoclinic. Basal cleavage is not well developed. The indices of refraction indicate a negative character; for the *D*-ray, $\alpha=1{\cdot}587$, $\beta=5{\cdot}593$, and $\gamma=1{\cdot}600$—all $\pm0{\cdot}002$. $\alpha$ for the *F*-line is 1·593; for the Tl-line, 1·590; and for the *G*-line, 1·585. No twinning of *strontia-felspar*, $SrAl_2Si_2O_8$, crystals was detected; and no well-formed crystals were observed. The crystals of radiating fibres did not permit a determination of crystallographic characters. The indices of refraction for the *D*-line were $\alpha=1{\cdot}574$, $\beta=1{\cdot}582$, and $\gamma=1{\cdot}586$—all $\pm0{\cdot}002$. The optical properties of anorthite and of strontia-felspar were very similar. Evidence showed that strontia-felspar probably forms a complete series of solid soln. with anorthite.

The crystals of celsian were first stated by H. Sjögren to be triclinic, but later they were shown by F. F. Strandmark to be monoclinic with axial ratios $a:b:c=0{\cdot}657:1:0{\cdot}554$, and $\beta=115°\ 2'$. Twinning according to the Carlsbad, Baveno, and Manebach types has been described. The crystals of hyalophane were examined by W. S. von Waltershausen, G. vom Rath, F. Rinne, and G. A. Kenngott. A. Hadding examined the X-radiograms of hyalophane, and celsian. According to A. von Obermayer, the axial ratios of the monoclinic crystals are $a:b:c=0{\cdot}658395:1:0{\cdot}55121$, and $\beta=64°\ 25'\ 15''$; P. Groth gave $0{\cdot}6584:1:0{\cdot}5512$, and $\beta=115°\ 35'$. The crystals of hyalophane have the adularia habit, and they sometimes have a zonal structure with the central portions richer in barium, and the outer portion richer in potassium. H. Sjögren gave $2V=86°\ 22'$ for the optic axial angle of celsian. The plane of the optic axes for hyalophane is vertical to the (010)-face; and the optic axial angle, according to A. des Cloiseaux, is $2E=60°$ at 20°; and, according to F. Rinne, for Li-, Na-, and Tl-light, $2H_a$ is respectively 83° 50′, 83° 25′, and 83° 2′; $2H_0$ respectively 107° 17′, 107° 30′, and 107° 52′; and $2V$, respectively 79° 21′ 14″, 79° 2′ 50″, and 78° 42′ 14″.

H. Sjögren gave for the sp. gr. of celsian 3·37; F. A. Genth found the sp. gr. of hyalophane with 3·71 per cent. of BaO is 2·692, and with 7·30 per cent. BaO, 2·835. W. S. von Waltershausen gave 2·771–2·832. F. F. Strandmark gave for the orthoclase (Or)-celsian (Ce) series of felspars:

| | Or | $Or_{10}Ce$ | $Or_{11}Ce$ | $Or_4Ce$ | $O_3Ce$ | $Ce_7Ce_3$ | Ce |
|---|---|---|---|---|---|---|---|
| Sp. gr. . . . | 2·550 | 2·593 | 2·645 | 2·725–2·733 | 2·756 | 2·818 | 3·384 |

F. Fouqué and A. Michel-Lévy's preparations had sp. gr., *baryta-oligoclase*, 2·906, *baryta-labradorite*, 3·333, and *baryta-anorthite*, 3·573; and his *strontia-oligoclase*, 2·610, *strontia-labradorite*, 2·862, and *strontia-anorthite*, 3·043. The effect of the at. vol. of potassium, sodium, and barium on the isomorphism of orthoclase and baryta-orthoclase has been discussed by E. T. Wherry. The hardness of celsian and the hyalophanes is about 6 or over. The indices of refraction of celsian, given

by F. F. Strandmark, are $\alpha=1{\cdot}5837$, $\beta=1{\cdot}5886$, and $\gamma=1{\cdot}5940$; for hyalophane, F. Rinne found Li-, Na-, and Tl-light, $\beta=1{\cdot}5388$, 1·5392, and 1·5416, respectively. The optical characters of celsian and hyalophane are negative. Hyalophane is scarcely affected by acids. A. S. Ginsberg studied the system $CaAl_2Si_2O_8$—$BaAl_2Si_2O_8$, and found the excess of the latter crystallizes as hexagonal plates corresponding with nephelite. Mixed crystals with up to 20 per cent. of nephelite have $2V=68°$, while anorthite has $2V=80°$.

F. L. Ransome [22] discovered a kind of hydrated anorthite in the glaucophanic schists of Tibaron Peninsula, California, and he called the mineral **lawsonite**—after A. C. Lawson. Since then, the mineral has been found in several other localities by C. Viola, A. Lacroix, E. Manasse, J. P. Smith, A. S. Eakle, S. Franchi. Analyses by F. L. Ransome and C. Palache, J. R. Schnell, W. T. Schaller and W. F. Hillebrand, F. Zambonini, A. F. Rogers, J. P. Smith, A. Lacroix, show that the composition approximates to $H_4CaAl_2Si_2O_{10}$, or **calcium dialuminium tetrahydroxydimetasilicate,** $(HO)_4CaAl_2(SiO_3)_2$. F. L. Ransome and C. Palache gave this formula, and also $(AlOH)_2H_2Ca(SiO_4)_2$; P. Groth gave $Ca\{Al(OH)_2\}_2(SiO_3)_2$; and F. W. Clarke tripled the formula:

$$\begin{matrix} Al{\equiv}SiO_4 \\ H_3{\equiv}SiO_4 \end{matrix}\!\!>\!Al\!-\!CaSiO_4\!-\!Ca\!-\!CaSiO_4\!-\!Al\!<\!\begin{matrix} SiO_4{\equiv}\{Al(OH)_2\}_3 \\ SiO_4{\equiv}H_3 \end{matrix}$$

Lawsonite is thus related to carpholite in which manganese replaces calcium. W. Vernadsky made some observations on the constitution of lawsonite. A. F. Rogers saw that the extinction is parallel in one part of a crystal from Calaveras Valley, and in the other part has an extinction angle of 5° to the long edge of the crystal. This may mean that lawsonite, like carpholite, is monoclinic. J. P. Smith saw that lawsonite represents the anorthite portion of plagioclase set free in the chemical adjustment during metamorphic changes, and the albite portion of plagioclase either furnishes albite crystals, or contributes to the formation of glaucophane. Lawsonite is pale blue or greyish-blue in colour. Hibscite is colourless or pale yellow. The large prismatic or tabular crystals belong to the rhombic system; and, according to C. Palache, have the axial ratios $a:b:c=0{\cdot}66524:1:0{\cdot}7385$. The crystals have also been studied by A. F. Rogers. The twinning plane is (110). The faces (110) and (011) are striated parallel with (001). The cleavage parallel to (010) and (001) is perfect; and the cleavage parallel to (110) is indistinct. The optic axial angles $2H_a=88°\ 27'$; $2H_0=103°\ 16'$; and $2V_a=84°\ 6'$ for yellow light. F. Cornu reported octahedral crystals of a mineral from Marienburg which had the same composition as lawsonite, but crystallized in the cubic system. He called the mineral *hibscite*, and considered it to be a dimorphous variety of lawsonite. The sp. gr. of lawsonite is 3·084–3·091, and the hardness $8\frac{1}{4}$. The sp. gr. of the ignited powder is 2·558. The sp. gr. of hibscite is about 3·5, and the hardness about 6. The indices of refraction of lawsonite are $\alpha=1{\cdot}6650$, $\beta=1{\cdot}6690$, and $\gamma=1{\cdot}6840$; and the birefringence $\gamma-\alpha=0{\cdot}019$ for yellow light. The optical character of lawsonite is positive. The index of refraction of hibscite is 1·67. Lawsonite resists attack by acids, but after ignition it is decomposed by acids with the separation of gelatinous silicic acid. According to F. Cornu, hibscite adsorbs the dye from soln. of fuchsine; the moistened powdered mineral has an acid reaction, but after calcination an alkaline reaction; it is strongly attacked by acids—even by acetic acid; and it is decomposed by alkaline soln.

The so-called *lime-mica* was described by F. Mohs [23] as *pearly mica*. C. C. von Leonhard said that the Tyrolese mineral dealers called it **margarite**—from $\mu\alpha\rho\gamma\alpha\rho\acute{\iota}\tau\eta\varsigma$, a pearl—its present-day name.

J. L. Smith designated the micaceous mineral accompanying the smirgel of Naxos and Asia Minor, *emerylite*; and J. L. Smith and G. J. Brush showed that emerylite is identical with the margarite of Tyrol. B. Silliman gave the name *clingmanite* to a mica accompanying the corundum of North Carolina, and the name *corundelite* to a mica associ-

ated with the corundum and smirgel of Unionville, Penn. J. D. Dana, and G. Tschermak showed that all these minerals are margarites. N. Nordenskjöld found a mica in the emerald mines of the Ural, to which he applied the term *diphanite*—from δίς, twice; φαίνω, to appear—in allusion to its appearance when viewed in different directions. A. Breithaupt showed that diphanite is identical with margarite.

C. F. Rammelsberg's review of the analyses correspond with $(H,R)_2CaAl_4Si_2O_{12}$, or $R_8SiO_4$. G. Tschermak, and R. Brauns gave for the idealized mineral $H_2CaAl_4Si_2O_{12}$; P. Groth, $R_2CaAl_4Si_2O_{12}$; and F. J. Wiik, $2\{(H_2Ca)Al_2SiO_6\}$. S. Weyberg assumed the existence of a *margaritic acid*, $H_2Al_2SiO_6$, and he claimed to have made salts of this acid by the action of potassium chromate on china clay; and addition products with calcium chloride or bromide. E. V. Shannon described a specimen coloured with chromium. F. W. Clarke made two suggestions:

$$HO-Al<\begin{matrix}SiO_4\equiv CaH\\SiO_4\equiv(AlO)_3\end{matrix} \qquad Ca<\begin{matrix}SiO_4\equiv(AlO)_2H\\SiO_4\equiv(AlO)_2H\end{matrix}$$

but prefers the former. This would make margarite, **calcium dihydrotetraaluminyldiorthosilicate.** K. von Chroustschoff claimed to have prepared margarite by melting together a mixture of lepidolite, silicic acid, alumina, and alkali fluorides. The statements, however, require confirmation.

The colour of margarite is white, with a grey, red, pink, or yellow tinge. Distinct crystals are rare. It usually forms aggregates of plates, or it may be massive with a scaly structure. The crystals are monoclinic with axial ratios close to those of biotite. The habit of the crystals is tabular. Twinning is common as in mica. The cleavage is like that of mica, but the laminæ are rather brittle and non-elastic, The percussion figure is like that of mica. A. des Cloizeaux gave for the optic axial angle $2E=109°\ 32'$–$128°\ 48'$ for red light; M. Bauer gave $2E=76°$–$80°$; G. Tschermak, $2E=120°$ for Na-light; and G. H. Williams, $114°\ 30°$. E. V. Shannon gave $2V=30°$ for the biaxial mineral. The sp. gr. ranges from 2·99–3·08; and the hardness from 3·5–4·5. G. Tschermak gave for the index of refraction $\beta=1·64$–$1·65$; and the birefringence is feeble for $\gamma-\alpha=0·009$. E. V. Shannon gave $\alpha=1·625$, $\beta=1·633$, and $\gamma=1·634$. The optical character is negative. E. S. Larsen made observations on the optical properties of margarite. A. Kenngott found that the moistened powder reacts feebly alkaline to litmus; and if it has been previously calcined the reaction is feebler. The mineral is slowly and imperfectly decomposed by hydrochloric acid. V. Iskyul studied the action of hydrochloric acid. F. A. Genth observed the transformation of margarite into dudleyite (*q.v.*) by the substitution of the calcium by magnesium.

A zeolite which occurs at Kilpatrick, Scotland, in amygdaloidal masses was called by H. J. Brooke [24] **thomsonite,** in honour of T. Thomson; and D. Brewster called that which occurs in the lavas of Monte Somma, *comptonite*—after S. J. A. Compton. T. Monticelli and N. Covelli, and A. Breithaupt grouped the two minerals together, and the analyses of C. F. Rammelsberg justified this.

A. Breithaupt called thomsonite *triphoclase*. J. J. Berzelius called the concretions with a lamellar radiating structure at Nalsö, Faröe Island, *mesole*—not mesolite—and M. F. Heddle, *farölite*. E. T. Wherry claimed that the composition of good representative samples of farölite approximate $Na_2Ca_3(Al_3Si_9O_{34})9H_2O$, and they have the average indices of refraction $\alpha=1·512$, $\beta=1·513$, and $\gamma=1·518$; and $\gamma-\alpha=0·006$. Hence, farölite is optically and chemically distinct from thomsonite, and he favoured its being regarded as a definite mineral species. A. and R. Brauns considered harringtonite is the same as farölite, and W. Haidinger, and A. des Cloizeaux showed that these minerals are varieties of thomsonite. R. D. Thomson called a mesole from Portrush, Antrim, *scoulerite*; T. Thomson, a reddish variety from the Donegore Mts., Antrim, *chalitite*; C. U. Shepard, a variety from the Ozark Mts., Arkansas, *ozarkite*; W. S. von Waltershausen, a variety in straw-yellow needles, from Berufiord, Iceland, *carphostilbite*; and S. F. Peckham and C. W. Hall, a green variety from Grand Marais, Lake Superior, *lintonite*—after L. A. Linton.

Quite a large number of analyses has been reported.[25] The proportion of soda ranges from virtually zero up to nearly 12 per cent. The magnesia is usually

below one-half per cent., but in the so-called *picrothomsonite*—from πικρός, bitter—of G. Meneghini and E. Bechi, the magnesia replaces soda, and may attain over 6 per cent. The sp. gr. is 2·278, and hardness 2. C. F. Rammelsberg [26] inferred from analyses of the mineral that there is a *soda-thomsonite*, $Na_2Al_2Si_6O_{16}.2\frac{1}{2}H_2O$, and a *lime-thomsonite*, $CaAl_2Si_2O_8.2\frac{1}{2}H_2O$. P. Groth accepted C. F. Rammelsberg's formula, and C. Hintze doubled it; C. Doelter represented the idealized mineral as a hydrated anorthite, namely, $CaAl_2Si_2O_8.2\frac{1}{2}H_2O$, because when melted and allowed to cool, crystals of anorthite were formed. This view was adopted by F. W. Clarke in his later work:

$$Al{\equiv}SiO_4{-}Al\begin{matrix}SiO_4\\SiO_4\end{matrix}\!\!\begin{matrix}\diagup Ca\\\diagdown Al\end{matrix}{-}SiO_4{\equiv}Al+5H_2O$$

If the analogy with anorthite be well-founded, idealized thomsonite would be $CaAl[Al(SiO_4)_2]2\frac{1}{2}H_2O$, or **hemipentahydrated calcium aluminium alumino-diorthosilicate.** The generalized formula, allowing for the soda, can be written $(Ca,Na_2)Al_2Si_2O_8.2\frac{1}{2}H_2O$, the $Na_2 : Ca$ ratio varying from 1 : 3 to 1 : 1. The replacement of up to about half the lime by soda, said F. W. Clarke, may be due to admixed carnegieite. S. G. Gordon found a variety with the ratio $CaO : Na_2O = 5 : 1$, and called it *calcio-thomsonite*. G. Tschermak assumed that there are three lime-thomsonites, and one soda-thomsonite. He further assumed that double salts can be formed with soda-thomsonite and the other lime-thomsonites. G. Tschermak suggested three possible types of formula; and for the sake of brevity, neglecting the oxygen atoms, these may be symbolized:

$$-Si\begin{matrix}\diagup Al\\\diagdown Al\end{matrix}\!\!\diagup Si-$$

Orthosilicate.

$$=Si\begin{matrix}\diagup Al\\\diagdown Al\end{matrix}\!\!\diagdown Si=$$

Metasilicate.

$$Ca\begin{matrix}\diagup Al=Si=\\\diagdown Al=Si=\end{matrix}$$

$$Ca=Si=Si\begin{matrix}\diagup Al=\\\diagdown Al=\end{matrix}$$

Disilicate.

where the free ends of the hyphens represent the attachments for the bivalent base. He assumed that the silicic acid obtained by treatment with acid would decide which type of formula is best fitted for a particular zeolite. He said that with 10 per cent. hydrochloric acid, orthosilicic acid is formed, and he accordingly favoured the corresponding formula. Thomsonite often carries an excess of silica or silicic acid, possibly in solid soln. S. G. Gordon assumed as end-members $CaO.Al_2O_3.2SiO_2.3H_2O$, and $Na_2O.Al_2O_3.3SiO_2.H_2O$ in order to represent the composition of the different thomsonites. The formulation of the composition of this mineral by the co-ordination theory with $Ca : Na_2$ approximately as 3 : 1 is

$$\left[SiO_6 : SiO_2\right]^{Al_2}_{(Ca,Na_2)}.2\tfrac{1}{2}H_2O$$

H. C. McNeil, and C. Hersch also proposed a structural formula for thomsonite. E. T. Wherry found that the analyses of thomsonite agree with that of the non-variable mineral $NaCa_2(Al_5Si_5O_{20})6H_2O$; and that the apparent variability is due to the admixture of this mineral with mesolite. O. B. Böggild found these two minerals show intergrowths.

F. Zambonini investigated the behaviour of the water on heating, and found that

| | 114° | 158° | 180° | 248° | 305° | 365° | |
|---|---|---|---|---|---|---|---|
| Loss in dry air . . . | 1·49 | 2·42 | — | 4·47 | 7·51 | 10·29 | per cent |
| Loss in moist air . . . | 1·12 | — | 2·25 | 3·43 | 5·38 | 8·86 | „ |

The evolution of water is greatly quickened at 400°, and the difference in the effects of dry and moist air becomes less marked. The rehydration of dehydrated thomsonite occurs in moist air; and the change is analogous to that which occurs with heulandite (*q.v.*). A. Damour found the mineral changes but slightly in moist air, but at 280° it loses 6·1 per cent. of water which it regains slowly when exposed to moist air. C. Hersch, and G. d'Achiardi also measured the loss of moisture which occurs when thomsonite is heated at different temp. The latter found

| | 80°–85° | 145°–150° | 205°–210° | 255°–260° | 325°–330° | Red heat. |
|---|---|---|---|---|---|---|
| Loss . . | 0·942 | 1·69 | 1·107 | 1·365 | 2·179 | 6·556 per cent. |

Thomsonite has not been prepared synthetically. It occurs in cavities in the more basic rocks and probably results from the alteration of the felspathic constituents and nephelite. It also occurs in crystalline schists as an alteration product of the lime-soda-felspars. Thomsonite occurs in snow-white, reddish, green, or brown columnar masses, in radiated concretions and massive. Euhedral crystals are not so common. The crystals belong to the rhombic system, and, according to W. C. Brögger,[27] they have the axial ratios $a:b:c=0{\cdot}99324:1:1{\cdot}00662$. The cleavage parallel to (010) is perfect; less so parallel to (100); and in traces parallel to (001). Twinning occurs on the (110)-plane, and this type has been discussed by E. Melly, and H. Guthe. The optic axial angle was found by A. Lacroix to be $2E=82°–93°\ 25'$ for the red ray, and $84°\ 11'–96°\ 53'$ for the blue ray. V. von Lang gave $2E=83°\ 56'$ and $2H=54°$; and G. Cesaro, $2E=78°–86°$ for the red ray. Observations were made by H. Backlund. A. des Cloizeaux gave $2E=85°\ 47'$; $2V=53°\ 50'$; $2H_0=132°\ 26'$; and $2H_a=55°\ 22'$; D. Hahn gave $2E=60°$. A. des Cloizeaux found at 17° $2E=78°\ 48'$, and at 146·5°, 78° 30′. The sp. gr. ranges from 2·3–2·4; and the hardness 5–6. A colourless and radiating variety of lime-thomsonite was found by S. G. Gordon to have a sp. gr. 2·405. When warmed, clear crystals of thomsonite become turbid. As indicated above, C. Doelter found that when fused, anorthite crystallizes from the slowly cooled mass. A. des Cloizeaux gave for the indices of refraction for the red ray, $\alpha=1{\cdot}497$, $\beta=1{\cdot}503$, and $\gamma=1{\cdot}525$. O. B. Böggild said that these values are too low, and gave $\alpha=1{\cdot}497$, $\beta=1{\cdot}503$, and $\gamma=1{\cdot}525$. E. T. Wherry found $\alpha=1{\cdot}520$, $\beta=1{\cdot}525$, and $\gamma=1{\cdot}540$; S. G. Gordon, $\alpha=1{\cdot}517–1{\cdot}529$, $\beta=1{\cdot}520–1{\cdot}531$, and $\gamma=1{\cdot}530–1{\cdot}541$, and for a colourless variety of lime-thomsonite, $\alpha=1{\cdot}530$, $\beta=1{\cdot}532$, and $\gamma=1{\cdot}542$; A. H. Phillips, $\alpha=1{\cdot}529$, $\beta=1{\cdot}531$, and $\gamma=1{\cdot}541$; A. Scheit, $\alpha=1{\cdot}524$, $\beta=1{\cdot}525$, and $\gamma=1{\cdot}537$. Observations were also made by H. Michel, A. des Cloizeaux, A. Michel-Lévy and A. Lacroix, and J. Königsberger and W. J. Müller. The birefringence is strong up to about 0·02 negative, or weak up to about 0·005. Next to pecolite, the birefringence is greater than that of any other zeolite, $\gamma-\alpha=0{\cdot}027$; G. Cesaro gave $\beta-\alpha=0{\cdot}0026–0{\cdot}04$. F. Rinne found that the double refraction is diminished when the mineral is warmed. Thomsonite is pyroelectric.

G. A. Kenngott[28] found that powdered and moistened thomsonite has an alkaline reaction, but if precalcined, the reaction is feebler. F. W. Clarke also found the moist mineral reacts strongly alkaline. Thomsonite decomposes when treated with acids, and, according to G. Tschermak, gelatinous orthosilicic acid is formed. A. Frenzel, K. D. Glinka, and J. R. Blum discussed the alteration of thomsonite in nature. K. D. Glinka obtained a crystalline substance which he called *hydro-thomsonite*, $(H_2,Na_2,Ca)Al_2Si_2O_8.5H_2O$, as a decomposition product of thomsonite or scolesite at Tschakaw, near Batum. The sp. gr. was 2·0. J. Lemberg found that when digested with a soln. of potassium carbonate, a *potash-thomsonite* was formed by replacement of calcium by potassium; *soda-thomsonite* is formed when this is digested with sodium carbonate soln.; and lime-thomsonite if calcium chloride soln. is used. He also investigated the action of soln. of sodium and potassium chlorides, and hydroxides. G. Steiger found that with a soln. of silver nitrate there is a partial replacement of the bases by silver, forming a *silver-thomsonite*. G. Steiger found that when heated in the vap. of ammonium chloride there is a partial decomposition and an ammonium derivative is formed. H. C. McNeil investigated the action of molten sodium chloride. C. Gismondi[29] described a zeolitic mineral which he obtained in octahedral crystals from the lava of Capo di Bove; he called it *zeagonite*—from ζεῖν, to boil; and ἄγονος, barren—and C. C. von Leonhard, in his translation of Gismondi's memoir, proposed calling the mineral **gismondite.** S. Breislak proposed the name *abrazite*—from ἀ, not; and βραζεῖν, to boil—and this term in some cases was corrupted to *aricite*. There seems to have been some confusion about the identity since properties described by T. Monticelli and

N. Covelli, and an analysis by P. Capri, do not agree with later observations. H. J. Brooke emphasized the relation of gismondite to phillipsite; and C. C. von Leonhard, the relations of both to harmotome; but it would appear from F. von Kobell that phillipsite from Capo di Bove and Vesuvius has been confused with gismondite from the same localities.

Analyses of gismondite have been reported by J. C. G. de Marignac,[30] F. von Kobell, F. Zambonini, A. Sachs, G. Tschermak, and S. J. Thugutt. As C. F. Rammelsberg showed, formulæ calculated from individual analyses are not always concordant—presumably for the reasons stated above. F. W. Clarke represented it as a hydrated anorthite, $CaAl_2(SiO_4)_2.4H_2O$, and gave a constitutional formula similar to that employed for thomsonite. F. Zambonini and P. Groth also used the anorthite formula. This would make gismondite a **tetrahydrated calcium aluminium aluminodiorthosilicate,** $CaAl[Al(SiO_4)_2].4H_2O$. The mineral usually contains some potash and soda, and similar hypotheses were suggested by S. J. Thugutt and G. Tschermak to explain their presence as were employed in the case of thomsonite. C. Friedel and A. Sarasin suggested the constitutional formula:

$$Ca<\begin{matrix}O.Si.O\\ \|\\ O.Si.O\\ \|\end{matrix}>Al_2\lessdot\!\!\!=$$

As in the case of thomsonite (*q.v.*), G. Tschermak obtained orthosilicic acid when gismondite is treated with 10 per cent. hydrochloric acid, and hence he favoured the orthosilicate type of formula. Since a mol of gismondite loses about a mol of water at 100°, he assumed that this represents the water of crystallization, and the remaining three mols of water are assumed to be an integral part of the mol which he symbolizes $H_6CaAl_2Si_2O_{11}$.

Gismondite has not been synthesized, and its high water-content indicates that it has been formed at a low temp. S. J. Thugutt showed that it is probably an *alteration product of nephelite, and by the action of soln. of calcium salts on* nephelite he was able to obtain a product somewhat like gismondite, and he assumed that in nature gismondite is formed in this manner. C. R. van Hise discussed the possible formation of gismondite from anorthite.

The habit of the crystals is a tetragonal pyramid more stumpy than that of the regular octahedron. The colour is white and may be tinged blue, grey, or red. J. C. G. de Marignac,[31] G. Rose and A. Streng measured the crystal angles, and supposed gismondite to be tetragonal. H. Credner, and V. von Lang supposed it to be rhombic. A. des Cloizeaux could not decide whether the mineral was uniaxial or biaxial. Irregularities in the angles led A. Schrauf to assume that the pseudo-tetragonal crystals are produced by the twinning of triclinic individuals, and A. von Lasaulx came to the same conclusions from a study of the optical properties. The later observations of A. des Cloizeaux proved that the crystals are penetration twins, and that the variations in the extinction angles caused by the irregular grouping of the twins do not confirm the assumption that the individuals are triclinic. F. Rinne showed that the crystals are formed by the twinning of monoclinic individuals, and that by the raising of the temp. the variations in the extinction-angle observed by A. des Cloizeaux disappear, and the crystals become rhombic in structure. This was confirmed by F. Zambonini. Gismondite is therefore monoclinic at ordinary temp., and rhombic at a higher temp. The cleavage is not perceptible. F. Rinne found the optic axial angles for Li-light to be $2H_a=86°\ 58'$, $2H_0=104°\ 11'$, and $2V_a=82°\ 11'\ 18''$; for Na-light $2H_a=87°\ 34'$, $2H_0=103°\ 38'$, and $2V_a=82°\ 42'\ 44''$; and for Tl-light $2H_a=88°\ 10'$, $2H_0=102°\ 54'$, and $2V_a=83°\ 18'\ 40''$. J. E. Hibsch gave $2V=86°\ 46'$. A. des Cloizeaux found $2H$ varied from 80°–93°. F. Rinne gave for the rhombic crystals $2H_a=24°\ 57'$. J. C. G. de Marignac gave 2·265 for the sp. gr., and 4–5 for the hardness. G. Tammann measured the vap. press. of the crystals with different proportions of water in equilibrium with water vap. at $p$ mm. press. The gismondite initially contained 21·86 per cent. of water.

| | | | | | |
|---|---|---|---|---|---|
| | 14·55 | 12·48 | 6·05 | 1·23 | 0·11 mm. |
| Loss . . . | 0·02 | 0·19 | 0·89 | 2·49 | 3·73 per cent. |

F. Rinne gave for the index of refraction $\beta=1{\cdot}5348$ for Li-light ; 1·5385 for Na-light ; and 1·5409 for Tl-light. J. E. Hibsch gave $\alpha=1{\cdot}5308$, $\beta=1{\cdot}5402$, and $\gamma=1{\cdot}5484$ for Na-light. A. Lacroix found the dispersion $\gamma-\alpha=0{\cdot}0082$ for Na-light. The optical character is negative. W. W. Coblentz found that the ultra-red transmission spectrum showed only those bands produced by water, *viz.* 1·5$\mu$, 2$\mu$, 3$\mu$, and 4·7$\mu$.

Gismondite is decomposed by acids, and according to G. Tschermak,[32] gelatinous orthosilicic acid separates out. S. J. Thugutt noted that gismondite is coloured red by a soln. of silver nitrate and potassium chromate ; and gismondite can be distinguished from phillipsite by its behaviour towards silver nitrate, and methylene blue. F. Grandjean found that dehydrated gismondite absorbs the vap. of mercury, cinnabar, calomel, iodine, bromine, or sulphur—*vide infra*, chabazite—and he measured the change which occurs in the optical properties of the products.

W. F. Foshag [33] applied the term *plazolite* to colourless rhombic dodecahedra occurring in the limestone of Crestmore, California. Analyses correspond with $3CaO.Al_2O_3.2SiO_2.2H_2O$, or **dihydrated calcium dialuminoxyldiorthosilicate,** $Ca_3(AlO_2)_2(SiO_4)_2.2H_2O$, in which some silica is replaced by carbon dioxide. The sp. gr. is 3·129 ; the hardness $6\frac{1}{2}$ ; and the index of refraction 1·710. The mineral is readily dissolved by hydrochloric acid, it reacts slightly alkaline when moistened with water ; and the reaction is strong after the mineral has been calcined.

J. N. von Fuchs [34] found a mineral at Mt. Monzoni, Fassa Valley, in isolated or aggregated crystals which he named **gehlenite**—after A. F. Gehlen. A. Breithaupt called it *stylobate*—from στυλόβατης, base of a pillar—in allusion to the resemblance of the crystals to a square foot under a column.

H. C. Lewis found square prisms of a pseudomorphous mineral at Wakefield, Ottawa, which he named *cacoclasite*—from κακός, bad ; and κλάσις, fracture—in allusion to its want of cleavage. The crystalline form is probably tetragonal. Its sp. gr. is 3·053, and hardness 5–6. It was analyzed by F. A. Genth. The mineral appears to resemble gehlenite, and also sarcolite. E. Weinschenk described thick, four-sided, light apple-green crystals of a mineral from Monzenithal, which he called *fuggerite*. The crystals probably belonged to the tetragonal system ; the basal cleavage was perfect ; the sp. gr. 3·18 ; and the hardness $6\frac{1}{2}$ ; and the index of refraction $\omega=\epsilon=1{\cdot}691$ for Na-light. The birefringence was low. The mineral is related to akermanite and gehlenite—*vide infra*.

Analyses of gehlenite have been reported by C. F. Rammelsberg, O. B. Kuhn, J. Lemberg, V. von Zepharovich, F. E. Wright, J. Percy, J. F. L. Hausmann, J. H. L. Vogt, H. Bauerman, etc. C. F. Rammelsberg calculated the formula $R''_3R'''_2Si_2O_{10}$, or $Ca_3Al_2Si_2O_{10}$. Z. Weyberg regarded it as a basic orthosilicate, $CaAl_2Si_2O_8.2CaO$ ; and P. Groth, $Ca_3(AlO)_2(SiO_4)_2$, *calcium dioxyaluminium diorthosilicate*. There are considerable deviations from these formulæ. F. W. Clarke represented gehlenite as an aluminato-orthosilicate :

$$(CaAlO_2)_3{\equiv}SiO_4{-}Al{<}\begin{matrix}SiO_4{\equiv}Ca_3{\equiv}SiO_4\\SiO_4{\equiv}Ca_3{\equiv}SiO_4\end{matrix}{>}Al{-}SiO_4{\equiv}(CaAlO_2)_3$$

W. T. Schaller showed that like the melitites all the fuggerites and gehlenites can be represented as isomorphous mixtures of akermanite, velardenite, sarcolite, and soda-sarcolite ; hence, he suggested that natural mixtures of two or more of these compounds be called by the group-name *melilite*, and that the terms *gehlenite* and *fuggerite* be dropped. J. B. Ferguson and A. F. Buddington call the silicate $2CaO.Al_2O_3.SiO_2$, gehlenite—*vide* gelardenite.

Gehlenite is found as a secondary mineral produced by contact metamorphism in limestone. It is not infrequently found in furnace scoriæ and slags, and reports of its occurrence in slags have been made by J. Percy, H. Bauerman, J. H. L. Vogt, P. Groth, J. F. L. Hausmann, and P. Heberdey. The mineral was synthesized by L. Bourgeois by simply fusing the constituents together. F. Fouqué and A. Michel-Lévy obtained good crystals by using mixtures containing magnesia, and iron

oxide. C. Doelter reported crystals resembling gehlenite to be formed when basalt is fused with limestone, and when vesuvianite is melted.

The crystals usually form short square prisms; they are sometimes tabular; and sometimes octahedral. The colour ranges from different shades of greyish-green to liver-brown. A. des Cloizeaux gave for the axial ratio of the tetragonal crystals $a : c = 1 : 0{\cdot}40006$. The cleavage parallel to (001) is imperfect, and parallel to (100) in traces. V. Schumoff-Deleano and E. Dittler studied the rate of crystallization of fused gehlenite. The sp. gr. ranges from 2·90–3·07; and the hardness from $5\frac{1}{2}$–6. A. Michel-Lévy and A. Lacroix gave for the indices of refraction for yellow light $\omega = 1{\cdot}663$ and $\epsilon = 1{\cdot}658$. The birefringence is weak being $\epsilon - \omega = 0{\cdot}005$, or, according to H. Rosenbusch, 0·00618. C. Hlawatsch measured the index of refraction for different spectral lines. The optical character is negative. When treated with hydrochloric acid, the (calcined or uncalcined) mineral is easily decomposed with the separation of gelatinous silicic acid, and the soln. obtained with the fresh mineral contains ferrous and ferric chlorides. J. B. Ferguson and A. F. Buddington studied the solid soln. formed by akermanite, $Ca_2MgSi_2O_7$, and gehlenite, $Ca_2Al_2SiO_7$, and found a minimum in the curve at 1388° corresponding with 74 per cent. akermanite, of m.p. 1458°. Sp. gr. of the glasses confirmed this. Observations on the alteration of gehlenite in nature have been made by A. Cathrein, P. von Sustschinsky, C. R. van Hise, and J. Lemberg.

In the third century B.C., Theophrastus, in his *Περὶ λιθων*, referred to a mineral which he called *ἄνθραξ*; and about the beginning of our era, Pliny, in his *Historia naturalis* (**37**. 25–27), referred to the *carbunculus*. Theophrastus' term, meaning a burning coal, alluded to the internal fire-like colour and reflection; the same term was applied to some rubies. Pliny's term was derived from *carbo*, coal, and had the same signification as *ἄνθραξ*. These minerals are thought to be designated *granatus* by Albertus Magnus in his *De mineralibus* (**2**. 7) of the thirteenth century. The term was adopted by G. Agricola,[35] and J. G. Wallerius; it was translated into French *grenat* by J. B. L. Romé de l'Isle, and into English **garnet** by R. Kirwan. The term *granatus*, meaning like a grain, alluded to likeness of some garnets to the seeds of the pomegranate, which are small, numerous, and of a red colour.

The garnets form a class of isomorphous minerals belonging to the cubic system; and there is also an artificial product, soda-garnet. Their general formula is $R_3''R_2'''(SiO_4)_3$, where calcium, manganese, and ferrous iron may replace one another as R″-bases; and aluminium, chromium, and ferric iron act as tervalent R‴-elements. In a few cases, titanium may act as a tervalent element replacing R‴, and it may also partially replace the silica. Thus, there are:

| | |
|---|---|
| Sodium garnet | LAGORIOLITE, $Na_6Al_2(SiO_4)_3$ |
| Calcium-aluminium garnet | GROSSULAR, $Ca_3Al_2(SiO_4)_3$ |
| Magnesium-aluminium garnet | PYROPE, $Mg_3Al_2(SiO_4)_3$ |
| Ferrous-aluminium garnet | ALMANDINE, $Fe_3Al_2(SiO_4)_3$ |
| Manganese-aluminium garnet | SPESSARTITE, $Mn_3Al_2(SiO_4)_3$ |
| Calcium-ferric garnet | ANDRADITE, $Ca_3Fe_2(SiO_4)_3$ |
| Calcium-chromium garnet | OUVAROVITE, $Ca_3Cr_2(SiO_4)_3$ |
| Calcium-ferrititano-garnet | SCHORLOMITE, $Ca_3(Fe,Ti)_2\{(Si,Ti)O_4\}_3$ |

L. L. Fermor described *grandite* as a garnet between grossular and andradite; and *spandite*, between spessartite and andradite. The sodium present in some grossulars is assumed to be present as isomorphous lagoriolite, when not present with an included mineral. The titanium is assumed to be present in the form of $Ca_3Ti_2(SiO_4)_3$, and also as $Ca_3Fe_2(TiO_4)_3$; the ferrous-iron in the ferric garnets is assumed to be present as $Fe_3Fe_2(SiO_4)_3$; the manganese as $Mn_3Fe_2(SiO_4)_2$; the vanadium as $Ca_3V_2(SiO_4)_3$; the yttrium as $Ca_3Y_2(SiO_4)_3$; and the cerium as $Ca_3Ce_2(SiO_4)_3$. The inter-relations of the garnets[36] have been discussed by W. C. Brögger and H. Bäckström, E. Weinschenk, W. E. Ford, W. Eitel, H. E. Boeke, and J. Uhlig. W. E. Ford obtained the results indicated in Table XXIX. Lagoriolite has been discussed in connection with the alkali aluminium

TABLE XXIX.—COMPARISON OF THE GARNETS.

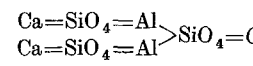
| | Index of refraction. | Sp. gr. | Mol. wt. | Mol. vol. |
|---|---|---|---|---|
| Pyrope . . . . | 1·705 | 3·510 | 404·5 | 115·2 |
| Grossular . . . . | 1·735 | 3·530 | 451·7 | 127·9 |
| Spessartite . . . | 1·800 | 4·180 | 496·4 | 118·8 |
| Almandine . . . | 1·830 | 4·250 | 499·1 | 117·4 |
| Ouvarovite . . . | 1·870 | — | — | — |
| Andradite . . . . | 1·895 | 3·750 | 509·3 | 135·8 |

triorthosilicates. The others will be discussed in connection with the corresponding bases, and the descriptions referred to that of grossular which is taken as the type-member of the class. W. Eitel investigated the miscibility of the garnetic minerals,

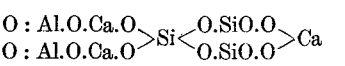
A. G. Werner[37] applied the term **grossular** to a pale green garnet from Siberia. The name was derived from *grossularia*, the botanical name for the gooseberry, and applied in allusion to the colour. Various terms have been applied to grossular garnets of different colours.

A cinnamon-brown variety from Ceylon was called by A. G. Werner *Kancelstein* or *cinnamon-stone*; R. J. Haüy called it *hessonite* or *essonite*—from ἧσσων, inferior—in allusion to its being less hard than the true hyacinth which it resembles. P. A. Dufrénoy applied the term *succinite* to an amber-yellow variety from Ala, Piedmont; and N. Nordenskjöld, *romanzovite*—after Count Romanzoff—to a brown variety from Kimito, Finland. A. Weisbach applied the term *tellemarkite* to a variety of grossular. Some of the green, yellow, and brown garnets may be iron-garnets. The lighter clear garnets are often called *hyacinths*, and regarded as gem-stones. The yellowish garnets thus furnish the so-called *jacinta la bella*; a yellowish-crimson garnet, the *guarnaccino*; a somewhat similar variety, the *vermeille*, or *hyacinth*-garnet; and a reddish-violet garnet, the *rubino di rocca*, and also the *grenat syriam*—from Syriam, Pegu—and probably also the *amethystzontes* of Pliny. The true precious garnet has a deep clear red colour like Burgundy wine, and is either a pyrope or an almandite.

Numerous analyses[38] of grossular have been made; some varieties are free from iron oxide, while other varieties may have up to about 8 per cent. A. Liversidge, G. A. König, and H. G. T. Wachtmeister found samples with up to 7·6 per cent. of manganese oxide; and L. Colomba, samples with nearly 5 per cent. of chromic oxide. C. F. Rammelsberg[39] summarized the various analyses by the formula $Ca_3Al_2Si_3O_{12}$, which in turn may be regarded as a substitution product of normal aluminium orthosilicate, $Al_4(SiO_4)_3$, **calcium dialuminium orthosilicate,** $Ca_3Al_2(SiO_4)_3$. This view is adopted by F. W. Clarke, W. C. Brögger and H. Bäckström, and P. Groth. The graphic formula thus becomes $(CaSiO_4)_3Al_2$, or




F. W. Clarke's formula.




G. Tschermak's formula.

W. and D. Asch represent the garnets as being compounded of two silicates of the types $18RO.6R_2O_3.18SiO_2$, and $16RO.6R_2O_3.16SiO_2$; and apply the hexite-pentite hypothesis to them. W. Vernadsky represents the garnets as being compounded of the mica nucleus (*q.v.*) with an orthosilicate, $R_2Al_2Si_2O_8.R_2SiO_4$. P. Erculisse regards the garnets as solid soln. of metasilicic acid and an aluminosilicic acid of the type $H_2SiAl_2O_6$. G. Tschermak claimed to have isolated mesotrisilicic acid, $H_4Si_3O_8$, from grossularite, and hence assumed that the mineral is a mesotrisilicate. The argument turns on the validity of the assumption that the product obtained actually represents the nature of the acidic radicle—*vide* the silicic acids.

W. C. Brögger showed that sodalite can be correlated with the garnets by substituting the bivalent AlCl″-group in place of sodium in soda-garnet; likewise

with the bivalent $NaSO_4$—Al''-group for nosean (*q.v.*). The helvite family is also related with the garnets if the bivalent S.Mn.S''-group be substituted for the base, and 3Be takes the place of 2Al, furnishing $(Mn,Fe)_2(MnS_2)Be_3(SiO_4)_3$.

Grossularite is found principally in crystalline limestones where it has been developed by contact metamorphism. Grossular is a pyrogenic mineral, but its synthesis is not easy. T. H. Smith [40] described a colourless grossularite formed by deposition from magnetic waters acting on serpentine and gabbro. C. Doelter and E. Hussak found that it decomposes when melted—*vide infra*—and L. Bourgeois, and J. H. L. Vogt fused a mixture eq. to grossular and obtained anorthite and monticellite. The production of grossular must therefore be restricted to a limited range of temp.; the observations of L. L. Fermor on the probable formation of garnets at great depths show that press. may be an important factor. E. S. Sheperd and G. A. Rankin produced grossular by the action of aluminium chloride on calcium orthosilicate under press. A. Gorgeu obtained crystals of a substance like grossular by fusing pipe-clay with an excess of calcium chloride.

The garnets all crystallize in the cubic system. Grossular furnishes euhedral crystals which are commonly dodecahedrons, and icositetrahedrons, or these in combination; octahedral and cubic crystals are rare. The anhedral crystals are often rounded or irregularly formed, and they may occur in grains and granular aggregates. Garnet may also occur massive, granular, or laminated. It may also appear to be compact and cryptocrystalline like nephelite. L. Cahn,[41] and V. Goldschmidt and R. Schröder found growths of needle-like crystals of topaz on crystals of garnet. The colour of grossular may be white, pale green, amber, yellow, brownish-yellow, cinnamon-brown, pale rose-red, and, when chromium is present, emerald-green. Although belonging to the cubic system, D. Brewster showed that the crystals may be optically anomalous in exhibiting double refraction. This subject has been studied by A. Breithaupt, A. des Cloizeaux, M. Websky, A. Wichmann, A. von Lasaulx, P. von Jeremejeff, J. Hirschwald, E. Mallard, etc. E. Bertrand explained the phenomenon by assuming that the crystals were really pseudorhombic or pseudocubic produced by the complex twinning of triclinic individuals. C. Klein showed that the normal form of the garnet is cubic, and that the anomalous optical structure is a secondary mol. condition—probably produced by contraction after crystallization. The structure of the crystals is immediately connected with the external form, for the crystals can be regarded as being made up of a series of similar pyramids whose vertices meet at the centre. Indeed, many garnets can be easily separated into parts corresponding with these pyramids. C. Klein distinguished four types: (i) The *octahedral type* corresponding with eight triangular pyramids each of which is uniaxial and negative with the optic axis normal to the octahedral face which forms its base. (ii) The *dodecahedral type* corresponding with twelve rhombic pyramids whose bases coincide with the faces of the dodecahedron. The axial plane is parallel to the longer diagonal to which the bisectrix is normal. (iii) The *icositetrahedral type* corresponding with twenty-four pyramids whose bases are formed by the faces of the tetragonal trisoctahedron to which the optic axis or bisectrix of the pyramid is normal. (iv) The *hexoctahedral or topazolitic type* corresponds to forty-eight triangular pyramids with bases corresponding to the position of the faces of the vicinal hexoctahedron of topazolite. Each pyramid is biaxial. W. C. Brögger showed that garnets in igneous rocks which have been formed from magmas, or which have been embedded in rocks by regional metamorphism, are uniformly isotropic; while the crystals which have separated from hot soln. in crevices, or have been formed by contact metamorphism, usually exhibit the anomalous double refraction. The dodecahedral faces of the crystals are sometimes striated parallel to the longer diagonal. The cleavage or parting parallel to (110) is sometimes distinct. S. Nishikawa studied the X-radiogram of a garnet.

The sp. gr. of grossular ranges from 3·4–3·6. W. E. Ford gave 3·530; and P. J. Holmquist, 3·621. The sp. gr. decreases after grossular has been melted;

thus, M. Seebach found a sample with a sp. gr. 3·506 before fusion, and 2·866 after fusion. Analogous observations were made by G. Magnus, F. von Kobell, and A. H. Church. The hardness is near 7. P. J. Holmquist found that if quartz be 1000, the hardness on the (111)-face is 835; on the (110)-face, 866; and on the (100)-face, 1261. P. W. F. Oeberg found the sp. ht. of garnets ranged from 0·1744–0·1758. The garnets can be readily fused; C. Doelter gave 1110° for the m.p. of hassonite. C. Doelter and E. Hussak found that when fused alone, meionite, melilite, anorthite, lime-olivine, lime-nephelite, hæmatite, and spinel are produced; the products vary with the composition of the garnet. C. Doelter fused grossular with sodium and magnesium fluorides and obtained biotite, anorthite, meionite, olivine, and magnetite. A. Dannholm found the sp. ht. of garnet. A. des Cloizeaux gave 1·74 for the index of refraction. H. Rosenbusch found for a colourless sample 1·7394, 1·7438, and 1·7480 respectively for Li-, Na-, and Tl-light; similarly, for a reddish sample, 1·7399, 1·7441 and 1·7482; for a pale yellow sample, 1·7520, 1·7569, and 1·7617; and for a brown sample, 1·7575, 1·7626, and 1·7676. M. Seebach gave 1·7320, 1·7364, and 1·7411. The index of refraction of grossular which has been fused is smaller—W. E. Ford gave 1·735. H. W. Vogel measured the absorption spectrum; and W. W. Coblentz, the ultra-red transmission spectrum. Absorption bands were found in the yellowish-green, and greenish-blue parts of the spectrum. In the ultra-red there is a wide absorption band extending from 1·2–2·6$\mu$, and complete opacity beyond 4·5$\mu$. S. C. Lind and D. C. Bardwell found that radium rays colour red garnet violet or purple; no fluorescence or thermoluminescence was observed. O. Mügge found specimens of garnet with radioactive haloes. B. Bavink measured the magnetic properties of garnet.

Grossular is not decomposed by acids, but after fusion acids decompose the product. G. A. Kenngott [42] found that moist and powdered grossular has an alkaline reaction. E. C. Sullivan found that an exchange of bases occurs when garnet is treated with a soln. of cupric sulphate. E. Reymond studied the action of chlorine and of hydrogen chloride on hessonite. The transformation of grossular into chloride, epidote, meionite, wollastonite, etc., has been discussed by C. R. van Hise, E. Millosevich, E. S. von Federoff, R. von Fellenberg, C. A. Kersten, R. Hermann, G. Rose, J. R. Blum, etc. J. Roth called an earthy product of the alteration of grossular, *achtaragdite*. J. Lemberg studied the action of a soln. of magnesium chloride on grossular which had been fused.

An isometric mineral from Achtaragda, Siberia, was named *achtaragdite* by E. F. Glocker; *achtarandite*, by A. Breithaupt; and *achtaryndite*, by F. Auerbach. It was analyzed by R. Hermann, and N. von Kokscharoff. The composition was 28·27–40·10 per cent. $SiO_2$; 11·11–13·06, $Al_2O_3$; 14·07–17·09, $Fe_2O_3$; 0·42, FeO; 11·27–14·41, CaO; 3·60–20·07, MgO; 8·64–12·27, $H_2O$. A. Breithaupt suggested that the crystals are pseudomorphs after helvite; G. Rose, after grossular; and R. Prendel, after boracite.

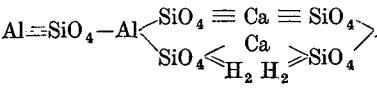
N. L. Bowen [43] found a fibrous white mineral in the calcite near the Abitibi River, Canada, and he named it **echellite**—from *échelle*, a ladder—in allusion to the ratio 1 : 2 : 3 : 4 for the components $(Ca,Na_2) : Al_2O_3 : SiO_2 : H_2O$, calculated from the analysis. He represents it by the formula $(Ca,Na_2)(AlOH)_2Al_2(SiO_4)_3.3H_2O$, or **calcium dihydroxytetraluminium triorthosilicate,** $Ca(AlOH)_2Al_2(SiO_4)_3.3H_2O$, a formula which recalls that of zoisite, $Ca_2(AlOH)Al_2(SiO_4)_3$. The mineral is probably rhombic; the indices of refraction are $\alpha$=1·530, $\beta$=1·533, and $\gamma$=1·545; the optic axial angle is 50°; and it is soluble in hydrochloric acid.

B. G. Sage,[44] and J. B. L. Romé de l'Isle mentioned a mineral resembling chrosoylite from the Cape of Good Hope, and the latter regarded it as a kind of schorl. A. G. Werner named it **prehnite**—after Col. Prehn. R. J. Haüy found specimens of the mineral in France. J. C. Delamétherie called a mineral similar from the Pyrenees, *coupholite*—from κοῦφος, tender—because it occurred in fragile masses made of small thin laminæ or scales. L. P. Walmstedt called a prehnite

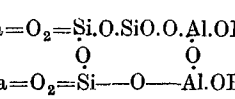
from Aedelfors, Sweden, *œdelite* or *edelite*; and specimens from Keweenaw Point, and Isle Royale were called by J. D. Whitney, *jacksonite*—after C. T. Jackson.

A mineral with radiated fibres found by J. D. Whitney [45] on Isle Royale, Lake Superior, was called *chlorastrolite*—from $\chi\lambda\omega\rho\acute{o}s$, green; and $\check{a}\sigma\tau\rho o\nu$, a star. Analyses were made by J. D. Whitney, and G. W. Hawes. P. Groth gave for the formula $(Ca,Fe,Na_2)\{(Al,Fe)OHSiO_4$. F. W. Clarke gave $H_2Ca_2Al_2(SiO_4)_3$, analogous to the formulæ of natrolite, and scolecite. C. F. Rammelsberg, G. W. Hawes, and C. Hintze regard chlorastrolite as an impure prehnite; J. D. Dana, and P. Groth, as analogous with carpholite; J. D. Whitney, a hydrated zoisite; and A. Lacroix, thomsonite. The colour is light bluish-green, and the mineral is slightly chatoyant on the rounded edges. The sp. gr. is 3·18; the hardness 5–6. It is decomposed by hydrochloric acid with the separation of flocculent silicic acid. W. M. Foote described a mineral occurring at Neepigon Bay, Lake Superior, which was called *zonochlorite* in allusion to its having banded zones with different shades of green. G. W. Hawes found the mineral is not homogeneous, and he regards it as impure prehnite. The sp. gr. is 3·113, and the hardness 6–7. M. F. Heddle found white or yellowish sheafy clusters of plates of a mineral at Uig, Isle of Skye, and he called it *uigite*. The sp. gr. is 2·284, and the hardness $5\frac{1}{2}$. It is regarded as a decomposition product of prehnite. C. W. Blomstrand found colourless crystals, tinged yellow or green, on Hvitholm, Spitsbergen. He called the mineral *arctolite*, or rather *arktolite*. The composition corresponds with $H_2(Ca,Mg)_2Al_2Si_3O_{12}$; it thus resembles prehnite with magnesium in place of some of the calcium—*calcium magnesium dialuminium dihydrotriorthosilicate*. Really, very little is known about arctolite. The sp. gr. is 3·03, and the hardness 5.

Early analyses were made by J. H. Hassenfratz,[46] M. H. Klaproth, L. N. Vauquelin, A. Laugier and A. F. Gehlen. A. G. Werner assumed that the contained water is zeolitic, and the mineral is sometimes regarded as a zeolite, but C. F. Rammelsberg showed that the water is expelled only at a red heat, and is therefore very different from zeolitic water. Numerous other analyses have been reported.[47] C. F. Rammelsberg [48] calculated from the analyses the formula $H_2Ca_2Al_2Si_3O_{12}$, and assumed it to contain silicic acid, and aluminium and calcium orthosilicates. F. W. Clarke gave $Al_2(SiO_4)_3Ca_2H_2$, **calcium dialuminium dihydrotriorthosilicate,** analogous to biotite, $Al_2(SiO_4)_3Mg_2KH$; graphically, he gave:



F. W. Clarke's formula.



C. Hersch's formula.

G. Tschermak gave $(O.Al.O.Ca.O)_2Si(O.SiO.O.H)_2$. The analyses indicated 2·66–5·30 per cent. of contained water. W. Dittrich and W. Eitel found that good samples contained about 4·88 per cent. As in C. F. Rammelsberg's experiment just cited, the water is retained very tenaciously up to a red heat. E. A. Schneider found only 0·17 per cent. is lost at 105°, and 0·31 between 250° and 300°. C. Hersch obtained a similar result. F. W. Clarke and G. Steiger observed the following percentage losses:

| | 100° | 180° | 250° | 350° | Red heat. | Bright red. | Blast-flame. |
|---|---|---|---|---|---|---|---|
| Loss . | 0·21 | 0·18 | 0·10 | 0·11 | 0·28 | 4·05 | 0·09 |

F. Zambonini similarly obtained small losses up to 430°, and hence he considered the water to be constitutional. E. Norin gave 725°–750° for the dehydration temp., and also showed that the water is constitutional. G. Tammann found the vap. press. of the mineral at 25° to be 0·39 mm. when 0·2 per cent. was removed.

Prehnite occurs principally in basic eruptive rocks—basalt, diabase, etc.—as a secondary mineral—may be in veins. It is often associated with zeolites, pectolite, datolite, calcite, etc. A. Lacroix [49] has described a case where it was formed by contact metamorphism. It has not been prepared synthetically, and it is doubtful if it has been formed at a high temp. Euhedral crystals are rare; their habit is generally tabular, sometimes prismatic and acute pyramidal. The aggregates of tabular crystals are united to make broken forms sometimes barrel-shaped. It also furnishes reniform, globular, or stactictic masses. The structure may be columnar, lamellar, or granular. The colour may be white, grey, or green, and the green colour

may fade on exposure. The crystals belong to the rhombic system, and A. Streng gave $a:b:c=0{\cdot}84009:1:0{\cdot}55494$ for the axial ratios; and A. Beutell gave $0{\cdot}8420:1:1{\cdot}1272$. Observations were made by W. H. Miller, G. Flink, V. M. Goldschmidt, C. F. Naumann, and A. des Cloizeaux. The cleavage parallel to (001) is distinct; but that parallel to (110) is not clear. A. des Cloizeaux found the optic axial angles are variable for the red ray, $2H$ varying from 73° 43′–76° 7′, and $2E$ from 122° 59′–129° 9′. A. Beutell found that for the red ray $2H=77°\ 41'$, and $2E=135°\ 16'$; for the yellow ray, $2H=77°\ 44'$, $2E=135°\ 26'$, and $2V=69°\ 22'$; and for the blue ray, $2H=77°\ 53'$, and $2E=135°\ 54'$. H. von Eckerman gave $2V=65°\ 52'$–$68°\ 40'$. A. des Cloizeaux found that raising the temp. from 9°–146½° changed $2E$ from 129° 48′ to 131° 50′; and in another case, raising the temp. from 9°–121° changed $2E$ from 52° 20′ to 50° 28′. Prehnite exhibits in some cases optical anomalies. The grouping of the parts in the aggregated forms is sometimes highly complex, and consequently there are marked variations in the optical characters. For instance, A. Mallard observed the crossed dispersion characteristic of the monoclinic system; and there may be microscopic lamination such as occurs with microcline. The subject has been investigated by A. des Cloizeaux, A. Mallard, B. K. Emerson, and A. Beutell.

The sp. gr. of prehnite ranges from 2·80–2·95; and the hardness is below 5. J. Joly gave 0·2003 for the sp. ht. of prehnite. According to C. Doelter, when prehnite is fused, and the melt slowly cooled, crystals of plagioclase and of wollastonite are formed: $H_2Ca_2Al_2Si_3O_{12}=H_2O+CaSiO_3+CaAl_2Si_2O_8$. E. Norin studied the thermal dissociation of prehnite. According to A. des Cloizeaux, and A. Michel-Lévy and A. Lacroix, the indices of refraction for yellow light are $\alpha=1{\cdot}616$, $\beta=1{\cdot}626$, and $\gamma=1{\cdot}649$. The double refraction is strong; A. Lacroix gave $\gamma-\alpha=1{\cdot}0336$. H. von Eckermann gave $\alpha=1{\cdot}6152$–$1{\cdot}6157$, $\beta=1{\cdot}6243$–$1{\cdot}6250$; and $\gamma=1{\cdot}6454$–$1{\cdot}6462$ for Na-light. The optical character is positive. R. J. Haüy, C. A. S. Hofmann, C. C. von Leonhard, P. T. Riess and G. Rose, and G. W. Hankel made observations on the pyroelectric properties. The polarity is central, the analogous poles are at the centre of the base, and the antilogous poles at the extremities of the brachydiagonal.

G. A. Kenngott [50] found that powdered and moistened prehnite has an alkaline reaction towards litmus. According to C. Doelter, prehnite is attacked with difficulty by hydrochloric acid, with the separation of granular silicic acid; but strongly calcined, or fused prehnite is readily attacked by acids with the separation of gelatinous silicic acid. Similar results were obtained by E. Norin. For thermal dissociation of prehnite, *vide supra*. E. C. Sullivan studied the action of soln. of cupric sulphate on prehnite. The natural transformations of prehnite into green earth, felspar, etc., have been discussed by C. R. van Hise, J. R. Blum, H. Laubmann, P. von Sustschinsky, V. von Zepharovich, C. N. Fenner, K. Peters, etc. When the mineral is heated in the vapour of ammonium chloride, F. W. Clarke and G. Steiger observed no absorption of ammonia. When prehnite is digested with water at 210°–220° for 342 hrs., J. Lemberg found that a hydrated silicate is formed, $Ca_2Al_2Si_3O_{11}.3H_2O$.

In 1806, A. G. Werner [51] received a specimen of a mineral from Baron von Zois; and it appears to have been called by the Carinthian mineralogists *saualpite*, being found on the Saualpe, Carinthia. A. G. Werner called it **zoisite**; C. C. von Leonhard, *illuderite*. R. J. Haüy, and J. J. Bernhardi associated zoisite with epidote, and in this they were followed by many others. H. Steffens emphasized the physical differences, and H. J. Brooke separated the two minerals on crystallographic grounds. In this, he was supported later by the optical work of A. des Cloizeaux.

H. J. Brooke applied the term *thulite*—after *Thule*, an ancient name for Norway—to a rose-red mineral from Tellemarken, Norway, which he regarded as a variety of epidote. The red colour of the *porfido rosso antico* is in part due to the presence of thulite produced by the alteration of felspar. A. des Cloizeaux, W. C. Brögger, and G. Tschermak showed

that thulite is a variety of zoisite. B. Silliman found a white mineral at Unionville, Penn.; he called it *unionite*. J. L. Smith and G. J. Brush at first regarded it as a variety of oligoclase, but later showed that it is a variety of zoisite. *Vide* saussurite, which often contains some zoisite.

The first analysis of zoisite was made by M. H. Klaproth,[52] and varieties were later analyzed by C. F. Bucholz, and A. Laugier. These were followed by analyses made by others. C. F. Rammelsberg[53] deduced the formula $Ca_6Al_8Si_9O_{36}$; and later gave $H_2Ca_4Al_6Si_6O_{26}$. G. Tschermak, and E. Ludwig recommended the same formula and assumed zoisite to be isodimorphous with $H_2Ca_4Fe_2Al_4Si_6O_{26}$. A. Breithaupt and F. Sandberger supposed that chromic oxide can take the place of part of the alumina. C. F. Rammelsberg showed that the boric oxide found by A. des Cloizeaux, and the zirconia reported by A. von Schrötter, are to be regarded as accidental impurities. H. Laspeyres tried to show that zoisite is a salt of silicic acid, $H_{4\cdot5}SiO_{4\cdot25}$; and G. Tschermak, that it is the salt of his garnitic acid, $H_4Si_3O_8$, namely, $(AlOH)(CaAlO_2)_2Si_3O_8$. W. Vernadsky regarded it as a complex $3Ca_2Al_2Si_2O_8.Ca(OH)_2$; and F. W. Clarke ascribed it to the formula, $Ca_2(AlOH)Al_2(SiO_4)_3$, **calcium dialuminium aluminohydroxytriorthosilicate :**

$$Al{\equiv}SiO_4{-}Al{<}\begin{matrix}SiO_4{<}Ca\\ SiO_4{>}AlOH\\ \qquad\quad Ca\end{matrix}$$

Part of the alumina can be replaced by ferric oxide owing presumably to the existence of an incomplete isomorphous series with the end-members, *aluminium-zoisite*, $HCa_2Al_3Si_3O_{13}$, and *iron-zoisite*, $HCa_2Fe_3Si_3O_{13}$—*vide infra*, epidote.

Zoisite is of secondary origin. It occurs chiefly in crystalline schists especially in those characterized by amphibolic minerals. It is also found in some granites, and in beds of sulphide ores. The formation of zoisite in nature has been discussed by A. Cathrein,[54] C. F. Chandler, F. Becke, F. A. Genth, C. R. van Hise, W. Vernadsky, and T. Hiortdahl and M. Irgens. A. Brun reported the formation of zoisite by fusing a mixture of silica, alumina, and lime. This conclusion is doubtful because the product contained no water.

Zoisite occurs in indistinct prismatic or columnar forms, and in fibrous aggregates. The euhedral prismatic crystals are sometimes striated or furrowed parallel to the *c*-axis. The colour may be white or tinged grey, yellow, green, brown, red, or, in the case of thulite, rose-red. H. J. Brooke,[55] as indicated above, showed that zoisite is crystallographically different from epidote; and A. des Cloizeaux found the crystals to be rhombic, not monoclinic like epidote. A. F. Rogers described the monoclinic crystals of clinozoisite. G. Tschermak gave for the axial ratios of zoisite $a:b:c=0{\cdot}61963:1:0{\cdot}34295$. Observations were also made by W. C. Brögger, F. Zambonini, G. H. Williams, H. Traube, and J. D. Dana. The cleavage parallel to (010) is perfect; and it is sometimes developed parallel to (100). G. Tschermak made observations on the twinning of the crystals. P. Termier assumed that there are polymorphous zoisites; in *α-zoisite*, the plane of the optic axis is parallel to (010), and in *β-zoisite*, this plane is parallel to (001). P. Termier suggested that both forms of crystals are really triclinic and pseudorhombic. This hypothesis has not been confirmed. F. Becke said that the alumino-zoisites correspond with P. Termier's α-zoisite, and the ferruginous-zoisites with the β-zoisites. The optic axial angles may be variable even in the same crystal. A. des Cloizeaux gave for red light, $2E=42°\,50'$; for green light, 50° 54′; and for blue light, 65°–70°. G. Tschermak gave $2E=94°\,59'$ for red and 93° 6′ for blue light. A. Lacroix gave $2E=95°$ and $2V=51°$. A. F. Rogers gave $2V=90°$ nearly. A. Arzruni gave $2H_0=108°\,14'$ for Li-light, 109° 48′ 20″ for Na-light, and 111° 13′ 30″ for Tl-light. A. des Cloizeaux found the optic axial angle increases rapidly with rise of temp., passing from 94° 59′ at 21·5° to 107° 28′ at 195° 8′.

E. Weinschenk proposed the name *clinozoisite* for the monoclinic epidotes which are near zoisite in composition, but monoclinic in crystallization—*vide* epidote. The pale

rose-red crystals of epidote from Goslerwand, Tyrol, may be regarded as clinozoisite. They are optically positive; index of refraction, 1·7195; birefringence, $\gamma-\alpha=0·0056$; optic axial angle, $2V=81°\ 40'$; and sp. gr., 3·372. The variety from Rothenkopf, Zillerthal, was optically negative, with the birefringence $\gamma-\alpha=0·0105$. The monoclinic mineral named *fouquéite*—after L. Fouqué—by A. Lacroix is white or yellow, and resembles zoisite in composition. It occurs in the gneiss at Salem and Candy, Ceylon. The optical character is negative; the birefringence $\gamma-\alpha=0·020$; and sp. gr., 3·24–3·31.

A. Breithaupt found the sp. gr. of a white variety to be 3·108, and that of a brown variety 3·381. The sp. gr. ranges from 3·1–3·4. The hardness is 6. J. J. Berzelius found that when heated before the blowpipe, zoisite swells up, forming a bubbly mass, and finally melts to a glassy slag. A. des Cloizeaux obtained a grey enamel. P. Herter made some observations on this subject. E. Norin studied the thermal dissociation of zoisite, and gave 900°–970° for the dehydration temp. R. Cusack gave 995° for the m.p.; A. L. Fletcher, 1045°; and C. Doelter, 1080°–1090°. G. A. König found that when heated in a tube, the red colour of zoisite becomes grey, and when cooled again, the original colour returns. C. F. Rammelsberg said that after calcination the proportion of $FeO : Fe_2O_3$ increases; H. Laspeyres showed that the opposite result obtains. E. Weinschenk gave for the indices of refraction $\alpha=1·6973$, $\beta=1·7002$, and $\gamma=1·7061$; A. Michel-Lévy, $\alpha=1·696$, $\beta=1·696$, and $\gamma=1·702$; K. Zimanyi, $\alpha=\beta=1·700$, and $\gamma=1·705$; and P. Termier, $\alpha=\beta=1·696$, and $\gamma=1·7034$. A. F. Rogers gave $\alpha=1·715$, $\beta=1·717$, and $\gamma=1·721$ for clinozoisite with Na-light. The respective birefringences are $\gamma-\alpha=0·0088$, 0·006, 0·005, and 0·0073. C. Doelter investigated the action of X-rays on zoisite and found its transparency relative to tin-foil to be as 1 : 14.

G. A. Kenngott[56] found that powdered and moistened zoisite reacts alkaline with litmus; he also reported that zoisite is scarcely affected, if at all, by nitric acid. C. F. Rammelsberg found that only zoisite which has been calcined is decomposed by hydrochloric acid with the separation of gelatinous silicic acid. E. Norin obtained a similar result. The observations of G. J. Brush, E. Ludwig, R. Hermann, F. Pisani, and T. Scheerer showed that the effect of acid is determined by the composition of the mineral. According to H. Laspeyres, the fine powder is completely decomposed by boiling hydrochloric acid. C. Doelter found that sulphur dioxide passed over the mineral at a red-heat has no appreciable influence. J. Lemberg studied the action of a soln. of potassium carbonate at 200°–210° for 708 hrs.; with sodium carbonate soln., a soda-lime-cancrinite was formed. C. Doelter passed water vap. over a molten mixture of manganous chloride and zoisite, and obtained anorthite and a lime-augite. The changes which zoisite undergoes in nature have been studied by J. R. Blum, and C. R. van Hise.

About 1783, J. B. L. Romé de l'Isle[57] and others referred to *schorl vert du Dauphiné;* J. C. Delamétherie called it *thallite*—from θαλλός, the colour of young twigs—in allusion to the colour; H. B. de Saussure, *delphinite*, after the locality where it was found, and *oisanite*, after Bourg d'Oisans; D. L. G. Karsten, *arendalite*, after Arendal; M. F. R. d'Andrada, *akanthikonite*—from ἀκανθίς, a goldfinch—in allusion to the colour; M. H. Klaproth, *scorza;* A. G. Werner, *pistacite*—from πιστάκια, pistachio nut—in allusion to the colour; and R. J. Haüy, **epidote**—from ἐπίδοσις, increase—in allusion to the base of the rhomboidal prism having one side longer than the other.

A. Lévy named a mineral from Arendal, *bucklandite*—after W. Buckland. G. Rose, and G. vom Rath referred to a mineral in such terms as to make it appear as if orthite was in question. G. Rose referred later to a black epidote from Achmatovsk which N. von Kokscharoff called bucklandite. A green mineral from the same locality was called *achmatite*—after B. von Achmaloff—by G. Rose. R. Hermann showed that M. von Kokscharoff's *bagrationite*—after P. Bagration—from Achmatovsk, is not an epidote but a variety of orthite. D. Brewster applied the term *withamite*—after H. Witham—to a red epidote from Glencoe, Scotland. J. A. Wagner called a mineral from Ekaterinburg, Ural, *puschkinite*—after M. Puschkin—A. Osersky, and N. von Kokscharoff showed it to be a variety of epidote. T. Scheerer called an epidote from Maggiathale, *escherite*—

after C. Escher van der Linth. G. Munteanu-Murgoci described green massive aggregates of a mineral from Lotru, Transylvania, which he called *lotrite*. Its composition approximates $3(Ca,Mg)O.2(Al,Fe)_2O_3.4SiO_2.2H_2O$, its sp. gr. is 3·23; its hardness 7½; index of refraction, 1·67; birefringence, $\gamma-\alpha=0·014$; $2E=30°$; $2V=18°$; and it is optically positive. It is supposed to be monoclinic. The mineral *hancockite*—after E. P. Hancock—was described by S. L. Penfield and C. H. Warren. It occurs at Franklin, New Jersey, and resembles epidote in its general properties. Its composition is $(Ca,Pb,Sr)_2(FeOH)Al_2(SiO_4)_3$. A. Breithaupt's *beustite*—after M. von Beust—from Predazzo, Tirol, is regarded as a variety of epidote. See clinozoisite. A. Damour and A. des Cloizeaux reported crystals of a kind of *magnesia-epidote* from Lake Baikal, Siberia. They called it *pieroepidote*.

H. V. C. Descotils [58] published the first analysis of this mineral, and this was followed by the analyses of L. N. Vauquelin, M. H. Klaproth, C. F. Bucholz, R. Hermann, C. F. Rammelsberg, R. Richter and T. Scheerer. Numerous other analyses have since been published.[59] E. Ludwig [60] made direct determinations of the water in a number of epidotes, and found from 1·67–2·35 per cent.: M. Dittrich and W. Eitel found from 0·32–2·14 per cent.; and F. Zambonini found after successively heating to the following temp.:

| | 80° | 120° | 370° | 460° | 471° |
|---|---|---|---|---|---|
| Water lost . . . . | 0·06 | 0·10 | 0·10 | 0·10 | 0·10 per cent. |

Attempts to deduce a formula were made by T. Scheerer,[61] R. Hermann, V. Hartwall, and A. Sobrero; and by C. F. Rammelsberg, who represented the idealized mineral by $Ca_6R_8Si_9O_{36}$. G. Tschermak, and G. A. Kenngott gave $H_2Ca_4Al_6Si_6O_{26}$. E. Ludwig confirmed this result, which was later accepted by C. F. Rammelsberg. As in the case of zoisite, more or less of the alumina can be replaced by ferric oxide, changing *aluminium-epidote*, $HCa_2Al_3Si_3O_{13}$, into *iron-epidote*, $HCa_2Fe_3Si_3O_{13}$. These form an incomplete series of solid soln., for the most ferruginous epidote known can have only 40 per cent. of iron-epidote. G. Tschermak first assumed that epidote and zoisite are isomorphous; C. F. Rammelsberg showed that these two minerals have the same composition but different crystalline forms; and G. Tschermak that they are isodimorphous. The subject was discussed by F. Kreutz, W. C. Brögger, E. Weinschenk, P. Termier, F. J. Wiik, A. Arzruni, A. Schwantke, and H. L. Barvir. Zoisite is the only representative of the rhombic epidotes. The monoclinic epidotes are:

| | |
|---|---|
| Clinozoisite . . . . . | $Ca_2(AlOH)Al_2(SiO_4)_3$ |
| Epidote . . . . . | $Ca_2\{(Al,Fe)OH\}(Al,Fe)_2(SiO_4)_3$ |
| Piedmonite . . . . . | $Ca_2(AlOH)(Al,Mn)_2(SiO_4)_3$ |
| Allanite or orthite. . . . | $(Ca,Fe)_2(AlOH)(Al,Fe,Ce)_2(SiO_4)_3$ |
| Hancockite . . . . . | $(Ca,Pb,Sr)_2(FeOH)Al_2(SiO_4)_3$ |

F. Balzac found an epidote approaching the end-member clinozoisite in the Ala Valley. H. Laspeyres assumed that epidote is a salt of a polysilicic acid with the empirical formula $H_{4·5}SiO_{4·25}$. E. Ludwig found no satisfactory evidence in favour of this hypothesis. G. Tschermak assumed epidote to be a salt of garnetic acid, $H_4Si_3O_8$; and he considered epidote to be like grossular with an atom of lime replaced by the radicle AlOH. W. and D. Asch postulated a series of nine typical epidotes and adapted their hexites and pentites to them. V. Goldschmidt regarded epidote as constituted: $3R''R_2'''Si_2O_8+H_2CaO_2$, and F. J. Wiik, as $H_2Ca_2(Al,Fe)_2Si_2O_{10}.2CaAl_2Si_2O_8$. F. W. Clarke employed a similar formula to that for zoisite (*q.v.*), thus making aluminium-epidote, $Ca_2(AlOH)Al_2(SiO_4)_3$, or **calcium dialuminium aluminohydroxytriorthosilicate;** and iron-epidote, $Ca_2(AlOH)Fe_2(SiO_4)_3$, or **calcium diferric aluminohydroxytriorthosilicate.** P. Groth gave for epidote $AlOH=SiO_4=Al_2(Si\equiv O_4)_2\equiv Ca_2$. W. Vernadsky regarded epidote and zoisite as addition products of the mica nucleus $3R_2(Al,Fe)_2Si_2O_8$ with $R''(OH)_2$.

Epidote is a mineral found in crystalline schists, and is common in gneiss, garnet rocks, amphibolitic, paragonitic, and glaucophanic rocks, and phyllites. It is a contact mineral in limestones; and when calcareous ferromagnesian minerals

form chlorite, epidote is simultaneously produced. Epidosite is an epidotic quartzose rock developed from diabase. C. R. Keyes [62] showed that epidote is probably a primary mineral in some granites; A. Michel-Lévy, B. S. Butler, etc., have given other examples. The epidotization of felspar, pyroxene, amphibole, biotite, scapolite, garnet, etc., has been discussed by numerous observers. Epidote has not been made artificially. C. Doelter [63] obtained indications of re-crystallization of epidote by fusing the powdered mineral with sodium and calcium fluorides. Garnet, meionite, anorthite, olivine, and magnetite were simultaneously produced. When epidote alone was fused, anorthite, and a lime-augite were produced. E. S. von Federoff made some observations on this subject.

Epidote occurs in crystals which are usually prismatic but sometimes acicular. It also occurs in fibrous and granular masses, and as epidote sand (scorza). The colour is usually a peculiar yellowish-green—pistachio green—seldom found in other minerals. This colour, however, shades into brownish-green, greenish-black, and black. The mineral also occurs white, grey, yellow, and red, the colour depending on the proportion of iron oxide. Measurements of the crystals were made by R. J. Haüy,[64] C. S. Weiss, A. T. Kupffer, F. Mohs, F. Hessenberg, W. Haidinger, L. J. Spencer, W. H. Miller, E. Artini, T. Scheerer, A. Lévy, K. Zimanyi, G. vom Rath, F. Babanek, G. Flink, J. C. G. de Marignac, J. Gränzer, B. Jezek and A. Krejci, M. von Tarassoff, A. des Cloizeaux, C. Bodewig, F. A. Quenstedt, A. Schrauf, F. Auerbach, V. von Zepharovich, etc. H. Bücking gave a historical review of the different observations which have been made on this subject. J. C. G. de Marignac measured the axial ratios of the monoclinic crystals, and N. von Kokscharoff gave $a : b : c = 1{\cdot}58073 : 1 : 1{\cdot}80574$, and $\beta = 64° 36'$, while his son gave $1{\cdot}57874 : 1 : 1{\cdot}80362$, and $\beta = 64° 36' 50''$. The latter values are considered to be more exact. For clinozoisite, with 1·68 per cent. $Fe_2O_3$, N. von Kokscharoff gave $1{\cdot}5853 : 1 : 1{\cdot}8117$, and $\beta = 64° 30' 24''$; F. Zambonini gave for an epidote with 14·99 per cent. $Fe_2O_3$, $1{\cdot}58187 : 1 : 1{\cdot}80758$, and $\beta = 64° 36'$; G. Boeris, for an epidote with 16·22 per cent. $Fe_2O_3$, $1{\cdot}57886 : 1 : 1{\cdot}80181$, and $\beta = 115° 22' 30''$; and N. von Kokscharoff, for bucklandite with 16·90 per cent. of $Fe_2O_3$, $1{\cdot}5807 : 1 : 1{\cdot}8057$ and $\beta = 64° 36'$. A. H. Westergard showed that an increase in the proportion of contained ferric-epidote increases all the mol. axial ratios. The twinning parallel to (100) is sometimes lamellar; twinning parallel to (001) is rare. The cleavage parallel to (001) is perfect; and imperfect parallel to (100). H. Baumhauer, and J. Gränzer found the corrosion figures corresponded with the symmetry of the monoclinic system. A. des Cloizeaux found the optic axial angle for red light to be $2H = 92° 1'$–$94° 6'$; $2H_0 = 115° 20'$; and $2V = 74°$–$87° 49'$. C. Klein gave for red light $2H_a = 91° 12'$–$91° 26'$; $2H_0 = 144° 56'$; and $2V = 73° 36'$–$73° 48'$; for yellow light, $2H_a = 91° 4'$ and $91° 20'$; $2H_0 = 145° 38'$; and $2V = 73° 26'$–$73° 39'$; and for green light, $2H_a = 90° 56'$–$91° 12'$; $2H_0 = 146° 36'$; and $2V = 73° 13'$–$73° 26'$. E. Artini gave for Na-light, $2H_0 = 144° 10'$; $2H_a = 96° 18'$; and $2V = 73° 59'$–$77° 54'$. E. H. Forbes, E. Weinschenk, M. Bauer, W. Ramsay, O. Andersen, C. Klein. E. Ludwig, and C. Schlemmer have noted the effect of ferric iron on the optical constants of epidote with $M$ molar per cent. of ferric epidote:

| $M$ | 0 | 3 | 11 | 14 | 19 | 23 | 27 | 37 |
|---|---|---|---|---|---|---|---|---|
| $2V_a$ | 114° 40′ | 98° 20′ | 90° 32′ | 87° 46′ | 79° 55′ | 73° 39′ | 73° 30′ | 68° 46′ |

A. des Cloizeaux found that the optic axial angles are not much affected by raising the temp., the maximum change being 1° 30′ when the temp. rose from 36·5°–146·5°. M. Goldschlag found for epidotes with 0 (clinozoisite), 19 (epidote), and 37 (pistacite) per cent. of ferric-epidote, respectively:

| $\lambda$ | 588·8 | 558·0 | 528·0 | 510·7 |
|---|---|---|---|---|
| Clinozoisite | 113° 47′ | 111° 29′ | 109° 41′ | 108° 11′ |
| Epidote | 79° 34′ | 79° 9′ | 79° 7′ | 78° 58′ |
| Pistacite | 68° 53′ | 68° 50′ | 68° 58′ | 69° 1′ |

H. Haga and F. M. Jäger studied the X-radiogram of epidote. The reported values for the sp. gr. of epidote vary from about 3·04–3·554. The former was obtained by D. Lovisato for an epidote with about 12 per cent. of $Fe_2O_3$ and is probably low, and the latter by V. von Zepharovich for a sample with about 18 per cent. of $Fe_2O_3$. J. Kehldorfer found 3·365 and E. Weinschenk 3·370 for samples with about 1·68 per cent. of ferric oxide. The relation between the sp. gr. and ferric oxide content is more or less obscured by other factors:

| | | | | | |
|---|---|---|---|---|---|
| $Fe_2O_3$ . . . | 3 | 3·52 | 5·67 | 9·67 | 12·03 per cent. |
| Sp. gr. . . . | 3·370 | 3·399 | 3·367 | 3·440 | 3·386 |

Determinations have been reported by A. Breithaupt, A. Renard, J. W. Mallet, C. Klein, O. Andersen, A. Lacroix, H. Wulf, R. Hermann, F. J. Wiik, G. vom Rath, C. Schlemmer, E. Ludwig, T. Scheerer, etc. The hardness is about 6. The sp. gr. is lowered by calcination; thus, G. vom Rath found at 13·5°, the sp. gr. of an epidote was so reduced from 3·361–3·316. F. von Kobell found for another sample a reduction from 3·46–3·38; and C. F. Rammelsberg, a reduction from 3·403–3·271. W. Suida, C. F. Rammelsberg, H. Laspeyres, D. Lovisato, etc., found that the proportion of ferric oxide in epidote was lowered by calcination, or by fusion with borax. The loss on ignition is therefore not all due to the loss of water and organic matter. T. Scheerer, E. Ludwig, and H. Laspeyres attributed the causes of the reduction of the ferric oxide to reducing gases from the flame; and C. F. Rammelsberg, and W. Suida to the dissociation of the ferric oxide at the temp. of the ignition. H. Fizeau found for the coeff. of linear expansion for the chief axis and for the two axes in the plane of symmetry, respectively $\alpha_1=0{\cdot}0_593126$, $\alpha_2=0{\cdot}0_533400$, and $\alpha_3=0{\cdot}0_4108600$; this makes the coeff. of cubical expansion $\alpha_1+\alpha_2+\alpha_3=0{\cdot}0_423335$; and the mean linear coeff. $0{\cdot}0_57778$. E. Jannettaz gave 0·634 for the square root of the ratios of the conductivities in the directions of the $a$- and $\gamma$-axes; and 1·088 in the directions of the $\beta$- and $\gamma$-axes; he also found the axial ratios $a:\beta:\gamma$ of the isothermal ellipse to be 0·934 : 1 : 1·088, and the ratios of the thermal conductivities in these directions, 0·87 : 1 : 1·18; he found that the vertical axis $c(001)$ and the principal axis made an angle −14° 30′. H. Fizeau made some observations on this subject. P. E. W. Oeberg found the sp. ht. of epidote to be 0·1861 between 16° and 100°; and J. Joly found 0·1877 between 13° and 100°. R. Cusack gave for the m.p., 954°–976°; A. L. Fletcher, 1004°–1026°; A. Brun, 900°–1250°; and C. Doelter, 1095°. E. Norin studied the thermal decomposition of epidote and gave 900°–1000° for the dehydration temp.

M. Goldschlag found the indices of refraction increase in magnitude as the proportion of ferric epidote increases. This is illustrated by the values of the indices of refraction for light of different wave-lengths, $\lambda$, shown in Table XXX. E. H. Forbes, E. Weinschenk, M. Bauer, W. Ramsay, O. Andersen, C. Klein,

TABLE XXX.—THE INDICES OF REFRACTION OF EPIDOTE.

| λ | Clinozoisite. | | | Epidote with 19 per cent. of ferric-epidote. | | | Epidote with 37 per cent. of ferric-epidote. | | |
|---|---|---|---|---|---|---|---|---|---|
| | $\alpha$ | $\beta$ | $\gamma$ | $\alpha$ | $\beta$ | $\gamma$ | $\alpha$ | $\beta$ | $\gamma$ |
| 656·3 | — | 1·7132 | — | 1·7174 | 1·7372 | 1·7445 | — | 1·7591 | — |
| 588·3 | 1·7136 | 1·7172 | 1·7188 | 1·7217 | 1·7422 | 1·7500 | 1·7291 | 1·7634 | 1·7796 |
| 558·0 | 1·7178 | 1·7204 | 1·7222 | 1·7244 | 1·7455 | 1·7540 | 1·7315 | 1·7655 | 1·7815 |
| 528·0 | 1·7182 | 1·7219 | 1·7237 | 1·7265 | 1·7479 | 1·7570 | 1·7339 | 1·7676 | 1·7836 |
| 523·2 | — | 1·7228 | — | 1·7270 | 1·7493 | 1·7579 | — | 1·7691 | — |
| 510·7 | 1·7201 | 1·7238 | 1·7258 | 1·7286 | 1·7504 | 1·7593 | 1·7375 | 1·7702 | 1·7857 |
| 476·9 | — | 1·7277 | — | 1·7319 | 1·7551 | 1·7651 | — | 1·7725 | — |

E. Ludwig, and C. Schlemmer have also investigated the indices of refraction of epidote with $M$ molar per cent. of ferric-epidote, and found

| $M$ | 0 | 3 | 11 | 14 | 19 | 23 | 27 | 37 |
|---|---|---|---|---|---|---|---|---|
| $\alpha$ | 1·7124 | 1·7176 | 1·7140 | 1·7240 | 1·7228 | — | 1·7336 | 1·7260 |
| $\beta$ | 1·7138 | 1·7195 | 1·7160 | 1·7244 | 1·7413 | 1·7532 | 1·7593 | 1·7620 |
| $\gamma$ | 1·7175 | 1·7232 | 1·7240 | 1·7344 | 1·7533 | — | 1·7710 | 1·7796 |
| $\gamma-\alpha$ | 0·0051 | 0·0056 | 0·0080 | 0·0144 | 0·0305 | 0·0350 | 0·0374 | 0·0536 |

The double refraction of the epidotes low in iron is positive and negative with those rich in iron. The transition occurs with epidotes containing 7–11 per cent. of ferric-epidote. The pleochroism and interference phenomenon were investigated by D. Brewster, J. B. Biot, A. Bertin, and W. Voigt; and H. Nagaoka examined the effect of temp. on the pleochroism. The absorption phenomena were studied by C. Klein, H. Laspeyres, C. Pulfrich, E. Carvallo, W. Ramsay, and H. Becquerel. V. Agafonoff studied the absorption of ultra-violet rays. W. W. Coblentz found the ultra-red transmission spectrum showed the hydroxyl band at $3\mu$; and additional bands at $4{\cdot}3\mu$, $4{\cdot}7\mu$, $5{\cdot}0\mu$, $5{\cdot}3\mu$, $5{\cdot}6\mu$, $5{\cdot}9\mu$, $6{\cdot}6\mu$, and $7{\cdot}4\mu$. Some of these are common with those of silica. W. Arnold, and L. P. Thompson studied the dichroism of epidote for X-rays; and C. Doelter found that the transparency of epidote for the X-rays is small. E. Jannettaz studied the electrical conductivity of epidote. W. Finke measured the magnetic susceptibility of epidote. A. des Cloizeáux found that fused epidote is non-magnetic. B. Bavink studied the properties of the crystals.

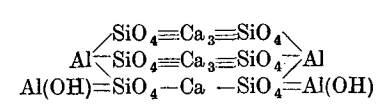
H. Laspeyres [65] found dark green or brownish-green globules of glass in epidote which had been calcined. W. Hermann heated epidote to dark redness in a stream of various gases; and found in oxgyen, the colour becomes more yellow and darker; in hydrogen, dark yellow; in coal gas, greener and darker; and in nitrogen, more yellowish-green. The changes are connected with the relative colouring effects of ferrous and ferric oxides. T. Scheerer, and E. Ludwig found that the water which is expelled from epidote by calcination has an acid reaction. G. A. Kenngott found that epidote powdered and moistened has a distinct alkaline reaction towards litmus, and the reaction is rather faster if the mineral has been calcined. G. A. Binder found that epidote heated, with carbonated water in a sealed tube at 160° for 4 weeks, is partly decomposed, but an inappreciable quantity passes into soln. E. W. Hoffmann, W. B. and R. E. Rogers, and C. G. C. Bischof have made observations on this subject. E. Ludwig, and C. F. Rammelsberg (1846) found that epidote is not attacked by hydrochloric acid, but the calcined mineral is completely decomposed with the separation of flocculent silicic acid. G. vom Rath said epidote is not soluble in hydrochloric acid whether the mineral has or has not been calcined. F. von Kobell, W. Baer, and C. F. Rammelsberg (1856) found epidote is partially decomposed by hydrochloric acid, but H. Laspeyres, L. Cordier, and A. E. Nordenskjöld said epidote is completely decomposed by the boiling acid. A. Renard said that epidote is completely dissolved by hydrochloric acid in a sealed tube at 125°–130°. C. Doelter found a small decomposition when epidote is heated in a stream of sulphur dioxide. H. Behrens and P. D. C. Kley found epidote to be only slightly attacked by sulphuric acid. G. A. Kenngott said that epidote is but slightly attacked by nitric acid, but the calcined mineral is easily decomposed with the separation of gelatinous silica. E. Norin obtained a similar result. E. Reymond studied the action of chlorine and of hydrogen chloride on epidote. E. C. Sullivan studied the exchange of bases which occurs in soln. of cupric sulphate. Epidote is less liable to alteration than a good many silicates; the contained iron is mostly present as ferric oxide. C. Simmonds found that epidote does not show any definite reduction by hydrogen at a red heat. The transformations of epidote in nature have been discussed by C. R. van Hise,[66] W. Haidinger, J. R. Blum, G. Rose, E. Döll, J. Morozewicz, C. Doelter, C. Heusser and G. Claraz, A. Lagorio, P. von Jeremejeff, etc.

The crystals of a mineral from Vesuvius were at first regarded as a variety of

hyacinth; accordingly, M. A. Cappellar[67] called it *hyacinthus octodecahedricus*; J. B. L. Romé de l'Isle, *hyacinte da Vesuve*; J. Demesté, *hyacinte volcanique*; P. S. Pallas, *Hyacinth-Krystalle*; and J. C. Delamétherie, *hyacinthine*. J. F. W. Widenmann called it *volcanic schorl*; A. G. Werner, and M. H. Klaproth, *vesuvian*—from the first known locality; and R. J. Haüy, *idocrase*—from εἶδω, I see; and κρᾶσις, mixture—in allusion to a resemblance between its crystalline forms and those of other species. J. D. Dana changed A. G. Werner's term *vesuvian* into **vesuvianite.**

A. G. Werner assumed that the mineral is exclusively volcanic. An identical mineral was found by C. A. Murray, at Gökum, Finland, and called by J. von Lobo *gahnite*—after J. C. Gahn; J. J. Berzelius called it *loboite*—after J. von Lobo da Silveira; and T. Thomson, *gökumite*. A magnesian variety from Frugard was called by N. Nordenskjöld, *frugardite*; it had a sp. gr. 3·349, while a non-magnesian variety of sp. gr. 3·390 from the same locality was called *jevreinovite*. A sub-columnar brown variety from Eger, Bohemia, was called *egeran* by A. G. Werner. J. J. Berzelius called a bluish variety containing a trace of copper *cyprine*. It was found at Tellemarken, Norway, and analyzed by G. Lindström. J. V. Lewis and L. H. Bauer found a specimen in Franklin, New Jersey, and it was analyzed and described by E. V. Shannon. T. Thomson called a yellowish-brown variety from Amity, New York, *anthite*—from ξανθός, yellow. R. Hermann found small green prisms of a variety of vesuvianite at Zlatoust, Ural, and called it *heteromerite*—from ἕτερος, other; μέρος, part—in allusion to a supposed variation in the normal composition. A. von Lasaulx called a manganiferous variety from St. Marcel, Piedmont, and from Pajsberg, *mangan-idocrase*, or *mangano-vesuvianite*. See colophonite. The mineral *wiluite* or *viluite* from Wilui or Vilui, Siberia, described by N. von Kokscharoff, A. T. Kupffer, P. S. Pallas, A. Estner, M. H. Klaproth, R. J. Haüy, C. C. von Leonhard, C. A. S. Hofmann, and V. von Zepharovich occurs associated with grossular, and is considered to be a boriferous variety of vesuvianite. The mineral *californite*, found by G. F. Kunz in California, has the appearance of jade, and it takes a high polish. It is a variety of vesuvianite.

M. H. Klaproth,[68] and F. von Kobell analyzed the mineral, but the results were not unlike those for garnet. G. Magnus believed that garnet and vesuvianite had the same composition; but R. Hermann held a different view. G. Magnus said that, on melting, the sp. gr. is reduced while the weight is not affected; but C. F. Rammelsberg showed that there is a 2–3 per cent. loss owing to the expulsion of water. This was later confirmed by G. Magnus, and T. Scheerer. The latter said that the water is not to be regarded as a secondary but rather as a primary constituent. M. Weibull, G. Lindström, L. Iwanoff, E. Grill, and J. H. Vogel found samples with up to nearly 2 per cent. of fluorine; and C. F. Rammelsberg, R. A. Prendel, P. Jannasch, E. T. Wherry and W. H. Chapin, samples with up to 10·20 per cent. of boric oxide. Many attempts have been made to find the primary compound in vesuvianite. It is probably a solid soln. of several minerals. C. F. Rammelsberg required four formulæ to represent the compositions of different varieties of the mineral. P. Jannasch and P. Weingarten gave $Ca_2(OH)AlSi_2O_7$; M. Weibull, $CaR''Al_2R'''(OH,F)Si_5O_{20}$, where R'' represents Mg, Fe, Ca, Mn, $Na_2$, $K_2$, $H_2$ or $(MgOH)_2$; while R''' represents Al, Fe, Ti, or B; H. Sjögren, $R''\{R''Al(SiO_4)_3\}_2$, where R'' denotes (AlOH)'', (AlF)'', Ca, Mg, $Na_2$, $H_2$, and $(CaOH)_2$; P. Groth, $\{Al(OH,F)\}Ca_6Al_2(SiO_4)_5$; G. Tschermak, $H_4Ca_{12}Al_6Si_{10}O_{43}$; and F. W. Clarke, $R'_4Ca_7Al_2Si_6O_{24}$, where $R'_4$ may be $Ca_2$, $(AlOH)_2$, $\{Al(OH)_2\}_4$, or $H_4$. There are some replacements of calcium by magnesium and iron; a little of the hydroxyl may replace fluorine, and some boric oxide may be present. F. W. Clarke gave the graphic formula:




which is very like that of epidote, but with $Ca_3$ in place of $Al_2$. E. V. Shannon represented its composition by $4R''O.R_2O_3.3SiO_2$ with part of the oxygen replaced by F- and HO-groups.

Vesuvianite is found among the ancient ejecta of Vesuvius, and in the dolomitic

blocks of Monte Somma. It occurs as a product of contact metamorphism in granular limestones, and it is then associated with pyroxene, scapolite, garnet, epidote, diopside, and wollastonite. It is also found in serpentines, gneiss, chlorite schists, and related rocks. V. Goldschmidt [69] considers that as a contact mineral it is formed by the association of garnet, wollastonite, and water; $Ca_3Al_2Si_3O_{12}+H_2O+CaSiO_3=2Ca_2AlSi_2O_7(OH)$. E. Mitscherlich, and R. A. Prendel found crystals of what was considered to be vesuvianite in blast-furnace slags, but F. Fouqué, and F. Fouqué and A. Michel-Lévy doubted the inference. A. Daubrée reported the synthesis of a product like vesuvianite by the action of silicon tetrachloride on a mixture of alumina and lime. H. St. C. Deville said that the product was probably something other than vesuvianite. F. Fouqué and A. Michel-Lévy, and C. Hintze said that it is doubtful if vesuviante has been synthesized. M. K. Klaproth obtained a crust of what he regarded as crystals of vesuvianite by cooling the molten mineral. A. des Cloizeaux obtained crystals in an analogous manner, but F. Fouqué and A. Michel-Lévy showed that they were a mixture of melanite, anorthite, and pyroxene. C. Doelter and E. Hussak also showed that the fusion of vesuvianite is attended by its decomposition, forming meionite, melilite, anorthite, and a calcium-chrysolite. C. Doelter also tried to obtain crystals by heating vesuvianite with calcium or ammonium fluoride, and by heating mixtures of grossular and wollastonite with sodium or calcium fluoride, but obtained *gehlenitartige Körper*, not vesuvianite.

Vesuvianite occurs in euhedral crystals; in irregular anhedral crystals; in aggregates of prisms; and in granular cryptocrystalline masses. The colour is brown to green, and sometimes sulphur-yellow or pale-blue. M. Weibull [70] has compiled a table showing the colours of crystals containing different proportions of ferrous and ferric oxides. He said that the yellow crystals have but little ferrous oxide, and up to about 3 per cent. of ferric oxide; the green crystals have up to about 1 per cent. of ferrous oxide, and 4 per cent. of ferric oxide; while the brown crystals have over 2 per cent. of ferrous oxide and about the same quantity of ferric oxide. The crystals were examined by J. B. L. Romé de l'Isle, R. J. Haüy, N. von Kokscharoff, A. Breithaupt, R. A. Prendel, P. Groth, L. Wiser, C. Doelter, A. Cathrein, W. J. Lewis, M. Tarassoff, G. Strüver, F. Tamnau, etc. A. T. Kupffer gave for the axial ratio of the tetragonal crystals $a:c=1:0{\cdot}537195$; and V. von Zepharovich, $1:0{\cdot}537541$. The cleavage parallel to (110) is not very distinct; and the cleavage parallel to (100) and (001) is still less so. There is sometimes a lamellar structure with a tendency to scale in thin layers. The corrosion figures were examined by F. Leydolt, and R. A. Prendel. Some crystals of vesuvianite are optically anomalous and exhibit biaxial phenomena; indeed, A. Brezina found crystals from Ala with an optic axial angle $2E=62°\ 25'$ for red rays, $62°\ 47'$ for yellow rays. The phenomenon was studied by A. Madelung, E. Mallard, A. von Lasaulx, F. Klocke, and R. A. Prendel. The crystals appear to be made up of segments with different optical properties, and oriented with respect to the outward form of the mineral as in the case of garnet, analcite, etc. The structure seems to have been produced by strains subsequent to crystallization. F. Klocke found that compression changed biaxial into uniaxial crystals. A. des Cloizeaux observed no change in the optical behaviour by raising the temp. from 12°–161°. C. Doelter found that by heating to redness the axial angle, if small, increased, and if large, decreased. R. A. Prendel found that near 300° biaxial wiluite became uniaxial.

The sp. gr. of vesuvianite ranges from 3·35–3·55. G. Magnus found the sp. gr. after fusion is reduced to 2·95; and F. Varrentrapp, to 2·93. The hardness is 6–7. A. Brun gave for the m.p. 800°–1000°; R. Cusack, 1024°–1025; and A. L. Fletcher, 1074°–1085°. As indicated above, the mineral decomposes when melted. R. A. Prendel found the coeff. of thermal expansion between 20° and 120° to be 0·00095–0·00111 parallel to the chief axis, and 0·00077–0·00091 perpendicular to the chief axis. J. Joly gave 0·19457–0·19529 for the sp. ht. E. Jannettaz found the square root of the ratio of the thermal conductivities perpendi-

cular and parallel to the chief axis to be 0·95. R. A. Prendel found the conductivity parallel to the chief axis is greater than perpendicular thereto. The indices of refraction are high. A. des Cloizeaux gave $\epsilon$=1·719–1·722, and $\omega$=1·718–1·720 for yellow rays; H. Rosenbusch, $\epsilon$=1·7226, and $\omega$=1·7235; C. Hlawatsch, $\epsilon$=1·701–1·726, and $\omega$=1·705–1·732; F. Zambonini, $\epsilon$=1·7004–1·7216, and $\omega$=1·7032–1·7324; and E. V. Shannon, $\omega$=1·710, and $\epsilon$=1·698. The birefringence is weak. F. Zambonini gave $\omega-\epsilon$=0·0018–0·0034: and C. Hlawatsch gave 0·00301 for the *B*-ray; 0·00274 for the *D*-ray; 0·00245 for the *F*-ray; and 0·00187 for the *G*-ray. The optical character is usually negative, that of wiluite is positive. As indicated above, the colour, optical character, and refractive index may be variable in successive concentric layers of the same crystal. The pleochroism is not usually strong. A. des Cloizeaux, and A. von Lasaulx reported that $\epsilon$ is colourless or yellowish, and $\omega$ is reddish, yellowish, or greenish. E. Bertrand found a manganiferous vesuvianite from Jakobsberg showed an orange and amethyst-violet colour. A. Sohncke, and A. Engelhardt observed the fluorescence of vesuvianite. H. Becquerel studied the absorption spectrum. C. Doelter found vesuvianite to be more transparent for X-rays than calcspar. G. W. Hankel studied the pyroelectric properties, and B. Bavink, the magnetic properties of vesuvianite.

G. A. Kenngott [71] found the powdered and moistened mineral reacts alkaline towards litmus. Hydrochloric acid has scarcely any effect on the mineral, but after calcination, or better, after fusion, vesuvianite is attacked by the acid with the separation of gelatinous silicic acid. E. C. Sullivan studied the basic exchange of vesuvianite in cupric sulphate soln. Vesuvianite under various natural conditions alters to clinochlore, mica, diopside, and garnet. These alterations have been investigated by J. R. Blum, P. Jeremejeff, P. Miklaschewsky, G. Sillem, G. Tschermak, and J. Lemberg. The last-named studied the action of soln. of magnesium sulphate and chloride on vesuvianite at 130°–180°.

F. E. Wright [72] found a mineral like gehlenite in the Velardena mining district, Mexico; and W. T. Schaller considers that the analysis corresponds with a mixture of what he called **velardenite,** $2CaO.Al_2O_3.SiO_2$, with about 20 per cent. of akermanite, $4MgO.8CaO.9SiO_2$. The composition of the assumed velardenite is that of **calcium dialuminatometasilicate,** $SiO(AlO_2.Ca.O)_2$, or, as W. T. Schaller writes it, $(CaAlO_2.O)_3Si.O.SiO.O.Si.(O.CaAlO_2)_3$. J. B. Ferguson and A. F. Buddington apply the term *gehlenite* to this compound. The compound was artificially prepared by Z. Weyburg by fusing china clay with a small proportion of calcium bromide, and washing out the matters soluble in water. The descriptions of the properties of the mineral by F. E. Wright, and of the artificial crystals by Z. Weyberg and G. A. Rankin and co-workers, are very much alike. Thus, writing the properties of the mineral first, both furnish tetragonal crystals, the cleavage (001) is imperfect and the prism cleavage is poor; the (001) cleavage is distinct. The sp. gr. is 3·039, and 3·038; the hardness 5 and 6; the m.p. 1590°; the indices of refraction, $\omega$=1·666 and 1·667, and $\epsilon$=1·661 and 1·658; while $\omega-\epsilon$=0·0055 and 0·009. E. V. Shannon gave $\omega$=1·657, and $\epsilon$=1·653. The refractive index of the glass is 1·638. The optical character of both is negative. G. A. Rankin and F. E. Wright's diagram, Fig. 158, shows the regions of stability of this compound. Its m.p. is 1590° ± 2°. F. E. Wright added further that the colour of velardenite is dark grey or greyish-black owing to minute inclusions of magnetite, etc.; the colour is rarely amber-yellow. The fracture is irregular and uneven, conchoidal to splintery. The mineral is gelatinized by acids.

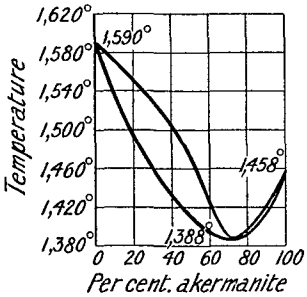



FIG. 178. — Freezing-point Curves of Mixtures of 2CaO.MgO.2SiO$_2$ and 2CaO.Al$_2$O$_3$.SiO$_2$.

J. B. Ferguson and A. F. Buddington obtained the f.p. diagram, Fig. 178 for

binary mixtures of akermanite, $2CaO.MgO.2SiO_2$, and gehlenite, $2CaO.Al_2O_3.2SiO_2$. There is a series of solid soln. with a minimum m.p. at 1388°, a little below the m.p. of diopside, and corresponds with 74 per cent. of akermanite and 26 per cent. of $2CaO.Al_2O_3.SiO_2$. They found for the sp. gr., the sp. vol. of crystals and glass of the binary series, at 25°:

| Akermanite . . | | 0 | 25 | 50 | 75 | 100 per cent. |
|---|---|---|---|---|---|---|
| Sp. gr. | Crystals . | 3·038 | 3·018 | 2·993 | 2·969 | 2·944 |
| | Glass . | 2·884 | 2·903 | 2·919 | 2·938 | 2·955 |
| Sp. vol. | Crystals . | 90·4 | 90·8 | 91·5 | 92·1 | 92·8 |
| | Glass . | 95·2 | 94·5 | 93·8 | 93·1 | 92·4 |

This conforms with the isomorphous character of the system. The optical characters of the crystals for Na-light are:

| Akermanite . . | 0 | 20 | 40 | 50 | 75 | 100 per cent. |
|---|---|---|---|---|---|---|
| $\omega$ . . . | 1·669 | 1·664 | 1·657 | 1·653 | 1·643 | 1·632 |
| $\epsilon$ . . . | 1·658 | 1·657 | 1·654 | 1·652 | 1·647 | 1·639 |
| $\omega-\epsilon$ . . . | 0·011 | 0·007 | 0·004 | 0·001 | 0·004 | 0·007 |
| Character . . | − | − | − | − | + | + |

The references of I. S. R. I. Eques a Born,[73] F. de St. Fond, and J. B. L. Romé de l'Isle, to a *zeolithus crystallisatus cubicus* or *zeolite en cubes*, probably apply to the zeolite called by B. d'Antic, and R. J. Haüy, *chabasie*, and by C. A. S. Hoffmann (1818), **chabasite**—from χαβάσιος, *qui désignoit une certaine espèce de pierre.*

The corrupted form *schabasite* was used by C. A. S. Hoffmann (1812), and *chabasin* by D. L. G. Karsten. C. S. Weiss called the mineral *Kuboizite.* The *acadiolite* or *acadialite* from Nova Scotia—the Acadia of the old French—mentioned by J. D. Dana, T. Thomson, and E. Hoffmann, is, according to the analyses of A. A. Hayes and C. F. Rammelsberg, nothing but a reddish chabazite. The *haydenite* of P. Cleaveland—named after H. H. Hayden—found near Jones' Falls, Baltimore, is, according to A. Lévy, H. J. Brooke, A. E. Delesse, and J. D. Dana, an altered chabazite. F. Tamnau found twinned crystals of a mineral at Leipa, Bohemia, and he called it *phacolite*—from φακός, a bean—in allusion to its lenticular shape. A. Breithaupt, G. Rose, and J. F. L. Hausmann showed that phacolite is only a variety of chabazite. This mineral was studied by G. F. H. Smith and co-workers. A. Lévy applied the term *herschelite*—after J. F. W. Herschel—to a rhombic mineral found in the lava at Aci Castello, Sicily. It was analyzed by A. Damour, and W. S. von Waltershausen, and shown by A. Breithaupt to be a variety of chabazite. According to W. Haidinger, the *mesolin* of J. J. Berzelius was probably chabazite, although J. D. Dana, C. Doelter, and A. des Cloizeaux regarded it as levyne. A siliceous herschelite from Australia was named *seebachite*—after K. von Seebach—by M. Bauer; but C. F. Rammelsberg, and G. vom Rath showed that it is an impure chabazite. T. Thomson's *doranite* from Antrim was shown by J. D. Dana to be a variety of chabazite; A. des Cloizeaux regarded it as a variety of analcite. E. Renevier found a mineral in cavities between the crystals of calcspar of Molasse, Lausanne. He called it *adipite*—from *adeps*, fat. J. D. Dana regarded it as chabazite. F. Gonnard found a zeolite in cavities in the basalts near Montbrison, Loire, in hexagonal plates. He called it *offretite.* V. Dürrfield described a similar mineral from Paul's Island. The analysis of offretite corresponded with $(K_2Ca)_2Al_6Si_{14}O_{39}.17H_2O$; and F. W. Clarke considers it to be compounded of potash- and lime-chabazites of the general formulæ $K_2HAl_3(Si_3O_8)_3.8H_2O$, and $CaHAl_3(SiO_4)_3.8H_2O$. The sp. gr. is 2·13.

The first analysis of chabazite was made by L. N. Vauquelin.[74] Numerous analyses of chabazite have since been reported. As in the case of other zeolites one species has been confused with others—*e.g.* chabazites have been confused with gmelinite and levyne—and, as just indicated, some impure or slightly altered chabazites have been given special names. This subject has been discussed by J. Lemberg,[75] A. Streng, G. vom Rath, G. Tammann, G. Rose, and F. Tamnau. C. F. Rammelsberg[76] was not very successful in 1875 in generalizing the chemical analyses into a formula. The formula $CaAl_2Si_4O_{12}.6H_2O$ is generally considered as representing the composition of the idealized mineral. This would make it **hexahydrated calcium dialuminium tetrametasilicate.** Structural formulæ have

been proposed by R. Gans, F. Singer, C. Hersch, and F. W. Clarke. The last-named gave

$$Al{\equiv}Si_3O_8{-}Al{<}\begin{matrix}SiO_4\\Si_3O_8\end{matrix}{\gtrless}\begin{matrix}Ca\\Al{-}SiO_4{\equiv}Al\\Ca\end{matrix}$$

A. Streng arranged the chabazites into three groups, $R''Al_2Si_3O_{10}.5H_2O$; $R''Al_2Si_4O_{12}.6H_2O$; and $R''Al_2Si_5O_{14}.7H_2O$. He regarded the chabazites as isomorphous mixtures of different silicates of the same type. C. F. Rammelsberg (1885–95), W. F. Fresenius, P. Groth, and J. Lemberg adopted similar hypotheses. G. Tschermak, and F. Doelter consider chabazite to be a compound of calcium aluminium silicate and silicic acid, and the former considers that the silicate $H_4CaAl_2Si_2O_{10}$ is the chabazite nucleus, Cz, and that the chabazites are formed by the association of this with four different silicic acids, making $H_8Si_4O_{12}.Cz.2Aq.$; $H_4Si_2O_6.Cz.2Aq.$; $H_4Si_2O_4,Cz.2Aq.$; and $H_2Si_2O_3.Cz.2Aq.$ E. Baschieri, and G. Tschermak believe that the silicic acid which is furnished by the decomposition of chabazite with dil. hydrochloric acid is of the leucitic acid type, $H_8Si_4O_{12}$.

The analyses of the chabazites indicate the presence of 17·83–22·32 per cent. of water. Attempts have been made to find out the nature of the water associated with chabazite.[77] S. J. Thugutt found that there is from 0·41–1·21 per cent. more water in chabazite of grain-size up to 10$\mu$, than in chabazite of grain-size 0·1–0·5 mm.—indicating that the finer the grain, the more the contained water. Presumably the greater the surface-area of the fine-grained powder, the greater the amount of absorbed water. G. Friedel, indeed, inferred that at ordinary temp. the chabazites are not in equilibrium with atm. moisture until they have absorbed 5–7 per cent. more. C. Hintze found that chabazite lost 2 mols. of water when kept over calcium chloride for a week; and A. Damour, 7·2 per cent. of water after five months' exposure to dry air. The lost water, and 0·15 per cent. more was regained on exposure for some months to ordinary air. Measurements of the loss of water at different temp. have been made by C. F. Rammelsberg, A. Damour, C. Bodewig, A. Streng, A. Bygden, E. Manasse, L. Pelacani, F. W. Clarke and G. Steiger, etc. C. Hersch found:

| | 102° | 125° | 155° | 195° | 240° | 265° | 290° | Red heat. |
|---|---|---|---|---|---|---|---|---|
| Loss . . | 5·77 | 6·51 | 9·22 | 11·29 | 13·55 | 14·44 | 14·81 | 22·47 per cent. |

He obtained similar results with phacolite. G. Friedel found the percentage loss (−) or gain (+) when chabazite is heated to $\theta°$ in a stream of air sat. with water at $\theta_0°$, to be:

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| $\theta$ . . | 12° | 66° | 112° | 148° | 263° | 410° | 570° |
| $\theta_0$ . . | 6·5° | 9·0° | 7·5° | 6·5° | 6·5° | 6·5° | 6·0° |
| Per cent. | +0·22 | −3·16 | −7·00 | −11·41 | −17·33 | −19·16 | −19·42 |

A correction is needed for the absorption of air, for chabazite can absorb up to 2·7 per cent. of air. Thus, a specimen which lost 21·9 per cent. of water at 800° when cooled 15 mins. in dry air appeared to have lost 19·56 per cent. The difference represents the air absorbed in cooling. Hence, the determination of water as loss on ignition may be vitiated by the absorption of air. G. Stoklossa obtained breaks in the rehydration curve of dehydrated chabazite representing 10 hydrates. G. vom Rath, G. Tammann, and E. Löwenstein measured the vap. press. of the water of chabazite. The last-named found at 25°, over sulphuric acid of different conc. and their corresponding different vap. press. of water in mm. of mercury:

| | | | | | | |
|---|---|---|---|---|---|---|
| Vap. press. . . . | 21·58 | 17·63 | 8·82 | 1·75 | 0·56 | 0·18 mm. |
| Loss water . . . | 0·21 | 0·64 | 0·97 | 2·94 | 4·67 | 6·90 per cent. |

A. Damour observed that the 19 per cent. loss which chabazite suffered at a red-heat was regained on exposure to a moist atm. for 3 days; but when calcined to dull redness, 21 per cent. was lost, and the mineral was no longer hygroscopic.

Similar results were obtained with phacolite. J. Lemberg found that artificial potash-chabazite which had lost 16·98 per cent. of water by gentle ignition, regained 16·10 per cent. on exposure to moist air; but after calcining to the sintering temp. only 3·84 per cent. was regained after immersion in water for 2 months. Soda-chabazite similarly lost 19·33 per cent. of water by gentle ignition, and regained only 8·39 per cent. on exposure to moist air. The differences, 0·88 per cent. in the case of potash-chabazite, and 10·94 per cent. in the case of soda-chabazite, were regarded as basic water.

G. Friedel's views [78] on the nature of zeolitic water—*vide* zeolites—are supported by the fact that the water in the dehydrated chabazite can be replaced by many other substances. G. Friedel showed that the water can be restored after dehydration, and F. Grandjean found that if the dehydrated mineral be placed in an atm. of dry ammonia, dry hydrogen sulphide, ethyl alcohol, and silicon tetrafluoride or tetrachloride, iodine, bromine, mercurous chloride, mercury, mercuric sulphide, and sulphur, these compounds are absorbed instead of water. He measured the optical properties of the products. F. Rinne found that carbon disulphide or dioxide, chloroform, benzene, aniline, and ether are absorbed; and O. Weigel and E. Steinhoff, water, methyl and ethyl alcohols, ether, acetone, benzene, and formic acid. R. Seeliger and K. Lapkamp, and R. Nacken and W. Wolff studied the absorption of helium, neon, nitrogen, oxygen, methane, nitric oxide, carbon dioxide, ethane, hydrogen, and ammonia by 80 per cent. dehydrated chabazite. The vol., $v$, of gas is a function of the press., $p$ cm., so that $v=ap^n$, where $a$ is a constant varying from 0·06–138·00, and is dependent on the nature of the gas; and $n$ is a constant also dependent on the nature of the gas varying from 0 to 96. The action is either a mechanical condensation of the gas or a mol. action. F. Rinne found that a partially dehydrated crystal plate of the mineral when placed in liquid carbon bisulphide exhibits a gradual change in extinction angles, and becomes more strongly birefringent; on heating the plate, the carbon bisulphide is expelled with a return to the original optical characters. The absorption of carbon dioxide, alcohol, chloroform, benzene, or aniline is accompanied by similar changes in the optical characters; R. Nacken and W. Wolff found that dehydrated chabazite absorbed 1·3 per cent. by weight of nitrogen; and that it absorbed air, carbon dioxide, and coal gas.

The formation of chabazite as a *Sekretionsprodukt* of archaic shales was discussed by F. Schalch,[79] A. des Cloizeaux, and O. Sismonda. E. Baur noted the formation of chabazite by hydrothermal processes, and A. Daubrée observed chabazite crystals were produced in cavities in the brick-masonry and about the thermal springs at Plombières, Luxeuil, Haute Saône; Bourbonne-les-Bains, Haute Marne; and Oran, Algiers. J. R. Blum found chabazite crystals on pieces of lignite, wood, etc. in a mine at Marienberg, Nassau. G. Tamnau found crystals of chabazite lining fossil shells of the *Venus islandica* in a recent deposit of Husavic, Iceland. C. Doelter, K. Hofmann, C. R. van Hise, A. Himmelbauer, and F. Cornu observed the formation of chabazite from other silicates—anorthite, plagioclase, trachyte, hauyne, etc. H. St. C. Deville obtained hexagonal plates of what he regarded as levyne by heating a soln. of potassium and sodium aluminates in a sealed glass tube. The product is now regarded as an alkali-chabazite. C. Doelter digested the powdered mineral in water sat. with carbon dioxide in a sealed tube for 9 days at 150°, and obtained minute rhombic crystals. Similar results were obtained with liquid carbon dioxide in place of carbonated water. C. Doelter obtained a similar product by the prolonged digestion of a mixture of freshly precipitated silicic acid, aluminium hydroxide, calcium hydroxide, and carbonated water in a sealed tube at 200°. R. Gans made soda-chabazite by dissolving silicic acid and aluminium hydroxide in soda-lye. C. Doelter obtained chabazite as a by-product in a number of reactions—*e.g.* by digesting okanite, ammonium chloride, sodium carbonate, and carbonated water in a sealed tube at 220°; the rhombohedral crystals of chabazite were decomposed by analcite and apophyllite. Chabazite was obtained by digesting a mixture

of powdered anorthite, freshly precipitated silicic acid, and carbonated water for 14 days at 200°.

Chabazite occurs massive, as incrustations, and in crystals of a white or brick-red colour. M. Websky[80] found that when brown or orange chabazite from Striegau is heated in a closed tube, it is blackened, and some tarry matters are distilled off; on cooling, the colour becomes bluish-grey. The crystals belong to the scalenohedral section of the trigonal system, and, according to W. Phillips, they have the axial ratio $a:c=1:1{\cdot}0860$. G. Tschermak regarded the crystals as monoclinic with $a:b:c=0{\cdot}4630:1:0{\cdot}3406$, and $\beta=83°\ 31'$, and as forming a family group with gmelinite, and levyne. G. F. H. Smith and co-workers also studied this family group. Euhedral crystals generally appear as simple rhombohedrons resembling a cube, with angles varying so little from 90° that the crystals have been mistaken for cubes. The crystals have been discussed by A. des Cloizeaux, W. H. Miller, A. Streng, A. Schrauf, G. vom Rath, F. Tamnau, etc. G. Tschermak said that chabazite crystals mimic monoclinic crystals of axial ratios $a:b:c=0{\cdot}4630:1:0{\cdot}3406$, and $\beta=83°\ 34'$. The cleavage parallel to $(10\bar{1}1)$ is rather distinct. Twinning by penetration is common; while contact twins about the composition plane $(10\bar{1}1)$ are rare. D. Brewster found that the crystals are optically anomalous because sometimes they appear distinctly biaxial. F. Becke assumed that the rhombohedral crystals are produced by the twinning of six or more triclinic individuals. C. Klein showed that different crystals or different parts of the same crystal exhibit wide variations in the double refraction, and inferred that these differences are connected with a loss in the zeolitic water, for as E. Mallard showed, heating increases the double refraction, and brings out areas which did not exist before, or develops the existing areas in extent and distinctness. When the crystals cool, the original conditions are not restored. F. Rinne concluded that by heat and consequent loss of water the chabazites gain the optical characters of the negative varieties; but they are changed into those with a strong positive double refraction. The distinction between optically positive and negative crystals is considered to be connected with the proportion of water present. R. Brauns, and G. Tschermak attribute the optical anomalies to the isomorphous association of different individuals. The optical anomalies of chabazite have been discussed by P. Groth, J. F. W. Johnston, A. des Cloizeaux, P. Groth and A. Arzruni, A. Streng, A. von Lasaulx, C. F. Rammelsberg, G. Tschermak, etc. L. Vegard and H. Schjelderup studied the X-radiogram of chabazite. A. Michel-Lévy and A. Lacroix gave for the optic axial angle $2V=0°$–$18°$; P. Groth and A. Arzruni, $2V=27°$–$40°$; and F. Becke, $2V=32{\cdot}3°$ for red light, and $2V=31{\cdot}6°$ for green light. The sp. gr. of chabazite ranges from 2·05–2·14; G. vom Rath found phacolite with a sp. gr. 2·135; and J. E. Hibsch and F. Seemann gave 2·096 for a sample of chabazite. A. Streng obtained evidence that the higher the ratio $SiO_2:Al_2O_3$, the lower the sp. gr.—thus, for the ratio $SiO_2:Al_2O_3=3{\cdot}85:1$, the sp. gr. was 2·133; 4·12 : 1, 2·115; 4·3 : 1, 2·112; 4·9 : 1, 2·093; and 4·93 : 1, 2·093. The hardness is from 4·0–5·5. The action of heat on the contained water, and the vap. press. have been previously indicated; A. Damour said all the water is lost at a bright red heat, and the residue fuses with intumescence to form a blebby mass. A. Kenngott, and V. Goldschmidt made some observations on this subject. C. Doelter found that by slowly cooling melted chabazite, crystals of anorthite embedded in a glassy matrix were obtained. E. Jannetaz found the ratio of sq. roots of the thermal conductivities in a direction parallel and vertical to the principal axis is 0·96. P. E. W. Oeberg found the sp. ht. of colourless crystals of chabazite to be 0·3799. O. Mulert found the rate of dissolution of chabazite in mixed hydrofluoric and hydrochloric acids is so slow, that it was not possible to measure the heat of soln. A. Michel-Lévy and A. Lacroix found for the index of refraction of chabazite 1·50, and for herschelite, 1·46. A. Lacroix gave $\omega-\epsilon=0{\cdot}0020$–$0{\cdot}0028$. The birefringence was feeble and generally negative, but as A. des Cloizeaux showed, it is

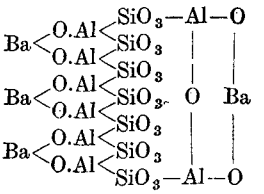
sometimes positive. As indicated above, F. Rinne found that the double refraction assumes a negative value on heating; and in all cases when still more strongly heated, the double refraction of chabazite becomes strongly positive. O. Weigel investigated the electrical conductivity of chabazite.

G. A. Kenngott[81] found that powdered and moistened chabazite reacts alkaline to litmus; the calcined mineral exhibits a feebler reaction. F. Cornu, and F. W. Clarke made similar observations. G. Steiger found that after standing in contact with water at 21° for a month, the water had dissolved a little soda. C. Doelter found the solubility to be greater in carbonated water; and the mineral also dissolves in liquid carbon dioxide. He also observed that some lime and silica are removed by a soln. of sodium carbonate. The action of soln. of sodium carbonate was also investigated by J. Lemberg, and S. J. Thugutt. J. T. Way, and H. Eichhorn showed that when chabazite is treated with a soln. of sodium chloride, calcium is displaced, and a *sodium-chabazite* is formed; J. Lemberg obtained the same compound by the action of sodium chloride soln. on potassium-chabazite, as well as on ordinary chabazite. J. Lemberg obtained sodium-chabazite by the action of a soln. of sodium silicate on albite. H. C. McNeil fused chabazite with sodium chloride, and obtained what was regarded as a substitution product, *sodium-chlorochabazite*, which F. W. Clarke considers to be a mixture $5Na_3Al_2(Si_3O_8)_2Cl + 3Na_3Al_2(SiO_4)_2Cl$. J. Lemberg, and S. J. Thugutt obtained *potassium-chabazite* by digesting chabazite with a soln. of potassium chloride at 100°. E. Löwenstein found that the vap. press. varied continuously as the water was removed. J. Lemberg obtained a product like potassium-chabazite by the action of a soln. of potassium carbonate on natrolite, spodumene, andesine, labradorite, jadeite, or analcite. H. Eichhorn, and J. Lemberg prepared *ammonium-chabazite* by the prolonged action of a hot soln. of ammonium chloride on chabazite. R. Gans, and I. Zoch also made the ammonium derivative in a similar manner; and G. Steiger, by the action of ammonium chloride on chabazite in a sealed tube at 350° for 5–6 hrs. I. Zoch treated chabazite with a soln. of cupric chloride, and obtained evidence that there is an exchange of a small proportion of the base, forming *copper-chabazite*. G. Steiger heated chabazite with silver nitrate for 24 hrs. at 250°–290°, and obtained a *silver-nitrato-chabazite*, which F. W. Clarke formulated $3Ag_3Al_2(Si_3O_8)_2NO_3 + Ag_3Al_2(SiO_4)_2NO_3$. J. Lemberg prepared *barium-chabazite* by the action of a soln. of barium chloride on chabazite for 5 months; and by digesting potassium-chabazite with a soln. of barium chloride, he obtained a *barium-chlorochabazite*; $Ba_3Al_4(Si_3O_8)_4Cl_2 + Ba_3Al_4(SiO_4)_4Cl_2$. If barium-chabazite be treated with a soln. of calcium chloride, calcium-chabazite is formed. J. Lemberg obtained *magnesium-chabazite* by the action of a soln. of magnesium sulphate on chabazite in a sealed tube at 180° for 12 hrs. By the action of thallium nitrate on chabazite in a sealed tube at 250°–290°, G. Steiger obtained *thallium-nitrato-chabazite*, which F. W. Clarke formulated $3Tl_3Al_2(Si_3O_8)_2NO_3 + Tl_3Al_3(SiO_4)_3$. S. J. Thugutt found that seebachite is not coloured by a soln. of methylene blue. G. Friedel found that natural or slightly dehydrated chabazite can absorb colouring matters from soln.; it also absorbs potassium permanganate, which is rapidly decomposed, staining the mineral yellow. J. Lemberg found that chabazite is stained red or orange by treatment with silver nitrate and potassium chromate. Chabazite is rapidly decomposed by acids with the separation of gelatinous silica which G. Tschermak considered to be analogous with leucitic acid, $H_4Si_2O_6$. V. Goldschmidt, E. Löwenstein, and F. Cornu studied the action of hydrochloric acid on chabazite. The transformation of chabazite into natrolite, etc., has been discussed by J. Roth, A. Streng, G. Suckow, J. R. Blum, J. D. Dana, T. Grandjean, R. Brauns, C. G. C. Bischof, C. R. van Hise, etc.

E. Artini[82] found fibrous radiated groups of crystals of a mineral in druses of the pegmatite at Baveno, Italy, which he called *bavenite*. The analysis corresponds with $Ca_3Al_2Si_6O_{18}.H_2O$. F. W. Clarke says that it is possibly a metasilicate, *monohydrated calcium dialuminium hexametasilicate*, $Ca_3Al_2(SiO_3)_6.H_2O$. The white

prismatic crystals are pseudorhombic; really monoclinic with axial ratios $a:b:c = 1{\cdot}1751:1:0{\cdot}7845$, and $\beta = 89°\ 17'\ 19''$. The sp. gr. is 2·72, the hardness $5\frac{1}{2}$; the optic axial angle, $2E = 78°\ 31'$; and the mean index of refraction, $\beta = 1{\cdot}580$. E. S. Larsen gave $\alpha = 1{\cdot}578$; $\beta = 1{\cdot}579$, and $\gamma = 1{\cdot}452$.

Z. Weyberg [83] reported the formation of crystals of complex barium and strontium aluminosilicates, $RO : Al_2O_3 : SiO_2 = 4 : 4 : 7$. If these substances are chemical individuals they may represent **tetrabarium octoaluminylheptametasilicate,** and **tetrastrontium octoaluminylheptametasilicate.** These substances are obtained by the prolonged fusion of mixtures of china clay with barium or strontium chloride. The crystals are hexagonal and hemimorphic, and are optically uniaxial and negative like nephelite.



In 1807, L. N. Vauquelin [84] analyzed flesh-red crystals of a mineral he found at Montecchio Maggiore, and called *sarcolite du Vicentin*—from σαρκός, flesh—the mineral was labelled *hydrolite* in E. de Drée's collection—in allusion to the contained water. H. J. Brooke and D. Brewster called a specimen from Vesuvius **gmelinite**—after C. G. Gmelin. R. J. Haüy regarded sarcolite as analcite; and A. Breithaupt identified it with melilite. F. de Fonseca considered sarcolite to be a distinct species of zeolite. F. W. Clarke gave a constitutional formula for this variety of chabazite, and C. F. Rammelsberg called it *natron-chabazite*. A. Streng, F. Tamnau, J. F. L. Hausmann, and P. Groth favoured the view that chabazite, levyne, and gmelinite are varieties of one mineral species; while A. des Cloizeaux, and C. Doelter, and J. D. Dana supposed them to be different.

C. T. Jackson applied the term *ledererite*—after C. Lederer—to a variety which A. des Cloizeaux, and O. C. Marsh showed was probably gmelinite. A. Arzruni applied the term *groddeckite*—after M. von Groddeck—to a zeolite from Andreasberg, Harz. The rhombohedral crystals have a hardness 3–4. The mineral closely resembles gmelinite in form and composition, but with magnesium and ferrous iron as impurities. G. Tschermak called it impure gmelinite.

The mineral was analyzed by L. N. Vauquelin,[85] A. Connell, C. F. Rammelsberg, A. A. Hayes, A. Arzruni, W. T. H. Howe, A. Damour, F. L. Walker, L. V. Pirsson, O. C. Marsh, and G. Tschermak. C. F. Rammelsberg [86] assumed that the composition of gmelinite is like that of chabazite, but with calcium largely replaced by sodium, hence he wrote $(Na_2,Ca)Al_2Si_4O_{12}.6H_2O$, or simply $Na_2Al_2Si_4O_{12}.6H_2O$, that is, **hexahydrated sodium dialuminium tetrametasilicate.** F. W. Clarke gave a constitutional formula for gmelinite like that of chabazite, but with $Na_2$ in place of Ca. G. Tschermak gave $Na_2Al_2Si_5O_{14}.6H_2O$; but later suggested that it is a mixture of three aluminosilicates. L. V. Pirsson, and P. Groth regarded it as a mixture of two such silicates. G. F. H. Smith and co-workers regarded chabazite, gmelinite, levyne, and phacolite as belonging to the same family.

The crystals of gmelinite may be colourless or white and tinged green, yellow, or red. The crystals belong to the trigonal system, and, according to L. V. Pirsson [87] they have the axial ratio $a:c = 1:0{\cdot}7345$. Euhedral crystals appear hexagonal and are produced by a combination of the hexagonal prism with plus and minus rhombohedrons. G. Tschermak regarded the crystals as monoclincic with $a:b:c = 0{\cdot}4571:1:0{\cdot}3385$, and $\beta = 82°\ 23'$. There are complex twinned forms as in the case of chabazite. The crystals have been studied by H. J. Brooke, D. Brewster, W. H. Miller, G. vom Rath, N. von Kokscharoff, F. Hessenburg, C. F. Rammelsberg,

E. Artini, A. des Cloizeaux, G. Rose, H. Guthe, R. P. Greg and W. G. Lettsom, etc. The cleavage parallel to $(10\bar{1}0)$ is fair; and that parallel to (0001) is sometimes distinct. L. V. Pirsson noted feeble optical anomalies; and F. Grandjean the optical axial angle $2V=0°–30°$. The sp. gr. ranges from 2·0–2·2. A. Breithaupt gave 2·083; H. J. Brooke, 2·05; G. B. Negri, 2·04; T. L. Walker, 2·135; and A. Fersmann, 2·08. The hardness is 4–5. G. Tammann measured the vap. press. by finding the partial press. $p$ mm. of the water vap. in equilibrium with crystals originally containing 21·51 per cent. of water, but for equilibrium lost the following percentage amounts of water:

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| $p$ . . | 15·72 | 12·48 | 9·11 | 6·05 | 2·93 | 1·23 | 0·39 | 0·11 mm. |
| Loss . | 0·05 | 0·18 | 0·42 | 0·75 | 1·40 | 2·48 | 3·81 | 4·58 per cent. |

The appearance of the crystals was not changed by the loss of water. L. V. Pirsson gave for the indices of refraction $\omega=1·4646–1·4770$, and $\epsilon=1·4637–1·4674$ for Na-light; and G. B. Negri obtained $\omega=1·48031$, and $\epsilon=1·47852$. L. V. Pirsson gave $\omega-\epsilon=0·0033$ for the birefringence; G. B. Negri, 0·0018; and F. Grandjean, 0·002. A. des Cloizeaux found that the optical character of crystals from some localities is negative, and from other localities positive. F. Grandjean found that the crystals of a negative character become positive when dehydrated.

Gmelinite is decomposed by acids with the separation of silicic acid. F. Grandjean found that like chabazite (*q.v.*), dehydrated gmelinite absorbs a relatively large proportion of the vap. of iodine, bromine, mercury, calomel, cinnabar, and sulphur; and that the product is pleochroic. J. Lemberg found that the exchange of bases which occurs when gmelinite is digested with aq. soln. of potassium chloride or carbonate furnished what he called *potassium-gmelinite*. If this product be treated with a soln. of sodium chloride, *sodium-gmelinite* is formed. If digested with a 10 per cent. soln. of sodium carbonate for 24 hrs. at 200°, analcite is formed; and if with a soln. of potassium carbonate, leucite is produced. I. Zoch made observations on this subject.

D. Brewster [88] applied the term **levyne** to a mineral collected by H. Heuland. There has been some discussion as to whether gmelinite and levyne are distinct species or whether they are varieties of chabazite—*vide supra*, gmelinite. There is also a question whether the mesolin of J. J. Berzelius, here regarded as a variety of gmelinite, would be better classed as a variety of levyne. Analyses were reported by A. Damour, J. J. Berzelius, A. Connell, W. F. Hillebrand and W. C. Cross, and G. A. Kenngott. C. F. Rammelsberg inferred from the analyses that the ratios $RO : Al_2O_3 : SiO_2 : H_2O$ are $1 : 1 : 3·2–3·8 : 4·6 : 5·0$. J. D. Dana gave the formula $CaAl_2Si_3O_{10}.5H_2O$, making the compound **pentahydrated calcium dialuminium orthotrisilicate.** F. W. Clarke gave for the constitution $Ca_3Al_6(SiO_4)_3(Si_3O_8)_2.15H_2O$. According to G. Tschermak, the constitution is best explained by assuming that it is formed by the isomorphous association of two silicates. G. F. H. Smith and co-workers grouped this mineral with the chabazite family. For the synthesis of levyne, *vide* chabazite.

The crystals may be colourless or white, tinged grey, green, red, or yellow. According to W. Haidinger, the trigonal crystals of levyne have the axial ratio $a : c=1 : 0·8357$. G. Tschermak represents the crystals as monoclinic with the axial ratios $a : b : c=0·4704 : 1 : 0·3433$, and $\beta=84° 54'$. Twinning is common as in the case of chabazite. The cleavage $(02\bar{2}1)$ is indistinct. F. Grandjean gave for the optic axial angle $2V=0°–30°$. The sp. gr. is 2·09–2·16; and the hardness 4–4½. A. Damour found the crystals lose 4 per cent. of water in dry air, and regain it all in ordinary air. When heated, the loss of water begins at about 70°; and 12–13 per cent. is lost at 225°; the partially dehydrated crystals remain hygroscopic provided the temp. of dehydration does not exceed 360°. The loss of water is complete at a white heat, when the mineral furnishes a white blebby enamel. A. Lacroix gave 1·50 for the index of refraction; and for the birefringence, $\omega-\epsilon=0·002$; and F. Grandjean gave 0·0075. E. S. Larsen gave $\omega=1·496$, and

$\epsilon$=1·491. The optical character is negative, and F. Grandjean found that after heating to 400° and cooling, the optical character is positive. He also found that the dehydrated mineral behaves like chabazite towards the vap. of iodine, bromine, mercury, calomel, cinnabar, or sulphur. Levyne is decomposed by acids with the separation of gelatinous silicic acid.

F. C. Wernekinck [89] noted that some crystals associated with barytiferous harmotome at Annerod and Schiffenberge, Giessen, were different chemically and crystallographically. J. F. C. Hessel and L. Gmelin also showed the same thing with respect to the assumed harmotome from Marburg; which they called *calcium-harmotome*. A. Lévy proposed the name **phillipsite**—after W. Phillips. A. Breithaupt called the mineral *normaline;* and A. des Cloizeaux, *christianite*—after Christian, King of Denmark.

A zeolite from the lava of Capo di Bove, Rome, was imperfectly described by P. Mantovani, and named *spangite*—after N. Spang. J. D. Dana considers it to be a variety of phillipsite. F. Zambonini found some bluish crystals from the lava at Casal Brunori, Rome, and he called the mineral *pseudophillipsite*. G. Tschermak considers it to be a variety of gismondite; F. Zambonini, an intermediate form between gismondite and phillipsite proper. J. Schill found fibrous concretions of a zeolite near Sasbach, Kaiserstuhl, which he called *sasbachite*. According to A. Knop, it is phillipsite.

Analyses were made by F. C. Wernekinck, L. Gmelin, and many others.[90] There is a wide variation in the relative proportions of lime, soda, and potash. C. F. Rammelsberg [91] first assumed phillipsite to be compounded of two silicates; and later he symbolized it $RAl_2Si_4O_{12}.4H_2O$, or **tetrahydrated calcium dialuminium tetrametasilicate.** W. Fresenius proposed a *Mischungshypothese* in which the mineral was supposed to be produced by the association of two silicates in various proportions. C. F. Rammelsberg did not favour W. Fresenius' hypothesis, but he assumed the existence of two *selbständigen Verbindungen*, with two *Zwischenstüfen*. In harmony with W. Fresenius' hypothesis, F. Zambonini noted that the potash increased and the lime decreased as the silica increased. P. Groth employed two formulæ. G. Tschermak assumed that the phillipsites are solid soln. of five different silicates. With hypotheses of this character it should be possible to formulate the composition represented by any conceivable set of analyses. He cites in favour of the mixture-hypotheses that when treated with dil. acid, phillipsite usually furnishes pulverulent silicic acid; phillipsite from Aci Castello, gelatinous silicic acid; and phillipsite from Eulenberg gives both forms. He represents these two silicic acids by the formulæ $H_4Si_2O_6$ and $H_2Si_2O_5$. J. H. Pratt and H. W. Foote represented phillipsite by the formula $RAl_2Si_4O_{12}.4\frac{1}{2}H_2O$; C. Hintze, $(Ca,K_2)Al_2Si_5O_{14}.5H_2O$; and F. W. Clarke:

$$Al{\equiv}Si_3O_8{-}Al\begin{matrix}<SiO_4<Ca\\<SiO_4>Al\end{matrix}{-}Si_3O_8{\equiv}Al+8H_2O$$

He added:

All phillipsites appear to be mixtures of orthosilicates and trisilicates, with the ratio $Si_3O_8 : SiO_4$ ranging between 3 : 1 and 1 : 3. Such a range and even a greater one is only to be expected when we remember that many zeolites are derivatives of plagioclase feldspars. The zeolites vary as the feldspars vary between end products, which may or may not be definitely known. Stilbite, for instance, represents a hydrated calcium albite or trisilicic anorthite, which in the anhydrous condition is yet to be discovered.

F. Zambonini [92] showed that in all probability no part of the 14·30–18·86 per cent. of water reported in the analyses is constitutional water; rather is it usually regarded as absorbed or zeolitic water. A. Damour showed that the crystals lose 8 per cent. on exposure to dry air for a month, and regain it all in ordinary air in 24 hrs. When exposed for an hour at 50°, the mineral loses 12·3 per cent., and recovers nearly all when exposed to ordinary air for 24 hrs., but it thereby becomes opaque and pulverulent; at 150°, 16 per cent. of water is lost, and only 0·8 per cent.

recovered after exposure to ordinary air for 4 days; and at 250°, the loss is 18·5 per cent., and about half of this can be recovered by exposure to ordinary air. F. Zambonini found that phillipsite which had been heated to 250° soon recovered the lost water on exposure to moist air; but if heated to 275°, the recovery was very slow. W. Fresenius found phillipsite becomes pulverulent, and opaque at 150°; the amount of contained water gradually decreases as the temp. rises, and increases as it falls, so that a definite proportion is retained by the mineral at a definite temp. With a gram of phillipsite from Aci Castello, for example, the percentage amount of contained water at different temp. was :

| | 20° | 50° | 100° | 150° | 260° | Dark redness |
|---|---|---|---|---|---|---|
| Contained water | 0·2183 | 0·2044 | 0·1738 | 0·1194 | 0·0645 | 0·0095 |

with pseudophillipsite, the percentage loss was :

| | 54° | 75° | 95° | 126° | 129° | 159° | 238° | Red heat |
|---|---|---|---|---|---|---|---|---|
| Loss | 1·37 | 2·07 | 3·03 | 6·00 | 6·28 | 12·77 | 14·71 | 20·48 per cent. |

There is a break in this curve at about 159°, and a break with phillipsite at 129°. The meaning of the break is not clear because all the water appears to be zeolitic. Phillipsite, in a stream of humid air, shows :

| | 115° | 175° | 215° | 250° | 275° | 320° | 360° |
|---|---|---|---|---|---|---|---|
| Loss | 2·90 | 8·95 | 10·96 | 12·40 | 13·45 | 14·66 | 15·09 per cent. |

Phillipsite is found in basalts, and various lavas. Minute crystalline aggregates and irregular crystalline groups were found in the deep-sea dredgings of the *Challenger* from the bottom of the central Pacific Ocean, south of the Hawaiian Islands. They are believed to have been formed at the bottom of the ocean by the decompositions of the augitic lavas of those islands. This subject has been discussed by J. Murray,[93] J. Murray and C. V. Leo, and A. Renard. A. Daubrée reported small transparent crystals of recent formation in the masonry of the thermal baths at Plombières; Bourbonne-les-Bains; Luxeuil, Haute Saône; and Oran, Algiers. H. St. C. Deville obtained a kind of potash-phillipsite by heating potassium aluminate, and silicate, silica, and water in a sealed glass tube at 200°. A little lime was derived from the glass.

The crystals of phillipsite are either isolated, or they occur in tufts or spherules with a radiating structure. The colour is white, may be with a reddish tinge. P. Groth[94] showed that the crystals belong to the monoclinic system, and A. Streng gave for the axial ratios $a : b : c = 0{\cdot}70949 : 1 : 1{\cdot}2563$, and $\beta = 55° 37'$; G. Tschermak gave $0{\cdot}5148 : 1 : 0{\cdot}3547$, and $\beta = 90°$. The subject was investigated by F. Köhler, P. Trippke, C. Stadtländer, W. Fresenius, and G. Cesaro. The crystals appear as penetration twins often simulating rhombic and tetragonal forms. The twins are sometimes simple and cruciform about a twinning plane (001). L. Langemann assumed that the individuals which form the complex twins of phillipsite are triclinic. F. Rinne found that heating did not change the character, and the twinning structure is retained, but the axial plane approaches (001) by some 10°, and the double refraction becomes weaker. The faces (010) are sometimes finely striated. The cleavage parallel to (001) and to (010) is rather distinct. The optic axial angle is large; A. des Cloizeaux gave $2H_a = 84° 8\frac{1}{2}'$ for the red ray, and $84° 54\frac{1}{2}'$ for the yellow ray. The angle is variable since for the red ray $2H_a$ ranged from 69° 55′–84° $8\frac{1}{2}'$; $2H_0$ from 98° 13′–129° 15′; and $2V = 65° 21'–81°$. The sp. gr. ranges from 2·15–2·20; and the hardness is just over 4. The action of heat has been previously discussed. A. des Cloizeaux found the index of refraction $\beta = 1{\cdot}48–1{\cdot}57$. The birefringence is low; A. Michel-Lévy and A. Lacroix gave $\gamma - \alpha = 0{\cdot}003$. The optical character is positive. J. Königsberger and W. J. Müller made observations on this subject. J. Lemberg studied the action of a soln. of potassium or sodium chloride or carbonate on phillipsite, and observed an interchange of bases. J. Roth, and C. R. van Hise discussed the transformation which phillipsite undergoes in nature—formation of albite, anorthite, and leucite. V. Goldschmidt said

dil. hydrochloric acid does not decompose the mineral; but with more conc. acid, flocculent and gelatinous silicic acid separates—*vide supra.*

J. H. Pratt and H. W. Foote [95] found crystals of a zeolite in the corundum mine of Buck Creek, North Carolina. They named the mineral **wellsite**—after H. L. Wells. The composition corresponds with $RAl_2Si_3O_{10}.3H_2O$, where R represents Ba : Ca : $K_2$=1 : 2 : 3. It may therefore be regarded as **trihydrated calcium dialuminium orthotrisilicate,** with some calcium replaced by potassium and barium. F. W. Clarke represents it by the formula :

$$Al{\equiv}SiO_4{-}Al{<}\begin{matrix}SiO_4{<}R\\SiO_4{<}R\end{matrix}{>}Al{-}Si_3O_8{\equiv}Al{+}6H_2O$$

The mineral is closely related to the phillipsite family, forming the isomorphous series :

| | | $a:b:c$ | $\beta$ |
|---|---|---|---|
| Wellsite . . . . | $RAl_2Si_3O_{10}.3H_2O$ | 0·768 : 1 : 1·2450 | 53° 27′ |
| Phillipsite . . . | $RAl_2Si_4O_{12}.4H_2O$ | 0·7095 : 1 : 1·2563 | 55° 37′ |
| Harmotome . . . | $RAl_2Si_5O_{14}.5H_2O$ | 0·7032 : 1 : 1·2310 | 55° 10′ |
| Stilbite . . . . | $RAl_2Si_6O_{16}.6H_2O$ | 0·7623 : 1 : 1·1940 | 55° 50′ |

G. Tschermak had doubts whether this is a distinct mineral species. The monoclinic crystals have the axial ratios $a:b:c$=0·768 : 1 : 1·245 and $\beta$=58° 27′. The small isolated crystals are invisible penetration twins closely resembling harmotome and stilbite. The crystals are colourless and transparent to white, and possess no cleavage. The optic axial angle is large, $2E$=120°–130°. E. S. Larsen found $2E$=60°, and $2V$=39°; the index of refraction $\alpha$=1·498 and $\gamma$=1·503, with the birefringence $\gamma-\alpha$=0·005. The optical character is negative. The sp. gr. is 2·278–2·366; and the hardness 4–4½. About one-third of the water is expelled between 100° and 200°; another third between 200° and 300°; and the remainder on ignition. Wellsite with 13·31 per cent. of water lost, at different temp. :

| | 100° | 125° | 175° | 200° | 260° | 295° | Red heat |
|---|---|---|---|---|---|---|---|
| Loss . | 0 | 1·93 | 1·48 | 0·92 | 2·45 | 1·24 | 4·96 per cent. |

After being heated to 265°, nearly all the water is regained by exposure to moist air. The birefringence is low; and the optical character negative. The mineral is decomposed by hot hydrochloric acid with the separation of silicic acid in a granular form. A. Fersmann found a similar zeolite near Simferepol.

R. J. Haüy [96] mentioned a *zéolithe efflorescente* which he called **laumontite**—after Gillet de Laumont, who found the mineral in the lead-mines of Huelgoet, Brittany, in 1785. C. C. von Leonhard used a similar term; but A. G. Werner corrupted it to *lomonite.* It was analyzed by H. A. von Vogel in 1810.

The *zéolithe rouge d'Aedelfors* of R. J. Haüy; the *aedeforsite* of C. G. Retzius—*vide* wollastonite; the *meal zeolite* of W. Hisinger; the red zeolite of Upsala; and a white zeolite from Fahlun, are considered by N. J. Berlin, and A. Ewert to be impure laumontites. A zeolite at Schemnitz, Hungary, was called *leonhardite*—after C. C. von Leonhard—by J. R. Blum, and a few occurrences have been reported elsewhere. Similar zeolites have been analyzed by G. O. Barnes, G. Lewinstein, A. Smita, J. Lemberg, A. E. Fersmann, and G. Tschermak. The mineral is very like laumonite in composition, and also furnishes monoclinic crystals. The sp. gr. is 2·25, and hardness 3–3½. N. Surgunoff distinguished three minerals belonging to one family—laumontite, $Ca_2Al_4Si_8O_{24}.8H_2O$; **α-leonhardite,** $(Ca,K_2,Na_2)_2Al_4Si_8O_{24}.7H_2O$, and **β-leonhardite,** $Ca_2Al_4Si_8O_{24}.7H_2O$. *β*-leonhardite was also described by A. Dwojtschenko; and *α*- and *β*-leonhardite by A. A. Twaltschrelidze. P. Savi, and L. Pilla described flesh-red monoclinic crystals of a zeolite which were found at Monte di Caporciano, and which P. Savi called *caporcianite;* its sp. gr. was 2·470, and hardness 2½. G. Meneghini said it resembled heulandite; J. J. Berzelius, and J. F. L. Hausmann, analcite; A. Breithaupt, crystalline chabasite; J. D. Dana, *desmin;* and E. F. Glocker, *mesotype.* It was analyzed by T. Anderson, and E. Bechi. According to G. A. Kenngott, A. d'Achiardi, and C. F. Rammelsberg, caporcianite is like laumontite in composition and properties. A mine at Monte Catini furnished G. Meneghini with a zeolite which was called *schneiderite*—after the director of

the mine. The mineral appears to have been formed by the alteration of serpentine by magnesian waters, and it is considered to be a variety of laumontite. H. Traube reported masses of radiating fibres of a white or pale yellow zeolite found on the phillipsite crystals at Lauban, Silesia, and he called the mineral *laubanite*. Its composition corresponds with hexahydrated *dicalcium dialuminium pentametasilicate*, $Ca_2Al_2(SiO_3)_5.6H_2O$; that is, $Ca{=}(SiO_3)_2{=}Al{-}SiO_3{-}Al{=}(SiO_3)_2{=}Ca{+}6H_2O$, the sp. gr. is 2·23, and its hardness $4\frac{1}{2}$–5. A. E. Fersmann called a variety from Antipoff having 2·5 per cent. $V_2O_5$, *vanadiolaumontite*.

Analyses have been made by H. A. von Vogel,[97] C. G. Gmelin, P. A. Dufrénoy, I. Domeyko, A. Connell, L. von Babo and C. Delffs, F. J. Malaguti and J. Durocher, and many others. The formula of the idealized mineral, according to C. F. Rammelsberg,[98] is $CaAl_2Si_4O_{12}.4H_2O$. C. Hintze, and J. D. Dana regarded two of the four mols of water as constitutional, and wrote $H_4CaAl_2Si_4O_{12}.2H_2O$; and P. Groth wrote $Ca\{Al(OH)_2\}_2(Si_2O_5)_2.2H_2O$. The generalized formula $CaAl_2(SiO_3)_4.4H_2O$ makes laumontite **tetrahydrated calcium dialuminium tetrametasilicate.** F. W. Clarke gave :

$$Al{\equiv}Si_3O_8{-}Al{<}\begin{matrix}SiO_4\\Si_3O_8\end{matrix}{\gtrless}\begin{matrix}Ca\\Al{-}SiO_4{\equiv}Al\\Ca\end{matrix}{+}8H_2O$$

The assumption that two mols of water are chemically bound in the mol. is based on the observation of F. J. Malaguti and J. Durocher that when the crystals are kept in vacuo for a month, they lose 2·26 per cent. of water, and if kept over conc. sulphuric acid, 3·85 per cent. The crystals regain their lost water when exposed to moist air. These workers found that 3·17 per cent. of water is lost at 100°, 6·08 per cent. at 200°, 7·28 per cent. at 300°; and the whole 13–14 per cent. is lost at a red heat. G. Tammann, however, found that as with other zeolites, the vap. press. at different temp. is a continuous function; and that the vap. press. curve exhibits no breaks. With atm. in which the vap. press. of water was respectively 14·55 mm. and 0·11 mm., the percentage losses were respectively 0·25 and 2·58 with laumontite originally containing 17·87 per cent. of water. Similar results were obtained with leonhardite. C. Doelter found that by slowly cooling molten laumontite he obtained a mixture of anorthite, a pyroxene, and a glassy matrix. C. Doelter, and G. Tschermak assumed that laumontite is really a mixture or solid soln. of anorthite and metasilicic acid : $CaAl_2Si_2O_8.2SiO(OH)_2.2H_2O$. Later on, G. Tschermak obtained orthosilicic acid by treating laumontite with acids, and he represented it by the formula with orthosilicic acid as a nucleus : $CaAl_2Si_2O_8.2H_4SiO_4$.

Laumontite occurs in cavities in porphyry, gneiss, and syenite rocks, in veins traversing clay slate with calcite. It is a secondary mineral formed at a low temp. It has not been synthesized. It occurs in columnar or radiating masses, and crystals. The colour is white, may be tinged grey, yellow, or red. The crystals were described by R. J. Haüy,[99] A. des Cloizeaux, F. Mohs, etc. According to W. H. Miller, the monoclinic crystals have the axial ratios $a : b : c = 1{\cdot}1451 : 1 : 0{\cdot}5906$, and $\beta = 68° 46\frac{1}{4}'$; while P. Groth gave 1·0818 : 1 : 0·5896, and $\beta = 99° 18'$. The cleavage is complete on the (010) and (110) faces, and incomplete on the (100) and ($\bar{2}01$) faces. Twinning occurs on the composition plane (100). A. Michel-Lévy and A. Lacroix gave for the optic axial angle $2V = 30°$; and A. des Cloizeaux, $2E = 52° 24'$ for red light, and 56° 15′ for blue light; while raising the temp. to 75° made no perceptible change in the optic axial angles. The sp. gr. ranges from 2·3–2·4; and the hardness is in excess of 3. The action of heat on the water content has been previously discussed. As with other zeolites, when the mineral is heated before the blowpipe flame, it swells up and froths before settling down to a glassy enamel. For the vap. press. *vide supra*. As indicated above, laumontite decomposes when fused and cooled slowly. A. Michel-Lévy and A. Lacroix found the indices of refraction to be $\alpha = 1{\cdot}513$, $\beta = 1{\cdot}524$, and $\gamma = 1{\cdot}525$; and the birefringence is weak, $\gamma - \alpha = 0{\cdot}012$. The optical character is negative.

G. A. Kenngott[100] found that powdered and moistened laumontite gives an alkaline reaction with litmus; but F. W. Clarke was in doubt about the result with phenolphthalein. G. Steiger found that with water there is a slow decomposition and a little alkali passes into soln. J. Roth noted that the weathering of laumontite produces some calcium carbonate; G. Leonhard and C. R. van Hise observed the passage of laumontite into prehnite; and C. G. C. Bischof, M. F. Heddle, G. Jentszch, J. Roth, R. P. D. Graham, and C. R. van Hise, the passage of laumontite into orthoclase and albite. F. F. Grout applied the term *pseudolaumontite* to a product which was derived from diabase, and which was regarded as a laumontite with much of the lime replaced by potash and magnesia. J. Lemberg found that when laumontite is treated with sodium or potassium carbonate, much of the lime is replaced by the alkali, and a product resembling analcite is formed. Similar results were obtained with alkali chlorides. He called the product obtained with sodium carbonate soln., *soda-caporcianite*. F. W. Clarke and G. Steiger found that after exposure to the vap. of ammonium chloride, the mineral is decomposed, and some 3·95 per cent. of ammonia is taken up by the residue.

St. Epiphany,[101] J. de Laet, and J. Beckmann have suggested that the *lyncurium* of Theophrastus' *Περὶ λίθων* and of Pliny's *Historia naturalis* (**8.** 38; **37.** 3, 7) may have been hyacinth. W. Watson argued in favour of tourmaline; but J. Beckmann said that if so, Theophrastus would have referred to the fact that heat is necessary to make this mineral attract light bodies. G. Noya-Caraffa suggested that the *theamedes* of the ancients was tourmaline; but A. B. de Boot, and J. Beckmann doubted this, and the latter has shown that Pliny's account of the *carbuncle* fits the known properties of tourmaline better than those of the other minerals named. Pliny said that this attracted chaff and light bodies after it had been heated by the beams of the sun, or by friction. J. Serapion the Arabian mentioned a red mineral resembling the hyacinth which "when strongly rubbed against the hair of the head, attracts chaff as the magnet does iron." As a matter of fact, this description would apply to most gem-stones.

The term **tourmaline** has been applied to a number of different silicates. It is a Singalese word first used for a reddish mineral brought to Europe from Ceylon by the Dutch Traders in 1703. A writer, "I. G. S.," at the beginning of the eighteenth century, said:

> The stone called *tourmaline, turmale,* or *trip* has the property that it not only attracts the ashes from the warm or burning coals, as the magnet does iron, but also repels them again, which is very amusing; for as soon as a small quantity of ashes leaps upon it, and appears as if endeavouring to writhe itself by force into the stone, the ash, in a little, springs from it again, as if about to make a new effort; and on this account tourmaline was by the Dutch called *Aschentrecker*—ashes-drawer. When the turf coals are cold, it does not produce these effects. I have no doubt that, if heated, it would attract other things beside ashes.

Similar remarks were made by F. Maurer in 1713; and L. Leméry likewise described the mineral in 1717. C. Linnæus called it *lapis electricus*. I. S. R. I. Eques a Born, S. Rinman, and R. Kirwan called it tourmaline. A black variety of tourmaline had long been called *schörl*. This word is of uncertain origin. It was spelt *schurl* by J. Matthesius in 1562; *shirl* by U. Brückmann in 1727; and *skiörl* by J. C. Wallerius in 1747. It is also referred to by C. Gesner, L. Ercker, F. von Kobell, A. Cronstedt, J. B. L. Romé de l'Isle, and C. A. S. Hofmann.

> It has been suggested that the word schörl is derived from the name of a German locality where the mineral occurred—Schorlau, meaning schörl-village; on the contrary, the word may be a miner's term of unknown origin, and that the village received its name because schörl was found near by. In the fifteenth century, the rejected material in auriferous and stanniferous ores was called schurl or wolfram. It has therefore been suggested that the word is derived from the old German word *schor*, meaning impurities or refuse.

J. B. L. Romé de l'Isle, A. Cronstedt, etc., regarded tourmaline and schorl as one species. Tourmaline is common in clay slates, crystalline schists, and in the

more siliceous rocks—*e.g.* the pegmatites. It is common in zones of contact metamorphism of schists and granites, and numerous kinds of rocks. H. B. Patton,[102] for instance, regards the tourmaline in some schists in Colerado as having been formed at the expense of the biotite in the pegmatites of the adjoining contact zone. Tourmaline occurs as a pyrogenetic mineral in igneous rocks—*e.g.* granites, pegmatites, porphyries, and lavas. In igneous rocks it seems to have been produced by the fumarole action, and not as a direct separation from magma. Tourmaline has not been made artificially. C. Doelter made some unsuccessful experiments in this direction.

A red schörl from Siberia was called by R. Kirwan,[103] *rubellite ;* by J. C. Delamétherie, *daourite*—from Daurien ; by C. Lermina, *siberite ;* by R. J. Haüy, *tourmaline apyre ;* and by J. F. L. Hausmann, *apyrite*, in reference to its fire-resisting qualities. M. F. R. d'Andrada called a black tourmaline from Kragerö, Norway, *apheizite*—from *αφρίζω*, foam, in allusion to its behaviour in the blowpipe flame—and a blue tourmaline from Utö, Sweden, *indigolite* (also *indicolite*). R. Hermann called a colourless tourmaline from Elba, *achroite*—from *ἀ*, without ; *χρόος*, colour. I. Domeyko called a variety from Taltal, Chili, *taltalite*. G. L. Ulex, and F. Pisani showed that taltalite is a mixture of tourmaline and a copper earth. G. Tschermak called the magnesium tourmaline from Unterdrauburg, Drave district, Carinthia, *dravite*. T. Thomson found a brown mass of interwoven acicular prismatic crystals at Huel Unity, Cornwall, which he called *zeuxite*—from *ζεῦξις*, the act of writing—in allusion to the locality where it occurred. R. P. Greg, and A. des Cloizeaux found the crystals to be a ferriferous tourmaline.

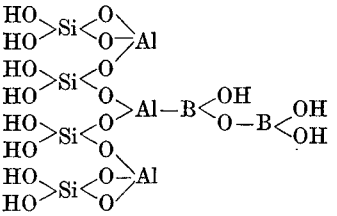
The first analysis of tourmaline is attributed to A. Wondraschek,[104] and analyses were soon afterwards reported by L. N. Vauquelin, R. J. Haüy, M. H. Klaproth, and C. F. Bucholz. The presence of boric oxide was discovered by H. A. von Vogel, and of lithium oxide by A. Arfvedson, W. Gruner, and C. G. Gmelin. An attempt was made by R. Hermann to show that carbon dioxide is an essential constituent ; but C. F. Rammelsberg found no carbon dioxide in numerous samples. He did, however, find in some samples a little phosphoric oxide and fluorine. The constitution with inadequate data was discussed by J. D. Dana, C. F. Naumann, G. A. Kenngott, and A. Mitscherlich. The combined water, and the ferrous and ferric oxides were studied by C. F. Rammelsberg in 1869. On account of the imperfections in the analytical methods, analyses prior to 1870 are usually omitted in discussions on the chemical nature of the mineral. Numerous analyses have been made [105] since that time.

In spite of the excellent analyses of tourmaline which are available, there is no general agreement as to the composition of the idealized mineral stripped from the accidental constituents which so commonly contaminate the products produced in Nature's laboratory. It is almost certain that tourmaline is a mixed crystal or solid soln. of a number of different silicates. The tourmalines represent a group of isomorphous minerals whose chemical relations have not yet been elucidated. In the *alkali tourmalines*, the chief bases are lithium, sodium, and potassium ; in the *magnesian tourmalines*, the chief base is magnesium—or, possibly, aluminium ; and in the *iron tourmalines*, iron (ous) replaces much of the magnesium. E. T. Wherry showed that the replacement of Fe″ by Li, and of Al by Mg, and the absence of calcium fit in well with the at. vol. theory of isomorphism. Before attempting to interpret the analyses, the imperfections to which analyses of complex silicates are liable must be taken into consideration. The main difficulties are (i) inaccurate determinations of the boron ; (ii) the adsorption of water from the air during the fine-grinding of the mineral ; and (iii) the ready oxidation of ferrous to ferric oxide during the fine-grinding which precedes analysis.

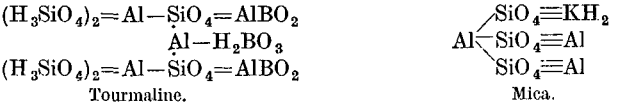
C. F. Rammelsberg,[106] in his paper : *Die chemische Natur der Turmaline* (Berlin, 1890), argued that tourmaline is a mixture of silicates of the types $R'_6SiO_5 : R''_3SiO_5 : R'''_2SiO_5$ in proportions between 1 : 2 : 6 and 15 : 1 : 90. He showed that the ratio R : Si in 64 good analyses ranges from 1 : 5·7–1 : 6·7. It is, however, necessary to consider the 8–10 per cent. of boric oxide in the mineral. The analyses discussed by R. B. Riggs, and E. A. Wülfing indicate that there

are three types with the group $3B_2O_3.12SiO_2.4H_2O$ constant, and in *lithium or alkali tourmaline*, $2(Na,Li)_2O.8Al_2O_3(3B_2O_3.12SiO_2.4H_2O)$; *ferrous tourmaline*, $Na_2O.4FeO.7Al_2O_3(3B_2O_3.12SiO_2.4H_2O)$; and in *magnesium tourmaline*, $\frac{2}{3}Na_2O.\frac{2}{3}MgO.5Al_2O_3(3B_2O_3.12SiO_2.4H_2O)$. There is, however, an excess of oxygen which is explained by assuming that AlO and HO groups are present. E. A. Wülfing inferred that the analyses are best summarized by regarding the tourmalines as solid soln. of the two silicates, $H_8Na_4Al_{16}B_6Si_{12}O_{63}$ and $H_6Mg_{12}Al_{10}B_6Si_{12}O_{63}$. P. Reiner bases his observations on these formulæ. R. B. Riggs, P. Jannasch and G. Kalb referred the analyses to the type $R_9BO_2(SiO_4)_2$, and P. Groth, $R_6(AlO).BO.(SiO_4)_2$. P. Jannasch and G. W. Kalb, W. and D. Asch, and G. Tschermak assume that there are three types of tourmalines, and V. Goldschmidt, two. H. Rheineck does not accept the view that the boric oxide and aluminium are in direct association.

S. L. Penfield and H. W. Foote argued that the tourmaline is a salt of a *tourmalinic acid*, $H_{11}Al_3B_2Si_4O_{21}$, or $(H_2SiO_4 : Al.H_2SiO_4)_2 : Al.H_3B_2O_5$ which contains the radicle $H_3B_2O_5$ of the acid $H_4B_2O_5$. Graphically, these formulæ become



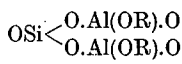
G. Cesaro regarded tourmaline as an orthosilicate with part of the silicon replaced by $B_2O$. F. W. Clarke has shown that although this formula fits most, but not all, the analyses of tourmaline, it does not harmonize with the characteristic change of the tourmalines into micas. W. T. Schaller, and P. Reiner avoid the difficulty by tripling the above formula. This gives the unwieldy and complicated tourmalinic acid, $H_{60}Si_{12}B_6O_{63}$. F. W. Clarke modified the type formula to



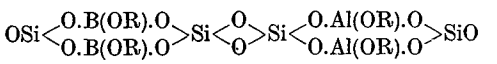
Tourmaline. Mica.

which would make the tourmalines *triboratotetraluminotetraorthosilicates*. He added that it is improbable that the boron is present partly as metaborate and partly as orthoborate; and as an alternative he said that it may be represented as $B_3O_7$, the quinquevalent radicle of a hypothetical acid $H_5B_3O_7$. He added that fluorine may in part replace the metaborate radicle. By replacing various hydrogen atoms with the univalent elements, K, Na, Li, and F; bivalent elements, Ca, Mg, Mn, and Fe; and tervalent elements, B, Al, Fe, Mn, and Cr, and compounding different proportions of two or three mols of the above type, it is possible to represent the different analyses of tourmaline. The alkali tourmalines usually have a high proportion of aluminium, and the magnesian and iron (ous) tourmalines have a low proportion of aluminium. The above scheme provides for *ferric tourmalines* although the existence of such has not been unequivocally established in normal tourmalines. The ferric oxide appearing in some analyses may have been the result of oxidation. In a few cases, part of the aluminium is replaced by chromium, furnishing the so-called *chrome-tourmalines*. If a mol. of the type indicated by F. W. Clarke's, and H. W. Foote's formula loses its boric oxide and an atom of aluminium, and takes up potash, two mols. of mica are formed. P. Erculisse represented the tourmalines as solid soln. of salts of different fluoaluminosilicic acids. J. Jakob applied the co-ordination theory and assumed tourmaline to be a

solid soln. of $4[Al(SiO_4)_3]R_9+[O.Al.(OBO)_2]Al_2$. W. Vernadsky assumed that tourmaline is an additive substance containing the kaolinite ring, $R'Al_2Si_2O_3$, *viz.*



W. Vernadsky's kaolinite nucleus.



W. Vernadsky's tourmaline nucleus.

because tourmaline is formed by the weathering of felspar, and it furnishes on weathering china clay or alkali-mica. He assumes that in tourmaline a similar ring is formed with boron in place of aluminium, and that the two rings are joined, furnishing the tourmaline nucleus $R'_4Al_2B_2Si_4O_{16}$. He postulates three groups: *kalbaite*, $R'_8Al_4B_2Si_4O_{21}$; *belbaite*, $R'_{14}Al_2B_2SiO_4O_{21}$; and *elbaite*, $R'_2Al_6B_2Si_4O_{21}$, one or more of which may form addition-compounds with the tourmaline nucleus. In this way it is possible to represent the composition of all the tourmalines. These hypotheses are to be regarded as tentative, though ingenious, attempts to solve the riddle—what is the chemical nature of tourmaline ?

Tourmaline is rarely colourless or white; the **colour** may be red, blue, or green; and most commonly brownish-black, bluish-black, or black. Some specimens are red internally, and green externally; others are red at one extremity, and green, blue, or black at the other. Sometimes there are different colours in concentric layers. R. Scharizer,[107] and W. Vernadsky made some observations on the relation between the colour and composition. According to the former, the iron tourmalines containing little or no manganese are brown to brownish-black. The intensity of the brown colour produced by iron is increased by increasing the titanium content. As the proportion of manganese increases, the colour passes from blue to green and to red. He considers that the blue and green colours are the result of an admixture of green manganate and reddish-violet permanganate. The passage of manganate into permanganate explains the change of colour which occurs when the tourmaline is heated in oxygen. From his observations on the action of oxidizing and reducing gases on the heated mineral, W. Hermann inferred that chromium, manganese, and iron are concerned in the coloration of tourmaline. The mineral is sometimes massive and compact, or in columnar masses. The **crystals** are prismatic, slender or acicular, short and thick, and rarely flattened; they are often much rounded and barrel-shaped, and they are sometimes isolated, but more commonly in parallel radiating groups. Doubly terminated crystals are rare; usually, the crystals are attached at one end. The crystals are commonly hemimorphic, and they furnish some of the most conspicuous examples of polar symmetry. The crystals belong to the trigonal system, and, according to V. von Worobieff, the axial ratio is $a:c=1:0{\cdot}45181$. M. Jerofejeff gave $1:0{\cdot}44805$ for this ratio; G. Seligmann, $1:0{\cdot}4513005$; and A. Cossa and A. Arzruni, $1:0{\cdot}45149$. Observations were also made by W. Ramsay, D. Brewster, J. D. Dana, A. T. Kupffer, W. E. Hidden, V. M. Goldschmidt, G. Rose, A. des Cloizeaux, A. d'Achiardi, W. H. Miller, A. N. Karnozhitsky, H. L. Ungemach, A. Lacroix, L. Duparc and co-workers, A. Ondrej, A. Krejci, C. M. Viola and E. Ferrari, W. P. Blake, P. Termier, E. Artini, O. B. Böggild, F. Slavik, A. Hamberg, W. Vernadsky, A. H. Westergard, and R. H. Solly. C. Hintze said that J. C. G. de Marignac's measurements more probably refer to phenacite than to tourmaline. W. T. Schaller said that the *c*-axis of red lithium tourmaline is largest for the ferruginous tourmalines. F. Rinne and M. Kemter, C. Kulaszewsky, H. Baumhauer, W. Ramsay, H. Traube, and T. L. Walker studied the **corrosion figures.** C. Kulaszewsky, and H. Haga and F. M. Jäger have studied the **X-radiograms** of tourmaline. The elementary parallelopiped is a prism of rhombic base, and 120° edge-angles; the edge-length of the rhomb is $16{\cdot}23\times10^{-8}$ cm., and the height $7{\cdot}26\times10^{-8}$ cm. The prismatic faces of the crystals are sometimes striated vertically. The **cleavage** is not noticeable, or is imperfect and parallel to $(11\bar{2}0)$ and $(10\bar{1}1)$. The alteration of analogous and antilogous patches on cross-sections indicates

supplementary **twinning** like that of hemimorphite. Juxtaposition twins or penetration twins with parallel axes are not common; cruciform twins are also very rare, but an example has been described by M. Bauer. A. E. Fersman found growths of felspar with tourmaline at Mursinka, Ural. L. Duparc and co-workers found the **optic axial angle**, $2E$, of anomalous biaxial crystals varied from 0°–14° 5′; and A. des Cloizeaux observed no change by raising the temp. from 12°–186°. C. Doelter also made observations on this subject.

The **specific gravity** of tourmaline ranges from 3·0–3·2. Determinations were made by many of those who analyzed the mineral. J. Joly gave 3·104–3·139 at 14°/4° for iron tourmalines, and 3·010 at 14°/4° for a magnesian tourmaline. L. Duparc and co-workers obtained numbers ranging from 2·978–3·127. K. Becht found values from 3·066–3·144. E. A. Wülfing found the sp. gr. increased linearly with the proportion of heavy metal present with the magnesian tourmalines. W. T. Schaller obtained the smallest value 3·05 and the greatest, 3·20–3·25; and with the magnesium-free tourmalines, the smallest values 3·00–3·05 and the greatest, 3·20–3·25. He represented his observations on the effect of alumina by the curves, Fig. 179. The **hardness** is about 7. W. Voigt found the **compressibility** of tourmaline to be $\beta=1{\cdot}15\times10^{-6}$, and E. Madelung and R. Fuchs, $0{\cdot}84\times10^{-6}$ ($p=125$ atm.). W. Voigt found the **modulus of elasticity** to be 15,560 kgrms. per sq. mm. at −45°; 16,330 at 0°; 17,160 at 45°; and 25,570 at 90°. W. Lissauer measured the elastic modulus at the temp. of liquid air. F. Pfaff gave 0·0009369 for the coeff. of **thermal expansion**, between 0° and 100°, taken in the direction of the $c$-axis, and 0·0007732 in the direction of the $a$-axis. R. Scharizer found that it is possible to change the colour of tourmaline by heating the mineral in a flame charged with oxygen. K. Simon found a red tourmaline lost its colour at 670° when heated in a stream of hydrogen, but the colour is restored at room temp.; a dark red crystal became green at 500°, and remained pale green at room temp.; a reddish-violet tourmaline became brownish-green when heated and the colour disappeared at 500°, and it remained colourless when cold. Red tourmalines became green when heated between 500°–800° in oxygen, and the green colour remained on cooling. R. Cusack gave 1012°–1102° for the **melting point** of tourmaline; A. L. Fletcher gave 1062°–1152°; and C. Doelter, 1010°. The m.p. must obviously depend on the composition. The last-named found that on fusion tourmaline yields olivine and spinel. This decomposition must interfere with observations on the m.p. J. Joly found the **specific heat** of an iron tourmaline to be 0·2004 between 9·1° and 100°; and 0·2111 for a magnesian tourmaline. S. P. Thomson and O. J. Lodge inferred that the **thermal conductivity** of tourmaline is probably unilateral, but F. Stenger found that it is not so. The ratio of the sq. roots of the conductivities in the direction of the $a$-axis and of the $c$-axis is 1·15–1·17. G. F. Fitzgerald made some observations on this subject.

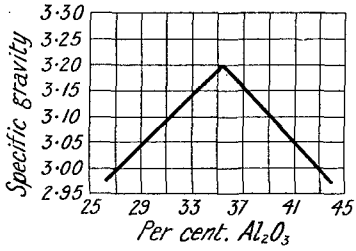



FIG. 179.—The Effect of Alumina on the Specific Gravity of Tourmaline.

A large number of observations have been made on the refractive indices of the tourmalines. A. des Cloizeaux found for a colourless tourmaline with Na-light, $\omega=1{\cdot}6366$, and $\epsilon=1{\cdot}6193$. Observations were made by M. Jerofejeff, P. H. Schwebel, A. Cossa and A. Arzruni, G. B. d'Achiardi, L. Duparc and co-workers, K. Becht, K. Zimanyi, etc. According to E. A. Wülfing, the lithium tourmalines have the lowest refraction; the magnesian tourmalines have intermediate values; and the iron tourmalines have the highest refraction. W. T. Schaller also found the ferruginous tourmalines have the highest refraction. The following is a selection of values from data furnished by the above-mentioned observers:

| | Colourless. | Dark green. | Green. | Red. | Dark red. | Straw yellow. | Dark brown. | Black. |
|---|---|---|---|---|---|---|---|---|
| $\omega$ . | 1·6424 | 1·6424 | 1·6401 | 1·6394 | 1·6448 | 1·6430 | 1·6481 | 1·6525 |
| $\epsilon$ . | 1·6223 | 1·6222 | 1·6220 | 1·6237 | 1·6251 | 1·6224 | 1·6250 | 1·6279 |
| $\omega - \epsilon$ | 0·0201 | 0·0202 | 0·0181 | 0·0157 | 0·0197 | 0·0206 | 0·0231 | 0·0246 |

P. Reiner found for the refractive index with alkali tourmaline $\alpha=1·625$, $\gamma=1·646$; with magnesian tourmaline, $\alpha=1·628$, $\gamma=1·640$; and iron tourmaline, $\alpha=1·639$ and $\gamma=1·668$. The **birefringence** is strong. E. A. Wülfing also found the magnesian tourmalines have the lowest birefringence; the lithium tourmalines have intermediate values, and the iron tourmalines, the highest double refraction. The optical character is negative. All the coloured tourmalines have a well-marked **pleochroism.** This was noted by J. G. Wallerius in 1778, and observations have been recorded by A. des Cloizeaux, E. Bertrand, A. Beer, C. F. Rammelsberg, G. Spezia, A. von Lasaulx, R. Scharizer, A. Cossa and A. Arzruni, and A. C. Gill. In the black varieties, $\omega$ is green or blue, and $\epsilon$ is brown or red; in the green varieties, $\omega$ is green or greenish-brown, and $\epsilon$ is green of a different tint; in the red crystals, both rays are red but of a different tint. The dichroism with ultra-red waves was studied by E. Merritt, and V. Agafanoff. The effect of the colouring pigment on the pleochroism was also investigated by V. Agafanoff. E. Bertrand, and T. Liebisch observed the idiophanous figures of tourmaline. The absorption of the ordinary ray is much greater than that of the extraordinary ray. In some dark brown crystals the difference is so great that a section parallel to the optic axis, transmits virtually only the extraordinary rays, and can therefore be used as polarizer or analyzer—*e.g.* the so-called tourmaline tongs. Observations on the **absorption of light** by tourmaline plates were made by W. Pulfrich, J. Ehlers, A. Potier, E. Carvallo, and P. H. Schwebel. W. W. Coblentz found the important bands on the **absorption spectrum** are at $1·28\mu$ and $2·82\mu$; and in the **reflection spectrum,** there are maxima at $7·5\mu$, $8·0\mu$, $9·2\mu$, $9·7\mu$, $10·2\mu$, and $10·7\mu$. A. Pflüger confirmed the law with respect to the proportionality of absorption and emission of light by tourmaline. E. Newbery and H. Lupton found that when green tourmaline is exposed to radium rays no visible effect is produced; a pink crystal became colourless when heated, but radium rays had no visible effect on the heated specimen, although the unheated crystal was slightly darkened in colour. Cathode rays did not change the colour of the heated or unheated mineral; the heated crystals alone have a fine orange glow. Colourless crystals assumed a faint pink colour by exposure to radium radiations. The **interference figures** are characteristic of uniaxial crystals, but sometimes the crystals are biaxial, may be as a result of press. strains. A. des Cloizeaux observed the biaxial interference figures about the boundary of differently coloured layers of a multi-coloured crystal. Observations on the **optical anomalies** of tourmaline crystals were made by E. Mallard, H. Bücking, L. Duparc, A. Madelung, etc. J. A. Anderson discussed the rotation of linearly polarized light by tourmaline crystals; and the motion of light in tourmaline crystals was investigated by C. Viola, E. A. Wülfing, and S. Nakamura.

K. Simon found that tourmaline which has been decolorized by heating in oxygen or hydrogen, has its colour restored by exposing the mineral to sunlight, or to **radium rays.** C. Doelter observed that a colourless tourmaline acquired a rose tint in radium rays; while other tourmalines were not changed. S. C. Lind and D. C. Bardwell found no change of colour, fluorescence, or thermoluminescence up to 300° with pink and green tourmalines. **Ultra-violet rays** act like radium rays, but more feebly. **Cathode rays** have but a slight action on colourless tourmaline. Tourmaline is either non-radioactive or it exhibits a feeble **radioactivity** which has been measured for a number of specimens by R. Piutti. F. Pockels investigated the influence of an **electrostatic field** on the optical properties of tourmaline; and J. Chaudier, the relation between the **electric double refraction** and the birefringence, and found that the former is smaller the less the value of the latter. The

**pyroelectrification** of minerals was first observed with tourmaline—*vide supra*. C. Linnæus stated that electricity is the cause of the property of attracting light bodies exhibited by warmed tourmaline. The phenomenon was studied by F. Æpinus, who showed that it was necessary to heat the mineral to between 37·5 and 100° in order to develop its attractive powers. The extremity of the crystal terminated by the six-sided prism then becomes positively electrified, and the other extremity negatively electrified. The chief axis of the crystal is thus an electrical axis. He added that when the crystal is large, flashes of light can be seen along its surface. J. Canton, and T. Bergman showed that the electrification is evoked by the *change* of temp. and is not produced when kept constantly in a heated condition. Observations were made by J. C. Wilcke, W. Watson, R. J. Haüy, M. Born, A. C. Becquerel, F. Köhler, J. D. Forbes, G. Rose, P. T. Riess and G. Rose, T. M. Gaugain, E. Riecke, H. Schedtler, and G. T. Techner. The relation between the electrical and morphological character of tourmaline was discussed by V. von Worobieff. Tourmaline exhibits **piezoelectrification,** and J. and P. Curie showed that by press. in the direction of the chief axis, the polar electrification is analogous to that which is developed by cooling the crystal. W. Lissauer studied the phenomenon at the temp. of liquid air. Observations on the piezoelectrification of tourmaline were made by E. Riecke and W. Voigt, D. H. Keys, and A. L. W. E. van der Veen. J. Curie found the **dielectric constant** in a direction parallel to the chief axis to be 6·05, and vertical to that axis, 7·10; R. von Fellinger gave the respective values 6·5382 and 7·12844; W. Schmidt, 5·65 and 6·75; and R. Coehn and A. Curs, 6·2 to 6·75. W. Lissauer found no change in the value of the dielectric constant in passing from room temp. to the temp. of liquid air. H. Saegusa measured the dielectric hysteresis of tourmaline. Tourmaline is paramagnetic. J. Königsberger measured the **magnetic susceptibility;** B. Bavink, the magnetic influence; and W. Voigt and S. Kinoshuto, the **magnetization numbers** parallel and vertical to the chief axis. B. Bavink studied the magnetic properties of tourmaline.

R. Piutti measured the occluded helium in some samples of tourmaline. H. Baumhauer studied the action of alkali hydroxide soln. J. Lemberg [108] investigated the action of soln. of sodium silicate at 200°, for 586 hrs., and obtained a product resembling analcite. E. C. Sullivan studied the basic exchange which occurs when tourmaline is placed in soln. of cupric sulphate. Some changes which occur in nature are produced by the addition of alkalies. The alteration of tourmaline to mica (lepidote), chlorite, cookeite, and steatite have been studied by G. Tschermak, W. T. Schaller, R. B. Riggs, C. R. van Hise, etc.

G. A. Kenngott [109] named a mineral erroneously thought to come from the Val Milar, Switzerland, **milarite;** it actually came from the Val Giuf, and hence J. Kuschel called it *giufite*. Analyses were made by R. Finkener, A. Frenzel, E. Ludwig, and F. P. Treadwell; and C. F. Rammelsberg calculated the formula $R'_6Ca_4Al_4Si_{24}O_{61}$; C. Hintze, $HKCa_2Al_2Si_{12}O_{30}$; P. Groth, $HKCa_2Al_2(Si_2O_5)_6$; and G. Cesaro, $K_2Ca_2Al_2(Si_2O_5)_6.H_2O$, or hemihydrated **potassium calcium aluminium trimesodisilicate,** $KCaAl(Si_2O_5)_3.\frac{1}{2}H_2O$. F. W. Clarke represents it by a constitutional formula analogous to that of beryl. The hexagonal prismatic crystals are colourless or pale green. In polarized light, the crystals are biaxial, and hence G. Tschermak, A. des Cloizeaux, and E. Mallard regarded them as pseudohexagonal; but F. Rinne showed that the anomalous characters are secondary, and that the crystals are hexagonal. W. Ramsay confirmed this, and found that the biaxial parts become uniaxial with rise of temp. F. Rinne gave for the axial ratio $a:c=1·06620$; and K. Busz, 1 : 0·66468. E. Bertrand gave for the optic axial angle $2H_a=79°$, and $2H_0=107\frac{1}{2}°$. The sp. gr. is 2·5–2·6; and the hardness 5–6.

F. von Kobell [110] found a massive, foliated, greyish-yellow mineral associated with the wollastonite and the edelforsite in the limestone of Gjellebäck, Norway; he called it **sphenoclase**—from *σφήν*, a wedge; and *κλάω*, I break—in allusion to its breaking into wedge-shaped pieces. C. F. Rammelsberg calculated the formula

$R_6Al_2Si_6O_{12}$ from the analysis where (Fe,Mn) : Mg : Ca=1 : 1·4 : 4·2. F. W. Clarke represents the idealized mineral as $Ca_6Al_2(Si_2O_7)_3$, analogous in structure with barylite and okenite, or **calcium dialuminium triorthodisilicate.** The sp. gr. is 3·2, and the hardness $5\frac{1}{2}$–6. Sphenoclase is slightly attacked by hydrochloric and sulphuric acids, but after ignition, the mineral is easily decomposed by hydrochloric acid with the separation of gelatinous silicic acid.

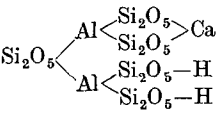
J. Söllner [111] reported a pale yellow or colourless mineral in the melilitic basalt of Kaiserstuhl, Baden, and he called it **deeckite**—after T. Deeck. The crystals are pseudomorphs after melilite. The analyses correspond with $(H,Na,K)_2(Mg,Ca)(Al,Fe)_2(Si_2O_5)_5.9H_2O$, or **potassium calcium dialuminium pentamesodisilicate,** $K_2CaAl_2(Si_2O_5)_5.9H_2O$. The crystals are apparently uniaxial with an index of refraction about 1·47, a weak birefringence, and optically negative. The sp. gr. is 2·1. The mineral becomes opaque when heated, and it is not attacked by hydrochloric acid.

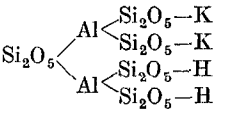
A. Damour [112] described a zeolite which he obtained from Sasbach, Baden, and named **faujasite**—after Faujas de Saint Fond. Analyses were made by A. Damour, and C. C. Hoffmann. The mineral has 22·49–27·02 per cent. of water. V. Goldschmidt found 27·5 per cent. The analyses were summarized by C. F. Rammelsberg, in the formula $H_{12}Na_2CaAl_4Si_9O_{32}.12H_2O$; J. D. Dana, and C. Hintze, $H_4Na_2CaAl_4(SiO_3)_{10}.18H_2O$; P. Groth, $H_2(Na_2,Ca)Al_2(SiO_3)_5.9H_2O$; and F. W. Clarke :

$$Al{\equiv}Si_3O_8{-}Al{<}\begin{matrix}Si_3O_8{=}Na_2\\ Si_3O_8{=}Ca\end{matrix}{>}Al{-}SiO_4{\equiv}Al{+}19H_2O$$

It is more probable that the sodium and calcium of faujasite belong to different mols. which form an isomorphous mixture of sodium and calcium aluminosilicates, say $CaAl_2(SiO_3)_5.10H_2O$, and $Na_2Al_2(SiO_3)_5.10H_2O$. This makes the idealized mineral **decahydrated calcium dialuminium pentametasilicate ;** and **decahydrated sodium dialuminium pentametasilicate.** G. Tschermak believed that faujasite is an isomorphous mixture of sodium and calcium aluminium silicates, each of which is combined with a silicic acid : $CaAl_2Si_2O_8.H_4O_2.H_8Si_4O_{12}+4Aq.$, and $Na_2Al_2Si_2O_8.H_4O_2.2H_4Si_2O_6+4Aq$. Whatever view is finally adopted will depend on the mode of association of the water. A. Damour found faujasite loses 15 per cent. of water when exposed to dry air for a month, but regains almost all during 24 hrs.' exposure to ordinary air. When heated to 50°–55° for one hour, it loses 15·2 per cent.; at 60°–65°, it loses 10·4 per cent.; and at 70°–75°, 19·5 per cent. Almost all is regained by exposure to moist air for a few weeks. P. Jannasch found that at 100° the mineral lost 18·66 per cent. of water ; at 200°–205°, 20·41 per cent., at 250°–260°, 22·67 per cent. ; over a gas-burner, 27·02 per cent. ; and over a blast-flame, 27·59 per cent. P. Jannasch also found that after being confined for 24 and 48 hrs. over calcium chloride, the losses were respectively 1·72 and 1·83 per cent. ; 65 and 100 hrs. over conc. sulphuric acid, respectively 4·60 and 6·52 per cent. ; and 118 and 190 hrs. over phosphorus pentoxide, respectively 7·44 and 10·88 per cent. The weight thereafter remained constant. The crystals usually occur in octahedra, and sometimes trisoctahedra. They are colourless, white, or brown. A. des Cloizeaux showed that the crystals are isotropic and belong to the cubic system. Twinning is common. The cleavage parallel to the (111) plane is clear. As with many other zeolites, the double refraction is anomalous. According to F. Rinne, the crystals, normally isotropic, are changed by the loss of a little water and form eight uniaxial individuals which are optically positive. The crystals at 150°, after losing 12 mols of water, become isotropic ; a further loss of water makes the crystals uniaxial and negative. When water is resorbed, the crystals again become uniaxial and positive. The sp. gr. is 1·923 ; and the hardness 5. The crystals are decomposed by hydrochloric acid, and only a fraction of the separated acid is gelatinous.

W. Cross and L. G. Eakins [113] found a zeolite on the Table Mts., and Silver Cliff, Colorado, which they named **ptilolite**—from πτίλον, wing down—in allusion to the light downy nature of the aggregates of the fine acicular crystals. It has also been found at Teplitz Bay by L. Colomba; San Piero, Elba, by G. d'Achiardi; and Teigarhorn, Iceland, by G. Lindström. K. Callisen described a mineral from Iceland which he called *flokite*. O. B. Böggild, however, showed that it is essentially the same as ptilolite—*vide infra*. Analyses of these specimens correspond with $CaAl_2Si_{10}O_{24}.5H_2O$ mixed with the isomorphous silicates $K_2Al_2Si_{10}O_{24}.5H_2O$, and $Na_2Al_2Si_{10}O_{24}.5H_2O$. F. W. Clarke represented this mineral by $H_2CaAl_2(Si_2O_5)_5.6H_2O$, etc. This corresponds with **hexahydrated calcium dialuminium dihydropentamesodisilicate;** similarly with the **hexahydrated potassium dialuminium dihydropentamesodisilicate,** and **hexahydrated sodium dialuminium dihydropentamesodisilicate.** Or, neglecting the $6H_2O$:




According to W. Cross and L. G. Eakins, a sample of ptilolite with 13·44 per cent. of water lost 3·84 per cent. of water when confined over sulphuric acid, and at

| | 110° | 125° | 300° | Red heat |
|---|---|---|---|---|
| Loss . . . | 2·61 | 1·31 | 2·41 | 3·10 per cent. |

L. Colomba found 0·81 per cent. loss over calcium chloride; 4·28 per cent. was lost at 85°, and 5·46 per cent. at 105°–110°. The mineral can reabsorb this water from moist air; but if heated to a high temp., the resorption is incomplete. The crystals are isotropic at ordinary temp., and doubly refracting at 120°–125°. L. H. Koch gave $\alpha=1{\cdot}574$, $\beta=1{\cdot}477$, and $\gamma=1{\cdot}478$. The optical character is negative. The sp. gr. is 2·30. The crystals are insoluble in hydrochloric acid, and slowly decomposed by sulphuric acid.

H. How [114] obtained a zeolite from Morden, Nova Scotia, which he named **mordenite;** L. V. Pirsson obtained the same mineral from the Noodoo, Wyoming. The analyses correspond with the formula $3RAl_2Si_{12}O_{24}.20H_2O$, where R represents $K_2 : Na_2 : Ca = 1 : 1 : 1$. C. S. Ross and E. V. Shannon gave $(Ca,Na_2)O.Al_2O_3.9SiO_2.6H_2O$. F. W. Clarke represents the constitution as an isomorphous mixture of three silicates associated with ptilolite. According to S. J. Thugutt, the so-called *comptonite* from the Swiss Alps is the same mineral. The tabular crystals are white, may be tinged yellow or pink. The crystals may occur in concretions with a fibrous texture. They resemble heulandite in habit and angles. L. V. Pirsson gave for the axial ratios of the monoclinic crystals $a : b : c = 0{\cdot}40099 : 1 : 0{\cdot}42792$, and $\beta=88°\ 29\frac{3}{4}'$. The cleavage parallel to (010) is perfect. The axial angle is large. The sp. gr. is 2·08–2·15; L. H. Hoch gave 2·30. The hardness is 3–4. The powdered mineral loses 3–6 per cent. of water when kept for an hour at 100°. O. B. Böggild found the index of refraction is about 1·480; L. H. Koch gave $\alpha=1{\cdot}475$, $\beta=1{\cdot}477$, and $\gamma=1{\cdot}478$. C. S. Ross and E. V. Shannon gave $\alpha=1{\cdot}470$–$1{\cdot}475$; $\beta=1{\cdot}473$–$1{\cdot}477$; and $\gamma=1{\cdot}475$–$1{\cdot}478$. The double refraction is weak, 0·002–0·003, and negative; and the extinction inclined at about 15°. O. B. Böggild said the extinction of ptilolite is parallel. The mineral is completely decomposed by acids. W. T. Schaller considers *flokite* to be the same as mordenite. T. L. Walker and A. L. Parsons regard ptilolite to be identical with mordenite; but W. T. Schaller regards mordenite, ptilolite, and *clinoptilolite*—crystallized mordenite—as distinct mineral species.

H. How found reddish, pink, or chalk-white balls in a red clay from Cape Split, Nova Scotia. He considered this mineral to be partially altered mordenite which he called

*steeleite*—after J. Steele. A zeolite found in British Columbia by R. P. D. Graham was named *ferrierite*. It is related to mordenite and ptilolite, and has the composition $(Mg,Na_2,H_2)_4Al_2(Si_2O_5)_5.6H_2O$. The crystals are rhombic, the indices of refraction $\alpha=1{\cdot}478$, $\beta=1{\cdot}479$, and $\gamma=1{\cdot}482$; and $\gamma-\alpha=0{\cdot}004$; the optic axial angle $2V=50°\ 25'$. When heated to 100°, water begins to be evolved; at 205°, 6·5 per cent. is lost; and at 275°, another one per cent. is given off.

R. J. Haüy [115] referred to a fibrous zeolite analyzed by L. N. Vauquelin as *mesotype*—from μέσος, middle; and τυπός, type—in allusion to form of the crystals whose square prisms were considered to be intermediate between the forms of stilbite and analcite. The fibrous zeolites were afterwards investigated by J. N. von Fuchs and A. F. Gehlen. They called natrolite, soda-mesotype, and lime-mesotype was called **scolecite**—from σκώληξ, a worm—in reference to the way some specimens curl up when heated before the blowpipe; mesotype, between scolecite and natrolite in composition, was called **mesolite.** H. J. Brooke called a specimen of scolecite from Poonah, India, *poonalite*. The two minerals from Antrim, Ireland, a fibrous variety named *antrimolite* and a massive chalk-like variety named *harringtonite*, were shown by G. A. Kenngott, and A. Lacroix to be scolecites; and A. and R. Brauns showed that harringtonite and faröelite are the same minerals.

Several analyses of scolecite have been made.[116] The results were represented by C. F. Rammelsberg,[117] $CaAl_2Si_3O_{10}.3H_2O$, *calcium dialuminium orthotrisilicate*, in which the water was represented as being eq. to water of crystallization. A. Damour found the eq. of about a mol of water was lost at nearly 230°, and the bulk of the water was driven off at a temp. approaching redness. F. Rinne hence concluded that there are two scolecites, one a rhombic form with a mol less water than the other; the one with the higher water-content he called *metascolecite—vide infra*. The fact that one-third of the water is more easily expelled than the rest was considered by J. Lemberg to have some bearing on the constitutional formula. The dehydration curve of scolecite was also investigated by F. W. Clarke and G. Steiger, and C. Hersch. F. Zambonini obtained the following results with moist air:

| | 120° | 217° | 240° | 275° | 305° | 365° | 445° |
|---|---|---|---|---|---|---|---|
| Water lost . | 1·03 | 4·22 | 5·33 | 6·52 | 7·23 | 11·16 | 11·99 per cent. |

There is said to be a break between 275° and 330°; with dry air, the loss at 275° is greater, being about 7·20 per cent. A. Damour found that the water is resorbed by the mineral dehydrated at 300°, but after it had been heated to redness, it was no longer hygroscopic. F. Zambonini also studied the resorption of moisture by the dehydrated mineral, and he compared the state of the water in scolecite with that in silica hydrogel. G. Stoklossa said that the water is in a combined state, and he reported that there are really six different hydrates shown by breaks in the rehydration curve of scolecite dehydrated between 17° and 390°. Hence, he doubled C. F. Rammelsberg's formula, and wrote: $Ca_2Al_4Si_6O_{20}.6H_2O$. P. Groth regarded scolecite as a metasilicate, $CaAl\{Al(OH)_2\}(SiO_3)_3.2H_2O$. G. Tschermak assumed that orthosilicic acid is associated with an aluminosilicate, and wrote the formula $CaAl_2Si_2O_8.H_4SiO_4$. He said no water of crystallization is present, but a mol of water is an intrinsic part of the mol. F. W. Clarke represented the constitutional formula like that of natrolite (*q.v.*) with Ca in place of $Na_2$, and $6H_2O$ in place of $4H_2O$. The water in mesolite was studied by G. Friedel, and E. T. Allen and J. K. Clement.

A. Daubrée [118] found crystals of scolecite in the masonry of the baths of the thermal springs at Plombières, and Bourbonne; and R. Hermann noted that crystals of scolecite are forming in the plastic mass between the basaltic columns of Stolpen, Saxony. C. Doelter did not obtain scolecite from soln. containing the theoretical proportions of silicic acid, alumina, and lime; but prismatic crystals were formed when powdered scolecite was heated in a closed tube at 150° as indicated in connection with natrolite. This, in conjunction with A. Daubrée's experiment, shows that a low temp. is needed for the formation of this silicate. Scolecite occurs

massive and in nodules; fibrous and radiating; and in slender prismatic crystals. The crystals were measured by W. Phillips,[119] W. H. Miller, S. Kreutz, A. des Cloizeaux, R. Köchlin, J. Königsberger, O. Luedecke, V. von Zepharovich, etc. D. Brewster, and G. Rose showed that the crystals are monoclinic; and G. Flink gave for the axial ratios $a:b:c=0{\cdot}9764:1:0{\cdot}3434$, and $\beta=90°\ 42'$; while S. Kreutz gave $0{\cdot}97636:1:0{\cdot}34338$, and $\beta=89°\ 18'$. The monoclinic crystals of scolecite are stated to be isomorphous with those of natrolite. F. Rinne, and H. Haga and F. M. Jäger have studied the X-radiogram of scolecite. G. Tschermak made observations on the relations between the crystals of various zeolites. G. Flink, and F. Rinne made observations on the corrosion figures. The prismatic cleavage parallel to the (110)-face is nearly perfect. The twinning plane is (100). O. Luedecke, G. Wyrouboff, and C. Schmidt made observations on the twinning of the crystals of scolecite. The optic axial angle is medium; A. des Cloizeaux found for the red ray, $2E=53°\ 41'$; for the blue ray, $2E=59°\ 37'$; and for the red ray, $2H_a=35°\ 57'$, $2H_0=156°\ 4'$, and $2V=35°\ 1'$. G. Flink gave $2E=16°\ 48'$ for white light. Observations were also made by G. Schmidt, V. von Zepharovich, and O. Luedecke. A. des Cloizeaux found the optical axial angle $2E=60°\ 28'$ at 8·8°, and 59° 46′ at 146·5°. The sp. gr. was determined on many of the samples analyzed; the results range from 2·2–2·4; and the hardness 5–5½. G. Tammann found that in an atm. with the vap. press. of water $p$ mm., the percentage amount of water lost by a sample of scolecite was:

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| $p$ | 15·7 | 14·6 | 12·3 | 9·1 | 6·1 | 2·9 | 1·2 | 0·11 mm. |
| Loss | 0 | 0·004 | 0·013 | 0·017 | 0·029 | 0·042 | 0·079 | 0·105 per cent. |

F. Rinne found a marked change in the optical properties when the mineral is heated; and scolecite which has been strongly heated is rhombic *metascolecite*. O. B. Böggild said the extinction is oblique up to about 17°. The refraction is like that of cedar oil. A. des Cloizeaux gave for the index of refraction 1·502 for red light; and C. Schmidt, 1·6470 for Li-light, 1·6570 for Na-light, and 1·6675 for Tl-light. H. Michel gave $\alpha=1{\cdot}509$, $\beta=1{\cdot}515$. A. Lacroix found for the birefringence $\gamma-\alpha=0{\cdot}0083$, and O. B. Böggild, 0·007. The optical character is negative. W. W. Coblentz found that the ultra-red transmission spectrum shows the absorption bands of water up to $5\mu$, where it becomes opaque. The $3\mu$ water-band is complex. Observations on the pyroelectric behaviour of scolecite were made by R. J. Haüy, D. Brewster, P. Riess and G. Ross, G. W. Hankel, C. Schmidt, G. Friedel and A. de Grammont, and F. Rinne. O. Weigel studied the electrical conductivity of scolecite.

The mineral first described by H. Michel[120] as *okenite* was later called *metascolecite* because its composition, $CaO:Al_2O_3:SiO_2:H_2O=0{\cdot}93921:1{\cdot}0323:3:2{\cdot}9941$, so closely resembles that of scolecite while the physical properties are different. It belongs to the rhombic system. The sp. gr. is 2·244; the indices of refraction, $\alpha=1{\cdot}504$–$1{\cdot}512$, $\gamma=1{\cdot}508$–$1{\cdot}515$.

C. Doelter[121] found scolecite to be partially soluble in carbonated water. J. Lemberg found that when digested with soln. of potassium or sodium carbonate, the calcium is nearly all replaced by the alkali metal; similarly with soln. of potassium or sodium chloride; and with a soln. of sodium sulphate. G. Steiger also found that much of the calcium in scolecite can be replaced by silver, when the mineral is digested with a soln. of silver nitrate. The product was called *silver-scolecite*. F. W. Clarke and G. Steiger studied the action of ammonium chloride in a sealed tube at 350°, when some lime is replaced by ammonium, forming *ammonium-scolecite*. I. Zoch experimented with soln. of ammonium chloride and likewise found an exchange of bases. The subject was investigated by R. Gans, and G. Tschermak. Scolecite is decomposed by acids with the separation of gelatinous silica in the form, according to G. Tschermak, of orthosilicic acid. J. M. Theile studied the nature of the silicic acid so obtained. M. F. Heddle, and C. R. van Hise studied the transformation of scolecite in nature.

Several analyses of mesolite have been reported.[122] C. F. Rammelsberg[123]

found that the composition could be represented as a mixture of natrolite and scolecite. C. Hintze, V. Goldschmidt, H. L. Bowman, and G. Tschermak also regarded mesolite as variable mixtures of these two minerals; while R. Görgey and J. N. von Fuchs and A. F. Gehlen supposed it to be a double salt. Mesolite occurs massive with radiating and interlaced fibres sometimes called *cotton-stone*. A. des Cloizeaux, on optical grounds, regarded the crystals as triclinic with penetration twinning. E. Hussak also found complex twinning in the apparently triclinic crystals from Brazil. O. Luedecke attempted to prove that mesolite is trimorphous —A. des Cloizeaux's triclinic variety, rhombic galactite (*q.v.*), and the monoclinic form from Iceland. R. Görgey represented the axial ratios of the triclinic crystals as $a:b:c=0{\cdot}9747:1:0{\cdot}3122$, and $\beta=92°$. C. Schmidt argued that the triclinic form is really monoclinic like scolecite. S. Kreutz gave for the axial ratios of the monoclinic crystals:

| | Natrolite. | Mesolite. | Scolecite. |
|---|---|---|---|
| $a:b:c$ | 0·97853 : 1 : 0·35362 | 0·9747 : 1 : 0·3122 | 0·97636 : 1 : 0·34338 |
| $\beta$ | 90° | 92° | 89° 18′ |
| $\alpha, \beta, \gamma$ | 1·480, 1·482, 1·493 | 1·505, 1·505, 1·506 | 1·512, 1·519, 1·519 |
| $\gamma-\alpha$ | 0·013 | 0·001 | 0·007 |

G. Flink regarded the three minerals as isomorphous. H. L. Bowman gave for the optic axial angles with Na-light $2E=76{\cdot}25°$, $2V=81{\cdot}5°$. The prismatic cleavage is perfect; the sp. gr. 2·2–2·4; and the hardness 5. P. E. W. Oeberg found the sp. ht. to be 0·2464 between 14° and 99°. O. B. Böggild found the index of refraction very nearly 1·505. R. Görgey gave for the index of refraction 1·5021 for Li-light, 1·505 for Na-light, and 1·5072 for Tl-light; and J. Königsberger and W. J. Müller gave $\alpha=1{\cdot}5048$, $\beta=1{\cdot}5050$, and $\gamma=1{\cdot}5053$ with Na-light. E. T. Wherry gave the values indicated above. R. Görgey gave for the birefringence, $\gamma-\alpha=0{\cdot}0005$; $\gamma-\beta=0{\cdot}00028$; and $\beta-\alpha=0{\cdot}00023$. O. B. Böggild said that there is no double refraction with thin needles of mesolite, in some cases the impure mineral has a weak positive or negative birefringence. J. Lemberg found that by treatment with a soln. of an alkali chloride the lime is replaced by alkali; and with a soln. of thallium nitrate, G. Steiger obtained *thallium-mesolite*. F. von Richthofen, C. R. van Hise, and K. D. Glinka studied the effect of natural agents on mesolite.

W. Haidinger[124] described a zeolite which was obtained from Kilpatrick, Scotland, by A. Edington, and which was accordingly named **edingtonite.** A. Breithaupt named it *antiëdrite* on account of its hemihedral crystals; and F. Mohs, *brithynspar*—from βριθύς, heavy. O. Nordenskjöld found it at Bohlet, Sweden. Analyses were reported by W. Haidinger, J. Lemberg, M. F. Heddle, and G. Lindström. C. F. Rammelsberg computed the formula $BaAl_2Si_3O_{10}.3H_2O$, or **trihydrated barium dialuminium orthotrisilicate.** P. Groth regarded it as a metasilicate, $BaO.\{Al(OH)_2\}(SiO_3)_3.2H_2O$. G. Tschermak regarded it as a mixture, $H_4SiO_4.H_2BaAl_2Si_2O_9.H_2O$. F. W. Clarke represents it by:

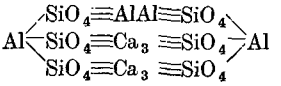
$$Al{\equiv}SiO_4{-}Al\begin{matrix}<SiO_4\\<SiO_4\end{matrix}\begin{matrix}\leqslant Ba\\\geqslant Al{-}Si_3O_8{\equiv}Al\\\leqslant Ba\end{matrix}+6H_2O$$

J. Lemberg obtained what he regarded as edingtonite by digesting artificial natrolite with a soln. of barium chloride for 12 days. The crystals are small and inconspicuous; and white with a grey or pink tinge. W. Haidinger regarded them as tetragonal with sphenoidal hemihedrism, with the axial ratio $a:c=1:0{\cdot}6725$; while O. Nordenskjöld represented them as rhombic with bisphenoidal hemihedrism, with axial ratios $a:b:c=0{\cdot}9872:1:0{\cdot}6733$. The cleavage is complete when parallel to (110). O. Nordenskjöld gave for the optic axial angles with Li-, Na-, and Tl-light, $2E=86°\ 51'$, $87°\ 17'$, and $88°\ 8'$ respectively; and $2V=52°\ 17'$, $52°\ 55'$, and $53°\ 10'$ respectively. The sp. gr. is 2·694–2·776; and the hardness 4–4½. A. des Cloizeaux found the double refraction strong and negative.

O. Nordenskjöld gave for the indices of refraction respectively with Li-, Na-, and Tl-light, $\alpha$=1·5344–1·5361, 1·5370–1·5395, 1·5401–1·5418; $\beta$=1·5466, 1·5492, and 1·5522; and $\gamma$=1·5511, 1·5540, and 1·5566. Edingtonite is decomposed by hydrochloric acid with the separation of gelatinous silicic acid.

T. Thomson found a mineral which he called *glottalite* near Port Glasgow, Scotland It occurred in octahedral crystals belonging to the cubic system. M. F. Heddle said that it is probably edingtonite mixed with harmotome. R. P. Greg and W. G. Lettsom regarded it as a chabazite. A. Sigmund's *galactite* from Weitendorf, Steiermark, was considered to be a mixture of natrolite and scolecite.

Flesh-coloured crystals of a rare mineral were found by T. Thomson[125] in the ejected masses on Monte Somma, Vesuvius, and called **sarcolite**—from *σάρξ*, flesh, in allusion to the colour. This mineral is not the same as the zeolitic sarcolite from Vicentin—*vide* gmelinite. R. J. Haüy seems to have considered these crystals to be analcite, and T. Monticelli and N. Covelli called it *analcime carnea*. A. Breithaupt regarded sarcolite as humboldtite or melilite; but A. des Cloizeaux, and *F. de Fonseca showed that it is more probably a definite mineral species.* The mineral was analyzed by A. Scacchi and M. del Lupo, C. F. Rammelsberg, and A. Pauly. C. F. Rammelsberg gave the formula $Na_6Ca_{27}Al_{20}Si_{30}O_{120}$; and P. Groth, $Na_2Ca_8Al_6Si_9O_{36}$. C. F. Rammelsberg supposed the mineral to be a complex of $Na_4SiO_4 : Ca_2SiO_4 : Al_4(SiO_4)_3$=3 : 27 : 10; or of $Na_6Al_2Si_3O_{12}$ +$9Ca_3Al_2Si_3O_{12}$. W. T. Schaller also favoured the hypothesis that in sarcolite, lime-sarcolite is in isomorphous admixture with soda-sarcolite, $3Na_2O.Al_2O_3.3SiO_2$; or **calcium dialuminyl-orthotrisilicate,** $Ca_3(AlO)_2Si_3O_{10}$, and **sodium dialuminyl-orthotrisilicate,** $Na_6(AlO)_2Si_3O_{10}$. The alternative view is to regard the one as *calcium dialuminium triorthosilicate,* $Ca_3Al_2(SiO_4)_3$, and the other as the corresponding sodium salt. F. W. Clarke takes this view and writes:




The mineral has not been prepared artificially, although it is possible that some of the reported syntheses of meionite may really refer to sarcolite. N. L. Bowen suggested that it has been formed in nature by the rapid cooling of a fused mixture of nephelite and pyroxene. R. J. Haüy assumed that the cubo-octahedral crystals belonged to the cubic system; but H. J. Brooke showed that the pseudo-cubic crystals are really tetragonal with pyramidal hemihedrism, and have the axial ratio $a : c$=1 : 0·88737; F. Zambonini gave 1 : 0·9861; and P. Groth, 1 : 0·4183. The crystals were studied by G. vom Rath, N. von Kokscharoff, F. Hessenberg, G. Strüver, C. F. Rammelsberg, and W. H. Miller. The cleavage is not apparent. A. Breithaupt gave 2·936 for the sp. gr.; C. F. Rammelsberg, 2·932; and F. Zambonini, 2·920. The last-named said that H. J. Brooke's value 2·545 is erroneous. The optical character of the uniaxial crystals is positive; F. Zambonini gave for the indices of refraction for Li-, Na-, and Tl-light respectively $\omega$=1·6000, 1·6035, and 1·6067; and $\epsilon$=1·6111, 1·6147, and 1·6180. He considers that A. Pauly's values $\omega$=1·6404 and $\epsilon$=1·6566 for Na-light must refer to some other mineral. The double refraction is strong and positive, $\epsilon-\omega$ being 0·0111, 0·0112, and 0·0113 respectively for Li-, Na-, and Tl-light.

In 1790, F. de Bellevue[126] discovered a yellow mineral at Capo di Bove, Rome, which J. C. Delamétherie called **melilite**—from *μέλι*, honey—in allusion to the colour—*vide supra*. The crystals which occur at Somma were called *humboldtitite*—after F. H. A. von Humboldt; *somervillite*, by H. J. Brooke; *zurlite*—after S. Zurlo—by V. Ramondini. The first attempt at analysis was made by P. Carpi. The mineral was subsequently analyzed by F. von Kobell, A. Damour, and many others.[127]

The selection of a formula for melilite has proved to be very difficult. The earlier analyses were not concordant. C. F. Rammelsberg[128] gave the

formula $(Na,K)_2(Ca,Mg)_{11}(Fe,Al)_4Si_9O_{36}$; A. des Cloizeaux gave the analogous formula $12RO.2R_2O_3.9SiO_2$; W. Stahl, $R_2O.29RO.3R_2O_3.20SiO_2$; C. Hintze, $(Ca,Mg,Fe)_6(Al,Fe)_2Si_5O_{19}$; and P. Groth, $(Ca,Mg)_6(Al,Fe)_2Si_5O_{19}$. J. H. L. Vogt suggested that the natural melilites are mixtures of gehlenite, $3CaO.Al_2O_3.2SiO_2$, and what he called akermanite, $4CaO.3SiO_2$—*vide* akermanite. This hypothesis failed, because, as W. T. Schaller expressed it, the end-member gehlenite is not a distinct and definite species, but is itself a variable mixture of definite end-members; and the other end-member akermanite was given a wrong formula—it should have been $4MgO.8CaO.9SiO_2$. F. Zambonini suggested three possible explanations of the composition of melilites: (i) they may be mixtures of the two types of compounds $R''SiO_3$ and $R''_3R'''_2Si_2O_{10}$; (ii) they may have the general composition $R''R'''_2Si_2O_8.nR''_2SiO_4$; and (iii), as G. Bödlander suggested, the optically negative melilites may be mixtures of $R''SiO_3$ and $R''R'''_2SiO_4$; and the optically positive melilites, of $R''SiO_3$ and $R''_3R'''_2SiO_6$. He considered that G. Bodländer's theory agreed well with the facts. W. Vernadsky gave $R''R'''_2Si_2O_8.5R_2SiO_4$. K. Busz and F. W. Rüsberg suggested that melilite is a mixture either of gehlenite and $R''_3Si_2O_7$, or of gehlenite, $Ca_2SiO_4$, and $CaSiO_3$. F. W. Clarke suggested that the melilites are mixtures of $2CaO.Al_2O_3.SiO_2$ and $9CaO.Al_2O_3.6SiO_2$. A. F. Buddington made a number of mixtures of akermanite, $Ca_2MgSi_2O_7$, gehlenite, $Ca_2Al_2SiO_7$, and $3R'O.R_2O_3.3SiO_2$, where $R'=Na_2$ or Ca; and $R=Fe$ or Al and found all types of melilite minerals as solid soln. of these constituents. A. N. Winchell represented the melilite minerals by $R_5O_7$, where R includes the silicon; gehlenite and akermanite are considered to be the dominant members of the series; and the alkalies assigned to $Na_2Si_3O_7$ or $NaAl_3SiO_7$. He said that unlike W. T. Schaller, and A. F. Buddington, he found grossular and andradite are not miscible with the melilites. An excess of silica may exist in the interatomic spaces in the molecules.

In nearly all these cases there is little evidence to show that the calcium meta- and ortho-silicates can be united in isomorphous mixture with the alleged end-members of the melilite group. The assumed end-members are in most cases quite imaginary compounds. It is generally admitted that the melilites are isomorphous mixtures of a certain number of end-products; and W. T. Schaller added that these products must satisfy the requirements of isomorphism; they must be related chemically; they must have a similar crystal form; they must form mixtures with the same crystal forms as the end-members themselves; and it must be possible to represent the composition of all natural melilites as mixtures of these end-members. He claimed that these conditions are satisfied by assuming that all members of the melilite and gehlenite series, including fuggerite, can be represented as isomorphous mixtures of the four primary compounds: sarcolite, $3CaO.Al_2O_3.3SiO_2$; soda-sarcolite, $3Na_2O.Al_2O_3.3SiO_2$; velardenite, $2CaO.Al_2O_3.SiO_2$; and akermanite, $4MgO.8CaO.9SiO_2$. These have been discussed individually elsewhere. See also gehlenite.

Melilite is always of pyrogenetic origin; but it is found only in the younger eruptive rocks; never in the plutonic rocks or crystalline schists. It is usually associated with nephelite, and leucite, and it sometimes takes the place of felspar.[129] This subject has been discussed by F. D. Adams, F. W. Clarke, E. S. Larsen and F. J. Hunter, C. H. Smyth, A. Stelzner, and A. E. Torneböhm. Melilite has been reported in slags by L. Bourgeois,[130] F. Fouqué, J. S. Dittler, P. Heberdey, J. H. L. Vogt, J. Percy, F. Bothe, C. J. B. Karsten, P. Berthier, K. Busz and F. W. Rüsberg, D. Forbes, A. Gurlt, F. Zambonini, G. Bödlander, A. Firket, etc. G. Bodländer observed it in portland cement; and L. Appert and J. Henrivaux found it to be produced in the melting of ordinary glass. L. Bourgeois prepared melilite by fusing a mixture of silica, lime, and alumina in the required proportions provided a salt of iron, magnesium, or manganese was present. It also forms more readily if some soda is present; and all natural melilites contain soda. Melilite was also produced by J. Morozewicz, and F. Fouqué and A. Michel-Lévy, by cooling

basaltic, augitic, and other rock magmas. Other minerals—olivine, plagioclase, augite, corundum, and spinel—were produced at the same time. *F. Fouqué* obtained it by crystallization from a fused mixture of lime and augitic andesine, or basalt. C. Doelter and E. Hussak found melilite among the products obtained by cooling fused garnet or vesuvianite. C. Doelter synthesized melilite by fusing tourmaline with calcium chloride and sodium fluoride; K. Bauer, by fusing mica-schist, nepheline, or andesine mixed with lithium chloride, and sodium and calcium fluorides; R. Medanich, by fusing a mixture of garnet, sodium hydrophosphate, sodium vanadate, and lithium chloride; and C. F. W. A. Oetling, by fusing a mixture of silica, alumina, iron oxide, magnesia, lime, alkali carbonate, and calcium fluoride. H. Buddington's work on the synthesis of the melilites is indicated above.

Melilite occurs in euhedral crystals and anhedral grains. The euhedral crystals are short square or octagonal prisms, or tetragonal plates. The colour is white, pale yellow, greenish-yellow, reddish-brown, or brown. The crystals belong to the tetragonal system, and A. des Cloizeaux [131] gave for the axial ratio $a:c=1:0{\cdot}45483$. The crystals may be cruciform twins with the vertical axes only slightly inclined, or nearly at right angles. The cleavage parallel to (001) is distinct, and indistinct parallel to (100). The crystals show some optical anomalies. The sp. gr. ranges from 2·9–3·1, and the hardness is 5. V. S. Deleano and E. Dittler gave 1180° for the m.p.; and J. H. L. Vogt, 1100°. The last-named estimated the latent heat of fusion to be 90 cals., and the total heat of fusion 390 cals. E. Jannetaz found the square root of the ratio of the thermal conductivities in the direction of the base and of the chief axis to be 1·19. The indices of refraction are moderately high. H. Rosenbusch reported for red light, $\omega=1{\cdot}6312$, and $\epsilon=1{\cdot}6262$; and for yellow light, $\omega=1{\cdot}6339$, and $\epsilon=1{\cdot}6291$. Values were also measured by E. S. Larsen and J. F. Hunter, and K. Busz and F. W. Rüsberg. The birefringence is weak. H. Rosenbusch reported for Li-light $\epsilon-\omega=0{\cdot}00530$; for Na-light, 0·00517; and for Tl-light, 0·00591. The double birefringence is weakest for yellow light and increases towards both ends of the spectrum. The optical character is positive or negative. The opposite characters appear in different parts of the same crystal, and are sometimes arranged concentrically in zones with intermediate isotropic portions. The two end-members sarcolite and akermanite are optically positive, whereas melilite is generally negative although positive varieties are known. W. T. Schaller [132] suggests two explanatory hypotheses. In one, a true compound of sarcolite and akermanite is formed which is optically negative; the melilites are solid soln. of this compound with smaller proportions of akermanite, sarcolite, and velardenite. If the indices of refraction $\epsilon$ and $\omega$ are not linear functions of the composition, as illustrated diagrammatically in Fig. 180, then the negative melilites may be isomorphous mixtures of two positive minerals. A. Stelzner studied the pleochroism of the crystals. Conc. hydrochloric acid decomposes the melilites with the separation of gelatinous silicic acid.

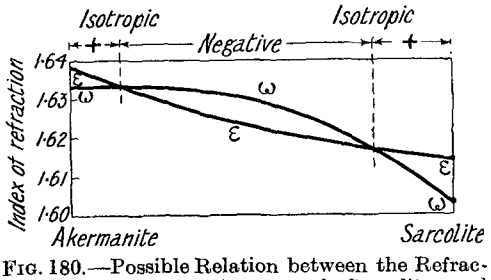



FIG. 180.—Possible Relation between the Refractive Indices of Mixtures of Sarcolite and Akermanite.

An alteration product of melilite from Cebolla Creek, Colorado, was reported by E. S. Larsen and W. T. Schaller, and named *cebollite*. The analysis corresponds with $Ca_5H_4Al_2Si_3O_{16}$. If, as F. W. Clarke suggested, the absence of the alkaline reaction with phenolphthalein when the powdered mineral is moistened with water indicates that CaOH-groups are absent, the graphic formula can be represented $Ca=SiO_4=[Ca.SiO_4 \equiv Ca\{Al(OH)_2\}]_2$, *calcium dihydroxyaluminium triorthosilicate*. The crystals are probably

rhombic, biaxial, positive, $\alpha=1{\cdot}595$, $\beta=1{\cdot}600$, and $\gamma=1{\cdot}628$. The sp. gr. is 2·96, and the hardness 5. The mineral gelatinizes with acids, and resembles the zeolites in its general properties.

The early observations on the distinction between heulandite and stilbite are indicated in connection with the latter. **Heulandite** is the *stilbite anamorphique* of R. J. Haüy,[133] and the *euzeolite* of A. Breithaupt.

The *beaumontite* of A. Levy—named after E. de Beaumont—was found in yellow crystals at Jones' Fall, Baltimore, and was considered by F. Alger, J. D. Dana, A. des Cloizeaux, J. J. Berzelius, A. Schmidt, E. Mallard, G. H. Williams, and W. Klein to be identical with heulandite. G. Rose did not agree that the two minerals are identical; but E. V. Shannon found the crystallographic and optical properties, and the chemical composition to be in such close agreement that beaumontite could be regarded only as a variety of heulandite. E. Hitchcock reported a mineral which he called *lincolnite* from Deerfield; but J. J. Berzelius, and A. des Cloizeaux showed that it is heulandite. Monoclinic crystals of a mineral from the granite blocks of Fonte del Prete, Elba, were named *oryzite*—from *ὄρυζα*, rice—by G. Grattarola, in allusion to the shape of the crystals. A. Arzruni, and P. Groth suggested that it is identical with heulandite. He also obtained minute acicular crystals of a mineral from the granite of San Piero, Elba, which he named *pseudonatrolite* on account of its resemblance to natrolite. He later showed that it more closely resembles heulandite. F. W. Clarke said that pseudo-natrolite has nearly the same composition as stellerite, but with 2 mols less water. G. d'Achiardi suggests it is a variety of pilolite. A variety called *metaheulandite* was studied by G. Stoklossa, O. Weigel, K. H. Scheumann, and F. Rinne.

The old analyses of J. C. F. Meyer,[134] and L. N. Vauquelin gave a very good approximation of the composition of heulandite. Many analyses have been made since then; and it is not always clear whether heulandite or stilbite was under examination. The bases are lime, and small proportions of soda and potash; a little lithia is sometimes present. P. Jannasch, F. Zambonini, B. Mauritz, O. Weigel, and F. W. Clarke and G. Steiger found samples with up to 3·65 per cent. of strontia; and D. Lovisato, a sample with 2·55 per cent. of baryta. C. F. Rammelsberg[135] first summarized the analyses by the formula $CaAl_2Si_6O_{16}.5H_2O$. P. Jannasch, and F. Rinne used somewhat similar formulæ. This is used to-day as the best representative formula; it makes heulandite **pentahydrated calcium dialuminium dimesotrisilicate,** $CaAl_2(Si_3O_8)_2.5H_2O$. C. F. Rammelsberg later modified the formula to $H_4CaAl_2Si_6O_{18}.3H_2O$, which C. Bodewig wrote $H_4CaAl_2(SiO_3)_6.3H_2O$. G. Tschermak used a similar formula. Later still, C. F. Rammelsberg considered the mineral to be a mixture of two such silicates. H. S. Washington used the formula $(CaSi_2)(AlSi_2O_8)_2.5H_2O$, regarding heulandite as a salt of the aluminosilicic acid, $H_5AlSi_2O_8$. C. S. Ross and E. V. Shannon gave $(Ca,K_2,Na_2)O.Al_2O_3.7SiO_2.5H_2O$. C. Doelter represented heulandite as a mixture of silicic acid and a silicate: $CaAl_2Si_4O_{12}.2H_2SiO_3.3H_2O$. S. Hillebrand, and E. Baschieri separated from heulandite what he called *heulanditic acid,* $H_{10}Si_6O_{17}$; and assumed that heulandite is a salt of this acid. G. Tschermak later said that the mineral is a complex of four calcium dialuminium silicates. F. W. Clarke represented heulandite by a formula like that employed for stilbite, but with a mol less water.

A. Damour[136] found that heulandite from Faröe loses part of its water in dry air, and regains it in ordinary air; at 100°, the mineral loses 2·1 per cent. of water, and 8·7 per cent. between 100° and 150°; the lost water is regained by exposure to air for 24 hrs. At 190°, the mineral loses 12·3 per cent. of water, and all but 2·1 per cent. is regained by two months' exposure to ordinary air. P. Jannasch found the loss with the fine-grained mineral was greater (or faster) than with the coarse-grained mineral. A. A. Ferro, C. Bodewig, and C. Hersch made observations on this subject. F. Rinne found the loss greater (or faster) in vacuo than in air dried by sulphuric acid; and F. Zambonini found the loss over sulphuric acid in vacuo to be:

| Time | 3 | 5 | 24 | 48 | 72 | 118 | 190 | 310 | 550 hrs. |
|---|---|---|---|---|---|---|---|---|---|
| Loss | 2·36 | 2·62 | 4·86 | 5·25 | 5·44 | 5·63 | 5·83 | 6·08 | 6·08 per cent. |

The losses in dry air at different temp. were:

| | 61° | 101° | 230° | 303° | 375° | 412° |
|---|---|---|---|---|---|---|
| Loss . . . | 2·99 | 4·70 | 12·04 | 13·9 | 14·30 | 14·80 per cent. |

and in moist air:

| | 61° | 101° | 151° | 234° | 272° | 284° | 369° | 420° |
|---|---|---|---|---|---|---|---|---|
| Loss . | 1·63 | 3·02 | 5·08 | 8·20 | 11·08 | 12·00 | 13·92 | 14·74 per cent. |

Although there is a break in the curves, there is nothing to show that any part of the contained water is constitutional. The lost water is rapidly regained if the temp. of calcination has not exceeded 300°. G. Stoklossa found that at 17°, in air sat. with moisture, heulandite is in equilibrium with the atm. when it contains about 16 per cent.—eq. to 5·5 mols.—of moisture, and therefore assumes that the ordinary formula should be doubled, $Ca_2Al_4Si_{12}O_{32}.11H_2O$. While the dehydration curve is continuous, he found that the rehydration curve of heulandite, which has been heated to a series of temp. between 17° and 380°, shows a number of breaks. A. Beutell also said that there are 11 mols. of water in heulandite, and all are present as water of hydration. O. Weigel inferred that the zeolites are neither adsorption products nor colloids of the nature of gels. Contrary to A. Beutell, O. Weigel maintained that the hydration and dehydration curves are practically reversible at temp. below 180°; and in agreement with K. H. Schümann, no permanent change is caused by dehydration up to a content of $3H_2O$; the dehydration curve is almost continuous; the breaks at higher temp. would not occur with integral mols if any considerable decomposition occurred; the curves of O. Weigel, and K. H. Schümann are concordant up to 200°; and optical observations give no evidence of decomposition. Hence, A. Beutell's hypothesis is not proven. O. Weigel considered the water to form a special kind of solid soln. which, as a result of the directing forces of the relatively rigid silicate lattice on the easily mobile water mols. shows some analogy to true hydrates. He added:

> The water in zeolites possesses the property of mobility to a high degree whilst the silicate space-lattice must be considered as relatively rigid. The water mols. entering into the mesh cavities of this lattice will tend, according to their thermal press., to become uniformly distributed; on the other hand, the silicate mols. (or portions thereof) in the crystal lattice will tend to hold by attraction the water mols., or a portion thereof, in position in entire conformity with the symmetry of the lattice. Both tendencies can be simultaneously satisfied only if the number of water mols. is a complete multiple of the number of silicate mols., for only under these conditions can the water mols. arrange themselves in identical formation round each of the other mols. of the silicate lattice. It is only exceptionally favourable mixtures such as these that give the straight line in the dehydration curve. All other mixtures correspond to points on the irregular curves. The zeolites are therefore considered to be solid soln., but it is an open question whether the water in this soln. reacts with the solvent, *i.e.* forms an intimate compound with the silicate, or whether it enters the lattice as a mol. dissociated into its atoms, or into ions.

U. Panicchi found that dehydrated zeolites absorb air and the absorbed air is richer in oxygen than is ordinary air; thus a gram of zeolite previously heated to 240° absorbed 1·093 c.c. of air which contained 28 per cent. of oxygen. G. Tammann, K. H. Schümann, and E. Löwenstein measured the vap. press. of heulandite and some of its substitution products—potassium-heulandite, and calcium-heulandite. The vap. press. is a continuous function of the combined water so that no breaks appear in the curve. The latter found that when in equilibrium with an atm. where the partial press. of the water-vap. was $p$ mm., the mineral lost:

| $p$ . | 21·58 | 19·60 | 17·63 | 13·45 | 8·82 | 4·41 | 1·75 | 0·56 | 0·18 mm. |
|---|---|---|---|---|---|---|---|---|---|
| Loss . | 0·06 | 0·12 | 0·24 | 0·35 | 0·50 | 0·79 | 1·15 | 1·56 | 3·70 per cent. |

Similar measurements were made with calcium- and potassium-heulandites.

Heulandite occurs principally in basaltic rocks associated with other zeolites, it also occurs in gneiss and occasionally in metalliferous veins. C. Doelter [137] recrystallized the powdered mineral by digesting it in water sat. with carbon dioxide,

in a sealed tube at 170° for 14 days. He also made it by digesting a mixture of powdered anorthite, freshly precipitated silica, and carbonated water in a sealed tube for 14 days at 200°.

Heulandite occurs in globular forms and granular; in flattened euhedral crystals; and in groups of subparallel crystals producing curved surfaces. The colour is various shades of white passing into grey, red, and brown. A. Breithaupt[138] considered heulandite belonged to the triclinic system; and G. vom Rath and F. Hessenberg obtained triclinic varieties from Elba and Iceland. A. des Cloizeaux showed that the crystals belong to the monoclinic system, and have axial ratios $a:b:c=0{\cdot}4035:1:0{\cdot}4788$ and $\beta=63°\ 40'$; recalculating the axial ratios to the pseudorhombic from $a:b:c=0{\cdot}40347:1:0{\cdot}8586$, and $\beta=88°\ 34\frac{1}{2}'$. The crystals were studied by F. Rinne, A. Sigmund, O. Tietze, and J. Königsberger. The twinning plane of the crystals is (100). The cleavage parallel to (010) is perfect. F. Rinne studied the corrosion figures; and also the X-radiograms. According to A. des Cloizeaux, the optic angles vary from 0°–92°, usually $2E=52°$ for the red ray, and 53° for the blue ray. P. Gaubert gave $2V=31°\ 22'$. E. Artini found $2E=81°\ 14'$–$94°\ 27'$ in yellow light, and 103° 50′ in white light at 150°. O. Tietze gave $2E=51°\ 49'$. F. Rinne, A. des Cloizeaux, E. Mallard, W. Klein, and G. B. Negri, measured the influence of temp. on the optic angles and the planes of the optic axes. E. Mallard found that raising the temp. to 150° changes the axial angles and plane, but the original condition is restored when the crystals regain their water; but if heated to 180° the sections become opaque, and the change is permanent. F. Rinne said that the various changes which occur are due to the loss of water; the high temp. form is called *metaheulandite*. The sp. gr. of heulandite is between 2·17 and 2·22; V. Goldschmidt found a sample of sp. gr. 2·202; and E. Billows, one, 2·17. F. Cornu has drawn attention to the quartz inclusions sometimes found in heulandite vitiating these determinations. P. Gaubert measured the sp. gr. of the mineral. After being heated to different temp. the hardness is between $3\frac{1}{2}$ and 4. The action of heat on heulandite is indicated above. C. Doelter obtained a pyroxenic mineral, anorthite, and a glassy matrix by slowly cooling molten heulandite. P. E. W. Oeberg gave for the sp. ht. of heulandite 0·2682. O. Mulert found the heat of soln. in dil. hydrofluoric acid to be 0·5501 Cal. per gram; and he calculated the heat of formation to be $CaO+Al_2O_3+6SiO_2+Aq.=CaO.Al_2O_3.6SiO_{2cryst.}+59{\cdot}44$ Cals., or 0·141 Cal. per gram. R. Brauns, and F. Rinne have discussed the optical anomalies. According to A. Michel-Lévy and A. Lacroix, the indices of refraction are $\alpha=1{\cdot}498$, $\beta=1{\cdot}499$, and $\gamma=1{\cdot}505$; P. Gaubert obtained $\alpha=1{\cdot}4996$–$1{\cdot}4998$; $\beta=1{\cdot}5003$–$1{\cdot}5008$; and $\gamma=1{\cdot}5069$–$1{\cdot}5070$. C. S. Ross and E. V. Shannon gave $\alpha=1{\cdot}482$; $\beta=1{\cdot}485$; and $\gamma=1{\cdot}489$. P. Gaubert measured the change in the indices of refraction on heating to 200°; $\alpha$ changed from 1·5004–1·4651; $\beta$, from 1·5015–1·4651; and $\gamma$, from 1·5078–1·4747. The birefringence is low; A. Michel-Lévy and A. Lacroix gave $\gamma-\alpha=0{\cdot}0066$. The optical character is positive. O. Weigel studied the electrical conductivity of heulandite.

According to P. Gaubert,[139] the coloration of heulandite by coloured liquids is due to the adsorption of the coloured liquid itself. F. W. Clarke found that powdered and moistened heulandite reacts feebly alkaline to phenolphthalein; and G. A. Kenngott, alkaline to litmus. G. Steiger, S. Hillebrand, and C. Doelter found that heulandite is perceptibly soluble in water; and the solubility in carbonated water or in soln. of sodium carbonate was found by C. Doelter to be greater. J. Lemberg digested heulandite with soln. of sodium and potassium chlorides for about a week; the lime was displaced by the alkali, forming respectively *sodium-heulandite*, and *potassium-heulandite*. He also studied the action of soln. of sodium silicate, borate, and phosphate. F. W. Clarke and G. Steiger heated heulandite with ammonium chloride in sealed tubes at 350°, and obtained an *ammonium-heulandite*. When heulandite is digested with hot hydrochloric acid, a granular to a gelatinous silicic acid may be formed; with conc. acid, E. Löwenstein obtained

finely powdered silicic acid. S. Hillebrand said that the air-dried acid is coloured pale blue by methylene-blue. F. Rinne, and F. Cornu also studied the action of acids on heulandite.

H. J. Brooke [140] found a zeolite mineral at Strontain, Scotland, and named it **brewsterite**—after D. Brewster. It has been found in a number of other localities. A. Breithaupt called it *diagonite*. Analyses were reported by A. Connell, T. Thomson, F. Rinne, and J. W. Mallet. C. F. Rammelsberg studied the relation of brewsterite to heulandite and to epistilbite; and finally represented it by the formula $R_2Al_4Si_{11}O_{30}.10H_2O$; and F. Rinne gave $R_2Al_4Si_{12}O_{32}.11H_2O$, where R represented (Sr,Ba,Ca,$Na_2$,$K_2$). C. Hintze gave a somewhat similar formula; and P. Groth gave $(Sr,Ba)Al_2Si_6O_{16}.5H_2O$; that is, **pentahydrated barium (and strontium) dialuminium dimesotrisilicate,** $BaAl_2(Si_3O_8)_2.5H_2O$, and $SrAl_2(Si_3O_8)_2.5H_2O$. F. W. Clarke represented it by

$$Al{\equiv}Si_3O_8{-}Al\begin{matrix}<Si_3O_8>Ba\\<Si_3O_8>Sr\end{matrix}Al{-}Si_3O_8{\equiv}Al+10H_2O$$

analogous with the formula for heulandite. It may possibly be a solid soln. of barium, strontium, calcium, and alkali salts. G. Tschermak considered it to be a solid soln. of two type silicates as in the case of heulandite.

The colour of brewsterite is grey, green, yellow, or brown. The crystals were measured by W. Haidinger, J. W. Mallet, W. H. Miller, etc. H. J. Brooke's data show that the prismatic crystals are monoclinic, with the axial ratios $a:b:c=0{\cdot}40482:1:0{\cdot}42042$, and $\beta=86°\ 20'$. The cleavage parallel to (010) is perfect, and traces of cleavage are found parallel to (100). A. des Cloizeaux gave for the optic axial angle $2E=94°$ for the red ray, and 93° for the blue ray; A. Lacroix and A. Michel-Lévy gave $2V=65°$. A. des Cloizeaux found that raising the temp. from 8·8°–105·5°, altered $2E$ from 93° 43′–95° 26′. W. Klein, and F. Rinne made observations analogous with those obtained with heulandite. The sp. gr. is 2·1–2·5; and the hardness 5–5½. A. Damour reported that brewsterite loses 1·65 per cent. of water when exposed to dried air at ordinary temp. for a month. At 100°, 0·2 per cent. was lost in 2 hrs.; at 130°, 7 per cent. was lost, and all but 2·7 per cent. regained by exposure to ordinary air for 48 hrs. At 190°, the loss was 8·2 per cent., and all was regained after 48 hrs.' exposure to ordinary air; at 270°, 10 per cent. was lost, and all but 1·2 per cent. was regained after 8 days' exposure. At a dull red-heat the loss was 12·8 per cent., and, at a bright red-heat, 13·3 per cent. O. Weigel showed that the loss of water appears to be a continuous process —*vide* heulandite. A. Lacroix and A. Michel-Lévy gave for the mean index of refraction 1·45, and for the birefringence $\gamma-\alpha=0{\cdot}012$. A. Damour found the crystals to be pyroelectric. Brewsterite is decomposed by acids with the separation of granular silicic acid.

A. Cronstedt [141] made references to *zeolites crystalli ad centrum tendentes* and *zeolites lammellaris;* and J. G. Wallerius, C. A. S. Hofmann, and J. C. F. Meyer regarded the latter as a foliated zeolite. A. G. Werner described four members of the zeolites and called them *Mehlzeolith* or *mealy zeolite; Faserzeolith* or *fibrous zeolite; Strahlzeolith* or *radiated zeolite;* and *Blatterzeolith* or *foliated zeolite.* J. C. Delamétherie called radiated zeolite, *zeolite nacrée* or stilbite; and R. J. Haüy regarded this zeolite as the type member of a species which he called **stilbite**—from στίλβη, lustre—and foliated zeolite was considered to be a variety which he called *stilbite anamorphique.* A. Breithaupt supposed radiated and foliated zeolite to be distinct species, and called the former *desmine*—from δέσμη, a bundle—and the latter *euzeolite.* H. J. Brooke followed R. J. Haüy and called radiated zeolite stilbite, and foliated zeolite, heulandite—after H. Heuland—in this H. J. Brooke has been followed by the French and British mineralogists; the Germans call H. J. Brooke's stilbite, *desmine;* and sometimes they call heulandite, *stilbite.*

F. S. Beudant studied two varieties of stilbite which he designated *hypostilbite* and *sphærostilbite*—the hypodesmine and sphærodesmine of A. Breithaupt. These varieties were discussed by E. F. Glocker, J. F. L. Hausmann, A. des Cloizeaux, and S. Haughton. J. D. Dana regarded hypostilbite as a separate species, but J. D. Dana later included it with stilbite with a rather low percentage of silica. L. Liebener and J. Vorhauser, and F. Bukeisen described a mineral from Puflerloch, Tyrol, which he called *puflerite*. G. A. Kenngott regarded it as a stilbite. J. W. Mallet regarded laumontites from Skye, and Bombay as hypostilbites. G. vom Rath called crystals of a mineral lining cavities in the granite of San Piero, Elba, *foresite*—after G. F. Forresi. It was analyzed by A. d'Achiardi, and F. Sansoni; and these analyses were recalculated by C. F. Rammelsberg. A. des Cloizeaux showing that it is a variety of stilbite. The *syhedrite* of C. U. Shepard is stilbite. V. Rosicky and S. J. Thugutt described a mineral which they called *epidesmine*. Its chemical composition is near that of stilbite, $3Ca(Na_2,K_2)Al_2Si_6O_{16}.20H_2O$; it furnishes rhombic crystals of sp. gr. 2·16.

The oldest analyses of stilbite are by W. Hisinger,[142] J. N. Fuchs and C. G. Retzius; numerous others have since been made. C. F. Rammelsberg[143] deduced the formula $CaAl_2Si_6O_{16}.6H_2O$, and assumed that this silicate was associated with $Na_2Al_2Si_6O_{16}.6H_2O$. This makes stilbite **hexahydrated calcium dialuminium dimesotrisilicate,** $CaAl_2(Si_3O_8)_2.6H_2O$. W. Fresenius postulated that stilbite is a mixture of two silicates. C. Doelter inferred from his observation on the formation of anorthite during the cooling of molten stilbite, and A. Damour's observations that two mols of combined water are present, that stilbite contains two mols of silicic acid in solid soln., *viz.* $CaAl_2Si_4O_{12}.2H_2SiO_3.4H_2O$. P. Groth used C. F. Rammelsberg's formula, $(Ca,Na_2,K_2)Al_2Si_6O_{16}.6H_2O$, but assumed that in some cases another silicate, $CaAl_2Si_2O_8.3H_2O$, is present. G. Tschermak first gave $H_2CaAl_2Si_6O_{18}.4H_2O$; later, he added another mol. of water; and later still, he assumed that the stilbites are really associations of four different calcium aluminium silicates. F. W. Clarke gave $CaAl_6(Si_3O_8)_6.18H_2O$, and later, he gave:

$$Al{\equiv}Si_3O_8{-}Al{<}\begin{matrix}Si_3O_8{>}Ca\\Si_3O_8{<}Ca\end{matrix}Al{-}Si_3O_8{\equiv}Al{+}12H_2O$$

E. Manasse used a graphic formula in which it was assumed that stilbite is a mixed orthosilicate and mesotrisilicate. C. Hersch also set up a constitutional formula for this substance.

A. Damour[144] found that stilbite loses 1·3 per cent. of water at 100°; 13 per cent. between 100° and 150°, and all but 3 per cent. of the lost water is regained by 5 days' exposure to ordinary air; at 170°, 16 per cent. of water was lost, and rather less than half of this is regained by 15 days' exposure to ordinary air. C. Hersch found the loss of water after two hours' heating at different temp. amounted to:

| | 104° | 150° | 210° | 250° | 290° | Red heat |
|---|---|---|---|---|---|---|
| Loss | 3·84 | 8·71 | 12·16 | 13·60 | 14·78 | 18·63 per cent. |

F. Rinne's observations agreed better with A. Damour's than with C. Hersch's. E. Manasse concluded that the water given off below 250° is zeolitic water, and that given off above that temp. is constitutional water. F. Zambonini measured the loss of water in dry and moist air suffered by stilbite with 18·61 per cent. of water; and found for dry air:

| | 112° | 175° | 210° | 265° | 328° | 385° | 440° |
|---|---|---|---|---|---|---|---|
| Loss | 7·88 | 11·51 | 13·56 | 14·68 | 15·66 | 15·97 | 17·56 per cent. |

and he inferred that the dehydration process is greatly dependent on the humidity of the air, because for moist air he found:

| | 118° | 173° | 215° | 260° | 310° | 380° |
|---|---|---|---|---|---|---|
| Loss | 3·71 | 9·69 | 12·59 | 13·85 | 14·65 | 15·75 per cent. |

E. Löwenstein found that when in equilibrium with water vap. at a partial press. $p$ mm., stilbite had lost the following proportions of water at 25°:

| $p$ | 21·58 | 19·60 | 17·63 | 13·45 | 8·52 | 4·41 | 1·75 | 0·56 | 0·18 mm. |
|---|---|---|---|---|---|---|---|---|---|
| Loss | 0·11 | 0·20 | 0·32 | 0·43 | 0·63 | 0·92 | 1·32 | 1·98 | 4·21 per cent. |

Similar measurements were made with calcium-, potassium-, and ammonium-stilbites. A. Beutell and K. Blaschke also measured the rehydration of stilbite dehydrated at different temp. and inferred that the breaks in the curve indicate that 14 hydrates are formed.

Stilbite occurs in cavities in amygdaloidal, basaltic, and other rocks. The high degree of hydration of the mineral favours the view that it is not a high temp. product. It is apparently being formed by the action of the thermal waters at Olette on the granite. E. Manasse discussed its formation from orthoclase at San Piero. E. Baur and F. Becke noted the formation of a stilbitic substance when a mixture of silica, alumina, lime, alkali hydroxide, and water is heated for 12–16 hrs. at 350°. E. Tischler found that when a mixture of 96 parts of kaolinite, 80 of silica, and 20 of lime is repeatedly exposed to the action of steam, after grinding, a silicate of the composition $CaAl_2Si_6O_{16}.6{\cdot}12H_2O$ is formed, and the crystals are sometimes found in sand-lime bricks.

The crystals of stilbite are often grouped in nearly parallel positions, forming sheaf-like aggregates; in divergent or radiated forms sometimes spherulitic; in thin lamellar prisms; and pseudo-rhombic pyramids; the colour is white, but may be tinged grey, yellow, brown, or red. R. J. Haüy [145] described the crystals as rhombic pyramids; but A. Breithaupt showed that like harmotome they belong to the monoclinic system and that the pseudo-rhombic form is produced by cruciform twinning. A. von Lasaulx found the axial ratios of the monoclinic crystals to be $a:b:c=0{\cdot}76227:1:1{\cdot}19401$ and $\beta=50°\ 49\frac{3}{4}'$. G. Tschermak gave $a:b:c=0{\cdot}4628:1:0{\cdot}3811$, and $\beta=89°\ 30'$. According to L. Langemann, the crystals are composed of triclinic individuals; and F. Rinne showed that when heated, the mol. structure becomes like that of a rhombic crystal. The crystals were studied by B. Jazek, and J. Königsberger. The crystals are always twinned, usually in thin tabular crystals parallel to (010), or else in cruciform penetration twins about the plane (001). The cleavage parallel to (010) is perfect. L. Langemann studied the corrosion figures which are best produced with hydrofluoric acid. A. Michel-Lévy and A. Lacroix found the optic axial angle $2V=33°$; A. von Lasaulx, $2V=52°$–$53°$ in blue light; and A. des Cloizeaux, $2E=51°\ 10'$ for red light and 52° for blue light. He also observed a small increase when the temp. is raised to 75°. The sp. gr. ranges from 2·094–2·205; and the hardness from $3\frac{1}{2}$–4. J. Joly found the sp. ht. to be 0·2621. The action of heat has been discussed above. C. Doelter found that when melted and slowly cooled, stilbite furnishes clusters of acicular crystals of a pyroxene-like mineral, and often anorthite in a glass-like matrix. The index of refraction is low; A. Michel-Lévy and A. Lacroix gave $\alpha=1{\cdot}494$, $\beta=1{\cdot}498$, and $\gamma=1{\cdot}500$. The birefringence is low, $\gamma-\alpha=0{\cdot}0093$. J. Königsberger and W. J. Müller found the indices of refraction to be $\alpha=1{\cdot}493$, $\beta=1{\cdot}501$, and $\gamma=1{\cdot}504$; and after treatment with a 25 per cent. soln. of potassium chloride, $\alpha=1{\cdot}478$, $\beta=1{\cdot}481$, and $\gamma=1{\cdot}483$. W. W. Coblentz found the ultra-red transmission spectrum gave all the water-bands superposed; but no important bands peculiar to the mineral itself. O. Weigel studied the electrical conductivity of stilbite.

G. A. Kenngott [146] found that the moist powder reacts alkaline to litmus: F. W. Clarke and G. Steiger confirmed this observation, and found that water extracts a little alkali from the mineral at 70°. J. Lemberg found that there is an exchange of bases when stilbite is treated with soln. of potassium or sodium chloride, forming respectively *potassium-stilbite* and *sodium-stilbite;* and with a soln. of barium chloride all the calcium is displaced by barium, forming *barium-stilbite.* F. W. Clarke and G. Steiger heated stilbite and ammonium chloride in a sealed tube and obtained a complex ammonia-derivative. J. Königsberger and W. J. Müller, A. Beutell and K. Blasche, R. Gans, H. Eichhorn, and I. Zoch studied the action of soln. of ammonium chloride on stilbite and concluded that an *ammonium-stilbite* is formed. The transformations of stilbite in nature into albite, orthoclase, sand quartz, were studied by M. F. Heddle, J. R. Blum, and C. R. van Hise.

Hydrochloric acid decomposes the mineral with the separation of granular and gelatinous silicic acid. F. Rinne heated the silica-gel from stilbite and obtained a pseudomorph of silica after stilbite.

In 1826, A. Breithaupt [147] described a *neue Species der Zeolithordnung* from Iceland and the Färoe Islands which he named *monophane*—μονοφάνης, appearance—in allusion to the lustre of the fractured surface. In a priority claim, G. Rose pointed out that he had named the same mineral **epistilbite** in two mineral collections. W. S. von Waltershausen named a specimen from Bogarfiord, Iceland, *parastilbite*; and F. Hessenberg refers to a specimen from Santorin, named *reissite*—after W. Reiss. C. A. Tenne identified parastilbite, and O. Luedecke, reissite, with epistilbite.

A number of analyses has been reported, and from these, C. F. Rammelsberg [148] computed the formula $(Ca,Na_2)Al_2Si_6O_{16}.5H_2O$; or $CaAl_2Si_6O_{16}.5H_2O$, making epistilbite into **pentahydrated calcium dialuminium dimesotrisilicate,** $CaAl_2(Si_3O_8)_2.5H_2O$. C. Bodewig, and C. Hintze gave $H_4CaAl_2Si_6O_{18}.3H_2O$; G. Tschermak, $CaAl_2Si_6O_{16}.5H_2O$; V. Rosicky and S. J. Thugutt, $3Ca(K,Na)_2Al_2Si_6O_{16}.20H_2O$; P. Jannasch, $H_2CaAl_2Si_6O_{17}.4H_2O$; F. Rinne, $CaAl_2Si_6O_{16}.5\frac{1}{2}H_2O$; and P. Groth, $H_6Ca_2Al_4(SiO_3)_{11}.7H_2O$. F. W. Clarke regarded heulandite (*q.v.*) and epistilbite as dimorphous forms of one silicate. F. A. Quenstedt, C. A. Tenne, P. Groth, and F. Rinne emphasized the relationship between epistilbite and heulandite. The second approximation to the formula is therefore largely dependent on which view is taken of the combined water. The amount of water in the reported analysis ranges from 12·52 to 15·68 per cent. V. Goldschmidt gave 15·5 per cent. C. Bodewig found samples containing 15·40 and 15·15 per cent. of water which retained 14·72 per cent. when dried over calcium chloride. P. Jannasch found that when epistilbite is confined over conc. sulphuric acid it lost 1·04 and 1·97 per cent. respectively in 5 and 48 hrs.; over phosphorus pentoxide, it lost in weight 1·03 and 2·14 per cent. respectively in 3 and 48 hrs.; over calcium chloride, it lost 0·54 per cent. in 5 hrs.; and over dry sand, 0·10 per cent. in 5 hrs. F. Zambonini found that when heated in a stream of moist air, epistilbite with 15·11 per cent. of water lost at:

| | 120° | 172° | 210° | 248° | 308° | 377° | 455° |
|---|---|---|---|---|---|---|---|
| Loss . | 2·06 | 4·70 | 7·31 | 10·33 | 12·69 | 13·27 | 14·09 per cent. |

He concluded that epistilbite contains neither water of crystallization nor constitutional water; the water is adsorbed as zeolitic water.

Epistilbite occurs associated with stilbite in various localities, in isolated crystals, or in tufts or spherules with an internally radiated structure. The colour is white, may be with a reddish tinge. G. Rose [149] supposed the crystals to be rhombic, but A. des Cloizeaux, and C. A. Tenne found them to be monoclinic; and the latter from G. Rose's measurements, calculated the axial ratios $a:b:c=0{\cdot}50430:1:0{\cdot}58006$, and $\beta=54°\ 53'$. Measurements were made by O. Luedecke, C. O. Trechmann, C. Hintze, and P. Jannasch. A. Levy emphasized the similarity between the crystals of heulandite and epistilbite. The twinning parallel to the (100) and (110) planes is common; there are also cruciform penetration twins. The cleavage parallel to (010) is perfect. The optic axial angle is large. A. des Cloizeaux gave $2E=67°$–$77°$ for the red ray, and 79°–83° for the blue ray. B. Mauritz gave $2E=70°$. For the Li-, Na-, and Tl-rays, C. A. Tenne found respectively $2E=73°\ 30'$, $75°\ 35'$, and $76°\ 40'$; L. Henniges, $2E=69°\ 12'$, $70°\ 45'$, and $71°\ 55'$. S. G. Gordon gave $2E=40°$ nearly. Raising the temp. from 12°–121°, was found by A. des Cloizeaux to raise $2E$ from $70°\ 25'$–$74°\ 56'$. F. Rinne showed that when the temp. of the monoclinic twins is raised, the crystals become rhombic; if these crystals be exposed to air, the expelled water is readsorbed, and the original optical characters are resumed. This does not occur if the crystals are embedded in Canada balsam. The sp. gr. of epistilbite is near 2·25, and the hardness over 4. The index of refraction found by A. des Cloizeaux

is $\gamma=1{\cdot}51$ for the red ray; A. Lacroix gave $\alpha=1{\cdot}512$ and $\gamma=1{\cdot}502$ for Na-light. S. G. Gordon gave $\alpha=1{\cdot}485$, $\beta=1{\cdot}495$, and $\gamma=1{\cdot}500$, and $\gamma-\alpha=0{\cdot}015$. A. Michel-Lévy and A. Lacroix found the birefringence is low, $\gamma-\alpha=0{\cdot}010$. V. Rosicky and S. J. Thugutt gave $\gamma-\alpha=0{\cdot}015$, and $\beta-\alpha=0{\cdot}010$. The optical character is negative. Epistilbite is almost completely decomposed by conc. hydrochloric acid with the separation of granular silicic acid.

A group of minerals called **scapolites** is analogous to the group of felspars in that they form a series with a gradual variation in composition between two end-members which G. Tschermak,[150] in his memoir: *Die Skapolithreihe*, regarded as *meionite*, $Ca_4Al_6Si_6O_{25}$, or Me, and *marialite*, $Na_4Al_3Si_9O_{24}Cl$, or Ma. There is no sharp line of demarcation in the series, but, as with the plagioclase felspars, certain members of the series have received special names—wernerite, mizzonite, etc. His three subdivisions are:

1. *Me to* $Me_2Ma_1$ or 100–67 per cent. meionite, or 40–48 per cent. silica. *E.g.* meionite, and wernerite (paranthine, nuttallite, glaucolite, stroganovite, algerite, and wilsonite).
2. $Me_xMa_1$ *to* $Me_1Ma_2$, or 67–34 per cent. meionite, or 48–56 per cent. silica. *E.g.* mizzonite, and scapolite (wernite, scapolite, ekebergite, porcelain spar, passauite, paralogite, and atheriastite).
3. $Me_1Ma_2$ *to Ma*, or meionite 34–0 per cent., or silica 56–64 per cent. *E.g.* marialite, and riponite (dipyre, prehnitoid, and coaseranite).

The following are given by J. D. Dana:

| | |
|---|---|
| Me to $Me_3Ma_1$ | Meionite |
| $Me_3Ma_1$ to $Me_1Ma_2$ | Wernerite |
| $Me_1Ma_2$ to $Me_1Ma_3$ | Mizzonite |
| $Me_1Ma_3$ to Ma | Marialite |

The scapolites all crystallize in the tetragonal system, they have nearly the same optic axial ratio, and they exhibit pyramidal hemihedrism. A. Lacroix also showed that the birefringence of the members of the series decreases in passing from meionite to marialite. The subject has also been discussed by C. F. Rammelsberg, G. vom Rath, E. T. Wolff, A. Himmelbauer, A. N. Winchell, L. M. Borgström, N. Sundius, R. Brauns, H. Eckermann, and V. M. Goldschmidt.

The first member of the series was also the first scapolite to be definitely recognized. J. B. L. Romé de l'Isle [151] described some crystals he obtained from geodes in the limestone at Monte Somma, Vesuvius, as *hyacinte blanche de la Somma*; R. J. Haüy called the mineral **meionite**—from μείων, less—because the pryamid of the crystals was less acute than is the case with vesuvianite (idocrase), harmotome, or zircon. The last member of the series was also the last to be recognized. It was obtained from the volcanic rock called *piperno*, occurring at Pianura near Naples. G. vom Rath called it **marialite**—after Marie, the daughter of G. Rose.

It has been suggested that the *white schorl-spar* obtained by A. Cronstedt [152] from Pargas, Finland, was a scapolite, although he regarded it as a lamellar pyroxene. M. F. R. d'Andrada applied the terms **wernerite**—after A. G. Werner—and **scapolite**—from σκάπος, a glossed form of κλάδος, a branch—to specimens from Norway. R. J. Haüy at first used the same terms for what he assumed to be distinct minerals, but later he, and J. A. H. Lucas arbitrarily proposed to call scapolite *paranthine*—from παρανθέω, to decay—in allusion to the inclination of the mineral to alter, and lose its lustre. J. A. Monteiro objected to the change, and showed that chemically and crystallographically, wernerite and scapolite were the same species, and he recommended applying the term wernerite to the species. P. C. Abildgaard called scapolite *rhapidolite* (not *rapidolite*)—from ῥαπίς, a rod. A. G. Werner referred to a scaly grey variety of wernerite as *arcticite*; J. J. Berzelius called wernerite *ekebergite*—after A. G. Ekeberg; A. G. Ekeberg called it *sodaite*; W. H. Wollaston, *natrolite*; C. F. Schumacher, *fuscite*—from *fuscus*, dusky; and C. C. von Leonhard, *gabbronite*—from its resemblance to gabbro—*vide* nephelite. C. C. von Leonhard regarded arcticite, paranthine, scapolite, ekebergite, gabbronite, and fuscite as synonyms of wernerite; and believed meionite to be a variety of the same mineral. This was later shown to be the case by A. Breithaupt.

The bluish or greenish scapolite from the vicinity of Lake Baikal, Siberia, was called *glaucolite*—from γλαυκός, greenish-grey or sea-green—by Fischer von Waldheim, and

J. F. John. R. Hermann, and G. Rose showed that this glaucolite is a scapolite; but W. C. Brögger has shown that the so-called glaucolites from Norway and Lake Baikal are really sodalites (*q.v.*). A pink scapolite from Bolton, Mass., is similar to glaucolite. A glassy scapolite from Galway, Ontario, was called *ontariolite* by C. U. Shepard. H. J. Brooke called a smoky brown variety from Bolton, Mass., *nuttalite*—after T. Nuttal—A. Breithaupt showed that it is a scapolite. J. D. and S. L. Dana found a grey, green, and red variety at Chelmsford, Mass., and called it *chelmsfordite*. J. D. Dana showed that it is a scapolite. J. N. von Fuchs referred to a *Porzellanspath* from Obernzell, near Passau, which was later called *porzellanite* by F. von Kobell, and *passauite* by C. F. Naumann. A. des Cloizeaux showed that these three minerals are scapolites. R. Hermann named a mineral from Sljudjanka, *strogonowite*—after Count Strogonowit—and it was shown by N. von Kokscharoff to be scapolite. T. S. Hunt described a mineral from Franklin, New Jersey, and named it *algerite*—after M. Alger. It was shown by J. D. Dana, and J. D. Whitney to be a scapolite. P. C. Weibye described a mineral from Arendal which he called *atheriastite* —from *ἀθέριστος*, neglected—and which was shown by J. F. L. Hausmann, G. A. Kenngott, and C. F. Rammelsberg to be a scapolite. The *wilsonite* of T. S. Hunt from Bathurst, Canada, was considered by E. J. Chapman to be a scapolite—*vide* mica. The *paralogite* of N. Nordenskjöld, obtained near Lake Baikal, was shown by N. von Kokscharoff to be a scapolite.

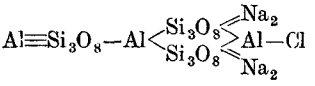
The *schorl blanchâtre de Mauleon* (Pyrenees) discovered by Gillet-Laumont in 1786, was called *leucolite*—from *λευκός*, white—by J. C. Delamétherie; *dipyre*—from *δίς*, twice; and *πῦρ*, fire, in allusion to the two effects of heat, *viz.* fusion and thermoluminescence, while H. Steffens called it *Schmelzstein*. J. F. L. Hausmann showed that dipyre was identical with common scapolite. J. F. W. de Charpentier observed two kinds of dipyre; one of these had a dark colour and was infusible at the fusion temp. of ordinary dipyre; and he called it *couseranite*—from Couserans or Conserans (Latin Consoranni), an old name for Ariège—where it occurs as a black schist. The work of A. des Cloizeaux, P. A. Dufrénoy, G. A. Kenngott, and F. Zirkel showed that couserite is a more or less altered form of dipyre. W. Salomon has recounted the history of dipyre and couserite. C. W. Blomstrand described a mineral from the vicinity of Solberg, Sweden, which he called *prehnitoid* owing to its resemblance to prehnite. G. A. Kenngott, and A. des Cloizeaux showed that it is a variety of scapolite. The *riponite* of G. Tschermak is a scapolite from Ripon, Canada. A. Scacchi called the crystals of a variety of scapolite he found in cavities in the trachyte of Monte Somma, Vesuvius, *mizzonite* (*mizonite*, or *meizonite*)—from *μείζων*, greater—because the axis of the prism is a little longer than that of meionite. N. Nordenskjöld found a water-free scolecite or scapolite at Ersby, Finland, which was harder than ordinary scapolite, and called by F. S. Beudant *scolexerose*; A. E. Nordenskjöld called it *ersbyite*. M. L. Frankenheim regarded ersbyite as a variety of labradorite, and C. F. Rammelsberg called it *Kalk-labrador*. A. des Cloizeaux, G. vom Rath, and E. T. Wolff showed that ersbyite is a variety of scapolite. N. Nordenskjöld's *pseudoscapolite* from Simonsby, Finland, was a mixture of scapolite and augite.

The oldest analysis of scapolite is that of a dipyre by L. N. Vauquelin;[153] more recent analyses of dipyre were made by A. Damour, V. Goldschmidt, A. des Cloizeaux, W. Salomon, A. E. Delesse, G. vom Rath, F. D. Adams, A. Lacroix, and A. Michel-Lévy; of meionite, by L. Gmelin, F. Stromeyer, E. T. Wolff, A. Damour, and G. vom Rath; of wernerite, by M. F. Heddle, P. C. Weibye, V. Hartvall, J. F. John, P. L. Simon, F. J. Wiik, P. Schafhäutl, L. Sipöcz, F. Becke, G. vom Rath, F. von Kobell, C. F. Rammelsberg, F. A. Genth, and A. Lacroix; of scapolite, by E. T. Wolff, G. vom Rath, F. J. Wiik, T. Tschernytscheff, A. Laugier, J. J. Berzelius, L. M. Berg, N. Nordenskjöld, L. Stadtmüller, R. Hermann, O. O. Baklund, H. Wurtz, T. S. Hunt, and A. Himmelbauer; of ekebergite, by E. T. Wolff, A. G. Ekeberg, and V. Hartwall; of glaucolite, by C. Bergemann, M. Giwartowsky, and G. vom Rath; of paralogite, by N. Nordenskjöld, E. T. Wolff, and C. F. Rammelsberg; of prehnitoid, by C. W. Blomstrand; of porcelain spar, by J. N. Fuchs, and F. von Kobell; of nuttalite, by T. Thomson; of paranthite, by F. P. Dunnington; of algerite, by T. S. Hunt, and W. Crossley; of wilsonite, by T. S. Hunt, and C. F. Rammelsberg; of stroganovite, by R. Hermann; of riponite, by F. D. Adams; of coaseranite, by A. des Cloizeaux, P. A. Dufrénoy, and L. Grandea; of mizzonite, by G. vom Rath; and of marialite, by G. vom Rath, and C. F. Rammelsberg. Analyses of samples with carbon dioxide were made by E. T. Wolff, G. vom Rath, R. Hermann, E. Neminar, L. Sipöcz, F. Becke, P. von Sustschinsky, F. A. Genth, V. Goldschmidt, and J. D. Dana; of samples with chlorine, but without carbon dioxide, were made by C. F. Rammelsberg, F. D. Adams, J. Lemberg, V. Goldschmidt, H. Lenk, and

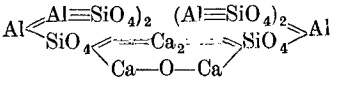
J. Eyermann; of samples with chlorine and sulphur trioxide were made by L. Sipöcz, H. Wulf, R. Brauns, and N. Sundius; and of samples with chlorine, carbon dioxide, and sulphur trioxide were made by L. Sipöcz, and L. H. Borgström. R. Brauns called the scapolite containing the sulphate radicle *silvialite*—after Silvia Hillebrand.

C. F. Rammelsberg showed that the composition of the scapolites is very variable, due, in part, to the partial alteration of the mineral. J. N. von Fuchs, P. Schafhäutl, E. Neminar, L. Sipöcz, N. Sundius, F. Becke, and F. D. Adams established the presence of chlorine as a constituent of most scapolites, and, after showing that the proportion of sodium increases as that of chlorine increases, he devised the mixture hypothesis indicated above, and assumed that all the scapolites can be represented as mixtures containing the primary constituents *meionite*, $Ca_4Al_6Si_6O_{25}$; and *marialite*, $Na_4Al_3Si_9O_{24}Cl$. L. M. Borgström emphasized the part played by carbonate and sulphate as well as the chloride radicles, and he said that the composition of the scapolites can be explained as isomorphous mixtures of marialite or *chloromarialite*, $Na_3Al_3Si_9O_{24}.NaCl$; *sulphatomarialite*, $Na_3Al_3Si_9O_{24}.Na_2SO_4$; and *carbonatomarialite*, $Na_3Al_3Si_9O_{24}.Na_2CO_3$; along with *sulphatomeinoite*, $Ca_3Al_6Si_6O_{24}.CaSO_4$, and *carbonatomeionite*, $Ca_3Al_6Si_6O_{24}.CaCO_3$. In each of these cases, the nucleus of the marialites, so to speak, corresponds with three mols of $NaAlSi_3O_8$, and that of the meionites with three mols of $CaAl_2Si_2O_8$. The compound $Ca_4Al_6Si_6O_{25}$, or $3CaAl_2Si_2O_8.CaO$, is regarded as *oxymeionite*. E. T. Wherry found that the at. vol. hypothesis of isomorphism fits in well with the various replacements or substitutions in the scapolite group. C. F. Rammelsberg assumed the different scapolites to be addition compounds of a metasilicate, a complex meta-orthosilicate, and a complex metasilicate and disilicate. G. A. Kenngott[154] calculated for meionite $Ca_7Al_{10}Si_{11}O_{44}$. P. Groth gave for meionite $Ca_4(AlO)Al_2(AlSi_2O_8)_3$, **calcium oxytrialuminium tri-monaluminodisilicate;** and for marialite, $Na_4(AlCl)Al_2(Si_3O_8)_3$, **calcium chlorotrialuminium mesotrisilicate.** He gave graphic formulæ for both these two compounds, and A. C. Brown also represented oxymeionite by a graphic formula. A. Himmelbauer considered meionite to be a complex of $2CaAl_2Si_2O_8+Ca_2Al_2Si_2O_9$; and marialite, a complex of $2NaAlSi_3O_8+Na_2AlSi_3O_8Cl$. H. S. Washington regarded the scapolites as complexes of the acid $H_{10}AlSi_3O_{12}$; and A. Himmelbauer obtained a metasilicic acid by treating meionite with dil. hydrochloric acid, and from marialite, *marialitic acid*, $H_{10}Si_9O_{23}$. W. and D. Asch applied their cumbrous hexite-pentite hypothesis to the scapolites.

F. W. Clarke emphasized the parallelism of the felspars and scapolites. He said: "Both groups of minerals are easily alterable, and both yield kaolinite as a final product of the change. Furthermore, both alter to muscovite, or to pinite, which is only an impure pseudomorphous mica." Crystallographically, kaolinite has close relations with the mica family as illustrated by the empirical and structural formulæ which he employed. F. W. Clarke gave:



Marialite.



Meionite.

where marialite is like sodalite, but with quadrivalent $Si_3O_8$ in place of quadrivalent $SiO_4$; and meionite is like anorthite, but with the bivalent Ca.O.Ca-group in place of $Ca^{II}$.

The scapolites occur in the volcanic rocks such as the ejected masses on Monte Somma. They principally occur in crystalline schists, gneisses, amphibolites, and altered limestones. They occur in crystallized limestones as a direct result of contact action. They also appear to be formed as alteration products of plagioclase felspars. This subject has been discussed by J. W. Judd,[155] A. Cathrein, A. Lacroix, H. Lenk, F. D. Adams and A. C. Lawson, F. Zirkel, W. Salomon, W. C. Brögger and H. H. Reusch, F. Becke, and A. E. Törnebohm.

L. Bourgeois [156] attempted to make meionite by fusing a mixture of its constituent oxides, but the product was anorthite; but he did obtain crystals of what was considered to be meionite by fusing a mixture of marble and a basaltic glass. K. B. Schmidt also prepared an artificial rock containing scapolite; and he obtained the same mineral from fused eclogite. C. Doelter fused epidote with calcium and sodium fluorides and recognized meionite in the products; he also observed meionite in a fused mixture of calcium oxide, silica, and alumina, and in a fused mixture of anorthite and sodium chloride. E. S. Shepherd and G. A. Rankin obtained crystals of meionite by heating a glass of that composition in contact with a soln. of sodium chloride in a bomb.

The scapolites occur in clear glassy or milk-white crystals; in crystal grains, and massive. Wernerite and mizzonite may be coloured white, with a grey, blue, green, or red tinge. The crystals belong to the tetragonal system and the different members have nearly the same axial ratio. N. von Kokscharoff [157] gave for meionite $a:c=1:0{\cdot}43925$; G. Tschermak for wernerite, $1:0{\cdot}4384$; N. von Kokscharoff for mizzonite, $1:0{\cdot}44235$; and G. vom Rath for marialite, $1:0{\cdot}4417$. Observations on the crystals of the scapolites were made by F. X. M. Zippe, A. Brezina, V. Goldschmidt, A. von Lasaulx, H. Fischer, etc. The crystals are characterized by pyramidal hemihedrism. The prismatic faces sometimes show vicinal prominences corresponding with the hemihedrism of the crystals. The corrosion figures also agree with the hemihedral character of the crystals. The cleavage parallel to (100) is perfect, and that parallel to (110) rather less so. Optical anomalies are rare, but are occasionally shown in the biaxial character of the interference figure, and a small angle between the optic axes.

The sp. gr. of many of the specimens analyzed were also determined. G. Tschermak calculated from the law of mixtures that the sp. gr. of the end-members is 2·815 for meionite, and 2·560 for marialite. The highest observed value is 2·737 for the meionite of Vesuvius, with its 12 per cent. of marialite. A. Himmelbauer, and N. Sundius have compiled sp. gr. tables of the scapolites from different localities. The mixture rule is in the main applicable, but there are disturbances due to the influence of potassium, the presence of sulphates and carbonates in place of chlorides, etc. The hardness is between 5 and 6. A. Brun found the m.p. of meionite to be 1138°–1130°; M. L. Fletcher, 1331° for meionite; and A. Himmelbauer, 1125°–1238° for various scapolites, and 1088°–1233° for marialite. J. Joly gave 0·2003 for the sp. ht. of wernerite. E. Jannettaz gave 0·845 for the sq. root of the ratio of the thermal conductivity in the direction of the base to that in the direction of the chief axis. A. Dannholm found the sp. ht. of scapolite. The indices of refraction are determined by the chemical composition and vary from $\omega=1{\cdot}594$–$1{\cdot}5545$, and $\epsilon=1{\cdot}557$–$1{\cdot}5417$ respectively for meionite and marialite. There is some confusion in the data, for the effects of variation in the proportions of meionite and marialite are affected by the presence of sulphates and carbonates. Similar remarks apply to the birefringence. Scapolite is optically negative. Observations have been recorded by H. Rosenbusch, A. Lacroix, L. M. Borgström, R. Brauns, P. Franco, A. Laitakari, N. Sundius, K. Zimanyi, O. O. Baklund, H. Preiswerk, etc. A. Himmelbauer gave for scapolites with different proportions of meionite, Me.

| Me | 4 | 31 | 32 | 54 | 55 | 72 | 85 per cent. |
|---|---|---|---|---|---|---|---|
| $\omega$ | 1·58968 | 1·58284 | 1·58534 | 1·56645 | 1·56062 | 1·55536 | 1·54630 |
| $\epsilon$ | 1·55638 | 1·56120 | 1·55641 | 1·54642 | 1·54402 | 1·54238 | 1·53949 |
| $\omega-\epsilon$ | 0·0333 | 0·03164 | 0·02893 | 0·02003 | 0·0166 | 0·01248 | 0·00687 |

According to G. A. Kenngott, [158] powdered and moistened meionite reacts strongly alkaline to litmus. The chloriferous scapolites gave the reaction for chlorides when treated with silver nitrate. According to G. Tschermak, the scapolites with a high proportion of meionite—Me to $Me_2Ma_1$—are completely or almost completely decomposed by hydrochloric acid; the $Me_2Ma_1$ to $Me_1Ma_2$ scapolites are incompletely decomposed; while the $Me_1Ma_2$ to Ma scapolites are not much affected by

the acid. The scapolites are very liable to change and particularly so towards the sodium or marialite end of the series. The introduction of water and carbon dioxide is a common change. By the substitution of potash, the mineral passes into pinite and potash-mica; with magnesia and potash, magnesia-mica is produced; with magnesia, steatite is formed; and with the acquisition of iron, epidote is produced. In some cases, a greenish chlorite is produced. By the loss of its bases, scapolite passes into kaolinite or china clay used in the manufacture of porcelain, etc. Hence, the name *porcelain-spar* for the scapolite at Passau—*vide supra*. C. F. Rammelsberg, C. R. van Hise, C. W. von Gümbel, J. N. von Fuchs, G. Forchhammer, L. Knafft, C. G. C. Bischof, V. Goldschmidt, G. vom Rath, etc., studied these transformations; and J. Lemberg, and H. Schneiderhölm investigated the action of soln. of potassium hydroxide, carbonate, and chloride; and of soln. of sodium carbonate, chloride, and sulphate, at 215°–220°.

A zeolitic mineral from Andreasberg, Harz, seems to have attracted attention in the latter half of the eighteenth century, but it was not given any specific name. I. S. R. I. Eques a Born [159] described it as a *spatum calcarium*, but, added T. Bergman, the crystals are not calcareous but siliceous, and he referred to it as *figure hyacinthica*. J. Deméste referred to it as *hyacinthe blanche*; J. B. L. Romé de l'Isle as *hyacinthe blanche cruciforme*; J. C. H. Heyer, and F. W. H. von Trebra, as *Kreuzkristalle*; A. G. Werner, D. L. G. Karsten, and L. A. Emmerling, as *Kreuzstein*, *Silex crucifer*, and *pierre de croix*; J. C. Delamétherie, as *andreasbergolite*, or *andreolite*; R. Kirwan, *staurolite*; C. A. G. Napione, *ercinite*: and A. J. M. Brochant, as *pierre cruciforme*. R. J. Haüy's term **harmotome** has been adopted; it is from ἁρμός, joint; and τέμνειν, to cut—alluding to the fact that the pyramid made by the prismatic planes in the twinning position divides parallel to the plane that passes through the terminal edges. T. Thomas called some well-developed crystals from Strontian, Scotland, *morvenite*; but A. Damour and A. des Cloizeaux showed that morvenite is the same as harmotome. C. Stadtländer has revived the history of harmotome.

J. C. H. Heyer first analyzed harmotome in 1789, and found it contained 24 per cent. of baryta; A. H. L. Westrumb, in 1794, found 20 per cent. of baryta; H. M. Klaproth, in 1797, found 18 per cent. of baryta; and R. J. Haüy, quoting Q. M. Tassaert's analysis, gave 16 per cent. of baryta. To distinguish it from phillipsite, called *lime-harmotome*, harmotome proper was sometimes called baryta-harmotome. Numerous analyses [160] of harmotome have been made. C. F. Rammelsberg [161] calculated from the analyses $BaAl_2Si_5O_{14}.5H_2O$, making harmotome **pentahydrated barium dialuminium mesopentasilicate**; C. F. Rammelsberg assumed that the corresponding isomorphous alkali salt, $R'_2Al_2Si_5O_{14}.5H_2O$, is present. G. Stoklossa doubled C. F. Rammelsberg's formula. P. Groth assumed that harmotome is produced by the isomorphous association of two silicates; and G. Tschermak, four silicates. J. Bruckmoser assumed that harmotome is a derivative of harmotomic acid, $H_8Si_5O_{14}$. F. W. Clarke, and C. Hersch used graphic symbolization. The former gave:

$$Al{=}Si_3O_8{-}Al\begin{matrix}<Si_3O_8\\<Si_3O_8\end{matrix}\begin{matrix}>Ba\\>Al{-}SiO_4{\equiv}Al+10H_2O\\>Ba\end{matrix}$$

According to A. Damour, harmotome from Strontian loses 4·3 per cent. of water by six months' exposure to dry air; at 100° it loses 1·8 per cent.; between 100° and 150°, 9·9 per cent.; and between 150° and 190°, 13·5 per cent. After 24 hrs.' exposure to ordinary air, the lost water is resorbed. At a dull red-heat, 14·65 per cent. of water is lost, and the mineral is disaggregated. C. Hersch found that the following percentage losses attended the heating of the mineral to:

| | 100° | 150° | 203° | 252° | 295° | Red heat |
|---|---|---|---|---|---|---|
| Loss . . . | 2·74 | 5·74 | 9·23 | 10·67 | 12·42 | 15·29 per cent. |

W. Fresenius made some observations on this subject; and G. Stoklossa measured the resorption of water by harmotome, dehydrated at different temp. The breaks in the curve, he said, indicate eleven hydrates; and that the water is chemically united in the mol.

Harmotome occurs in basalt and similar eruptic rocks; in phonolyte; trachyte, and gneiss rocks; and in some metalliferous veins. It has not been recorded in barytiferous gangue. It is commonly associated with calcite and quartz. J. Lemberg assumed that it is like chabazite, and he found traces of baryta and strontia in chabazite. He assumed that harmotome is formed by the action of barytiferous waters on chabazite. Harmotome, however, has not been prepared artificially.

Harmotome occurs in various twinned forms coloured white or tinged grey, yellow, red, or brown. L. von Buch [162] first described the crystals of harmotome in 1794. R. J. Haüy considered the fundamental form to be a tetragonal pyramid. A. Breithaupt assumed the crystals were triclinic. This was discussed by C. F. Rammelsberg, C. F. Naumann, and G. A. Kenngott. The morphological features of the twinned crystals were studied by F. Köhler, and A. des Cloizeaux investigated their optical properties, and assumed that the rhombic crystals have monoclinic symmetry. A. Gadolin explained the structure on the assumption that the individual members of the twinned system are monoclinic. This view was supported by A. des Cloizeaux, R. Brauns, E. Mallard, H. Baumhauer, etc. A. des Cloizeaux gave for the axial ratios of the monoclinic crystals $a:b:c$ $=0{\cdot}70315:1:1{\cdot}2310$, and $\beta=55°\ 10'$. G. Tschermak gave $a:b:c=0{\cdot}5053:1:0{\cdot}3516$, and $\beta=90°$. The crystals occur in cruciform penetration twins united as simple or as double twins; the double twins may have the aspect of a square prism with a diagonal pyramid having feather-like striations from the median line. More complex twins—*e.g.* three double twins—are known. As in the case of phillipsite, L. Langemann assumed that the individuals are triclinic because they deviate optically from monoclinic crystals. F. Rinne showed that the optical characters which refer the crystals to the triclinic system are not changed by heat, though there is a movement of the axial plane, and an increase in the double refraction. The cleavage (010) is well marked, but the (001) less so. A. des Cloizeaux gave for the optic axial angles $2H_a=86°\ 31'$–$98°\ 33'$; and $2V=85°\ 52'$ for red light. He also measured the change which occurs on raising the temp. The sp. gr. is 2·45–2·50; and the hardness 4–5. A. des Cloizeaux found $\beta=1{\cdot}516$ for the index of refraction with the red ray; and for Na-light, A. Michel-Lévy and A. Lacroix gave $\alpha=1{\cdot}503$, $\beta=1{\cdot}506$, and $\gamma=1{\cdot}508$.

G. A. Kenngott [163] found that the moistened powdered mineral reacts alkaline to litmus. Conc. hydrochloric acid attacks the mineral with the separation of pulverulent silicic acid; J. Bruckmoser obtained pseudomorphs of silica after harmotome, and the silicic acid has the composition $H_8Si_5O_{14}$, *harmotomic acid.* G. Friedel found that dehydrated harmotome absorbs ammonia so violently that it decrepitates. F. Grandjean found the vap. of iodine, bromine, mercury, calomel, cinnabar, and sulphur are absorbed by dehydrated harmotome, and he measured the corresponding changes in the optical properties. J. Lemberg found that only a little barium is displaced by six months' digestion with soln. of calcium sulphate and sodium chloride at 100°. He found that with a soln. of potassium chloride the barium is rapidly displaced, and a *potassium-harmotome* formed. By digesting the latter with a soln. of sodium chloride, a *sodium-harmotome* is produced.

A. Meister [164] analyzed the crystals of a dark grey mineral found near the Tatarka, Siberia. The mineral was called *didymolite*, or *didjumolite*. Its composition corresponded with $2CaO.3Al_2O_3.9SiO_2$. A little ferric oxide may take the place of alumina; and a little magnesia, the place of lime. In view of the absence of any definite information of the mol. structure, a number of hypotheses could be suggested for its constitution, but this would be unprofitable until more evidence is available. The mineral belongs to the monoclinic system, and the axial ratios are $a:b:c=0{\cdot}6006:1:0{\cdot}2867$, and $\beta=106°$. The sp. gr. is 2·71; the hardness $4\frac{1}{2}$–5; the index of refraction $\beta=1{\cdot}5008$; the birefringence is negative, $\gamma-\alpha=0{\cdot}015$; and the optic axial angle $2V=81°\ 26\frac{1}{2}'$. The mineral is not decomposed by acids other than hydrofluoric acid.

J. Morozewicz [165] found a zeolite in the diabase tuff on one of the Commander Islands, and he called it **stellerite**—after W. Steller. Its analysis corresponds with $CaAl_2Si_7O_{18}.7H_2O$, and F. W. Clarke represents it by the formula $Al:Si_3O_8.Al(Si_2O_5)_2Ca.7H_2O$. J. Morozewicz considers it to be a salt of the aluminosilicic acid, $H_2Al_2Si_nO_{2n+4}$. Stellerite occurs in rhombic crystals with axial ratios $a:b:c=0{\cdot}98:1:0{\cdot}75$. G. Tschermak gave $0{\cdot}49:1:0{\cdot}40$, and $\beta=90°$. The cleavage parallel to (010) is complete; less complete parallel to (100). The optical axial angle $2V=43{\cdot}5°$. The sp. gr. is 2·124 at 15°, and the hardness 3½-4. It loses 2 mols. of water at 125°, and 4 mols. at 200°. The water lost at 125° is regained on exposure to air. The index of refraction $\alpha$ is=1·484, and $\gamma$=1·495. *Pseudonatrolite* (*q.v.*) is considered by F. W. Clarke to be stellerite.

A. Lacroix [166] obtained a white, silky, fibrous mineral from cavities in the doleritic basalt of Gignat, Puy-de-Dôme, and named it **gonnardite**—after F. Gonnard. Its composition approximates $(Ca,Na_2)_2Al_2Si_5O_{15}.5\frac{1}{2}H_2O$. It is probably rhombic. The sp. gr. is 2·246–2·260; and the hardness 4½–5. It is optically biaxial, and positive. E. S. Larsen gave $2E=83°\pm10°$; $2V=52°\pm6°$; and the indices of refraction $\alpha$=1·514, $\beta$=1·515, and $\gamma$=1·520.

A. S. Eakle [167] found slender white fibres of a mineral in the rhyolitic tuff at Durkee, Oregon, and he named it **erionite**—from ἔριον, wool. Its composition approximates $H_2CaK_2Na_2Al_2Si_6O_{17}.8H_2O$. Its sp. gr. is 1·997. It is optically biaxial; and positive. The crystals belong to the rhombic system. E. S. Larsen gave for the indices of refraction $\alpha$=1·438, and $\gamma$=1·452. The birefringence is high. It readily dissolves in hydrochloric acid.

A. Cronstedt [168] referred to a mineral *Röd Magnesia;* C. A. G. Napione, to *manganèse rouge;* and R. J. Haüy, to *manganèse oxyde violet silicifère*. H. B. de Saussure also described the mineral, and L. Cordier showed that it was an *epidote manganésifère*. C. A. S. Hofmann called it *Piemontischer Braunstein*. The mineral from St. Marcel, Piedmont, was called *piemontite*, that is, **piedmontite**, by G. A. Kenngott. Analyses of piedmontite were made by E. Geffken, W. Eitel, B. Koto, V. Hartwall, A. Sobrero, H. St. C. Deville, C. F. Rammelsberg, H. Laspeyres, G. Flink, A. W. Tamm, L. J. Igelström, and N. Svensson. The composition corresponds with that of the epidotes with some manganese replacing aluminium, $Ca_2(AlOH)(Al,Fe)_2(SiO_4)_3$; presumably, the clinozoisite, $Ca_2(AlOH)Al_2(SiO_4)_3$, is in solid soln. with the isomorphous *manganic-epidote*, $Ca_2(AlOH)Mn_2(SiO_4)_3$, **calcium dimanganic aluminohydroxytriorthosilicate.** The general properties of piedmontite resemble those of epidote, to which reference must be made. Piedmontite does not occur so abundantly as epidote and zoisite; and it is mainly confined to crystalline schist. B. Koto found it to be quite common in the manganiferous schists of Japan. N. Yamaski, and G. H. Williams found it associated with rhyolite.

Piedmontite is reddish-brown or black. H. Laspeyres gave for the axial ratios of the monoclinic crystals $a:b:c=1{\cdot}6100:1:1{\cdot}8326$, and $\beta=64°\ 39'$; G. Flink gave $1{\cdot}5807:1:1{\cdot}8657$, and $\beta=64°\ 36'$. The cleavage and twinning resemble those of epidote. A. des Cloizeaux gave for the optic axial angles, $2H_a=82°$–$90°$, and $2H_0=121°$–$126°$. A. Breithaupt gave for the sp. gr. 3·404–3·518; and the hardness 6½. The pleochroism is pronounced and characteristic. It has been investigated by H. Laspeyres, A. Lacroix, and B. Koto—*vide* epidote.


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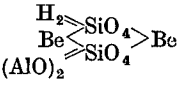
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## § 45. Beryllium Aluminium Silicates

R. Rieke [1] studied the fusibility of mixtures of beryllia and clay. In an early issue of his *Tableau méthodique de minéraux*, R. J. Haüy [2] referred to a mineral, brought to Europe from Brazil, which he named **euclase**—from εὖ, easily; κλάσις, fracture—in allusion to its easy cleavage. J. C. Delamétherie also made some references to the mineral. The first analysis was made by L. N. Vauquelin, and other analyses were made by J. J. Berzelius, J. W. Mallet, and A. Damour. The last-named summarized the analysis by the formula $HBeAlSiO_5$; C. F. Rammelsberg gave $H_2SiO_3.2Be_3SiO_5.3Al_2SiO_5$; and P. Groth, $Be(AlOH)SiO_4$, **beryllium aluminohydroxyorthosilicate,**



analogous to those employed by him for datolite, homilite, and gadolinite. Euclase, said G. Cesaro, corresponds to datolite except that aluminium is present instead of boron, and beryllium instead of calcium. Euclase occurs with topaz in the chloritic schist of Villa Rica, Brazil; with topaz, etc., in the auriferous sands of Orenburg, Ural; with pericline, etc., in the mica schist of Gramsgrube, Austrian Alps; and also with pericline at Möllthal. The association with pericline indicates that the

mode of formation of each has been similar. F. Kolbeck and M. Henglein found euclase associated with pegmatite. V. Dürrfield argued that the fluorite which accompanies the mineral indicates that euclase has been formed by the action of fluoriferous vap. A. Daubrée's synthesis of the beryllium silicates by the action of silicon tetrachloride on beryllia, was questioned by H. St. C. Deville. C. Doelter heated a mixture of alumina, silica, and beryllia under a layer of sodium fluoride in a magnesite crucible and obtained crystals corresponding in composition with an anhydrous euclase; but the product was not euclase.

Euclase occurs only in crystals with a prismatic habit, and with a colour ranging from white, blue, or green. The crystals, according to J. Schabus, are monoclinic with the axial ratios $a:b:c=0{\cdot}32369:1:0{\cdot}33324$, and $\beta=79°\ 44'\ 4''$. C. F. Rammelsberg gave $0{\cdot}6303:1:0{\cdot}6318$, and $\beta=91°\ 42'$. Observations on the crystals have been made by V. Dürrfield, E. Hussak, R. Köchlin, A. Levy, P. von Jeremejeff, A. T. Kupffer, K. Zerrenner, N. von Kokscharoff, W. H. Miller, A. des Cloizeaux, P. Guyot, N. Kulibin, C. S. Weiss, L. J. Spencer, and V. Goldschmidt. C. F. Rammelsberg said that the euclase is isomorphous with datolite, homilite, and gadolinite. The cleavage parallel to (010) is perfect; but the cleavages parallel to (100) and to (001) are imperfect. A. des Cloizeaux gave for the optic axial angles $2V=49°\ 37'$; and $2E=88°\ 47'$ for the red ray, and $88°\ 7'$ for the blue ray. Raising the temp. to 176° increased $2E$ by $2°\ 18'$. A. des Cloizeaux found that a colourless variety of euclase had a sp. gr. 3·089, and a blue variety, 3·097. A. Breithaupt found the sp. gr. of Brazilian euclase ranged from 3·094–3·095. In general, the extremes are 3·051–3·111. The hardness ranges from 7–8. A. des Cloizeaux found the indices of refraction to be $\alpha=1{\cdot}6520$, $\beta=1{\cdot}6553$, and $\gamma=1{\cdot}6710$ for Na-light. A. Worobieff measured the indices with light of different wave-lengths. The optical character is negative. The coloured crystals are distinctly pleochroic. C. Doelter found the colourless euclase acquires a soft blue tint when exposed to radium rays; and pale green euclase became a shade darker. Exposure to ultra-violet light bleaches these colours. With the exception of hydrofluoric acid, the mineral is not affected by acids.

P. Hautefeuille and A. Perrey [3] melted together a mixture of potassium hydroxide, beryllium oxide, silicic acid, and an excess of neutral potassium vanadate; washed the product well with water and dil. alkali-lye; and separated the crystalline constituents by flotation in soln. of cadmium borotungstate of different sp. gr. They thus obtained what has been called *beryllia-leucite*, $KBe(SiO_3)_2$, **potassium beryllium dimetasilicate.** They also claimed to have made other complex beryllium silicates with $K_2O:Be_2O:SiO_2=2:1:8$; $1:1:4$; $2:1:10$; and $1:1:5$. They also obtained icositetrahedral crystals of beryllia-leucite by rapidly heating the constituents to a high temp. and cooling slowly. They assumed that in these complex salts the beryllia can replace alumina and also ferric oxide, and that it is a sesquioxide; so that in some cases beryllium oxide functions as a monoxide like magnesia, and in other cases, as a sesquioxide like alumina. The evidence is not satisfactory.

The history of **beryl** in its bearing on the evolution of our knowledge of the element beryllium has already been discussed—**4.** 28, 1—and various analyses of the mineral were indicated at the same time. T. Uemura [4] found a Japanese beryl containing beryllium, calcium, sodium, magnesium, scandium, silicon, aluminium, and iron, but no chromium.

W. Vernadsky applied the term *vorobyevite*, *worobieffite* or *worobyewite*—after M. Vorobyey—to cæsia-beryl. G. F. Kunz called rose-red beryl *morganite*—after J. P. Morgan. The terms *aquamarine*, *emerald*, and *smaragd* applied to beryl have already been discussed. T. Thomson called a greenish-yellow beryl from Aberdeen, *davidsonite*; C. U. Shepard, a colourless or white beryl from Goshen, Mass., *goshenite*; A. Grattarola, a slightly altered rose-red variety from Elba, *rosterite*—after G. Roster; and A. Atterberg, and J. J. Berzelius, an altered variety, *pseudosmaragd* or *pseudoemerald*. A. Eppler investigated a yellow beryl called *heliodor* containing 0·58 per cent. of ferric oxide; it became luminous in the cathode rays.

C. F. Rammelsberg summarized the analyses by the formula $BeAl_2Si_6O_{18}$. E. T. Allen and J. Clement found the small proportion of water in beryl is expelled very slowly on calcination, and they assumed that the water is dissolved in the mineral. S. L. Penfield, however, argued that the, approximately, 2 per cent. of water is chemically combined, and wrote the formula $H_2Be_6Al_4Si_{12}O_{37}$. T. Uemura wrote the formula $4BeO.Al_2O_3.4SiO_2$. W. Vernadsky supposed that in beryl there is a nucleus of a mineral $m BeAl_2Si_4O_{12}$ associated with $n BeSiO_3$. F. W. Clarke considers some of the methods of synthesizing beryl, the alteration of beryl into mica, and the common changes which occur involving the replacement of beryllium, do not agree with the formula $Be_2(Si_3O_8)_2Be(AlO)_2$; but rather with the metasilicate formula of **beryllium dialuminium hexametasilicate,** $Be_3Al_2(SiO_3)_6$:

$$Be<\begin{matrix}SiO_3\\SiO_3\end{matrix}>Al.SiO_3.Be.SiO_3.Al<\begin{matrix}SiO_3\\SiO_3\end{matrix}>Be$$

Beryl is commonly found in pegmatite veins, and also in clay slate, and in mica schists. *J. J. Ebelmen* [5] found that if beryl be dissolved in fused boric oxide, crystals of beryl separate out on cooling or on volatilization of the boric oxide. H. St. C. Deville treated a heated mixture of alumina and beryllia with silicon tetrachloride, and obtained, not beryl, but a silicate with the composition $6BeO.5SiO_2$. P. Hautefeuille obtained beryl by fusing a mixture of alumina, beryllia, and silica, using lithium molybdate as a flux and *agent minéralisateur;* with potassium vanadate as a flux, beryllia-leucite, $K_2Be_3Si_4O_{12}$, was formed. H. Traube treated a mixed soln. of aluminium and beryllium sulphates with sodium metasilicate; and crystallized the precipitate from a soln. of fused boric oxide. It is assumed above that since the start was made with a metasilicate, the same kind of silicate is obtained at the end.

Beryl usually occurs in long prismatic crystals, but rarely in tabular crystals. G. F. Kunz [6] found a large crystal of aquamarine weighing 110·5 kgrms., at Marambaya, Brazil. A beryl from Grafton, Mass., weighed 2900 lbs., and measured 4 ft. 3 ins. in one direction, and transversely 32 ins.; and another weighed nearly 2½ tons. A. Lacroix discussed the beryl crystals from Madagascar. Beryl occasionally occurs in compact, columnar, or granular masses. The **colour** may be emerald green, pale green, light blue, yellow, rose-red, or white. W. Hermann attributed the colour to iron oxide; and G. O. Wild and R. E. Liesegang found the emerald-green varieties owe their colour to chromium; but the other varieties have no chromium, but possess an iron content nearly proportional to the colour intensity. Rose-beryl is thought to be coloured by cerium—*vide* quartz. The **crystals** belong to the hexagonal system; and, according to N. von Kokscharoff, have the axial ratio $a:c=1:0{\cdot}498855$. The crystals were studied by R. Scharizer, H. Panebianco, C. Anderson, R. Fellinger, H. Rubens, H. Ungemach, P. Siedel, W. F. P. McLintock and T. C. F. Hall, H. Thiene, A. Lacroix, L. Duparc and co-workers, A. S. Eakle, O. Dreher, C. S. Middlemiss and L. J. Parshad, W. E. Ford, E. Kaiser, C. Anderson, E. Romanovsky, H. Reis, P. von Jeremejeff, E. S. Dana, O. Lehmann, G. A. Kenngott, F. Hessenberg, G. vom Rath, P. Groth, A. d'Achiardi, C. Busz, W. Müller, G. Strüver, A. Schrauf, M. Websky, P. von Jeremejeff, W. E. Hidden, and S. L. Penfield. The **cleavage** (0001) is imperfect and indistinct. The crystals are sometimes striated vertically, rarely transversely. P. von Jeremejeff has discussed the twinning of the crystals of beryl. Beryl is often optically anomalous and may appear to be biaxial. This subject has been investigated by D. Brewster, J. Babinet, W. F. Salm-Horstmar, A. Breithaupt, A. Madelung, A. des Cloizeaux, F. Pfaff, E. Mallard, E. Bertrand, F. J. Wiik, R. Brauns, B. Lévy, A. Schrauf, A. N. Karnojitzky, A. Grattarola, and J. Hirschwald. L. Duparc and co-workers found that a beryl from Madagascar had the **optic axial angle** $2V=2°\ 34'$, and $2E=10°\ 12'$ for Na-light. H. Bücking studied the effect of press. on the axial angle; C. Doelter, and A. Offret, the effect of heat; and F. Pockels, the effect of heat and press. The **corrosion**

**figures** were studied by F. J. Wiik, R. C. Hills, W. Pettersson, H. Traube, A. Arzruni, K. Vrba, W. Kohlmann, A. P. Honess, C. Anderson, and S. L. Penfield. The **X-radiogram** was investigated by F. Rinne. The **specific gravity** of beryl ranges from 2·6–2·9; L. Duparc and co-workers obtained numbers ranging from 2·7116–2·8808; and A. Piutti, numbers from 2·628–2·886. A. H. Church gave for aquamarine, 2·702. W. E. Ford studied the rise in the sp. gr. with increasing proportions of alkalies. The **hardness** is 7–8. According to H. Vater, the coeff. of **elasticity** increases with increasing load, but with an alternation of loading, there is a steady decrease. W. Voigt found in directions 0°, 45°, and 90° to the chief axis, the coeff. of elasticity 21650, 17960, and 23120 kgrms. per sq. mm. respectively; and the **modulus of torsion,** parallel and perpendicular to the chief axis, 6666 and 8830 kgrms. per sq. mm. He also found the coeff. of **compressibility** to be $\beta=0{\cdot}0_6 75$, or 70 times smaller than with water; E. Madelung and R. Fuchs gave $\beta=0{\cdot}0_6 57$ ($p$=125 atm.).

F. Pfaff found the coeff. of **thermal expansion** of beryl to be $\alpha=0{\cdot}0000017214$ in the direction of the $c$-axis, and $\alpha=0{\cdot}0_5 1316$ in the direction of the $a$-axis; or, for the coeff. of cubical expansion, $0{\cdot}0_5 105$. H. Fizeau gave at 40° parallel to the chief axis, $\alpha=0{\cdot}0_5 106$; and perpendicular to that axis, $\alpha=0{\cdot}0_5 137$; or, for the coeff. of cubical expansion at 40°, $0{\cdot}0_5 168$. The maximum density lies at −42°; H. Panebianco gave −47° for this temp. A. Offret found that unit vol. at 0° became 1·000743 at 500°. According to R. Benoit, the coeff. of linear expansion at $\theta°$ is $\alpha=-(1304{\cdot}9-8{\cdot}06\theta)10^{-9}$ parallel to the chief axis, and $\alpha=(993{\cdot}7+9{\cdot}316\theta)10^{-9}$ perpendicular to that axis. H. de Sénarmont found elliptical melting figures were obtained by the experiment described **1.** 11, 5, Fig. 18. According to E. Jannetaz, the ratio of the sq. roots of the **thermal conductivities** perpendicular and parallel to the chief axis is 1 : 0·92. J. Joly gave 0·2066–0·2127 for the **specific heat** of different samples of beryl; P. E. W. Oeberg gave 0·1979. A. Brun gave 1410°–1430° for the **melting point** of beryl from Limoges. A. S. Watts found the softening temp. of mixtures of ground microcline and beryl, and of orthoclase and beryl. J. Joly found that yellow and green beryls became colourless at 357°. C. Doelter found that a higher temp. was needed for aquamarine; green beryls became paler but were not decolorized by heating in oxygen or in reducing gases. E. Newbery and H. Lupton found that a green beryl became blue after it had been heated by the Bunsen flame.

The **index of refraction** of beryl has been measured by F. Kohlrausch, A. des Cloizeaux, J. C. Heusser, J. Danker, H. Dufet, B. Jezek, A. Offret, L. Duparc and co-workers, E. Rengade and A. Lacroix, and L. Maddalena. The results vary for Na-light from $\omega$=1·571–1·6033; and from $\epsilon$=1·566–1·5955. W. E. Ford found that with increasing proportions of alkalies, the index of refraction of most minerals is reduced, but, with beryl, the converse rule obtains; cæsia, on account of its high mol. wt., exerts an overpowering influence. A. Schrauf measured the effect with different spectral lines. L. Duparc and co-workers found that with Li-light, $\epsilon$ varied from 1·5728–1·5740, and $\omega$ from 1·5787–1·5865; with Na-light, $\epsilon$ varied from 1·5756–1·5831, and $\omega$ from 1·5818–1·5899; and with Tl-light, $\epsilon$ varied from 1·5791–1·5864, and $\omega$ from 1·5850–1·5931. A. Offret found the effect of temp. to be as follows:

| | | Li-ray. | Na-ray. | Green Cd-ray. | Blue Cd-ray. |
|---|---|---|---|---|---|
| 20° | $\omega$ | 1·570980 | 1·574043 | 1·576570 | 1·580448 |
| | $\epsilon$ | 1·566050 | 1·569027 | 1·571497 | 1·575348 |
| 320·4° | $\omega$ | 1·575089 | 1·578219 | 1·580862 | 1·584904 |
| | $\epsilon$ | 1·569887 | 1·572936 | 1·575439 | 1·579306 |

H. Dufet represented the change which occurs by raising the temp. to $\theta°$, $\delta\omega/\delta\theta\times10^7=189{\cdot}4-10{\cdot}34\theta+0{\cdot}2735\theta^2$; and $\delta\epsilon/\delta\theta\times10^7=180{\cdot}3-10{\cdot}314\theta+0{\cdot}2735\theta^2$. The **double refraction** is not strong; L. Duparc and co-workers obtained $\omega-\epsilon$ =0·0081–0·0084; and H. Dufet gave for the effect of temp., $\delta(\omega-\epsilon)/\delta\theta=0{\cdot}0_6 91-0{\cdot}0_8 26\theta$. The **optical character** is negative. W. E. Ford, and A. Lacroix studied

the effect of increasing proportions of alkalies on the optical properties. The crystals are **pleochroic.** This subject was discussed by G. Tschermak. F. M. Stapff found a beryl from West Africa showing a distinct asterism, and the so-called cat's-eye effect. W. Vernadsky found the crystals to be **triboluminescent.** According to L. Sohnke, the crystals are fluorescent, but J. Schincaglia could not confirm this. E. Newbery and H. Lupton found that a crystal which had been exposed to radium rays gave a feeble bluish-white **thermoluminescence** which appeared only on the basal planes. S. C. Lind and D. C. Bardwell found no fluorescence or change of colour by exposing aquamarine or emerald to **α-rays.** A synthetic emerald which had been exposed to radium radiations for 10 days gave a faint green thermoluminescence at 200°. E. Engelhardt observed some crystals have a pale green fluorescence in ultra-violet light. C. Doelter observed no fluorescence in **radium rays,** but on exposure the colour darkens a little. He also found that beryl is opaque to the **X-rays,** and aquamarine was darkened a little by exposure to X-rays. C. Baskerville and G. F. Kunz found that a rose-coloured beryl became cherry-red by the action of X-rays. V. Goldschmidt and R. Brauns studied the origin of a circle of light found on aquamarine from Brazil. W. G. Hankel found the **pyroelectricity** of the crystals to be small. J. Curie found the **dielectric constant** to be 6·24 parallel to the optic axes and 7·58 perpendicular to that direction; W. Schmidt gave 5·55 and 6·05 respectively. The **paramagnetism** was investigated by J. Plücker; and W. Voigt and S. Kinoshuto investigated the **magnetic susceptibility.**

Beryl is insoluble in acids other than hydrofluoric acid. G. A. Kenngott [7] found that the moistened and powdered mineral shows no reaction with litmus, but it reacts distinctly alkaline after calcination. According to J. Lemberg, when beryl is digested with a 12 per cent. soln. of sodium silicate at 200°, up to about 19 per cent. passes into sodium silicate decomposed by hydrochloric acid. The transformation of beryl into kaolinite and muscovite has been discussed by H. Müller, A. Grattarola, A. Damour, and A. Atterberg.


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## § 46. Magnesium Aluminium, Thallium, and Rare Earth Silicates.

H. Abich [1] observed that one part of spinel intimately mixed with 1·2 parts of silica, fuses to a grey mass which does not adhere to the platinum crucible, and is not attacked by the strongest acids. It is decomposed by fusion with potassium carbonate. W. Heldt fused a mixture $MgO : Al_2O_3 : SiO_2 = 1 : 3 : 3$; P. Berthier, mixtures 3 : 1 : 3, and 3 : 1 : 6; N. G. Sefström, 3 : 1 : 3; and L. Bourgeois, 12 : 2 : 9, and 2 : 1 : 5. J. Lemberg replaced part of the calcium in many calcium aluminium silicates with magnesium, by digesting them in a soln. of a magnesium salt. H. Mäckler, A. E. Hœttinger, L. E. Barringer, G. Flach, and R. Rieke studied the effect of heating mixtures of china clay and magnesia, with and without quartz

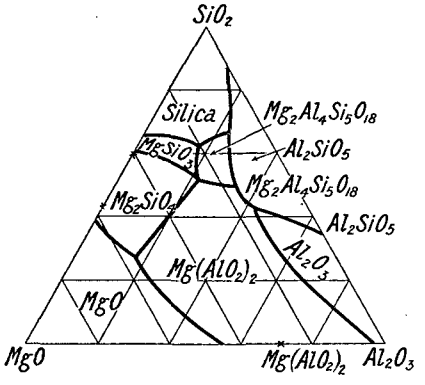



FIG. 181.—Equilibrium Diagram of the Ternary System: $MgO$–$Al_2O_3$–$SiO_2$.

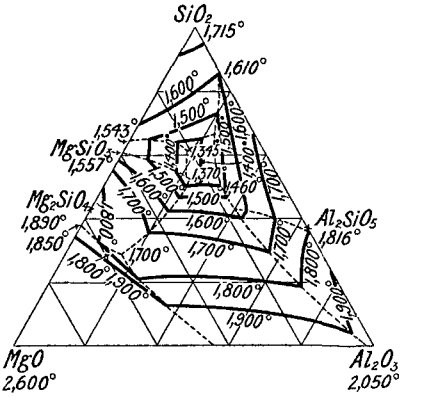



FIG. 182.—Melting-point Curves of the Ternary Mixtures: $MgO$–$Al_2O_3$–$SiO_2$.

addition. The magnesium aluminium silicates are not so numerous as those of calcium. The ternary system $MgO$–$Al_2O_3$–$SiO_2$ for dry melts of the constituent oxides has been explored by G. A. Rankin and H. E. Merwin,[2] and the results are summarized in Figs. 181 and 182. The latter shows the m.p. of all ternary mixtures of these oxides. The binary compounds have been discussed elsewhere. The sole ternary compound is represented by cordierite, $2MgO.2Al_2O_3.5SiO_2$, now to be considered. A. Meissner, and P. Niggli described the ternary system.

E. von Schlotheim [3] referred to a blue mineral from Cabo de Gata as *Spanish lazulite*. A. G. Werner, and D. L. G. Karsten called it *iolite*—from ἴον, violet—λίθος, stone; L. Cordier called it *dichroite*—δίχροια, double coloured—in allusion to its dichroism; J. Gadolin, *steinheilite*—after C. A. Steinheil; Y. Kikuchi, *cerasite*—from κέρασος, cherry—in allusion to the Japanese name of cherry-stone

for the rock containing the altered mineral; and C. A. S. Hofmann, *peliome*—from πελιός, livid—in allusion to its smoky-blue colour. J. A. H. Lucas, and R. J. Haüy finally adopted the term **cordierite** because names derived from the colour are not always applicable, and dichroism is found in many other minerals. L. Cordier, and C. C. von Leonhard showed that peliome and dichroite are identical; and F. Stromeyer[4] that stenheilite and cordierite are the same.

Early analyses were made by C. G. Gmelin, R. Brandes, and F. Stromeyer. Numerous analyses have been since made, and from them C. F. Rammelsberg calculated the formulæ $R''_2Al_4O_5O_{18}$ and $R''_3Al_6Si_8O_{28}$; O. C. Farrington, $(Mg,Fe)_4Al_8Si_{10}O_{36}.H_2O$; A. Osann, $(Mg,Fe)_3(Al,Fe)_6Si_8O_{28}$; W. E. Hidden and J. H. Pratt, $(Mg,Fe)_4Al_8Si_{10}O_{36}.H_2O$; P. Groth, $(Mg,Fe)_4(OH)_2Al_8(Si_2O_7)_5$; and E. A. Wülfing and L. Oppenheimer, $Mg_3Sl_6Si_8O_{28}$. The best representative value is $Mg_2Al_4Si_5O_{18}$. The latter formula agrees with the work of G. A. Rankin and H. E. Merwin. Cordierite may then be represented as **magnesium dialumyl-aluminium orthopentasilicate,** $Mg_2Al_2(AlO)_2Si_5O_{16}$. The analyses of cordierite have up to 2·5 per cent. of water. Most observers consider that the water is due to the partial alteration of cordierite by weathering. M. Weibull found that the cordierite he investigated contained the hydrated silicates, muscovite, talc, and kaolinite, which could be detected microscopically; and he considers that the mineral itself is anhydrous. O. C. Farrington, and F. Zambonini observed the loss of water at different temp. The latter found with two different samples:

| | 125° | 205° | 255° | 300° | 350° | 400° | 480° |
|---|---|---|---|---|---|---|---|
| Loss . . | 0·35 | 0·45 | 0·56 | 0·65 | 0·66 | 0·75 | 0·95 |
| Loss . . | 0·08 | 0·13 | 0·23 | 0·27 | – | 0·34 | – |

F. Zambonini, and F. W. Clarke think that the water is an intrinsic part of the mineral. F. W. Clarke writes the formula:

$$\begin{matrix}AlMg\equiv Si_2O_7\\AlMg\equiv Si_2O_7\end{matrix}>(AlOH)_2Si_2O_7<\begin{matrix}Si_2O_7\equiv AlMg\\Si_2O_7\equiv AlFe\end{matrix}$$

Since the proportion of water varies from sample to sample, and anhydrous cordierite can be obtained synthetically, it is assumed that cordierite itself is not a hydrated silicate.

Cordierite is found in a great variety of rocks—both eruptive and metamorphic—*e.g.* gneiss, granite, basalt, porphyry, trachyte, dacite, andesite, etc. It is thought to have been formed by crystallization from the fused magma after biotite but before the felspars. This subject has been discussed by H. Bücking,[5] E. Hussak, J. Szabo, A. Harker, E. O. Hovey, G. A. F. Molengraaff, A. Lacroix, A. E. Bergeat, K. Jimbo, etc. It has been found as a product of contact metamorphism. H. Bücking, and F. Zirkel, for instance, found it in sandstone vitrified in contact with basalt; A. Scott, in shale metamorphosed by contact with essexite; and Y. Kikuchi, in slate in contact with granite. R. Brauns, and A. Lacroix have also made observations on the formation of cordierite by pyrometamorphic actions. C. Doelter, E. Hussak, and L. Bourgeois made cordierite by fusing a mixture of silica, magnesia, and alumina in proper proportions. J. Morozewicz obtained it in his experiments on artificial magmas supersaturated with alumina. When magnesia and iron were present in magmas of the composition $RO.mR_2O_3.nSiO_2$, and $n$ was greater than 6, cordierite was formed. G. A. Rankin and H. E. Merwin have shown the region of stability of this compound in the ternary system, $MgO–Al_2O_3–SiO_2$. Crystals are best obtained from melts in which it (or sillimanite) is the primary phase. This compound was found to be unstable at its m.p., and is considerably affected by solid soln. with the boundary compounds, Fig. 177. There are two forms. An unstable **β-cordierite** crystallizes from glasses at temp. below about 950°; and at somewhat higher temp., it passes into stable **α-cordierite.** The properties of both forms—but particularly those of

the α-form—are close to those of the mineral cordierite. G. A. Rankin and H. E. Merwin added :

Aggregates with the ternary compound as the chief constituent were prepared by heating for periods of 15 mins. to 5 hrs. at 900°–1400°. While the glass was heating, the μ- or unstable form of the ternary compound began crystallizing at 900° or less as fine fibres which radiated from points on the surface of the grains. At temp. of 925°–1150° this form inverted to the α-form. The inversion in different portions of the same charge, and in different aggregates from glasses of the same composition, had an extreme temp. range of about 200°. This range is mostly accounted for in a lag in the starting of the inversion. When once started in a grain the inversion proceeded so rapidly that only in a few instances was a grain found, after quenching, to contain both forms.

Cordierite occurs in short prismatic, six- or twelve-sided crystals, often with rounded edges ; it also occurs massive, and in embedded grains. The colour is various shades of blue, grey, yellow. The transparent blue pebbles of Ceylon are cut as gem-stones so as to display the colour to the best advantage. As a gem-stone, pale blue cordierite is known as *saphir d'eau*, and the darker varieties as lynx-sapphire. Blue corundum is harder and posseses a higher sp. gr. than cordierite. L. Cordier,[6] and R. J. Haüy assumed that the crystals are hexagonal ; F. Mohs showed that they belong to the rhombic system, and W. H. Miller gave for the axial ratios $a : b : c = 0{\cdot}58709 : 1 : 0{\cdot}55835$. Observations were made by V. Goldschmidt, A. des Cloizeaux, G. vom Rath, F. Tamnau, A. Breithaupt, A. Lévy, J. F. L. Hausmann, etc. F. Rinne studied the X-radiograms of cordierite. G. A. Rankin and H. E. Merwin found that the artificial crystals are advantageously studied when they occur in melts of higher refractive index, say in melts with less than 55 per cent. silica. The crystals were usually stout six-sided prisms with basal termination, and negative elongation. The prism angle was 120°, and basal sections gave a nearly or quite uniaxial negative interference figure. In one case there was evidence of rhombic symmetry. These crystals had the 120° prism, and the side and basal pinacoids corresponding to the faces on the other crystals ; they also had the front pinacoid and a second prism which bevels the edge between the side pinacoid and axial prism. Penetration twinning of cordierite is parallel to (110) and oft repeated, furnishing pseudohexagonal forms ; the twinning parallel to (130) also furnishes pseudohexagonal forms. The faces (100) and (010) are sometimes vertically striated. The crystals often show a lamellar structure parallel to (001) especially when partially weathered. The cleavage parallel to (010) is distinct, and that parallel to (001) is indistinct. A. des Cloizeaux gave for the optic axial angle $2V = 39°\ 32'–84°\ 28'$ ; $2E = 63°\ 45'–125°\ 16'$ ; and $2H = 82°\ 21'$. L. Duparc and co-workers gave $2V = 69°\ 38'–71°\ 12'$ ; A. Offret gave $2E = 115°\ 38'$ ; A. Osann, $2E = 85°\ 50'$ ; and L. Oppenheimer, $2E = 70°\ 30'–161°\ 34'$, and $2V$ from $40°\ 46'–87°\ 12'$ for Na-light. The axial angle was found to increase from $43°\ 36'–85°\ 34'$ as the iron-content and sp. gr. decreased. A. des Cloizeaux found that raising the temp. increased the axial angle $2E$ from $63°\ 56'$ at 8·8° to $71°\ 40'$ at 150·8° with the red ray. W. Klein found that $2E$ passed from $68°\ 9'$ at 16° to $77°\ 43'$ at 200°. F. Rinne studied the X-radiograms of cordierite.

The sp. gr. is between 2·581 and 2·660; when iron is present, the sp. gr. is higher ; thus, E. A. Wülfing and L. Oppenheimer obtained 2·625–2·628 with samples containing about 12 per cent. of iron oxide. The hardness is 7–7½. A. Brun gave for the m.p. 1310°. In Figs. 181 and 182, the mixture corresponding with $Mg_2Al_4Si_5O_{18}$ is outside the region representing mixtures containing this compound. The compound dissociates when melted, and therefore has no definite m.p. C. Doelter and E. Hussak found that cordierite crystals were not changed when dipped in molten augite. G. A. Rankin and H. E. Merwin found a ferruginous cordierite after heating half an hour at 1440°, consisted of glass and sillimanite.

The indices of refraction have been measured by A. des Cloizeaux, K. Zimanyi, A. Offret, A. Osann, A. Michel-Lévy and A. Lacroix, etc., and the values range from $\alpha = 1{\cdot}5320–1{\cdot}5918$ ; $\beta = 1{\cdot}5360–1{\cdot}5970$ ; and $\gamma = 1{\cdot}5390–1{\cdot}5992$, with Na-light. L. Duparc and co-workers found $\alpha = 1{\cdot}5359$, $\beta = 1{\cdot}5414$, and $\gamma = 1{\cdot}5440$ for

Li-light; $\alpha$=1·5392, $\beta$=1·5443, and $\gamma$=1·5475 for Na-light; and $\alpha$=1·5423, $\beta$=1·5473, and $\gamma$=1·5506 for Tl-light. L. Oppenheimer gave for Na-light $\alpha$=1·5330–1·5520; $\beta$=1·5381–1·5599; and $\gamma$=1·5406–1·5610. A. Offret measured the effect of temp. and nature of light on the refractive index, and found:

| | | Li-ray. Red. | Cd-ray. Red. | Na-ray. Yellow. | Cd-ray. Grey. | Cd-ray. Blue. |
|---|---|---|---|---|---|---|
| $\alpha$ | 20° | 1·588620 | 1·589503 | 1·591786 | 1·594482 | 1·598731 |
| | 313° | 1·592947 | 1·593834 | 1·596196 | 1·598947 | 1·603209 |
| $\beta$ | 20° | 1·593798 | 1·594656 | 1·596995 | 1·599848 | 1·603972 |
| | 313° | 1·567920 | 1·598875 | 1·601180 | 1·603918 | 1·608327 |
| $\gamma$ | 20° | 1·596010 | 1·596921 | 1·599189 | 1·601980 | 1·606315 |
| | 313° | 1·600282 | 1·601262 | 1·603621 | 1·608500 | 1·610818 |

G. A. Rankin and H. E. Merwin found that the refractive indices of the artificial crystals $\alpha$=1·519, $\beta$ and $\gamma$=1·522; and $\alpha$=1·524, $\beta$ and $\gamma$=1·528. The birefringence of cordierite is feeble, $\gamma-\alpha$=0·0047, $\gamma-\beta$=0·0013, and $\beta-\alpha$=0·0058. The range for $\gamma-\alpha$ is 0·011–0·0047. The birefringence found by G. A. Rankin and H. E. Merwin for the artificial crystals $\gamma-\alpha$=0·003–0·004. The optical character is negative. A. Beer investigated the absorption spectrum of cordierite with red light. The effect of polarized light was described by D. Brewster, W. Haidinger, A. Bertin, T. Liebisch, etc. A. Agafanoff measured the absorption spectrum of cordierite in ultra-violet light. The pleochroism of many coloured crystals of cordierite is strong. Observations were made by W. Haidinger, A. Osann, H. Rosenbusch, and A. Offret. Crystals from Ceylon gave $\alpha$, light yellow; $\beta$, deep violet; $\gamma$, pale violet; from Bodenmais: $\alpha$, yellowish-white; $\beta$, milk-white; $\gamma$, greenish-white; from Simiutak: $\alpha$, smoke-brown; $\beta$, leather-brown; $\gamma$, honey-yellow; and from Orijarfoi: $\alpha$, clove-brown; $\beta$, dark Berlin blue; and $\gamma$, light Berlin blue. There are often pleochroic spots in cordierite in the zones of contact metamorphism. These are bright yellow with light vibrating parallel to the *c*-axis, and colourless with light vibrating parallel to either of the other two axes. The pleochroic haloes disappear when heated, and they are absent in cordierite from igneous rocks. They are thought to be produced by an organic pigment about the inclusions, but J. Joly has shown that in many cases, if not all, they are caused by the radioactive properties of a particle in the centre of the halo. O. Mügge produced colours of like tint by exposing cordierite to the rays from specks of radium—*vide* mica. O. Anscheles confirmed the radioactive origin of these haloes by exposing the mineral to radium rays. M. Weber discussed the development of a pleochroic halo in zircon by contact with a cordierite crystal. G. Hövermann, and M. Weber made observations on the subject. E. Reymond studied the actions of chlorine and of hydrogen chloride on cordierite.

Cordierite is readily altered by exposure, so that the mineral is most commonly found in an altered state or surrounded by a crust of altered cordierite. The alteration of cordierite has been discussed by F. W. Clarke,[7] A. Wichmann, W. Haidinger, C. R. van Hise, etc. The change may involve simple hydration as in the formation of fahlunite; some of the lime may be removed by carbon dioxide; and iron oxide or alkalies may be introduced. Mica in some of its forms is a common product of the change and a number of pseudomorphs after cordierite have received special names.

T. Scheerer reported a mineral from Kargarōe, Norway, which he named *aspasiolite*—after *ἀσπάζομαι*, welcome—and it has been discovered by W. Haidinger, J. R. Blum, F. P. Möller, F. Zirkel, A. Wichmann, A. Lacroix, etc. The sp.gr. is 2·764. P. A. von Bonsdorff described a "hydrated iolite" from Abo, Finland. It was called *auralite*; and T. Thomson called it *bonsdorffite*. W. Haidinger, J. R. Blum, A. des Cloizeaux, H. J. Holmberg, A. Lacroix, and F. J. Wiik have made observations on the mineral. For *catapilite*, *vide* mica. C. T. Jackson described a mineral which he named *chlorophyllite*—from *χλωρός*, green; *φύλλον*, leaf—and obtained from Unity, Maine. Its sp. gr. was 2·77. It was discussed by C. U. Shepard, W. Haidinger, P. Barbier, C. F. Rammelsberg, F. Gonnard, C. Baret, M. F. Heddle, A. Wichmann, F. Zirkel, and G. A. Kenngott. A. Erdmann obtained a mineral which he named *esmarkite*, from Bräkke, Norway. F. Pisani regarded it as a scapolite; and W. Haidinger, F. P. Möller, A. Lacroix, J. J. Berzelius, and

J. R. Blum, as an altered cordierite. W. Hisinger obtained a mineral which he named *fahlunite* from Fahlun, Sweden; J. F. L. Hausmann called it *triclasite* in allusion to the three cleavages which are in part due to the original cordierite. It was described by R. J. Haüy, J. R. Blum, F. J. Wiik, A. Wichmann, and W. Haidinger. The minerals *gignatolite* and *gongylite* are discussed in connection with mica. L. F. Svanberg found a mineral which he called *groppite* at Gropptorf, Sweden. It was discussed by A. des Cloizeaux, G. Tschermak, and H. Fischer. T. Thomson described a mineral occurring near Lake Huron, and he called it huronite. J. D. Dana described it as an altered fahlunite; B. J. Harrington, as a decomposed felspar. L. F. Svanberg's minerals, *iberite* and *oosite*, were described in connection with mica. C. P. Carlsson described a mineral *peplolite* from Ramsberg, Sweden, as an altered cordierite. The mineral *pinite* is described in connection with mica. P. C. Weibye described prismatic crystals of *polychroilite*—from πολύς, many; χροιά, colour—obtained from the gneiss at Krageröe, Norway. It was described by J. D. Dana, and A. des Cloizeaux. A. Erdmann found a mineral in the granite at Bräkke, Norway, and he called it *prasiolite*—from πράσιος, leek-green. It was also described by W. Haidinger, P. C. Möller, F. Zirkel, F. Gonnard, A. Wichmann, and J. R. Blum. N. Nordenskjöld found a mineral in the granite at Helsingfors, Finland; he named it *pyrargillite*—from πῦρ, fire; ἄργιλλος, clay. It was described by L. F. Svanberg, J. R. Blum, A. Wichmann, F. J. Wiik, and A. Lacroix. P. A. von Bonsdorff obtained from Raumo, Finland, a mineral which he called *raumite*, and which A. E. Nordenskjöld showed to be like prasiolite. H. G. T. Wachtmeister found a mineral at Fahlun, Sweden, which he named *weissite*—after C. S. Weiss. It was discussed by W. Haidinger, S. Tennant, and J. D. Dana. A. Brusoni[8] described a rhombic mineral from Volpedo, Piedmont, which he called *zebedassite*, its composition is $5MgO.Al_2O_3.6SiO_2.4H_2O$. A. N. Winchell described a mineral from Bingham, Utah, which he called *racewinite*. It is hydrated calcium ferric aluminium silicate of sp. gr. 1·94–1·98.

J. Lorenzen[9] described a mineral from Fiskernäs, Greenland, which he called **kornerupine**—after M. Kornerup—and A. Sauer independently described a mineral from Waldheim, Saxony, which he called *prismatine*. The two descriptions are so much alike that N. V. Ussing said that it can hardly be doubted that they refer to the same mineral species. The analyses correspond approximately with the formula $MgAl_2SiO_6$, or **magnesium aluminium aluminatorthosilicate**, $Al{\equiv}SiO_4{-}MgAlO_2$; although J. Uhlig's analysis corresponds better with $NaH_3Mg_6Al_{12}Si_7O_{40}$, which F. W. Clarke regards as a heptaorthosilicate; and for the simpler analysis, he gave $(Al{\equiv}SiO_4)_2{=}Al{-}SiO_4{\equiv}(MgAlO_2)_3$. It is assumed that augites (*q.v.*) are mixtures of silicates in isomorphous association with silicates of this type. A. Lacroix and A. de Gramont represented kornerupine as a boriferous mineral, $Mg_8\{(Al,Fe,B)O\}_{12}(SiO_4)_7$. C. Doelter, and J. Morozewicz prepared pryoxenes (*q.v.*) containing 73 per cent. of $MgAl_2SiO_6$, but it was not found possible to isolate either $MgAl_2SiO_6$ or $CaAl_2SiO_6$, since both decompose in molten fluxes. C. Doelter and E. Dittler reported rhombic crystals of magnesium aluminium aluminato-orthosilicate, $MgAl_2SiO_6$, were produced by sintering a mixture of the constituent oxides. E. Fixek fused a mixture of magnesium metasilicate, diopside, alumina, and ferric oxide, and obtained mixed crystals containing 30 per cent. of the silicate in question. *Vide* Z. Weyberg's $KAl''_2SiO_6$. Kornerupine occurs in colourless, white, or yellowish-brown fibrous or columnar aggregates resembling sillimanite, and it shows prismatic zones (110), (100), and (010). The crystals belong to the rhombic system with the axial ratios $a:b:c = 0{\cdot}862:1:-$, to $0{\cdot}854:1:-$, according to N. V. Ussing. The cleavage is prismatic and well-defined. The optic axial angles are $2E = 65\frac{1}{2}$, $2V = 37°\ 34'$ $37°\ 7'$ for Na-light. According to N. V. Ussing, the sp. gr. is 3·273–3·341; and the hardness 6·5. The indices of refraction are $\alpha = 1{\cdot}6691$, $\beta = 1{\cdot}6805$, and $\gamma = 1{\cdot}6818$ for Na-light. The coloured crystals are pleochroic. According to A. Sauer, prismatine alters into a fine fibrous mineral of a light green colour which he called *cryptotite*—from κρυπτός, hidden; τίλαι, fibre. According to P. Groth, the composition approximates $HAlSiO_4$—*vide supra*.

C. d'Ohsson[10] noted the occurrence of a granular honey-yellow mineral in the limestone of Pargas, Finland, and he called it **chondrodite**—from χονδρός, a grain. H. Seybert noted a similar mineral at Sparta, New Jersey, and he called it *maclureite*—after W. Maclure. The analyses of maclureite by H. Seybert, and W. Langstaff showed that it is a magnesium fluosilicate. The presence of fluorine was

overlooked by C. d'Ohsson. P. Cleaveland's suggestion to call the mineral *brucite*—after A. Bruce—was not adopted, since F. S. Beudant employed the term for native hydrated magnesia. J. L. de Bournon named some dark reddish-brown crystals from Monte Somma, **humite**—after A. Hume. T. Monticelli and N. Covelli regarded humite, maclureite, and brucite as synonyms of chondrodite. R. J. Haüy showed that chondrodite is monoclinic, and W. Phillips, that humite is rhombic. The results of the studies of A. Lévy, J. C. G. de Marignac, C. F. Rammelsberg, J. F. L. Hausmann, A. Scacchi, W. H. Miller, J. D. and E. S. Dana, A. E. Nordenskjöld, N. von Kokscharoff, F. Hessenberg, G. vom Rath, M. Websky, E. S. Breidenbaugh, G. W. Hawes, C. Klein, and A. des Cloizeaux were thus summarized by P. Groth. There are three types of crystals of magnesium fluosilicate occurring in nature. The first type furnishes rhombic crystals which may be called *humite;* the second type furnishes monoclinic crystals which may be called *chondrodite;* and the third type also gives monoclinic crystals for which he proposed the name **clinohumite.** H. Sjögren found yet a fourth type furnishing monoclinic crystals which he called **prolectite**—from προλέγειν, to foretell—in allusion to the prediction of S. L. Penfield and W. T. H. Howe that a member of this family corresponding with this mineral remained to be discovered.

The axial ratios of members of the series were measured by G. vom Rath A. Scacchi, E. S. Dana, H. Sjögren, etc. With the scale of reference employed by A. Scacchi, and E. S. Dana, the results can be summarized:

| | | $a:b:c$ | |
|---|---|---|---|
| Prolectite, $Mg(MgF)_2SiO_4$ | Monoclinic | 1·0803 : 1 : 2·3877 | (or 0·7959×3) |
| Chondrodite, $Mg_3(MgF)_2(SiO_4)_2$ | Monoclinic | 1·0863 : 1 : 3·1447 | (or 0·6290×5) |
| Humite, $Mg_5(MgF)_2(SiO_4)_3$ | Rhombic | 1·0802 : 1 : 4·4033 | (or 0·6290×7) |
| Clinohumite, $Mg_7(MgF)_2(SiO_4)_4$ | Monoclinic | 1·0803 : 1 : 5·6588 | (or 0·6288×9) |

This is a good example of P. Groth's *morphotropische Riehe*, where the addition of a $Mg_2SiO_4$-mol. adds a certain length to the vertical axis, without affecting the other axes or the axial angle $\beta=90°$, so that the vertical axis of prolectite is nearly $\frac{3}{9}$ths, that of chrondrodite $\frac{5}{9}$ths, and that of humite $\frac{7}{9}$ths of that of clinohumite. The relations of these minerals was also discussed by T. V. Barker.

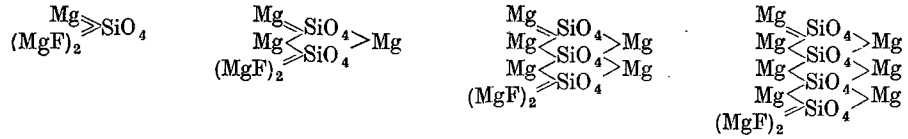
No analysis of prolectite is available; analyses of chrondrodite were made by C. F. Rammelsberg, G. vom Rath, F. C. von Wingard, H. Sjögren, F. Berwerth, W. Fischer, G. W. Hawes, E. S. Breidenbaugh, N. von Kokscharoff, M. Siewert, and S. L. Penfield and W. T. H. Howe; analyses of humite by C. F. Rammelsberg, G. vom Rath, W. Langstaff, H. Seybert, W. Fischer, T. Thomson, F. C. von Wingard, H. Sjögren, and S. L. Penfield and W. T. H. Howe; and analyses of clinohumite by C. F. Rammelsberg, F. C. von Wingard, G. vom Rath, A. K. Coomaraswamy, and S. L. Penfield and W. T. H. Howe.

The analytical difficulties in the accurate determination of silica, fluorine, and small quantities of combined water prevented for a long time the establishment of the chemical relations of these minerals. A. Scacchi supposed that chondrodite, humite, and clinohumite represented three types of crystallization of one and the same chemical substance; C. F. Rammelsberg, and G. vom Rath suggested the formula $Mg_5Si_2O_9$ for the whole group provided part of the oxygen be replaced by fluorine. They noted that the percentages of silica varied in the different types. E. Mallard made a guess at the composition by assuming it to be a mixture of olivine, pericline, and sellaite. P. Groth suggested that part of the fluorine is replaced by hydroxyl; and F. C. von Wingard concluded that the three minerals have the same chemical composition, *viz.* $Mg_{19}F_4(OH)_2Si_8O_{38}$. H. Sjögren recalculated the older analyses, and after a consideration of the neglected water, concluded that each of these minerals should be represented by a separate formula, and he emphasized the isomorphous replacement of fluorine by hydroxyl. S. L. Penfield and W. T. H. Howe employed specially selected materials purified by hand picking and the flotation of the powders. They showed that these minerals form a chemical

series progressing from prolectite to clinohumite by an increase of one mol of $Mg_2SiO_4$. Thus:

| | Magnesium. |
|---|---|
| Prolectite . . | tetrafluohydroxyorthosilicate, $Mg\{Mg(F,OH)_2\}_2SiO_4$ |
| Chondrodite . | tetrafluohydroxydiorthosilicate, $Mg_3\{Mg(F,OH)_2\}_2(SiO_4)_2$ |
| Humite . . | tetrafluohydroxytriorthosilicate, $Mg_5\{Mg(F,OH)_2\}_2(SiO_4)_3$ |
| Clinohumite . | tetrafluohydroxytetraorthosilicate, $Mg_7\{Mg(F,OH)_2\}_2(SiO_4)_4$ |

The first member of this series was not known when S. L. Penfield and W. T. H. Howe published their work, but they said that it is "a possible and a most likely compound to occur," and it was discovered soon afterwards at Nordmark, Sweden, by H. Sjögren. See leucophœnicite, and gageite. According to F. W. Clarke, the chondrodite group gives indications of the possible polymerization of fosterite, $Mg_2SiO_4$. In the first member of the family, one bivalent magnesium atom is replaced by two univalent MgF-groups furnishing prolectite, $Mg(MgF)_2SiO_4$; a similar replacement in $(Mg_2SiO_4)_2$ furnishes chondrodite, $Mg_3(MgF)_2(SiO_4)_2$; likewise $(Mg_2SiO_4)_3$ furnishes humite, $Mg_5(MgF)_2(SiO_4)_3$; and $(Mg_2SiO_4)_4$ furnishes $Mg_7(MgF)_2(SiO_4)_4$. Structurally



Prolectite. Chondrodite. Humite. Clinohumite.

where part of the fluorine may be replaced by HO-groups. Fosterite or chrysolite is closely related to the members of this group; and, as shown by G. vom Rath, a few of its forms are like those of humite — $a : b : \frac{1}{9}c$ for clinohumite is 1·0803 : 1 : 0·6288, and $b : 2a : c$=1·0735 : 1 : 0·6296 for chrysolite. Since the latter contains no fluorine or hydroxyl, it naturally deviates considerably in chemical type from the members of the humite group, and its crystal habit is also different.

The following remarks refer mainly to humite, chondrodite, and clinohumite. The colour of all three minerals is much the same—white, yellow, or chestnut-brown; chondrodite and clinohumite also appear hyacinth-red. The crystals of chondrodite vary in habit; they are often flattened parallel to (010). Chondrodite also occurs massive both compact and in embedded grains. The euhedral crystals of humite are rare. The anhedral crystals of all three minerals may be irregularly shaped, rounded, or ellipsoidal. Humite crystallizes in the rhombic system; the other members of the humite group are monoclinic. The axial ratios are indicated above. The crystals of chondrodite were investigated by A. Scacchi, G. vom Rath, A. des Cloizeaux, F. Hessenberg, H. Sjögren, A. E. Nordenskjöld, C. F. Rammelsberg, N. von Kokscharoff, J. D. Dana, and E. S. Dana; those of humite, by A. Scacchi, G. vom Rath, A. des Cloizeaux, F. Hessenberg, H. Sjögren, and E. S. Dana; and those of clinohumite, by A. Scacchi, E. Scacchi, G. vom Rath, F. Hessenberg, W. H. Miller, A. des Cloizeaux, and E. S. Dana. B. Jazek, and A. Ondrej gave for the axial ratios of chondrodite, $a : b : c$=1·08506 : 1 : 3·13937, and $\beta$=90° 0′. Humite crystals usually show penetration twinnings, or lamellar polysynthetic twinnings. Trilling sometimes occurs. The twinning plane with humite crystals is (017) with the two $c$-axes at 60° 26′; also (037) with the $c$-axes at 59° 34½′. Chondrodite and clinohumite show crossed and polysynthetic twinning with the lamellæ parallel to (001). The cleavage parallel to (001) is distinct in humite, and rather less so with chondrodite and clinohumite. The axial angle is large. H. Sjögren gave for red, yellow, and green rays respectively $2V$=68° 1′, 67° 54′, and 67° 44′ for humite; $2V$=79° 40′, 79° 40′, and 79° 38′ for chondrodite; and $2V$=76° 29′, 76° 27′, and 76° 24′ for clinohumite. A. des Cloizeaux obtained $2H_a$=78° 18′ for humite with the red ray. H. Sjögren also found for $2H_a$ with the red ray 85° 53′–86° 6′,

and 85° 41′–86° 8′ for the blue ray with a yellow chondrodite; and with a brown chondrodite 89° 8′–89° 20′ for the red ray, and 88° 28′–89° 14′ for the blue ray. A. des Cloizeaux found for the red, yellow, and blue rays respectively $2H$=82° 6′–83° 19′, 82° 9′–83° 27′, and 82° 31′–84° 7′; and $2E$=148° 38′–154° 2′, 149° 24′–155° 24′, and 154° 10′–163° 52′. Observations were also made by A. Michel-Lévy and A. Lacroix, C. Klein, and E. S. Dana. The sp. gr. of humite is 3·1–3·2; and similar results apply to chondrodite and clinohumite. The observations of W. Barlow and W. J. Pope, and T. V. Barker on the valency vol. of the series has been discussed **1.** 5, 18. P. E. W. Oeberg gave 0·2142 for the sp. ht. of chondrodite. The indices of refraction are moderate. A. Michel-Lévy and A. Lacroix gave $\beta$=1·643 for humite, and $\alpha$=1·607, $\beta$=1·619, and $\gamma$=1·639 for chondrodite, while H. Sjögren gave $\beta$=1·659 for the same mineral. L. Brugnatelli gave $\beta$=1·638 for chondrodite, and 1·670 for clinohumite. The birefringence is strong; A. Michel-Lévy and A. Lacroix gave $\gamma-\alpha$=0·032–0·028 for humite, and 0·032 for chondrodite. The optical character of all three minerals is positive. Pleochroism is well marked particularly in the brown varieties. The minerals are all decomposed by acids with the separation of gelatinous silica. The transformation of the humites in nature has been discussed by E. S. Dana, and H. Sjögren.

According to F. Stromeyer,[11] K. L. Giesecke found a sapphire-blue mineral at Fiskernäs, Greenland, which was named **sapphirine,** a term wrongly applied by C. A. S. Hofmann to haüyne. Analyses were made by F. Stromeyer, A. Damour, E. Schluttig, J. Lorenzen, and N. V. Ussing. Formulæ were given by J. F. L. Hausmann, N. von Kokscharoff, and G. A. Kenngott. The best representative formula is $Mg_5Al_{12}Si_2O_{27}$. F. W. Clarke represents it by the formula $(AlO_2)_2AlSiO_4 \equiv (MgAlO_2)_3$, **magnesium aluminium pentaluminato-orthosilicate;** and A. Lacroix and A. de Gramont, $9MgO.10(Al,Fe,B)_2O_3.4SiO_2$.

Sapphirine usually occurs in disseminated grains or granular aggregates, and in indistinct tabular crystals. The colour is pale blue or green. G. Forchhammer attributed the colour to the presence of ferrous phosphate. The monoclinic crystals, according to N. V. Ussing, have the axial ratios $a:b:c$=0·65 : 1 : 0·93 and $\beta$=79° 30′. The cleavage is not distinct. The optical axial angles were found by N. V. Ussing to be $2H_a$=68° 50′, $2H_0$=111° 13′, and $2V_a$=68° 49′, for yellow light; A. des Cloizeaux gave for red, yellow, and green light, $2H_a$=77° 50′–83° 29′, 83° 55′, and 83° 34′. The sp. gr. is 3·420–3·486; and the hardness 7½. A. des Cloizeaux gave for the indices of refraction $\alpha$=1·705, $\beta$=1·709, and $\gamma$=1·711 for red light, and N. V. Ussing, $\alpha$=1·7055, $\beta$=1·7088, and $\gamma$=1·7112. A. Michel-Lévy and A. Lacroix gave $\gamma-\alpha$=0·009 for the birefringence. The optical character is negative. The crystals are pleochroic.

G. Agricola [12] referred to *carbunculii carchedonii in Boëmorum agris* which were called *Bohemian garnets* by A. G. Werner, and M. H. Klaproth. The former called the mineral **pyrope**—from πυρωπός, fire-like—and A. Weisbach, *vogesite.* Many analyses [13] have been made. The composition calculated by C. F. Rammelsberg, and C. von John, approximates **magnesium dialuminium triorthosilicate,** $Mg_3Al_2(SiO_4)_3$. Calcium and iron are often present, and the mineral sometimes contains chromium. The work of C. F. Rammelsberg,[14] E. Cohen, and C. von John agrees with the assumption that the chromium is present as sesquioxide in a *magnesium dichromium triorthosilicate,* $Mg_3Cr_2(SiO_4)_3$. H. E. Boeke found evidence that there is a continuous series of mixed crystals between pyrope and almandine—*i.e.* magnesia-garnet and ferrous-garnet.

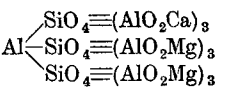
Pyrope is often found in peridotites and the serpentines derived from them. The colour of pyrope is various shades of red, brown, and black. When transparent, pyrope is prized as a gem; and it is the common red garnet of the jewellers. Pyrope does not appear on the ternary diagram, Fig. 177. The general crystallographic properties have been described in connection with grossular—lime-garnets (*q.v.*). The sp. gr. ranges from 2·69–2·78. W. E. Ford gave 3·150, the hardness is 7–7½. P. E. W. Oeberg gave 0·1758 for the sp. ht. C. Doelter found the m.p.

to be 1185°, or rather fusion begins at that temp. He also found that the mineral decomposes when melted, forming spinel, etc., as indicated in connection with grossular. According to C. Doelter, when pyrope is heated in gases the colour is not changed. The indices of refraction given by H. Rosenbusch, P. A. Wagner, and M. Seebach are 1·7369–1·7422 for Li-light; 1·7412–1·7466 for Na-light; and 1·7451–1·7508 for Tl-light. W. E. Ford gave 1·705. B. Jezek found for different samples, 1·73721–1·73914 for Li-light; 1·74301–1·74606 for the *D*-line; 1·74696–1·75258 for Tl-light; and 1·75748–1·76134 for blue light. C. Doelter found the colour of pyrope is not changed by exposure to radium rays; but with some varieties the red colour is deepened both by radium rays and by X-rays. E. Reymond studied the action of chlorine and of hydrogen chloride on pyrope; and V. Iskyul, the action of hydrochloric acid, and the solubility of silica in pyrope.

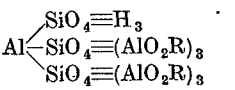
The alterations which pyrope undergoes in nature have been discussed by A. Schrauf,[15] A. E. Delesse, F. Becke, H. von Fouillon, G. Linck, J. S. Diller, A. von Lasaulx, J. Mrha, J. Lemberg, G. Tschermak, and C. R. van Hise. Pyrope changes into chlorite, serpentine, and various more or less indefinite substances; thus, A. Schrauf found near Krems, Bohemia, a substance which he called *kelyphite* —from κέλυφος, a nut-shell—as a crust about a nucleus of pyrope. A. von Lasaulx found that it is not a homogeneous substance.

The minerals seybertite, brandisite, and xanthophyllite belong to the clintonite family of brittle micas. They are complex calcium magnesium aluminosilicates. According to W. W. Mather,[16] seybertite was discovered at Amity, New York, in 1828, by J. Finch and co-workers; it was named *clintonite*, after W. Clinton; and in 1829, J. Finch described the mineral under the name *bronzite*. In 1832, J. G. Clemson described the mineral as **seybertite**—after H. Seybert. A. Breithaupt called the mineral from Amity, *chrysophane*; T. Thomson, *holmite*; and G. Rose, *xanthophyllite*. A related clintonitic mineral from Fassathal, Tyrol, was called **brandisite** —after M. Brandis—by W. Haidinger, and *disterrite*—from δίς, twice; and στερρός, hard—by A. Breithaupt. Another clintonitic mineral from the Urals was called **xanthophyllite**—from ξανθός, yellow; and φύλλον, a leaf—by G. Rose, and *waluewite* or *valuevite*—after P. A. von Waluew—by N. von Kokscharoff.

Analyses of seybertite have been reported by T. G. Clemson, G. J. Brush, G. Tschermak and L. Sipöcz, T. Thomson, and A. Breithaupt; of brandisite, by F. von Kobell, G. Tschermak and L. Sipöcz, and U. Panichi; and of xanthophyllite, by G. Rose, M. Meitzendorff, A. Knop, P. D. Nikolajeff, R. Schläpfer, and F. W. Clarke and E. A. Schneider. C. F. Rammelsberg calculated formulæ for these minerals from the analyses and obtained for seybertite $R''_5Al_4Si_2O_{15}.2H_2O$; for brandisite, $H_{10}R''_{24}Al_{24}Si_{10}O_{85}$; and for xanthophyllite, $R''_5Al_6Si_2O_{18}.2H_2O$, or $H_4R''_5Al_6Si_2O_{20}$. P. Groth gave for seybertite, $H_6(Mg,Ca,Fe)_{10}Al_{10}Si_4O_{36}$; for brandisite, $H_8(Mg,Ca,Fe)_{12}(Al,Fe)_{12}Si_5O_{41}$; and for xanthophyllite: $H_8(Mg,Ca)_{14}(Al,Fe)_{16}Si_5O_{22}$. G. Tschermak considered these three minerals to be isomorphous mixtures of different proportions of an aluminate and a silicate. F. Zambonini considered these minerals to be hydrated mixtures of a disilicate, $H_2R_2Si_2O_7$, an aluminate, $R''Al_2O_4$, and water in the proportions 1 : 2·33 : 1; with brandisite 1 : 2·5 : 0·75; and with xanthophyllite, 1 : 3 : 1. V. Goldschmidt gave for brandisite. $Ca_4(Mg,Fe)_8Al_{12}Si_5O_{40}.4H_2O$. P. Erculisse regards the clintonites as solid soln. of the micas and spinels. F. W. Clarke regards these minerals as morphologically like biotite and having the univalent radicle $AlO_2R''$, where R'' represents Mg, Ca, Fe″. or Mn. Xanthophyllite is considered to be the most basic member of the series :



Xanthophyllite.



Seybertite.

This makes xanthophyllite **calcium magnesium ennealuminoxy-aluminotri-**

**orthosilicate ;** and seybertite, **calcium magnesium trihydrohexaluminoxy-aluminotriorthosilicate.**

The colour of seybertite is yellow, reddish-brown, or copper-red; that of brandisite is yellowish-green, leek-green, or reddish-grey ; and that of xanthophyllite is usually leek- or bottle-green. These minerals all belong to the monoclinic system. Some measurements of the crystal constants have been made by G. Tschermak; and N. von Kokscharoff gave for xanthophyllite the axial ratios $a:b:c$ $=0{\cdot}57736:1:1{\cdot}62214$, and $\beta=90°\ 0'$. The crystals are usually tabular; those of seybertite are sometimes hexagonal in outline. The symmetry of xanthophyllite approximates to that of the rhombohedral system, and the forms simulate the octahedron. Complex twinning occurs as in the case of the other micas. The basal cleavage is perfect. The folia are brittle. Percussion and press. figures correspond to those of the micas. The corrosion figures of xanthophyllite and of seybertite have been studied by F. J. Wiik. G. Tschermak gave for the optic axial angle of seybertite, $2E=3°–13°$ ; and A. des Cloizeaux found that for the red ray, $2E=20°\ 23'$ at 21·5° ; 20° 32′ at 95·5° ; and 20° 40′ at 171°. For brandisite, G. Tschermak gave $2E=18°–35°$ ; and A. des Cloizeaux found in some cases $2E=0°$, in others $2E=15°–20°$, and in another case $2E=28°$, and increase of the angle with a rise of temp. was not unequivocally proved. For xanthophyllite, G. Tschermak found $2E=17°–32°$; H. Bücking, $2E=20{\cdot}5°$; and A. des Cloizeaux, $2E=20°$, with a decrease of about 1° when the temp. rises 26·5°–146·5°. The sp. gr. of all three minerals is near 3·0–3·1 ; and the hardness between 4 and 5. According to F. W. Clarke, xanthophyllite decomposes when heated, forming a portion soluble and a portion insoluble in hydrochloric acid. The insoluble portion has the composition of spinel, $Mg(AlO_2)_2$. F. Zambonini investigated the dehydration of some xanthophyllite from the Urals, and found in a current of air :

| | 130° | 210° | 256° | 350° | 450° |
|---|---|---|---|---|---|
| Percentage loss . . . | 0·19 | 0·31 | 0·37 | 0·51 | 0·64 |

Only 1·98 per cent. was lost by heating the mineral in a porcelain crucible over a Bunsen's burner ; and 5·10 per cent. in a platinum crucible over a gas blowpipe flame. Hence, he concluded that all the combined water is not to be regarded as constitutional water ; a part is extrinsic. A. Knop made some observations on the dehydration of this mineral. A. Michel-Lévy and A. Lacroix found the indices of refraction of seybertite to be $\alpha=1{\cdot}646$, $\beta=1{\cdot}657$, and $\gamma=1{\cdot}658$. The crystals are optically negative. A. S. Eakle found the sp. gr. of xanthophyllite to be 3·081, and A. Laitakari, 3·093 ; for the indices of refraction, A. S. Eakle gave $\beta-\gamma=1{\cdot}660$, and A. Laitakari, $\gamma=1{\cdot}638$, and $\beta-\gamma=0{\cdot}0003$. The crystals are optically negative. The three minerals are pleochroic. Seybertite is readily and completely decomposed by hot conc. hydrochloric acid; brandisite is readily attacked by conc. sulphuric acid, but not so rapidly by conc. hydrochloric acid. F. W. Clarke and G. Steiger found that ammonium chloride vap. attacks xanthophyllite only feebly.

In connection with pyroxene and diopside, it was found convenient to apply the term **augites** to the monoclinic pyroxenes with sesquioxides—alumina, ferric oxide, etc., as essential constituents. The aluminous pyroxenes are also augites. A. G. Werner[17] applied Pliny's term *augite*—from *αὐγή*, lustre—to the black volcanic schorl of the early writers—J. B. L. Romé de l'Isle, F. de la Fond, and J. Démeste ;. A. G. Werner's term, and the *volcanite* of J. C. Delamétherie, included only the black igneous rocks ; while L. A. Emmerling, and A. Estner did not clearly distinguish augite as a definite mineral species. R. J. Haüy included a number of species as pyroxenes (*q.v.*) as A. G. Werner did with augite.

The amphibole of H. Seybert was called *macluerite* by T. Nuttall ; a variety of augite was called *basaltine* by R. Kirwan, and basaltic hornblende by A. G. Werner ; a variety from Fassathal, Tyrol, was called *fassaite* by C. A. S. Hofmann, and *pyrgom*—from *πύργωμα*, a tower—by A. Breithaupt. V. Zsivny analyzed a sample of fassaite from Hodrusbanja (Comitat Hont). A white aluminous augite analyzed by T. S. Hunt was called *leucaugite*

—from λευκός, white—by J. D. Dana. L. Tokody studied the optical properties of fassaite, and V. Zsivny, the composition. E. F. Glocker referred to needle-like crystals of augite in the porous lavas of Eifel and Laacher-See. It was named *porricine*, and described by H. Laspeyres, F. Sandberger, and A. des Cloizeaux.

R. J. Haüy [18] applied the term *diallage* to a green or brown mineral which is found in gabbros and related rocks. The name—from διαλλαγή, difference—was intended to emphasize the dissimilar cleavages or planes of fracture. Typical augite exhibits schillerization, and closely resembles bronzite in appearance. There has been much discussion as to whether diallage is a distinct mineral species, or a variety of pyroxene. G. Tschermak regarded diallage as a member of the augite family, and it has a lamellar or thin foliated structure and parting. It resembles diopside in composition, but usually contains alumina. Analyses were made by G. vom Rath,[19] H. Traube, M. F. Heddle, A. Hilger, T. Petersen, W. Wahl, A. Cossa, A. Cathrein, O. Luedecke, A. R. Leeds, D. Hummel, etc.

The earliest analyses of augite were made by L. N. Vauquelin, and W. Roux; and since then numerous others have been made. The mineral is essentially a metasilicate of calcium, magnesium, and ferrous iron plus ferric and aluminium silicates. Manganese and alkalies are often present, and up to 1·5 per cent. of titanic oxide is present in the so-called *titanic-augites* analysed by A. Knop, P. Merian, E. Lord, A. Streng, C. Becker, B. Mauritz, and F. Gonnard and P. Barbier. There are also pyroxenes with up to nearly 3 per cent. of chromic oxide—*chromic-diopside* and *chromic-augite*. These were analyzed by C. W. von Gümbel, A. Schrauf, R. Scharitzer, E. Jannettaz, A. Knop, F. P. Mennell, H. Lenk, C. F. Rammelsberg, K. Oebbeke, and R. Brauns. Here the chromium replaces part of the aluminium. The mineral *omphazite* or *omphacite* of C. A. S. Hofmann, and A. Breithaupt was named—after ὄμφαξ, an unripe grape—in allusion to the colour; it is a variety of chromic-augite. Analyses were made by L. Hezner, J. Ippen, and O. Luedecke. The character of omphascite was discussed by C. A. S. Hofmann,[20] C. C. von Leonhard, R. J. Haüy, F. Mohs, W. Haidinger, A. Breithaupt, A. des Cloizeaux, J. F. L. Hausmann, G. Tschermak, H. Rosenbusch, and P. T. Riess. A *vanadic-augite* with up to 3·65 per cent. of vanadic oxide was called *lavrovite*, or *lavroffite*, or *lavroffite*—after N. von Lavroff—by N. von Kokscharoff; it was analyzed by K. von Schafhäutl, and P. Hermann—*vide* diopside.

The composition of augite as a mineral is so variable that it has not been possible to formulate the composition of an idealized augite. C. F. Rammelsberg [21] regarded the augites as mixtures of diopside, $CaMgSi_2O_6$, with alumina. G. Tschermak at first supposed alumina-augite to be an isomorphous mixture of diopside with a silicate of the composition $MgAl_2SiO_6$, or $R''Al_2SiO_6$. This silicate is hypothetical, but its composition approximates to that of cornerupine or prismatine (*q.v.*). Here it is assumed that the proportion of calcium is less than that of magnesium. C. Doelter found that this is not always the case, and he assumed the augites to be isomorphous mixtures of diopside with one or more of the silicates $MgAl_2SiO_6$, $MgFe'''_2SiO_6$, $CaAl_2SiO_6$, $CaFe'''_2SiO_6$, and $Fe''Fe'''_2SiO_6$. A. Knop regarded the augites as mixtures of $RSiO_3$, $(Al,Fe)_2O_3$, and $Fe_2Si_3O_9$. N. Parravano, A. Merian, J. Uhlig, A. Cathrein, J. Hampel, F. W. Clarke, J. Götz and E. Cohen, P. Mann, J. W. Retgers, W. Wahl, A. H. Phillips, and others also advocated the view that the augites are solid soln. of different silicates. In the augites which contain alkalies it is assumed that silicates analogous to acmite or jadeite are also in isomorphous association with the other silicates. E. T. Wherry found the at. vol. theory of isomorphism fits in with (i) the complete replaceability of Mg and Fe''; (ii) the slight tendency of Mg or Fe'' to replace Ca; (iii) the existence of Na and Li, and the absence of K, pyroxenes; and (iv) the improbability of G. Tschermak's mol. $R''R'''_2SiO_6$. H. S. Washington regards the pyroxenes as mixtures of jadeite, $Na_2O.Al_2O_3.4SiO_2$; acmite, $Na_2O.Fe_2O_3.4SiO_2$; and diopside, $(Ca,Mg,Fe)O.Al_2O_3.2SiO_2$ mols. Augite and ægirite are composed of acmite and diopside with $Fe_2O_3$ and $Al_2O_3$ in solid soln. P. Erculisse regarded

the augites (and hornblendes) as solid soln. of derivatives of metasilicic acid and the aluminosilicic acid, $H_2Al_2SiO_6$.

Augite is a pyrogenetic mineral, and is commonly found in igneous rocks of all classes. Augite was found by F. Mohs,[22] G. Rose, C. F. Rammelsberg, M. Jerofeeff and P. Latschinoff, E. Ludwig, and G. Tschermak in meteorites. Crystals of augite have been reported in many slags by J. Percy,[23] E. Mallard, N. S. Maskelyne, C. Gruner, G. J. Brush, J. F. L. Hausmann, E. Mitscherlich, J. Nöggerath, C. C. von Leonhard, F. Sandberger, C. F. Rammelsberg, F. von Kobell, C. Vélain, G. vom Rath, T. Scheerer, P. W. von Jeremejeff, J. H. L. Vogt, and E. Reynolds and V. Ball. Augite is readily obtained by simply fusing a mixture of the constituents. It was so obtained by P. Berthier,[24] H. J. Johnston-Lavis, F. Fouqué and A. Michel-Lévy, A. Daubrée, A. Lacroix, C. J. St. C. Deville, S. Meunier, etc. J. Morozewicz found both ordinary augite and the alkaline augites in his work on artificial magmas, when over 50 per cent. silica was present, and when the alumina is in excess of that required for felspar and mica. G. V. Wilson obtained it by the action of glass on fragments of lime. K. Bauer, J. Lenarcic, L. Bourgeois, and C. Doelter obtained augite among the products of the fusion rock magmas—*e.g.* garnet vesuvianite, epidote, biotite, and clinochlore; he also obtained augite by fusing diopside with alumina or ferric oxide. J. Lenarcic obtained augite by fusing a mixture of labradorite and magnetite; and B. Vucnik, by fusing hedenbergite with anorthite, albite, or corundum.

The general properties of the augites are like those of diopside (*q.v.*). The colour of the augites depends on the composition; usually it varies from a dark green to black, and in thin section, colourless to pale green. Augites with no iron may be white—*e.g.* the *leucaugite* of J. D. Dana[25]—*vide supra*. Vesuvian augite is yellow. The titaniferous augites are often pale violet-brown. G. Becker made some observations of the colour of titaniferous augites. Manganese oxide introduces a violet or rose-red colour into the augites—*e.g.* the *violan* of A. Breithaupt, and A. des Cloizeaux. In general, augite crystals appear in short thick prisms, rarely tabular or bladed. The axial ratios of the monoclinic crystals vary but little with wide variations in composition. The change in form with varying amounts of ferrous and ferric oxides has been discussed by G. vom Rath, and G. Flink. Thus, a colourless diopside with 0·51 per cent. $Al_2O_3$, 0·98 $Fe_2O_3$, and 1·91 FeO had the axial ratios $a:b:c=1{\cdot}09126:1:0{\cdot}58949$, and $\beta=74°\ 8\frac{5}{6}'$; while an augite with 5·6 per cent. of $Al_2O_3$, and 9·5 FeO had the ratios $1{\cdot}09547:1:0{\cdot}59035$, and $\beta=74°\ 13\frac{5}{6}'$. Diopside, augite, ægirite, acmite, and jadeite are probably isomorphous. H. Baumhauer, and G. Greim studied the corrosion figures of the augites. The commonest form of twinning is on the composition plane (100); the twinning on the (001)-plane is usually repeated in thin lamellæ; the twinning on the (101)-plane furnishes cruciform twins; and the twinning on the $(\bar{1}22)$-plane furnishes stellate groups. The last two forms are rare. The cleavage parallel to (110) is often well-developed, but sometimes quite imperfect. In cross-section, the obtuse angles of the traces of this cleavage intersect at 92° 50′, and the acute angles at 87° 5′. This is shown diagrammatically in Fig. 183. The outer dotted lines represent the form of the primary; the continuous lines represent the cleavage-solid; and the broken lines represent the rhombic cleavage. A second cleavage parallel to (100) is highly developed in some augites, and the crystals then separate into thin plates. There may also be an imperfect cleavage parallel to (010). A parting parallel to (001) is well developed in many crystals twinned in lamellæ parallel to this plane. It is considered to be a result of multiple twinning, and not a true cleavage. E. A. Wülfing gave for the optic axial angle $2V=61°\ 12'$; and G. Tschermak, 68°. E. Goens examined the optic axial angle in the ultra-red. For the X-radiograms, *vide* diopside.

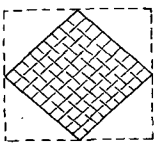


FIG. 183.—Transverse Section of a Prismatic Crystal of Augite.

The sp. gr. ranges between the limits 3·15 and 3·60, and it naturally depends on the composition, *e.g.* the replacement of magnesium by sodium lowers the sp. gr., while calcium, iron, and manganese in place of magnesium raise the sp. gr. Similarly, the replacement of aluminium by ferric iron raises the sp. gr. The m.p. also depends on the composition. In general, the augites with sodium, aluminium, iron, and manganese have a lower m.p. than diopside. C. Doelter found for various augites 1090°–1260°; for diallage, 1160°–1180°; and for soda-augites, 1085°–1115°. A. Brun gave 1230° for the m.p. of an augite from Monte Rossi. R. Cusack gave 1187°–1199° for the m.p. of augite, and A. L. Fletcher, 1237°–1249°. R. Cusack gave 1264°–1300° for the m.p. of diallage; and A. L. Fletcher, 1328°–1350°. L. H. Adams and E. D. Williamson found the compressibility, $\beta$, of augite to be $2{\cdot}34\times10^{-6}$ at 0 megabar, $2{\cdot}27\times10^{-6}$ at 2000 megabars, and $1{\cdot}04\times10^{-6}$ at 10,000 megabars. F. E. Naumann obtained numbers between 0·1930 and 0·1950 for the sp. ht. of augite; P. E. W. Oeberg, 0·1830 between 15° and 99°; and R. Ulrich, 0·1931 between 19° and 98°. H. Fizeau gave for the coeff. of thermal expansion of the two axes in the plane of symmetry; $0{\cdot}0_5 2730$ and $0{\cdot}0_5 7910$, and for the axis at right angles to this plane, $0{\cdot}0_4 13856$. This makes the coeff. of cubical expansion $0{\cdot}0_4 25971$. G. Tschermak gave $\beta=1{\cdot}74$ for the index of refraction; E. A. Wülfing, $\alpha=1{\cdot}6975$, $\beta=1{\cdot}7039$, and $\gamma=1{\cdot}7227$ for Na-light; and A. Michel-Lévy and A. Lacroix, $\alpha=1{\cdot}706$–$1{\cdot}712$, $\beta=1{\cdot}712$–$1{\cdot}717$, and $\gamma=1{\cdot}728$–$1{\cdot}733$. For the birefringence E. A. Wülfing gave $\gamma-\alpha=0{\cdot}0252$, and A. Michel-Lévy and A. Lacroix 0·021–0·022. The optical character is positive. The more strongly coloured augites are often pleochroic; but ordinary augite is hot perceptibly pleochroic. This subject has been discussed by G. Tschermak. According to L. van Werncke, A. Pelikan, J. Blumrich, and A. Scott, titaniferous augites are generally pleochroic and exhibit, in section, an hour-glass structure, the crystals consisting of a number of sectors. A. Scott showed that the extinction angles, indices of refraction, and optic axial angles differed in the various sectors. W. Vernadsky found augite to be triboluminescent. C. Doelter found that augites free from iron are as transparent as calcspar for the X-rays, while the ferruginous augites are less permeable. At ordinary temp., augite is a non-conductor of electricity, but it becomes a conductor at higher temp. Thus, with an augite with a m.p. 1225°, C. Doelter found the sp. electrical resistance of the compressed powder to be:

| | 1000° | 1050° | 1100° | 1160° | 1200° | 1270° |
|---|---|---|---|---|---|---|
| Ohms . . | 8315 | 5361 | 2936 | 1119 | 28·88 | 5·4 |

and for the cooling of molten augite:

| | 1215° | 1200° | 1160° | 1115° | 1050° | 1000° |
|---|---|---|---|---|---|---|
| Ohms . . | 7·54 | 9·45 | 17·7 | 172·0 | 493·4 | 669·0 |

B. Bavink studied the magnetic properties of crystals of augite.

G. A. Kenngott[26] found green and black augites powdered and moistened with water react markedly alkaline; F. Sestini found that powdered and moistened Vesuvian augite behaves similarly. Water dissolved 0·057 per cent., and water sat. with carbon dioxide dissolved 0·095 per cent. in 50 hrs. It was assumed that water breaks augite into two parts, the calcium and magnesium silicates appear in the soluble part, the aluminium and iron silicates in the insoluble part. A. Daubrée observed that the augites are not so readily decomposed by steam at 400° as diopside. C. Simmonds found that augite does not show any definite reduction by hydrogen at a red heat. Acids have but a slight action on augites, and in the case of the aluminiferous augites the action is inappreciable. E. Lord observed no separation when titaniferous augite is digested with hydrochloric acid. G. Becker investigated the action of hydrochloric acid. H. Lotz, and W. B. Schmidt studied the action of sulphurous acid on augite and observed but a slight action after 12

months' exposure. E. C. Sullivan found a basic exchange occurs when augite is treated with a soln. of cupric sulphate. V. P. Smirnoff studied the action of humic and crenic acids on augite. The natural transformation products of augite in nature are numerous.[27] Picrophyll, pitkarantite, pyrallolite, traversellite, pyroschlerite, grengesite, and strakonitzite have been previously indicated. Cimolite, steatite, mica, epidote, and green-earth or glauconite, have also been reported. J. Roth has discussed the various changes; and other reports have been made by J. Lemberg, T. S. Hunt, A. Streng, G. Tschermak, and G. A. Kenngott. A. Erdmann found a yellow, slightly altered pyroxene at Bergen, Norway, and he called it *monradite*—after M. J. Monrad. S. H. Cox reported a greenish pyroxenic mineral from the serpentine rocks of the Dun Mts., New Zealand. He called it *hectorite*—after J. Hector. G. Friedel and F. Grandjean discussed the transformation of augite into chlorite; C. F. Rammelsberg, the alteration to opal; and M. F. Heddle, and N. Kispatic, the serpentinization of augite.

The mineral **hornblende** or *Hornstein* probably received its name from the old miners in allusion to its toughness. C. A. S. Hofmann[28] indicated that the term may be of Swedish origin. J. G. Wallerius designated it *corneus fissilis*, *corneus solidus*, *corneus crystallosatus*, and *skiorl*. A. Cronstedt called it *skörl*, etc. J. B. L. Romé de l'Isle classed it as a *schorl*. A. G. Werner, L. A. Emmerling and A. Estner used the term *hornblende* for the mineral.

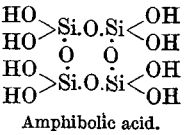
The term *pargasite* was applied by G. von Steinheil to green, bluish-green, or greyish-black crystals of hornblende from Pargas, Finland. A. Breithaupt called the black hornblende from Nordmark, Wermlande, *diastatite*—from διαστατός, standing apart—and later *wallerian*. He called the black hornblende from Vesuvius, *syntagmatite*—from σύνταγμα, arranged; and the colourless or grey hornblende from Edenville, New York, *edenite*. The light-coloured hornblende with but little iron is often called *edenite*, and the darker varieties *pargasite*. N. Nordenskjöld called a variety from Lake Baikal, Siberia, *kokscharoffite*—after N. von Kokscharoff—and J. D. Dana, one from Nora, Westmanland, *noralite*. A. Breithaupt obtained a green mineral from Gamsigrad, Serbia, which he called *gamsigradite*, and which A. Lacroix showed to be a hornblende. P. Lucchetti obtained needle-like crystals of a hornblende from Monte Altino, Bergamo, Italy, which he called *bergamaskite*. J. Lorenzen obtained crystals of a hornblende at Kaersut, North Greenland, and he called the mineral *kaersutite*. Its composition was examined by B. Gossner. T. Thomson, A. des Cloizeaux, and T. S. Hunt described *rhaphilite*—from ῥαφίς, a needle—found by the first-named at Perth, Lanarkshire. It is a variety of hornblende. F. D. Adams and B. J. Harrington reported a hornblende in the nepheline-syxnite of Dungannon, Hastings, Ontario, and they called it *hastingsite*. T. L. Walker gave for the indices of refraction, $\alpha = 1{\cdot}695 - 1{\cdot}697$; $\beta = \gamma = 1{\cdot}710 - 1{\cdot}711$; and pleochroism with $\alpha$ pale yellow, and $\beta$ and $\gamma$, a deep greenish-blue. G. Platania referred to a variety occurring in minute crystals in the hæmatite of Acicatena, Sicily; it was named *xiphonite*—after Xiphonia, an old town near the locality. R. A. Daly applied the name *philipstadite* to an amphibole from Philipstad, Sweden. W. C. Brögger found an amphibole intermediate in properties to barkevikite and arfvedsonite which he named *cataphorite*. It came from South Norway. Its composition was examined by B. Gossner. A. Lacroix mentioned a similar mineral from Haute-Loire. L. Duparc and F. Pearce named an amphibole from Koswinsky, Urals, *soretite*—after C. Soret; and another related to riebeikite and arfvedsonite, was called *tschnichewite*. J. A. Krenner called an amphibole occurring with the jadeite of Central Asia, *szechenyiite*—after Count Szechenyi. L. L. Fermor called a blue amphibole from the manganese mines of Central India, *winchite*—after H. J. Winch. L. C. Beck applied the term *hudsonite* to a mineral from Cornwall in the vicinity of the Hudson River, New York. Hudsonite is black, lamellar, massive, and often has a bronze lustre. It was shown by S. Weidman to be an amphibole, not, as formerly supposed, a pyroxene. A. G. Werner called a dark-coloured hornblende from Sanalpe, Carinthia (Kärnten), *karinthine*. A. Breithaupt regarded it as a special species of amphibole, but J. F. L. Hausmann showed that it is a variety of hornblende. E. Denaeyer described *torendrikite* as a magnesian ferric amphibole from Tine, Ouadai.

Among the more or less altered hornblendes which have been reported are T. Thomson's *kirwanite*—after R. Kirwan—which is a green chlorite-like mineral whose nature was established by A. Lacroix. The *loganite* of T. S. Hunt—named after J. R. Logan—occurs at Calumel Falls, Quebec, and it is near penninite in composition. G. A. Bertels described a yellow, fibrous, hornblende-like mineral which he called *phœactinite*—from φαιός, black; and ἀκτίς, a ray. A. Knop, G. A. Kenngott, and C. F. Rammelsberg described a green mineral from Waldheim, Saxony, which was called *waldheimite*, and which was found to be an altered product of hornblende.

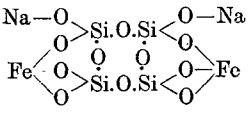
R. J. Haüy [29] regarded the *variété verte* of diallage as synonymous with the *smaragdite* of H. B. de Saussure. A. G. Werner regarded smaragdite from Corsica as a granular kind of hornblende (Steahlstein). Observations were made by W. Haidinger, G. Rose, G. Tschermak, R. von Drasche, H. Rosenbusch, and F. Zirkel. Analyses were made by J. V. Lewis, J. B. Trommsdorff, F. A. Genth, etc. C. Boulanger has described a chromiferous smaragdite. Smaragdite has a light grass-green colour, and is a thin foliated variety of amphibole, which closely resembles actinolite in composition, but contains some alumina. Usually, it has probably been derived from pyroxene or diallage, and it retains much of the structure of diallage. Saussurite and smaragdite form the greenish rock called saussuritic gabbro; and the Corsican mineral is from the rock *verde di Corsica duro* used in the arts.

G. Rose [30] applied the term *uralite* to a mineral which had the crystalline form of augite and the structure of hornblende; this name was selected because the mineral is widely distributed in the Urals. The mineral is a pyroxene which has been changed to an amphibole. The uralitization of pyroxene is generally attended by an increase in the proportion of magnesium, and a decrease in the proportion of calcium. The change was discussed by G. Rose, W. Haidinger, F. Becke, R. J. Haüy, H. Rosenbusch, C. A. Müller, and H. Fischer. L. Duparc and T. Hornung say that uralitization is not a case of mol. transformation, nor a case of hydrochemical alteration. They suggest that after the pyroxene had crystallized from the magma, it was acted on by the residual magma and transformation occurred in patches into amphibole. Analyses have been reported by C. F. Rammelsberg, B. J. Harrington, P. Dahms, L. Duparc and T. Hornung, G. vom Rath, and J. Kudernatsch. Traversellite—*vide* diopside—has probably been formed by a similar process to uralite.

P. A. von Bonsdorff [31] made an analysis of hornblende, and since then numerous analyses have been reported. As with the augites, the composition of the hornblendes is very variable. The hornblendes bear the same relation to the amphiboles as the augites bear to the pyroxenes. E. T. Wherry [32] applied the at. vol. theory of isomorphism to explain the various replacements in the amphiboles. S. L. Penfield and F. C. Stanley quoted a number of analyses to show that in the hornblendes, magnesium and iron preponderate over calcium, while the reverse condition prevails among the augites. The constitution of hornblende is generally assumed to be analogous to that of augite. C. F. Rammelsberg made attempts to deduce a formula for hornblende. C. G. C. Bischof, T. Scheerer, and J. Roth discussed the nature of the sesquioxides in this mineral; E. T. Allen and J. K. Clement, the nature of the water. G. Tschermak regarded hornblende as an isomorphous association of the silicates $CaMg_3(SiO_3)_4$, $CaFe_3(SiO_3)_4$, $Na_2Al_2(SiO_3)_4$, $K_2Al_2(SiO_3)_4$, $CaMgAl_4Si_2O_6$, and $CaMgFe_4Si_2O_{12}$, which he afterwards reduced to the first three, and $CaMg_2Al_3Si_3O_{12}$. P. Groth gave for hornblende $(Mg,Fe)_3Ca(SiO_3)_4$, and $(Mg,Fe)_2Al_2(SiO_3)_2(AlO_3)_2$; and for richterite, $(Mg,Fe,Mn)_3Ca(SiO_3)_4$, and $Na_2(Al,Fe)_2(SiO_3)_4$. A. Sauer assumed that $Al_2SiO_5$ is present in hornblende from Darbach. R. Scharitzer regarded hornblende and richterite as mixtures of an actinolite, $CaMg_3(SiO_4)_3$, with a silicate of the garnet type, $R''_3R'''_2Si_3O_{12}$, to which he applied the term *syntagmatite*. F. Berwerth, F. R. van Horn, G. F. Becker, J. Soellner, H. Haeffke, and F. D. Adams and B. J. Harrington also assumed the presence of orthosilicates—first, because the proportion of oxygen is larger than that required for metasilicates, and second, because they alter into mixtures containing orthosilicates. The first argument is not strong because some hornblendes have more oxygen than is required for the orthosilicate ratio, and the excess in both cases can be explained by assuming the existence of basic radicles. S. L. Penfield and F. C. Stanley suggest that hornblendes may be regarded as polymetasilicates with the bivalent radicles $Al_2OFe_2''$, $Al_2O(OH)_2''$, $R'Al_2O_3''$, $Na_2R'Al_2O_4''$, and the univalent radicle $MgF'$; this explains the presence of water, and fluorine. X. Galkin, and B. Gossner supported this hypothesis. E. T. Allen and J. K. Clement assumed that the water in these minerals is adsorbed, occluded, or in solid soln. In agreement with G. Tschermak, S. L. Penfield and F. C. Stanley assumed that the hornblendes are salts of an *amphibolic acid*, $H_8Si_4O_{12}$; and H. S. Washington suggested a constitutional formula for kaersutite, based on this assumption.



Amphibolic acid.



Kaersutite.

P. Erculisse argued that the hornblendes (and augites) are solid soln. of derivatives of the aluminosilicic acid, $H_2Al_2SiO_6$, and of metasilicic acid. Hornblende is found in both igneous and metamorphic rocks; it is a common constituent of granite, syenite, dionite, trachyte, diabase, gabbro, norite, gneiss, chlorite schist, mica schist, etc. Edenite occurs in crystalline limestone and seems to have been produced by contact metamorphism; pargasite is found in metamorphic rocks, gneisses, and crystalline limestones. Basaltic hornblende is an early secretion in andesite, dacite, phonolite, basalt, and other eruptive rocks. The reports of T. Scheerer, and C. W. C. Fuchs [33] of the occurrence of hornblende in slags were shown by C. C. von Leonhard, and G. Tschermak to be unreliable. H. J. Johnston-Lavis reported finding hornblende on fossil bones in the volcanic tufa of Faiano, Nocera, and he assumes that it was formed under press. and at a temp. insufficient to carbonize or discolour the organic matter of the bones. K. von Chrustschoff synthesized hornblende by heating a mixture of dialyzed silica, alumina, ferric and ferrous hydroxides, magnesium hydroxide, calcium hydroxide, and water in an autoclave for 3 months at 550°. C. Doelter also prepared crystals of hornblende by fusing a mixture of magnesia, iron oxide, alumina, silica, and boric oxide. He also recrystallized amphiboles from fused borax, or a fused mixture of magnesium and calcium chlorides. Olivine, scapolite, magnetite, anorthite, or orthoclase were also produced. K. Bauer obtained hornblende by fusing at 800° a mixture of biotite, boric acid, sodium phosphate, and calcium fluoride. A. Becker showed that when hornblende is fused, a pyroxene, possibly mixed with olivine, is formed; and A. Lacroix found that heat alone, or contact with molten magmas, must have converted hornblende into augite in the volcanic rocks of Auvergne. Indeed, the amphiboles are not stable at elevated temp. Their appearance as pyrogenic minerals is therefore conditioned by the rapid cooling of the mother magma, the presence of water, or some undetermined influence of press. An excess of magnesia favours the development of the hornblendes, while an excess of lime favours the formation of the augites—*vide* magnesium metasilicate. E. T. Allen and co-workers found that when magnesium metasilicate is heated above its m.p. and rapidly cooled, amphiboles are produced; and if slowly cooled, pyroxenes are formed. When rhombic amphibole and water are heated at 375°–475°, the monoclinic form is produced; and the latter is obtained when a soln. of magnesium ammonium chloride or of magnesium chloride and sodium hydrocarbonate is heated along with sodium silicate or amorphous silica in a steel bomb for 6 days at 375°–475°. Some quartz and forsterite were formed at the same time.

The colours of argasite and common hornblende vary from light to dark green, bluish-green, and black. G. Murgoci discussed the blue amphiboles. A zonal structure is sometimes developed and the central portion is brown while the outer portion is green, or *vice versâ*. Hornblende is often free from inclusions, but it sometimes contains apatite, magnetite, and titanite when of igneous origin, and rutile when formed by metamorphosis. Gas, glass, and liquid inclusions are rare. Parallel growths of pyroxene and amphibole are not uncommon. According to A. E. von Nordenskjöld,[34] the axial ratios of the monoclinic crystals of hornblende are $a:b:c=0{\cdot}54826:1:0{\cdot}29377$, and $\beta=75°\ 2'$. Observations were made by A. des Cloizeaux, N. von Kokscharoff, W. H. Miller, J. D. Dana, A. Lévy, and C. F. Naumann, M. Vendl, A. Schrauf, P. Groth, G. H. Williams, F. A. Quenstedt, G. vom Rath, C. S. Weiss, G. Tschermak, etc. The crystals often appear as slender prisms, and short thick prisms. The forms common to all monoclinic amphiboles are (110), (010), and less often, (100) and (130); the common terminal planes are (011),

($\bar{1}01$); sometimes ($\bar{1}01$) and (211); and rarely (001). The faces of the crystals of hornblende are usually quite simple, the unit prisms have (110) strongly developed, the second pinacoid (010) is subordinate, and less frequently, the first pinacoid (100) is quite small. The terminal faces are usually (011) and ($\bar{1}01$). The relations between the crystals of augite and of hornblende were discussed by G. Rose. H. Haga and F. M. Jäger studied the X-radiograms of hornblende. The common case of twinning has the composition plane (100), and in some cases there are several lamellæ twinned between larger parts. A second form of twinning, rather rare, is parallel to the basal pinacoid (001), and is usually polysynthetic. As in the case of pyroxene, it is produced by press. Observations on the twinning were made by E. Cohen, K. Oebbeke, F. Becke, C. H. Williams, O. Mügge, E. Dathe, and W. Cross. The cleavage parallel to (110) is highly developed, yielding 55° 30′, as illustrated diagrammatically in Fig. 184, where the outer dotted line represents the primary form; the continuous line, a secondary form of that of the cleavage solid. Cleavages parallel to (100) and (010) are sometimes distinct, but rare. Parting parallel to the twinned lamellæ is sometimes developed. A. des Cloizeaux gave for the optic axial angle $2H=92°\ 37'$; G. Tschermak gave $2E=107°\ 30'$ and $2V=59°$. M. Vendl gave $2V=82°\ 45'$. Observations were also made by J. D. Dana, H. Rosenbusch, G. Flink, A. Michel-Lévy and A. Lacroix, and K. Zimanyi. A. des Cloizeaux found that for pargasite, $2E=95°\ 53'$ at 17°, and 100° 38′ at 170° 8°. A. Belowsky, and A. Schrauf also studied this subject. G. Tschermak, C. Schneider, A. Belowsky, and F. J. Wiik studied the effect of composition on the axial angles; and F. Rinne, the effect of heat.

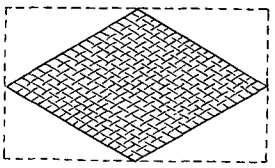


Fig. 184.—Cleavage of Hornblende.

The sp. gr. of most of the samples analyzed were determined; the numbers range from 2·9–3·4. M. Vendl gave 3·178 at 20°. The actual number naturally depends on the composition—thus the greater the iron-content, the greater the sp. gr. The hardness ranges from 5–6. F. Pfaff found the coeff. of thermal expansion in the direction of the crystallographic axes $b$ and $c$ to be $b=0{\cdot}000000843$ and $c=0{\cdot}000009530$, and for $a$, at right angles to $b$ and $c$, 0·000008119; and for the coeff. of cubical expansion 0·00002845. H. Fizeau gave for the coeff. of cubical expansion 0·000025971. F. E. Naumann gave for the sp. ht. 0·1958–0·1976; R. Ulrich, 0·1941 between 21° and 98°; and J. Joly, 0·2113. A. Brun gave 1070° for the m.p. of hornblende; R. Cusack, 1187°–1200°; A. L. Fletcher, 1237°–1250°; C. Doelter, 1150°–1220°; and H. Leitmeier, 1180°–1200° for coarse-grained hornblende, and 1130°–1180° for the fine-grained mineral. The indices of refraction for hornblende given by A. Michel-Lévy and A. Lacroix are $\alpha=1{\cdot}680$, $\beta=1{\cdot}725$, and $\gamma=1{\cdot}752$; for pargasite, K. Zimanyi gave $\alpha=1{\cdot}616$, $\beta=1{\cdot}620$, and $\gamma=1{\cdot}635$; and M. Vendl, $\alpha=1{\cdot}698$, $\beta=1{\cdot}6825$, and $\gamma=1{\cdot}6929$. Other observations were made by H. Rosenbusch, A. Belowsky, G. Tschermak, A. des Cloizeaux, and A. Franzenau. For the birefringence, H. Rosenbusch gave $\gamma-\alpha=0{\cdot}0264$, $\gamma-\beta=0{\cdot}0114$, and $\beta-\alpha=0{\cdot}0148$. The optical character is negative, rarely positive. Attempts to find a relation between the composition and the optical properties have been made by G. Tschermak, F. J. Wiik, W. C. Brögger, G. Murgoci, S. Kreutz, A. Laitakari, W. E. Ford, S. L. Penfield and F. C. Stanley, and A. N. Winchell. G. Tschermak, A. Michel-Lévy and A. Lacroix, H. Rosenbusch, M. Vendl, and F. Becke studied the pleochroism of the crystals. W. Vernadsky found the crystals are triboluminescent. O. Mügge studied the pleochroic halos produced by radium radiations. C. Doelter found the non-ferruginous hornblendes are transparent to the X-rays, but not so with the ferruginous hornblendes.

C. Schneider studied the action of steam on heated hornblende. According to G. A. Kenngott,[35] powdered and moistened tremolite, hornblende, and maragdite, calcined or uncalcined, react alkaline to litmus. R. Müller found that carbonated water has a strong action on hornblende, and about 1·536 per cent. is dissolved.

E. A. Stephenson studied the action of alkaline soln. on hornblende. C. Doelter found that when heated to redness for 3 hrs. in a stream of hydrogen chloride, about 4·25 per cent. of lime and 1·57 per cent. of magnesia was rendered soluble in water. The ferruginous varieties of hornblende are attacked by hydrochloric acid, but the non-ferruginous varieties are not appreciably affected. J. W. Mellor found that an hour's treatment of coarse-grained and fine-grained hornblende with hot conc. sulphuric acid decomposed respectively 1·79 and 15·09 per cent. W. B. Schmidt, and H. Lotz investigated the action of sulphurous acid and found about 6·7 per cent. was dissolved. A. Becker, and C. Doelter studied the corrosive action of molten silicate magmas on hornblende. E. C. Sullivan studied the action of soln. of cupric sulphate on amphibole. G. Tammann and C. F. Grevemeyer found that magnesia does not act on hornblende at 1000°; lime acts slowly at 500°; and baryta acts quickly at 275°–300°. For the transformation of hornblende into pyroxene, *vide supra*. The transformation of hornblende in nature has been discussed by C. F. Rammelsberg, J. Lemberg, M. F. Heddle, K. Vrba, C. R. van Hise, J. D. Dana, C. A. Joy, F. Becke, and B. Kolenko. The mineral alters into pyroxene as indicated above, and also into biotite, calcite, chlorite, epidote, quartz, siderite, etc.

T. von Saftschenkoff [36] found and analyzed a soft, tough, white, fibrous mineral in the Paligoris mine of the Permian mining district, Ural; it was regarded as an altered asbestos, and called **paligorscite.** Analyses were also made by A. Fersmann, and G. Friedel. The composition approximates $H_{16}Mg_2Al_4Si_{11}O_{38}.3H_2O$; and A. Fersmann called it *α-paligorscite*, to distinguish it from a similar mineral with the composition $H_{10}Mg_2Al_2Si_7O_{24}.4H_2O$, and called *β-paligorscite*. The latter was also analyzed by A. Kasakoff, G. S. Whitby, M. F. Heddle, G. Tschurowsky, and A. Rzehak. A variety high in lime was called *calcio-paligorscite*. The sp. gr. of paligorscite is 2·217; it is not acted on by acids. According to P. A. Schemjatschensky, it is an altered asbestos. M. F. Heddle [37] applied the term **pilolite**—from πῖλος, felt—to a fibrous, more or less flexible, and tough mineral resembling the so-called *mountain-cork*, or *mountain-leather*, the colour white, buff, or grey. Analyses were also made by A. E. Delesse, Z. Rozen, A. F. Collins, T. Thomson, and A. Fersmann. The last-named called samples approximating $H_{14}Mg_4Al_2Si_{10}O_{34}.6H_2O$, *α-pilolite*, and those approximating $H_{18}Mg_6Al_2Si_{13}O_{44}$ $8H_2O$, *β-pilolite*. G. Friedel described snow-white masses of a fibrous mineral from the antimony mine of Miramount, France, etc., and named it **lasallite**—after M. Lasalle. He considers it to be a variety of pilolite. F. W. Clarke represented the analyses of the two minerals by the formulæ:

$$Mg_2.Si_2O_7<\begin{matrix}Al(Si_2O_7AlH_2)_2\\Al(Si_2O_7H_5)_2\end{matrix}+7H_2O \qquad Mg_2Si_2O_7<\begin{matrix}Al(Si_2O_7.MgH_2)\\Al(Si_2O_7.H_5)_2\end{matrix}+7H_2O$$

Lasallite. Pilolite.

E. F. Glocker [38] applied the term **xylotile**—from ξύλον, wood—to a kind of asbestos which is green or brown in colour, and very delicately fibrous. Analyses were made by A. Erdmann, A. Fersmann, M. C. J. Thauloff, C. von Hauer, and W. Lindgren and W. F. Hillebrand. The composition approximates to that of paligorscite. R. Hermann's *xylite* is a kind of hydrated asbestos. G. A. Kenngott regarded xylotile as an altered chrysotile. The sp. gr. is 2·40–2·56. A. Fersmann concluded that all these minerals, paligorscite, pilolite, lassallite, mountain-cork, mountain-leather, and the like, should be grouped together as *paligorscites*. The composition of the group is explained by assuming that they are various mixtures of two components—the one, called **parasepiolite,** has the composition $H_8Mg_2Si_3O_{12}$; and the other, called **paramontmorillonite,** has the composition $H_2Al_2Si_4O_{12}.5H_2O$.

P. Pusirewsky [39] found a massive white or rose-red mineral resembling lithomarge near Nertschinsk. He called it **nefedieffite** or *nefedjewite*, and represented its analysis by the formula $H_4MgAl_2Si_5O_{16}$, or $MgAl_2Si_5O_{14}.2H_2O$. When confined over

sulphuric acid, about 11·3 per cent. of water is given off in 22 days, and this water is restored on exposure to a moist atm.; at 250°, the mineral loses 19·23 per cent. of water, and 4·73 per cent. more when heated to the m.p. A. Fersmann and L. Zitladeffa represented it by the formula $(Mg,Ca)Al_2Si_5O_{14}.7H_2O$, or **magnesium aluminium mesopentasilicate,** $MgAl_2Si_5O_{14}.7H_2O$. The sp. gr. is 2·25, and the hardness $1\frac{1}{2}$. Water dissolves 0·2 per cent. of this mineral and acquires an alkaline reaction.

T. S. Hunt [40] described a green clay-like mineral which he found at Springfield, Penn., and which he called *venerite*—after Venus, the alchemist's symbol of copper. It contains 18·55 per cent. of magnesia; 17·58, cupric oxide; 5·35, ferric oxide; 14·67, alumina; 30·73, silica; and 12·83, water.

G. Steiger [41] obtained a number of thalliferous silicates by the action of thallous nitrate on the zeolites in a sealed tube at 250°–290°—*e.g. thallo-analcite, thallo-leucite, thallo-chabazites, thallo-stilbite, thallo-natrolite,* and *thallo-mesolite.* A. Lamy, and G. Müller made observations on *thallium glasses* (*q.v.*) with thallium oxide as one of the bases. H. Flemming dissolved silica in a boiling aq. soln. of thallous hydroxide, and on cooling obtained a white crystalline mass which, when dried over sulphuric acid, lost 5·38 per cent. of water, and no more when heated to 150°. The composition approximates $3Tl_2O.10SiO_2$. The soln. deposits silica when treated with carbon dioxide, and the hot soln. of thallous carbonate redissolves silica. The soln. becomes turbid on cooling, and clarifies when heated. G. Wyrouboff obtained yellow needles of **thallous silicate,** $Tl_6Si_2O_7.H_2O$, which belong to the tetragonal system, and have the axial ratio $a:c=1:0·3946$. The crystals are not altered by heating to 130°, but at 150° they become opaque, and at a higher temp. lose weight by the expulsion of water. L. Bourgeois [42] failed to make **silicates of cerium, lanthanum, and didymium** by heating mixtures of the oxides of these elements and silica.


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## § 47. The Silicates of the Phosphorus Family

W. Skey [1] melted quartz and other silicates with a mixture of alkali carbonate and phosphate, treated the product with hydrochloric acid, and washed the insoluble matter until the wash-water was free from phosphoric acid. Aq. ammonia dissolves both silica and phosphoric acid from the residue, which is considered to be a mixture of silicic and phosphoric acids or a *silicophosphoric acid*, *silicon phosphate*, or *phosphorus silicate*. For P. Hautefeuille and P. Margottet's *silicyl metaphosphate*, $SiO_2.P_2O_5$, or $SiO(PO_3)_2$, and $SiO_2.2P_2O_5.4H_2O$, *vide* silicon phosphates. H. N. Stokes reported $SiO_2.P_2O_5$ to be formed when $SiP_2O_6Cl_2$ is heated until no more phosphoryl chloride is evolved. The **calcium phosphatosilicates**—*carnotite*, *steadite*, and *ciplyte*—and the **calcium ferrous phosphatosilicate**—*thomasite*—were discussed, **3**. 24, 25, and 30. G. Saring also reported a series, $Ca_3(PO_4)_2.(CaO)_2(K_2O)SiO_2$, with the silica replaceable by analogous oxides from the same family group of elements. For the **sodium cerium phosphatosilicate**, *erikite*; and the **calcium cerium phosphatosilicate**, *britholite*—*vide* the rare earths. O. Meister referred to the uses of **tin phosphatosilicate** for weighting silk. S. J. Thugutt obtained *arsenitosodalite*, $6(Na_2O.Al_2O_3.2SiO_2)Na_4As_2O_5.6H_2O$, or **sodium aluminium arsenitosilicate**, by heating in an autoclave a mixture of kaolinite, arsenic trioxide, sodium hydroxide, and water for 54 hrs. at 207°–208°. By using arsenic pentoxide, he obtained acicular crystals of *arsenatosodalite*, $6(Na_2O.Al_2O_3.2SiO_2)Na_3AsO_4.nH_2O$, or **sodium aluminium arsenitosilicate**, when $n=7$ and 14. G. Flink described a **manganese arsenitometasilicate**, $(HOMn)_2Mn_3SiO_3(AsO_3)_2$, whose X-radiogram corresponded with the hexagonal or rhombohedral symmetry. The mineral was called *dixenite*; the sp. gr. was 4·20; the hardness, 3–4; and the mean index of refraction, 1·96. It was uniaxial and positive. R. B. Gage and co-workers

described a hydrated **manganese arsenatometasilicate** which occurs in veinlets in the normal zinc ore at Franklin, New Jersey, and which they called *schallerite* —after W. T. Schaller. Its companion is $12MnO.9SiO_2.As_2O_5.7H_2O$, or $9MnSiO_3.Mn_3As_2O_8.7H_2O$, and recalls that of friedelite, $9MnSi_3.MnCl_2.7H_2O$. It occurs massive, light brown in colour, with a conchoidal fracture, and a vitreous or waxy lustre; its sp. gr. is 3·368, and its hardness 4·5 to 5·0. It fuses with difficulty, gives off water at a low red-heat, and arsenic is evolved at a higher temp. The mineral is uniaxial, and has a perfect basal cleavage. The indices of refraction are $\omega=1·704$, and $\epsilon=1·679$; the optical character is negative. A. Raimondi mentioned a mineral from the vicinity of Tibaya, Arequipa, Peru, which he called *arequipite*, and which he stated to be a **lead antimonatosilicate**. T. L. Walker reported a yellowish-green, pulverulent mineral from Ontario with a composition corresponding with **ferrous antimonatosilicate**, $5FeO.Sb_2O_5.5SiO_2.2H_2O$. He called it *chapmanite*. It has a sp. gr. 3·58; indices of refraction $\alpha=1·85$, $\gamma=1·96$, and is doubly refracting. It is dissolved by hydrofluoric acid, but not by other acids. G. Flink reported iron-black hexagonal crystals of a **manganese ferrous antimonatosilicate**, $37Mn_5SiO_7.10Fe_3(SbO_4)_2$, from Längban, Wermland, Sweden. It was named *längbanite*, or *longbanite*. The axial ratio $a:c=1:1·6437$. The sp. gr. is 4·918, and the hardness 6·5.

C. M. Kersten [2] found a reddish-brown mineral, sometimes yellow or black, at Schneeberg, Saxony, and he called it *eulytine*—from εὔλυτος, easily dissolved or fusible. Analyses were made by C. M. Kersten, and G. vom Rath. The composition represents **bismuth orthosilicate**, $Bi_4(SiO_4)_3$. The crystals belong to the cubic system. A. Frenzel found monoclinic crystals of a mineral with the same composition at Johanngeorgenstadt, Saxony. He called it *agricolite*—after G. Agricola. Bismuth orthosilicate thus appears to be dimorphous. According to A. Frenzel, agricolite is the arsenical bismuth of A. Breithaupt, and A. G. Werner. The sp. gr. of eulytine is 6·106, and the hardness $5\frac{1}{4}$–6. It is decomposed by hydrochloric acid with the separation of gelatinous silica. A. Frenzel also found a ferruginous bismuth silicate in the same locality, which he called *bismutoferrite*; its composition approximated $Bi_2O_3.2Fe_2O_3.4SiO_2$, and its sp. gr. was 4·47.

According to J. J. Berzelius,[3] when a vanadyl salt is added to a soln. of an alkali silicate, a pale grey precipitate of **vanadyl silicate** is formed. On exposure to air, this silicate turns brown, and finally green, and at the same time becomes insoluble in water. A. von Lasaulx [4] noticed a mineral at Salm Chateau, Ardennes, which he called *Mangandisthene* on account of its supposed resemblance to cyanite; and later **ardennite.** F. Pisani called it *dewalquite*—after G. Dewalque. Analyses were made by A. Lasaulx and A. Bettendorff, and F. Pisani; and the results agree roughly with the formula $H_{10}Mn_{10}Al_{10}Si_{10}V_2O_{55}$ or $H_5Mn_4Al_4Si_4VO_{23}$, or $8MnO.4Al_2O_3.V_2O_5.8SiO_2.5H_2O$, **manganese aluminium vanadatosilicate.** Some arsenic may replace vanadium, ferric iron the aluminium, and magnesium and calcium the manganese. The prismatic crystals of ardennite are yellow or yellowish-brown in colour. According to G. vom Rath, the rhombic crystals have the axial ratios $a:b:c=0·4663:1:0·3135$. The cleavage 010 is perfect, and the 110-cleavage is distinct. There are partings parallel to $c$ with horizontal striations like cyanite. The sp. gr. is 3·577–3·620; and the hardness 6–7. The mineral is pleochroic. A. Michel-Lévy and A. Lacroix made some observations on the optical properties of the mineral. J. Blake [5] found a *vanadium-mica* at Granite Creek, El Dorado, Cal., and named it *roscoelite*—after H. E. Roscoe. Other finds were reported and analyses made by F. A. Genth, W. F. Hillebrand and co-workers, E. S. Simpson, and H. E. Roscoe. Attempts to derive a formula have not been very successful. H. E. Roscoe concluded that the mineral has the composition $4AlVO_4.K_4.Si_9O_{20}.H_2O$; F. A. Genth gave $K_4(Mg,Fe)_2(Al,V)_8Si_{24}O_{64}.8H_2O$, or $H_8K(Mg,Fe)(Al,V)_4(SiO_3)_{12}$. F. W. Clarke, and P. Groth assumed that the mineral is compounded of three different silicates; and the former considers that the idealized mineral has the composition **potassium divanadium dihydroalumino-**

**triorthosilicate,** $KH_2V_2Al(SiO_4)_3$, or $(V{\equiv}SiO_4)_2{=}Al{-}SiO_4{\equiv}KH_2$, analogous to phlogopite, $KH_2Mg_3Al(SiO_4)_3$. Roscoelite occurs in minute scales often in stellate or fan-shaped groups coloured dark brown, greenish-brown, or brownish-green. F. E. Wright observed that the corrosion figures agree better with the monoclinic than with the triclinic system. According to F. A. Genth, the sp. gr. is 2·92–2·94; H. E. Roscoe, 2·902; and F. E. Wright, 2·5–3·0. H. E. Roscoe said that the hardness is 1. F. E. Wright found that the cleavage parallel to (001) is perfect and good when parallel to (010); the optic axial angles $2E=42°$–$69°$ for Na-light, and 34°–60° for Li-light; the indices of refraction are $\alpha=1{\cdot}610$, $\beta=1{\cdot}685$, and $\gamma=1{\cdot}704$. The optical character is negative. The mineral is pleochroic. A. des Cloizeaux made some observations on the optical properties. The mineral is but slightly attacked by boiling conc. sulphuric acid; but it is rapidly decomposed by dil. sulphuric acid in a sealed tube at 180°.

According to C. Friedheim and C. Castendyck,[6] when ammonium vanadate and ammonium silicomolybdate are mixed into a paste with water, interaction occurs, and a clear red soln. is obtained. The intensity of the colour is greatest when the mol. ratio $(NH_4)_2O.V_2O_5 : 2(NH_4)_2O.SiO_2.12MoO_3.8H_2O$ is 2 : 1, and the soln. deposits large, lustrous red crystals of **ammonium silicovanadatomolybdate,** $3(NH_4)_2O.SiO_2.V_2O_5.11MoO_3.27H_2O$—often 2 cms. in length. These crystals are easily soluble in water, and during their formation become contaminated by sparingly soluble ammonium vanadiomolybdates of varying composition, the latter being separated mechanically. The composition of these ammonium vanadiomolybdates, according to the order of their separation, is as follows: (1) $2(NH_4)_2O.2V_2O_5.5MoO_3.8H_2O$, yellow; (2) $(NH_4)_2O.V_2O_5.2MoO_3.4H_2O$, yellowish-green; (3) $2(NH_4)_2O.3V_2O_5.4MoO_3.11H_2O$, bright brown; (4) $(NH_4)_2O.2V_2O_5.2MoO_3.8H_2O$, reddish-brown; (5) $4(NH_4)_2O.12V_2O_5.5MoO_3.24H_2O$, brownish-red. The first three of these are microcrystalline whilst the two last form felted needles. On recrystallizing the foregoing ammonium silicovanadiomolybdate from water, either hot or cold, decomposition occurs, and a series of compounds, (1) $3(NH_4)_2O.SiO_2.V_2O_5.9MoO_3.20H_2O$; (2) $3(NH_4)_2O.SiO_2.V_2O_5.10MoO_3.21H_2O$; (3) $3(NH_4)_2O.SiO_2.V_2O_5.15MoO_3.24H_2O$, is obtained; these differ little from the parent substance and from one another in colour and crystalline form, but are differentiated by the behaviour of their sat. soln. with silver, lead, and mercurous nitrates. The following table gives their principal physical properties:

| Ammonium silicovanadiomolybdate. | Sp. gr. of solid at 18°. | Sp. gr. of saturated soln. at 18°. | Solubility in grams per c.c. |
|---|---|---|---|
| $3:1:1:9+20H_2O$ | 2·8020 | 1·21322 | 0·32016 |
| $3:1:1:10+21H_2O$ | 2·8044 | 1·25275 | 0·35026 |
| $3:1:1:11+27H_2O$ | 2·8074 | 1·29266 | 0·38086 |
| $3:1:1:15+24H_2O$ | 2·8162 | 1·43761 | 0·48997 |

It is noteworthy that the addition of each mol. of molybdenum trioxide causes a regular increase of approximately 0·00237 unit in the sp. gr. of the solid salt; 0·037 unit for the sp. gr. of the sat. soln.; and 0·030 unit for the solubility. The salts containing $9MoO_3$ and $15MoO_3$ can be recrystallized unchanged from water, but that containing $10MoO_3$ yields a mixture of the other three salts. Their formulation is illustrated by:

$$R_6H_2\left[Si\begin{matrix}(V_2O_6)\\(W_2O_7)_5\end{matrix}\right]nH_2O$$

When potassium chloride is added to cold sat. soln. of these salts, crystalline **potassium ammonium silicovanadatomolybdates** are formed in which $2(NH_4)_2O$ of the parent substance is replaced by $2K_2O$. The physical properties of these complexes are as follows:

| Composition. | Sp. gr. of solid. | Sp. gr. of sat. soln. at 18°. | Solubility in grams per c.c. |
|---|---|---|---|
| $(NH_4)_2O.2K_2O.SiO_2.V_2O_5.9MoO_3.20H_2O$ | 2·8648 | 1·17031 | 0·24021 |
| $(NH_4)_2O.2K_2O.SiO_2.V_2O_5.10MoO_3.21H_2O$ | 2·8682 | 1·19184 | 0·25914 |
| $(NH_4)_2O.2K_2O.SiO_2.V_2O_5.11MoO_3.12H_2O$ | 2·8704 | 1·21378 | 0·27914 |
| $(NH_4)_2O.2K_2O.SiO_2.V_2O_5.15MoO_3.14H_2O$ | 2·8803 | — | — |

. Similar laws to those obtaining in the case of the original ammonium compounds regulate the change of sp. gr. and solubility of these salts; moreover, the replacement of 4K for $4NH_4$ in the original salts increases the sp. gr. in each case by a constant amount equal to 0·0634 unit. On the other hand, the difference between the sp. gr. of sat. soln. of the corresponding ammonium and potassium salts increases by approximately 0·02 unit for each addition of $1MoO_3$, whilst a similar increase of 0·01 unit is observed in the solubility.

According to C. Friedheim and W. H. Henderson, silicovanadatotungstates can be obtained by the action of hydrofluosilicic acid on a mixture of tungstate and vanadate. From the product of reaction between ammonium vanadate and ammonium silicotungstate a hydrated **ammonium silicovanadatodecatungstate** of the formula $(NH_4)_6SiV_2W_{10}O_{40}.21H_2O$ has been obtained. It forms reddish-brown, octahedral crystals of sp. gr. 3·428 at 20°. One c.c. of its sat. soln. at 17° contains 0·6652 grm. of the hydrated salt. If the product be not evaporated to dryness, but subjected to fractional crystallization, a salt of the formula $(NH_4)_6SiV_2W_9O_{37}.24H_2O$ is obtained having a sp. gr. 3·396. Two series of salts have been produced, a deca-series with the ratio of $SiO_2$ to $WO_3$ 1 : 10, and a series with the ratio 1 : 9. The deca-salts which have been prepared are: hydrated **sodium silicovanadatodecatungstate,** $Na_6SiV_2W_{10}O_{40}.29H_2O$, in reddish-brown crystals of sp. gr. 3·344° at 20°; the potassium salt, $K_6SiV_2W_{10}O_{40}.22H_2O$, in the form of reddish crystals with a sp. gr. 3·664 at 20°, the barium silicovanadatodecatungstate, $Ba_3SiV_2W_{10}O_{40}.28H_2O$, with a sp. gr. 3·66 at 20°. One c.c. of the sat. soln. of the barium salt contains 0·0384 grm. of salt. A **potassium ammonium silicovanadatodecatungstate,** $NH_4K_5SiV_2W_{10}O_{40}.23H_2O$, soluble to such an extent that 1 c.c. of its sat. soln. contains 0·5072 grm., and an **ammonium potassium barium silicovanadatodecatungstate,** $(NH_4)_2K_2BaSiV_2W_{10}O_{40}.25H_2O$, which crystallizes in holohedral forms of the regular system, have also been obtained. **Potassium and barium silicovanadatoenneatungstates** are obtained at the same time as the deca-salts. By the action of potassium silicotungstate on potassium vanadate, a salt of the formula $K_{14}Si_2V_6W_{18}O_{80}.42H_2O$ is produced, and it gives the salt $K_{12}Si_2V_6W_{18}O_{79}.31H_2O$ on crystallizing from water; both these are red solids which form crystals belonging to the monoclinic system. The **barium silicovanadatoenneatungstates** are: $BaSi_2V_4W_{18}O_{80}.83H_2O$ and $Ba_6Si_2V_4W_{18}O_{79}.50H_2O$; they are both red and form rhombic crystals. These salts are all decomposed by conc. acids or alkalies; they give characteristically coloured precipitates with lead, silver, and mercurous salts. Their formulation is illustrated by:

$$R_6H_2\left[Si\begin{matrix}(V_2O_6)\\(W_2O_7)_5\end{matrix}\right].nH_2O \qquad F_8\left[Si\begin{matrix}(V_2O_6)_2\\(W_2O_7)_4\end{matrix}\right].nH_2O$$

G. Flink [7] found small octahedral cubic crystals, sometimes hollow and otherwise irregular, associated with ægirite at Narsarsuk, Greenland. The mineral was named *chalcolamprite*—from χαλκός, copper; and λαμπρός, lustre—in allusion to the copper-red metallic iridescence. The composition approximates **calcium fluocolumbatosilicate,** $CaSiO_3.CaCb_2O_6F_2$, and there are small proportions of the cerium earths, alkalies, manganese oxide, and tantalic oxide also present. The colour is dark greyish-brown inclining to red. No cleavage was observed. The sp. gr. is 3·77, and the hardness 5·5. O. B. Böggild described a mineral from the nephelite-syenite region of Julianehaab, and Kangerdluarsuk, Greenland. It was named *epistolite*—from ἐπιστολή, a letter—in allusion to the flat rectangular form and white colour. The composition approximated to that of a **sodium fluocolumbatotitanosilicate,** $10Na_2O.4NaF.(Ca,Mg,Mn,Fe)O.4TiO_2.19SiO_2.5Cb_2O_5.21H_2O$. F. Zambonini discussed the chemical composition; and showed that the water is not constitutional. At 22°, over sulphuric acid of sp. gr. 1·835, the mineral lost 0·66 per cent. of water in 1 hr. and 1·83 per cent. in 143 hrs.; and when heated, the percentage losses were:

| | 65° | 120° | 170° | 195° | 240° | 310° | 345° | 390° | 400° |
|---|---|---|---|---|---|---|---|---|---|
| Loss . | 1·13 | 2·90 | 6·35 | 7·16 | 7·92 | 8·86 | 9·10 | 9·40 | 9·47 |

The total loss was 10·52 per cent. According to O. B. Böggild, the rectangular tabular crystals belong to the monoclinic system, and have the axial ratios $a : b : c = 0{\cdot}803 : 1 : 1{\cdot}206$, and $\beta = 74° 42'$. The 001-cleavage is very perfect yielding thin plates, and the 110-cleavage is distinct. The sp. gr. is 2·885; the hardness 1–1·5; the optic axial angle, $2V = 80°$; and the refractive index, 1·67. The optical character is negative. G. Flink [8] found a chocolate-brown mineral at Narsarsuk, Greenland, which he named **endeiolite**—from ἔνδεια, want; and λίθος, stone—in allusion to the fact that the analysis showed a considerable loss. The composition approximates **calcium hydroxycolumbatosilicate,** $CaCb_2O_6(OH)_2.CaSiO_3$. The minute octahedral crystals belong to the cubic system. The sp. gr. is 3·44; and the hardness 4. The mineral was also examined by O. B. Böggild and C. Winther.

The minerals epistolite, dysanalyte, pyrochlore, æschynite, euxenite, blomstrandine, priorite, marignacite, and boranskite are either complex columbatotitanates or complex tantalatotitanosilicates, and they have been discussed in connection with the rare earths, and scandium.


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## § 48. The Silicates of the Titanium-Lead Family

R. Rieke [1] found that mixtures of silica and titanic oxide give a **V**-eutectic at about 1530° with 40 per cent. of titantic oxide; and there is here inconclusive evidence of a maximum corresponding with the formation of a **titanium silicate,** $TiO_2.SiO_2$. Observations with titanic oxide and slag or clay (*q.v.*) were made by H. A. Seger and E. Cramer, H. Ries, C. Bryce, R. Rieke, and G. F. Comstock. The softening temp. of binary mixtures of titanic oxide and clay, by R. Rieke, were:

| $TiO_2$ | 0 | 10 | 20 | 30 | 40 | 50 | 60 | 80 | 100 per cent. |
|---|---|---|---|---|---|---|---|---|---|
| Temp. | 1770° | 1740° | 1660° | 1580° | 1530° | 1610° | 1670° | 1660° | 1610° |

For colloidal titanium silicates, *vide supra,* water-glass. L. Bourgeois obtained crystals containing the dioxides by fusing the dioxides of tin, silicon, or titanium with calcium fluoride.

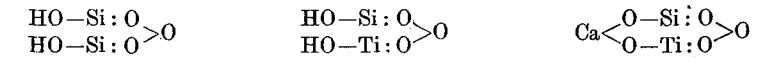
In 1787, M. A. Pictet [2] described *une nouvelle substance minérale* from Chamouni, which J. C. Delamétherie called *pictite.* M. H. Klaproth analyzed the mineral from Passau, and he named it **titanite.** L. J. M. Daubenton designated the mineral *titane siliceo-calcaire.* A. G. Werner called it *Braunmenakerz*—after Menaccan, Cornwall. H. B. de Saussure referred to it as *schorl rayonnante en gouttière ;* and R. J. Haüy called a related mineral *sphene*—from *σφήν,* a wedge. The chemical identity of titanite and sphene was established by the analyses of P. L. A. Cordier, M. H. Klaproth, and G. Rose.

An apple-green variety of sphene from Liguria, Apennines, was called by D. Viviani [3] *ligurite ;* a brown variety from Lewis Co., New York, was called *lederite* by C. U. Shepard ; and a red variety from Piedmont was called *greenovite*—after G. B. Greenough—by P. A. Dufrénoy. It was also described by A. Breithaupt, J. C. G. de Marignac, A. Delesse, and A. des Cloizeaux, and is coloured by manganese. The Norwegian mineral, the *eucolite-titanite* of T. Scheerer, resembles eucolite or eudialyte, and, according to W. C. Brögger, it contains 2–3 per cent. cerium oxide, and 35 per cent. titanic oxide—*vide* rare earths. A greenish variety from Maronne, Dauphiné, was called by F. de Bellevue *semeline* from its resemblance to flax-seed—*semen lini,* and by R. J. Haüy, *spinthere*—from *σπινθήρ,* spark—in allusion to its lustre. A dark brown titanite from Plauen Grund, Dresden, was investigated by P. Groth, and called by J. D. Dana, *grothite.* The sp. gr. is 3·5, and the hardness 6. It contains from 2–5 per cent. of yttria and 31 per cent. titanic oxide. C. W. Blomstrand described a greyish or brown mineral from Alsheda, Smäland, Sweden, with a sp. gr. 5, and hardness 3 ; he called it *alshedite—vide* rare earths. P. C. Weibye called a yellowish-green variety occurring in lanceolate crystals at Arendal, Norway, *aspidelite.* A. von Lasaulx applied the term *titanomorphite* to a white altered variety from Lampersdorf, Silesia, which was considered by A. Bettendorff to be calcium titanite, but A. Cathrein showed its relationship to titanite. W. von Gümbel applied the term *leucoxene* to a greyish-white opaque alteration product of titaniferous iron. A. Cathrein, H. Rosenbusch, and F. Zirkel showed it to be a variety of titanite. C. U. Shepard applied the term *xanthitane* to a yellow alteration product of titanite from Green River, Henderson Co., North Carolina. L. G. Eakins regarded it as a clay with titanic oxide in place of silica. C. U. Shepard called a reddish-brown or black mineral from McDowell Co., North Carolina, *pyromelane ;* it is a variety of titanite. A. Breithaupt found yellow monoclinic crystals of a mineral which he called *castellite,* at Holenkluk Mt., near Prolscht. A. Erdmann applied the term *keilhauite*—after B. M. Keilhau—to a dirty brown or black titanosilicate of calcium, aluminium, ferric iron, and the yttrium elements approximating $15CaTiSiO_5.(Al,Fe,Y)_2(SiTi)O_5$, and containing about 26–36 per cent. of titanic oxide, 12 per cent. of ceria earths, and 6–9 per cent. of yttria earths. T. Scheerer called it *yttrotitanite—vide* titanosilicates. The monoclinic crystals are isomorphous with those of titanite. The sp. gr. varies from 3·52 to 3·77, and the hardness is 6·5. F. S. Beudant referred to what he called a *minéral de Coromandel,* and this has been identified with the black mineral *tscheffkinite* found by G. Rose in the Ilem Mts., Ural. Analyses were made by H. Rose, etc.—*vide* rare earths. C. F. Rammelsberg, and A. des Cloizeaux gave formulæ for the mineral. R. C. Price's analysis corresponds with $(Ca,Fe)_2(Di,Ce,La,Fe)_2(Si,Ti)_5O_{15}$. R. Hermann found thoria present in the Russian mineral, but A. Damour found no thoria in the Indian mineral. The mineral analyzed seems to be an alteration product, and is possibly related to keilhauite.

Analyses were made by M. H. Klaproth,[4] G. Rose, P. L. A. Cordier, H. Rose, C. Busz, H. Rosales, F. A. Genth, F. W. Clarke, M. Schmöger, A. Cathrein, J. N. von Fuchs, A. Delesse, W. C. Brögger, J. C. G. de Marignac, J. Lemberg, M. F. Heddle, A. Erdmann, D. Forbes, C. F. Rammelsberg, G. Lindström, C. W. Blomstrand, E. B. Knerr and E. F. Smith, A. E. Arppe, J. Harrington, R. Soltmann, T. S. Hunt, J. Bruckmoser, P. Groth, C. Hintze, H. Lenk, F. Zambonini, etc.

H. Rose [5] represented titanite by a formula in which the titanic oxide was considered to be basic, but J. J. Berzelius showed that titanic oxide is more probably acidic, and he regarded titanite as a compound of calcium silicate and calcium titanate. C. W. Blomstrand favoured H. Rose's hypothesis and represented the mineral by the formula $Ca : O_2 : Si : O_2 : TiO$. F. W. Clarke, F. Zambonini, and O. Hauser, like C. W. Blomstrand, regard titanite as a basic salt, **calcium titanyl orthosilicate,** $Ca(TiO)SiO_4$. P. Groth regarded titanite as the calcium salt of

mesosilicic acid, **calcium mesotitanosilicate,** in which part of the silicon is replaced by titanium :



Mesosilicic acid, $H_2Si_2O_5$. Mesotitanosilicic acid, $H_2SiTiO_5$. Titanite, $CaSiTiO_5$.

The varieties of titanite which contain sesquioxides are supposed by P. Groth to be mixtures of $CaTiSiO_5$ and $(Al,Y)_2SiO_5$ ; while C. W. Blomstrand supposed that the complexes $Al_2O_2$, $Fe_2O_2$, etc., can replace the titanyl group, while bivalent iron and manganese can replace calcium. According to F. W. Clarke, xanthitane approximates to $Al{\equiv}Ti_3O_7{\equiv}H_3$ ; tscheffkinite to $(Fe,Ca)_3Ce_6Ti_4Si_6O_{32}$ ; and keilhauite resembles titanite with Ca or TiO replaced by $R'''OH$ or $R'''(OH)_2$.

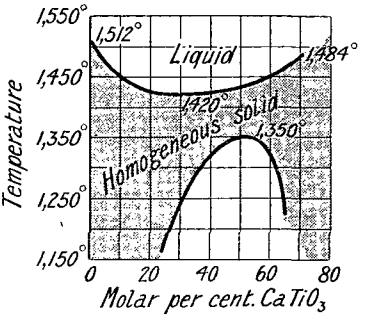



FIG. 185.—Freezing-point Curves of Mixtures of Calcium Metasilicate and Metatitanate.

Titanite is a pyrogenic mineral and is found as secretions in the oldest siliceous rocks—granites, diorites, syenites, and trachytes. It occurs as a secondary mineral derived from rutile or ilmenite. Titanite does not seem to be easily synthesized. S. Smolensky measured the f.p. of mixtures of calcium metasilicate and metatitanate, and found two breaks in the cooling curve. The upper ones correspond with the crystallization of the mixture to form homogeneous solid soln., and the lower one is produced by the resolution of the solid soln. into the component metasilicates. The f.p. curve has a minimum at 1420° and 33·4 molar per cent. of calcium metatitanate ; and the decomposition curve has a maximum at about 1350°. J. J. Ebelmen [6] observed greenish-yellow crystals of titanite were formed in fused mixtures of titanic oxide, silica, and an alkali or alkaline earth carbonate. F. Fouqué and A. Michel-Lévy made a similar observation. P. Hautefeuille melted a mixture of silica and titanic oxide or rutile with an excess of calcium chloride ; if some manganese oxide is also present the resulting crystals of titanite are rose-red. L. Bourgeois, and S. Smolensky also observed the separation of crystals of titanite from various magmas containing silica and titanic oxide. S. Smolensky found the blue artificial crystals enclose small crystals of perowskite. L. Michel found titanite crystals were formed by heating mixtures of titaniferous iron, calcium sulphide, silica, and carbon. P. Sustschinsky, and E. van der Bellen observed titanite crystals were formed after heating to 1400° a mixture of lime, quartz, and rutile.

The **colour** of titanite may be brown, grey, yellow, green, rose-red, and black ; and it may be transparent or opaque. The monoclinic **crystals** vary in habit ; they are wedge-shaped and flattened, or prismatic. The mineral is sometimes massive and compact—rarely lamellar. The crystals have been studied by A. des Cloizeaux,[7] C. Busz, W. H. Miller, V. Goldschmidt, F. Hessenberg, V. von Zepharovich, A. C. Lane, J. C. G. de Marignac, A. Lévy, G. vom Rath, H. B. Patton, A. Streng, H. Credner, P. Groth, H. Traube, R. Helmhacker, F. Becke, O. Mügge, J. F. Kemp, F. Kretschmer, A. von Lasaulx, A. Schmidt, C. Palache, W. J. Lewis, I. Bachinger, L. J. Igelström, F. J. Wiik, G. Flink, A. von Elterlein, D. F. Wiser, E. Artini, A. Arzruni, J. D. Dana, W. C. Brögger, J. F. Williams, P. von Jeremejeff, etc. The axial ratios, according to A. des Cloizeaux, are $a : b : c = 0{\cdot}75467 : 1 : 0{\cdot}85429$, and $\beta = 60° 17'$. Both contact and cruciform penetration twins are common, the former yielding forms apparently hemimorphic. The **twinning** plane (100) is common, and (001) rare. Polysynthetic twinning lamellæ occur sometimes giving rise to easy parting. Parting produced by twinning has been studied by P. von Jeremejeff, G. H. Williams, and O. Mügge. The faces 100 and (112) are often striated. The

**cleavage** (110) is distinct; and (100) and ($\bar{1}12$) imperfect; in greenovite, the (111) cleavage is easy, and ($\bar{1}11$) is less so. According to C. Busz, the **optic axial angle** $2E=57°\ 20\frac{1}{2}'$ with Li-light, $52°\ 29\frac{2}{3}'$ with Na-light, and $47°\ 54\frac{2}{3}'$ with Tl-light; and $2V=29°\ 30\frac{1}{2}'$ with Li-light, $27°\ 0\frac{1}{3}'$ with Na-light, and $24°\ 27\frac{1}{2}'$ with Tl-light. The optic axial angles vary widely, but the effect of composition is not clear. C. Busz observed no marked change in the optic axial angles when the temp. was raised to 200°; and A. des Cloizeaux found that at 26·5°, $2E=53°\ 34'$; at 171°, $2E=55°\ 48'$.

The **specific gravity** of titanite ranges from 3·4–3·8; that of yttrotitanite is 3·8. The **hardness** is nearly 5; that of yttrotitanite is nearly 6. I. I. Saslavsky studied the **molecular volume** and the **compressibility**. According to R. Cusack, the **melting point** of titanite is 1127°–1142°; A. Brun gave 1210°; S. Smolensky, 1221°; and C. Doelter, 1230°. A. L. Fletcher found that various titanites begin to show signs of melting at about 1250° and 1350°; keilhauite melted at 1110°. According to L. Bourgeois, titanite when melted is unstable, and it furnishes perowskite, and calcium metasilicate. G. A. Kenngott said that the coloured varieties become paler when heated, but become darker just before fusion. C. Busz found for the **indices of refraction** of titanite, $\beta=1·8839$ and $\gamma=1·9987$ for Li-light; $\beta=1·8940$ and $\gamma=2·0093$ for Na-light; and $\beta=1·9041$ and $\gamma=2·0239$ for Tl-light. H. Rosenbusch found the **pleochroism** gave *a* almost colourless; *b*, yellow with a greenish tinge; and *c*, reddish-yellow to brownish-red. C. Pulfrich, W. C. Brögger, and T. Liebisch made observations on this subject. The **optical character** is positive. G. W. Hankel studied the **pyroelectric** properties of titanite.

G. A. Kenngott found that the moistened powdered mineral—calcined or uncalcined—reacts alkaline to litmus. The mineral is but partially dissolved by hot hydrochloric acid; it is completely decomposed by sulphuric acid; but best broken down by conc. hydrofluoric acid. According to J. Bruckmoser, hydrochloric acid acts slowly at ordinary temp., and only a part of the titanic acid goes into soln.; at higher temp. the decomposition is faster and almost all the titanic acid goes into soln. The residual silica has the properties of mesosilicic acid, $H_2Si_2O_5$. J. Lemberg found that when titanite is treated with a soln. of magnesium chloride part of the calcium is replaced by magnesium; but no interchange of bases occurs with soln. of sodium carbonate or silicate. A. Johnsen found that the ferrous oxide in sphene could be oxidized by heating in oxygen, or reduced by heating in hydrogen. L. G. Eakins noted the transformation of sphene into xanthitane; P. Mann reported the alteration of titanite into rutile; B. Doss observed pseudomorphs of anatase after titanite; and K. Schneider showed that titanite can be altered into perowskite.

G. Flink [8] found minute acicular crystals, colourless or tinged violet or brown, in the pegmatite of Narsarsuk, Greenland, and he called the mineral **lorenzenite**—after J. Lorenzen. The analysis by R. Mauzelius corresponds with **sodium titanyl orthodisilicate,** $Na_2(TiO)_2Si_2O_7$, in which part of the titanium is replaced by zirconium. P. Groth regarded it as a salt of a polysilicic acid, $Na_2(Ti,Zr)_2Si_2O_9$, with Ti : Zr=9 : 2. F. W. Clarke gives $4Na_2(TiO)_2Si_2O_7.Na_2(ZrO)_2Si_2O_7$. F. Zambonini also regarded it as a double salt. The crystals belong to the rhombic system and have the axial ratios $a:b:c=0·6042:1:0·3592$. The (120) cleavage is distinct; the sp. gr. 3·42; the hardness 6–$6\frac{1}{4}$; the optic axial angle $2E=72°$; and the indices of refraction, $\alpha=1·7320$ and $\gamma=1·7786$ for red light; and $\alpha=1·7785$ and $\gamma=1·7876$ for yellow light. The optical character is positive. E. E. Kostyleva described a mineral with the same composition as lorenzenite which was collected by A. E. Firsman in the pegmatite veins of Khibinskii and Lovozerskii tundras. It was named **ramsayite**, after W. Ramsay, the Finnish geologist. The mineral occurs in black or dark brown aggregates; and possesses a metallic lustre. The rhombic crystals have the axial ratios $a:b:c=1·2116:1:1·6520$. The (100)-cleavage is perfect; the (110)-cleavage is less good. The sp. gr. is 3·43, and the hardness 6. The mineral readily fuses to a black bead. The mean index of

refraction is 1·9; and the birefringence $\gamma-\alpha=0{\cdot}09$; the dispersion is strong; and the pleochroism marked.

G. Flink [9] found a mineral which he named **narsarsukite** in several localities near Narsarsuk, Greenland. According to F. W. Clarke, C. Christensen's analysis corresponds with **sodium titanium dimesotrisilicate,** $Ti(Si_3O_8Na_2)_2$, in which about one-sixth of the sodium is replaced by the univalent radicle FeO. F. Zambonini represents it by the formula $6Na_2Si_4O(FeO_9)_2Ti_4O_9$, which is regarded as a salt of tetrerosilicic acid, $H_2Si_4O_9$, where the silicon is in part replaced by titanium and, may be, zirconium. The colour is yellow or reddish-brown. The tabular or cubic crystals belong to the tetragonal system, and have the axial ratio $a:c=1:0{\cdot}5235$. The cleavage (110) is distinct. The sp. gr. is 2·751, and the hardness 7–7¼. The indices of refraction are $\omega=1{\cdot}5532$, and $\epsilon=1{\cdot}5842$ for Na-light. The optical character is positive. The mineral is not attacked by ordinary acids.

H. A. Brouwer [10] described a mineral from Rustenberg, Transvaal, which he called **molengraaffite**—after G. A. F. Molengraaff. The analysis corresponds closely with that of yttrotitanite; and F. W. Clarke represents its composition as a hydrated **sodium calcium titanosilicate,** $HNa_3Ca_4Ti_3Si_4O_{20}$. The yellowish-brown imperfect crystals are probably monoclinic, possibly rhombic. Polysynthetic twinning is common; the (100) cleavage is perfect; the pleochroism is feeble; the refractive indices are $\alpha=1{\cdot}735$, $\beta=1{\cdot}770$; the optic axial angle $2E=50°$; and the optical character is positive.

G. D. Louderback mentioned a titanosilicate of calcium and iron from Joaquin, California. H. Leitmeier called it *joaquinite*. It has not been examined carefully.

G. Flink [11] obtained a mineral near Igaliko, Greenland, which he called **neptunite.** A sample from San Benito, California, was named *carlosite* by G. D. Louderback. Analyses by G. Flink, W. M. Bradley, and O. A. Sjöström correspond with $R'_2R''TiSi_4O_{12}$. The mineral is thus closely related to titanite. F. W. Clarke regarded neptunite as **sodium ferrous titanium trimetasilicate,** with part of the sodium replaced by potassium; and part of the bivalent iron by manganese:

$$\begin{matrix}(Na,K)-SiO_3\\(Na,K)-SiO_3\end{matrix}>Ti<\begin{matrix}SiO_3\\SiO_3\end{matrix}(Fe,Mn)$$

The colour of the mineral is black, but in thin splinters, blood-red. The crystals were described by O. B. Böggild, A. Wallenström, G. Nordenskjöld, W. E. Ford, etc. According to G. Flink, the prismatic crystals are monoclinic, with the axial ratios $a:b:c=1{\cdot}3164:1:0{\cdot}8076$, and $\beta=64°\ 22'$. Twinning occurs about the plane (001); the (110) cleavage is distinct. The optic axial angle $2V=48°$. The optical character is positive. The mineral is pleochroic. The sp. gr. is 3·234, and the hardness 5–6.

P. C. Weibye, and T. Scheerer [12] found a mineral on the islands of the Langesund fiord, Norway, and named it **astrophyllite**—from ἄστρον, star; and φύλλον, leaf—in allusion to the stellate aggregation and foliated micaceous structure. J. Lorenzen found it at Kangerdluarsuk, Greenland; G. Gürich, on the Los Island, Africa; and G. A. König, at Pike's Peak, Colorado. A yellowish-brown related mineral from Kola, Lapland, was called by W. Ramsay and V. Hackman, *lamprophyllite.* Analyses have been reported by T. Scheerer, F. Pisani, C. F. Rammelsberg, H. Bäckström, G. A. König, and L. G. Eakins. W. C. Brögger writes the formula $R''_4R'_4Ti(SiO_4)_4$; and P. Groth gave $(K,Na,H)_4(Fe,Mn)_4TiSi_4O_{16}$. The composition varies, but the dominant molecule seems to be **sodium potassium ferrous titanium orthosilicate,**

$$\begin{matrix}FeH{\equiv}SiO_4\\FeH{\equiv}SiO_4\end{matrix}>Ti<\begin{matrix}SiO_4{\equiv}FeK\\SiO_4{\equiv}FeNa\end{matrix}$$

with some ferrous iron replaced by manganese, and ferric-iron as FeOH''. F. W. Clarke regarded the Colorado mineral as a mixture of 3 molar proportions of the above with one of $TiOH(SiO_4{\equiv}FeH)_3$. The colour of astrophyllite is bronze-

yellow or gold-yellow. The crystals are often elongated into thin strips or blades, sometimes arranged in stellate groups. The faces are often striated. A. Nordenskjöld, and A. des Cloizeaux made the crystals rhombic; H. Bücking, monoclinic; and W. C. Brögger, triclinic. The last-named later showed that the variation in the angle and optical character earlier noted is probably without significance, being due to deformation produced by press. The axial ratios of the rhombic crystals are $a:b:c=1{\cdot}0098:1:4{\cdot}7556$. The (100) cleavage is perfect, and (001) very imperfect. The percussion figure on a cleavage surface has two rays crossing at 81°–85°. A. des Cloizeaux gave for the optic axial angle $2H_0=118°–124°\ 11'$ with the red ray, and $2V=103°\ 25'$; H. Bücking gave $2H_0=122°\ 18'$ for the Li-ray and 124° 52′ for the Na-ray; and W. C. Brögger, $2H_0=114°\ 37\frac{1}{2}'–123°\ 28'$, and $2E=160°$ for white light. A. des Cloizeaux found that raising the temp. to 146·5° produced no perceptible change in the optic axial angles. The sp. gr. of astrophyllite is 3·324–3·375; and the hardness is 3. A. Michel-Lévy and A. Lacroix gave for the indices of refraction $\alpha=1{\cdot}678$, $\beta=1{\cdot}703$, and $\gamma=1{\cdot}733$ for yellow light. The crystals are pleochroic, $a$=deep orange-red, $b$=citron-yellow, and $c$=orange-yellow. The optical character is positive. The mineral is decomposed by hydrochloric acid with the separation of flocculent silicic acid.

According to F. W. Clarke, the minerals *johnstrupite* and *rinkite*—*vide* titanium silicates—can be regarded as fluoriferous astrophyllites. In the former, a little zirconia, thoria, and ceria may replace some titania. Johnstrupite is essentially a hydrated **sodium calcium titanium orthosilicate,** with some cerous fluoride in place of sodium:

$$\begin{matrix}\mathrm{CaNa{\equiv}SiO_4}\\ \mathrm{CaNa{\equiv}SiO_4}\end{matrix}\!\!>\!\mathrm{Ti}\!<\!\begin{matrix}\mathrm{SiO_4{\equiv}CaH}\\ \mathrm{SiO_4{\equiv}Na(CeF_2)}\end{matrix}$$

and rinkite is supposed to be a mixture of 3 mols of $\mathrm{Ti(SiO_4{\equiv}CaNa)}$ and 2 mols of $\mathrm{TiF{\equiv}SiO_4{-}Ti\{SiO_4{\equiv}Ca(CeF_2)\}_3}$. He also represents *mosandrite*—*vide* rare earths—by $\mathrm{4RF(SiO_4{\equiv}CaH)_3.R(OH)[SiO_4{\equiv}HNa\{Ce(OH)_2\}]_3}$, where R is used in place of Ce″ : Zr : Ti = 1 : 2 : 2.

S. Smolensky[13] found that barium metasilicate and metatitanate give a complicated system, but determined only the m.p. of binary mixtures with the following molar percentage proportions of $BaTiO_3$:

| | 0 | 10·8 | 21·4 | 31·9 | 42·1 | 52·2 | 62·1 | 71·8 |
|---|---|---|---|---|---|---|---|---|
| m.p. . . . | 1470° | 1461° | 1450° | 1420° | 1405° | 1376° | 1384° | 1409° |

G. D. Louderback found crystals of a mineral which he called **benitoite** associated with the neptunite and natrolite near the head waters of the San Benito River, California. The composition approximates **barium titanotrisilicate,** $BaTiSi_3O_9$; this would make benitoite the barium salt of teterosilicic acid, $H_2Si_4O_9$, with an atom of silicon replaced by one of titanium. E. H. Kraus considers the mineral as a metasilicate isomorphous with beryl, $Ba_2Ti_2(SiO_3)_6$, but W. C. Blasdale has shown that the titanium is not likely to be basic. F. W. Clarke regards benitoite as a *barium titanyl mesotrisilicate,* $TiO{=}Si_2O_8{=}Ba$. The ditrigonal crystals were found by G. D. Louderback to have the axial ratio $a:c=1:0{\cdot}17326$; C. Palache gave 1 : 0·7319; and B. Jezek, 1 : 0·7353. F. Rinne found that the X-radiograms of benitoite correspond with the ditrigonal bipyramidal class. The colour is usually sapphire blue to light blue; colourless or green crystals are rare. The mineral is used as a gem-stone. G. D. Louderback, and B. Jezek gave 3·64–3·67 for the sp. gr., and $6\frac{1}{4}–6\frac{1}{2}$ for the hardness. C. Hlawatsch found the indices of refraction for the *D*-line to be $\omega=1{\cdot}756$, and $\epsilon=1{\cdot}802$; C. Palache gave $\omega=1{\cdot}77$, and $\epsilon=1{\cdot}80$. The mineral is strongly dichroic, $\epsilon$ being deep blue, and $\omega$, colourless. Benitoite is insoluble in hydrochloric, but is decomposed by hydrofluoric acid.

G. Flink[14] found a white or greyish-blue mineral which he called **leucosphenite**—from λευκός, white; and σφήν, a wedge—occurring sparsely in the pegmatite at Narsarsuk, Greenland. The composition approaches that of petalite or eudidymite; and R. Mauzelius' analysis corresponds with $Na_4Ba(TiO)_2(Si_2O_5)_5$, which makes leucosphenite **sodium barium titanyl mesodisilicate.** P. Groth writes the formula $BaNa_4Ti_2Si_{10}O_{27}$, where the titanium is anionic. F. W. Clarke writes

the formula $Na_3Ba_2Ti_4(Si_3O_8)_7$. F. Zambonini makes leucosphenite a double salt, $BaSi_4O_9.2Na_2TiSi_3O_9$. G. Flink found that the monoclinic crystals have the axial ratios $a:b:c=0{\cdot}5813:1:0{\cdot}8501$, and $\beta=93°\,23'$. The crystals are wedge-shaped. Twinning is common; the twinning plane is (001); the cleavage (010) is distinct. The sp. gr. is 3·05; and the hardness 6·5. The indices of refraction for the red ray are $\alpha=1{\cdot}6401$, $\beta=1{\cdot}6572$, and $\gamma=1{\cdot}6829$; and for the yellow ray, $\alpha=1{\cdot}6445$, $\beta=1{\cdot}6609$, and $\gamma=1{\cdot}6878$. The optic axial angle $2V=79°\,26'$ for the red ray, and .77° 4′ for the yellow ray. The optical character is negative. Leucosphenite is decomposed by hydrofluoric acid. A titanium ultramarine of a green colour has been reported by F. Singer[15] to be formed when the zeolitic substance, with a composition approximating $Na_2O.Al_2O_3.2TiO_2.4H_2O$, is treated with sodium sulphide.

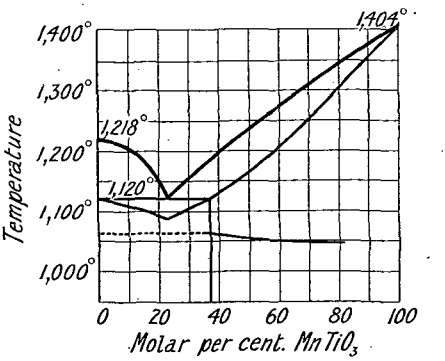


Fig. 186.—Freezing-point Curves of Mixtures of Manganese Metasilicate and Metatitanate.

S. Smolensky[16] measured the f.p. of binary mixtures of manganese metasilicate and metatitanate, and obtained the curves shown in Fig. 186. There is a eutectiferous series with a eutectic at 1120° and 22·3 molar per cent. of $MnTiO_3$. Solid soln. are formed with from 38·3 to 100 molar per cent. of manganese metatitanate but not at the other end of the series. A decomposition of the solid soln. occurs at about 1050°.

A. Breithaupt[17] found black prismatic crystals of a mineral associated with the arfvedsonite of Greenland. He called it *kölbingite*—after F. Kölbing—and another similar mineral was called **ænigmatite**—from αἴνιγμα, an enigma—and regarded as a pseudomorph after kölbingite. Ænigmatite had a sp. gr. 3·833–3·863, and kölbingite a sp. gr. 3·60–3·61. J. Lorenzen showed that the crystals of ænigmatite cannot be pseudomorphs; and W. C. Brögger showed that kölbingite is probably a parallel intergrowth of arvedsonite and ænigmatite. Analyses of ænigmatite were reported by W. C. Brögger, and H. Förstner. The mineral is essentially **sodium ferrous titanometasilicate,** with part of the silicon replaced by titanium, and a small admixture of a basic salt, $RFe'''_2SiO_6$. J. Söllner represented it as a mixture of $Fe''_2Fe'''_4Si_2O_{12}$ and $(Na_2,K_2,Fe)_4(Si,Ti)_4O_{12}$. The crystals approximate closely to those of the monoclinic amphiboles in habit, angle, and form. The prismatic crystals of ænigmatite, however, are triclinic. J. D. Dana recalculated H. Förstner's values for the axial ratios, and obtained $a:b:c=0{\cdot}6778:1:0{\cdot}3506$, and $\alpha=90°$, $\beta=72°\,49'$, and $\gamma=90°$. Contact twinning on the (010) plane is common, and there are twinning lamellæ giving striations on the terminal planes and on the (100)-face. The prismatic cleavage is distinct. The sp. gr. is indicated above. The optic axial angle $2E=60°$, according to W. C. Brögger. The optical character is positive. The pleochroism is well-marked. The radioactive haloes were studied by O. Mügge.

J. Söllner obtained triclinic crystals of a black or brownish-black mineral isomorphous with ænigmatite but containing less ferrous oxide and alkalies, and approximating $(Ca,Na_2,K_2)_2Mg_4Fe_2''Fe_3'''Al_4(Si,Ti)_6O_{30}$. The mineral was first found in the Rhön district, and called *rhönite*. The crystals are short prisms or tabular; the twinning plane is (010); the cleavages parallel to (110) and to $(1\bar{1}0)$ are good. The sp. gr. is 3·587. H. Förstner found minute black crystals in the liparyte lavas of the Island of Pantellaria whose ancient name was Cossyra; and he called the mineral *cossyrite*. Analyses were made by J. Söllner, and H. Förstner. The composition and crystal form were shown by W. C. Brögger, J. Söllner, B. Gossner, and H. Förstner to be like those of ænigmatite. The sp. gr. is 3·802; the hardness is $5\frac{1}{2}$; the index of refraction is near that of hornblende; and the double refraction is feeble. The mineral is but little affected by the ordinary acids, but is completely decomposed by hydrofluoric acid.

For the so-called *titanolivine*, $(Mg,Fe)_2(Si,Ti)O_4$, *vide* olivine. There are numerous titaniferous pyroxenes and amphiboles—*e.g.* the triclinic *œnigmatite* (*q.v.*). A number of garnets carrying titanium have been reported by A. Damour,[18] A. Knop, A. Stromeyer, W. Petersson, A. Claus, G. A. König, F. A. Genth, and A. Sauer. The proportions here run up to 10·84 per cent. $TiO_2$. The *ferrotitanite* of J. D. Whitney had 22·10 per cent. $TiO_2$. C. U. Shepard called this mineral **schorlomite,** owing to its resemblance to schorl. The analyses approximate $Ca_3(Fe,Ti)_2\{(Si,Ti)O_4\}_3$, or *calcium diferric tetrorthotitanatosilicate.* The sp. gr.. is 3·81–3·88 ; and the hardness 7–7½. It furnishes trapezohedral and dodecahedral crystals belonging to the cubic system. C. U. Shepard regarded the mineral as hydrated silicate of ferric oxide, yttria, and possibly thoria ; but C. F. Rammelsberg, and G. A. König showed that the mineral is really a garnet. N. Nordenskjöld obtained a mineral from Ivaara, Finland, which he called *ivaarite.* It closely resembles schorlomite. H. S. Washington gave for the refractive index 1·94 ; for ivaarite, 2·01 ; and for melanite, 1·86–1·88.

R. Rieke [19] made some observations on the fusibility of mixtures of zirconia and clay. The history of **zircon** is discussed in connection with the history of zirconium (*q.v.*). Although zircon is not itself readily altered, it is gradually hydrated and transformed by weathering, forming a whole series of products containing 3–70 per cent. of zirconia ; at the same time other bases like alkalies, alkaline earths, and the rare earths have been taken up, producing minerals of great complexity. Most of them have been reported from Norway, Sweden, Greenland, and Russia. Some of the altered forms have received special names ; very few of them are of general interest. T. Scheerer [20] described a brown mineral from Hitterö, Norway, which he called **malacone**—from μαλακός, soft—in allusion to its being softer than ordinary zircon. A. des Cloizeaux found malacone at Chanteloube, Haute Vienne, occurring in thin plates 3–4 mm. thick ; and occasionally with crystals on their surface ; and he regarded it as hydrated zircon. C. F. Rammelsberg said that without doubt malacone is *eine Pseudomorphose des Hydrate nach der wasserfreien Verbindung.* Analyses were made by T. Scheerer, A. Hermann, E. S. Kitchin and W. G. Winterson, A. C. Cumming, R. Hermann, and A. E. Nordenskjöld. Malacone contains from 47–67 per cent. of zirconia, about 32 per cent. of silica, 3–4 per cent. of water, and traces of yttria, magnesia, iron oxide, and manganese oxide. V. M. Goldschmidt and L. Thomassen found that malacone from Hitterö, Norway, contained hafnium. Idealized malacone approximates to **zirconium dihydroxytriorthosilicate,** $Zr_3(SiO_4)_3.H_2O$—*vide infra.* E. S. Kitchin and W. G. Winterson stated that it is one of the few minerals known to contain argon. From the radioactivity of the mineral, R. J. Strutt suggested some uranium is present, and E. S. Kitchin and W. G. Winterson found 0·33 per cent. $U_3O_8$, but A. C. Cumming found none. A brownish-yellow powder from Rosendal, Finland, was shown by A. E. Nordenskjöld to resemble malacone very closely. The crystals of malacone were described by T. Scheerer, E. Zschau, and W. C. Brögger. The sp. gr. is 3·9–4·05, and the hardness 6·5.

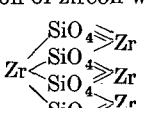
W. J. Knowlton [21] found a mineral in the granite at Rockport, Mass., and he named it **cyrtolite**—from κυρτός, bent—in allusion to the curvature of the pyramidal faces of the tetragonal crystals which appear like rhombic dodecahedra. Analyses were made by C. W. Blomstrand, J. P. Cooke, F. A. Genth and S. L. Penfield, and A. E. Nordenskjöld. The mineral appears to be a brownish-red variety of malacone with zirconia from 60–67 ; of silica, 26–28 ; ceria, 1·4–2·1 ; iron oxide, 2·5 ; water, 2·2–4·7 per cent. Although under ordinary conditions the dominant constituents of minerals are alone determined in analyses, the composition appears exceedingly complex when the constituents present in smaller proportions are determined. For example, the following is compiled from three analyses of cyrtolite from Devil's Head Mountain, Colorado, by W. F. Hillebrand :

| $SiO_2$ | $Ta_2O_5$ | $SnO_2$ | $ZrO_2$ | $ThO_2$ | $Ce_2O_3$ | $(La,Di)_2O_3$ | $Er_2O_3$ | $Y_2O_3$ |
|---|---|---|---|---|---|---|---|---|
| 19·90 | 0·71 | 0·03 | 47·81 | 1·16 | 0·06 | 0·19 | 4·69 | 2·63 |

| $Fe_2O_3$ | MnO | CaO | MgO | $K_2O$ | $Na_2O$ | $H_2O$ | $P_2O_5$ | F |
|---|---|---|---|---|---|---|---|---|
| 5·45 | 0·46 | 2·02 | 0·12 | 0·19 | 0·46 | 12·61 | 1·44 | 0·36 |

G. Hevesy and V. T. Jantzen found 9 per cent. of hafnia in cyrtolite from the United States. This was previously included in analyses with the zirconia. F. W. Clarke represented the mineral as **zirconium octohydroxydiorthosilicate,** $Zr\{SiO_4)_2(OH)_2\{H(ZrO_2H_2)\}_2$—*vide infra.* The sp. gr. is 3·29–4·04; and the hardness 5–5·5—after ignition, the hardness is 7–7·5. C. W. Blomstrand found a cyrtolitic mineral near Ytterby to which H. Bäckström applied the term *anderbergite.* The mineral is honey-yellow to coal-black in colour and is microscopically amorphous, but with a pseudomorphous tetragonal form. It was analyzed by A. E. Nordenskjöld, and G. K. Almström; it approximates $2CaO.R_2O_3.6ZrO_2.8SiO_2.12H_2O$. F. W. Clarke's view of the constitution is indicated below. The sp. gr. is 3·28–3·33; and the hardness 5·5–6. D. Forbes and T. Dahll found at Alve and Narestö, Norway, crystals of a reddish-brown mineral which they called **alvite.** It also occurs at Ytterby, Sweden. It is a zirconosilicate of the rare earth metals, calcium, magnesium, beryllium, copper, aluminium, and zinc, and a small proportion of water. V. M. Goldschmidt and L. Thomassen found that alvite from Hitterö, Norway, contained some rare earths, tungsten, yttrium, thorium, manganese, and hafnium; and they represented its composition by the formula $(Zr,Ha,Th)O_2.SiO_2$. G. Hevesy and V. T. Jantzen found 16 per cent. of hafnia in alvite from Kragerö and this was formerly regarded as zirconia. The analysis of the Ytterby mineral was reported by A. E. Nordenskjöld, and it appears different from that of D. Forbes and T. Dahll—but the analysis by the latter is not satisfactory. B. Szilard, W. C. Brögger and co-workers, and R. J. Strutt have made some observations on this subject. The ceria earths amount to 3·98 per cent.; the yttria earths, 22 per cent.; and zirconia, 30·5–61·4 per cent. F. W. Clarke's view of the composition is indicated below. The crystals are tetragonal, optically isotropic, forming pseudomorphs after zircon. The sp. gr. is 3·3–4·3; and the hardness 5–6. P. C. Weibye [22] found dark reddish-brown crystals in gneiss near Kragerö, Norway, to which he applied the term **tachyaphalite**—from *ταχύς*, quick; and *ἄφαλτος*, flying to pieces—in allusion to the ready separation of the mineral from the gangue when struck. N. J. Berlin's analysis gave: zirconia, 38·96 per cent.; silica, 34·58; thoria, 12·8; iron oxide, 3·7; and water, 8·5 per cent. Its sp. gr. is 3·6; hardness, 5·5. G. Forchhammer applied the term **oerstedite**—after H. C. Oersted—to a reddish-brown mineral from Arendal, Norway. It has 68·9 per cent. of zirconia; 19·7, silica; 2·05, magnesia; 2·61, lime; and 5·5 of water. Its sp. gr. is 3·629, and hardness, 5·5. P. C. Weibye found that the mineral always crystallized in the form of zircon. R. Hermann applied the term **auerbachite,** to a brownish-coloured crystalline mineral found by J. Auerbach in Mariupol, Russia. It has 55·18 per cent. zirconia; 42·9, silica; 0·93, iron oxide; and 0·95, water. The sp. gr. is 4·06; and the hardness, 6·5. The mineral was also studied by N. von Kokscharoff, P. von Jeremejeff, and J. D. Dana.

Analyses of zircon have been reported by M. H. Klaproth,[23] L. N. Vauquelin, M. H. Cochran, C. W. Nylander, A. Corsi, A. Liversidge, F. A. Genth, G. A. König, K. von Chrustschoff, A. Osann, J. J. Berzelius, T. S. Hunt, C. F. Rammelsberg, G. Grattarola, G. Woitschach, G. P. Tschernik, P. J. Holmquist, A. Schmidt, A. Knop, C. M. Wetherill, W. Gibbs, J. F. John, W. Henneberg, C. F. Chandler, J. P. Cooke, W. J. Knowlton, A. Damour, R. Hermann, N. J. Berlin, etc. G. von Hevesy and V. T. Jantzen reported 1·3–6 per cent. of hafnium (or celtium) dioxide in samples of zircon from various localities. The composition of the purer varieties of zircon approximates to that of **zirconium orthosilicate,** $ZrSiO_4$, or $ZrO_2.SiO_2$, with up to about 3 per cent. of thoria, yttria, and other oxides. Zircon is either an isomorphous mixture of the two oxides or a zirconium silicate. Since the ratio $ZrO_2 : SiO_2$ in the various analyses varies between 39 : 44 and 30 : 65, and since the mixture 1 : 2 behaves very like zircon, C. Doelter and E. Dittler [24] incline to believe that zircon is an isomorphous mixture of the two oxides. W. C. Brögger regards zircon as zirconyl metasilicate, $ZrO.SiO_3$, and, in agreement with P. J. Holmquist, writes this graphically $O{=}Zr{=}O_2{=}Si{=}O$. This view is based on the close morphological relations between zircon, rutile, and cassiterite. The minerals cassiterite, $SnSnO_4$; rutile, $TiTiO_4$; zircon, $ZrSiO_4$; thorite, $ThSiO_4$; polianite, $MnMnO_4$; plattnerite, $PbPbO_4$; and xenotime, $YPO_4$, are analogous in form and composition even if they are not strictly isomorphous. The absence of any information as to the mol. wt. of a mineral is tacitly considered to be a license to adopt any desired mol. wt. F. W. Clarke assumes the tetradic association $Zr_4(SiO_4)_4$, in order to harmonize the constitution of zircon with those of some related minerals.



The space lattice of the zircon family, as revealed by the X-radiograms of L. Vegard, and C. M. Williams, shows that the silicon and zirconium atoms are arranged as atomic centres in tetragonal lattices of the diamond type, and the tetragonal arrangement is not produced by the atomic centres but by the tetragonal arrangement of the oxygen atoms. Consequently, the lattice has a kind of mol. structure with units of the type $MO_2$, where M represents an atom of silicon, zirconium, titanium, or tin; the three atoms form one mol. and are situated on a straight line with M in the central position. The straight line or mol. axis is always perpendicular to the tetragonal axis. The distance apart of the atoms, and the geometrical relations of the lattice vary with the nature of the central atom M. This supports the view that the groups $MO_2$ form chemically bound molecules. The space lattice of xenotime does not belong to the zircon type, for there is a different arrangement of the oxygen atoms. In xenotime, the oxygen atoms are arranged in groups of four around each atom of phosphorus so that the space lattice gives the constitutional formulæ $YPO_4$ and $ZrO_2.SiO_2$ respectively for xenotime and zircon. The specimens of the mineral thorite examined by L. Vegard preserved the outer form isomeric with zircon, but internally, the crystals had become isotropic. The space lattice was completely broken down, and no X-radiogram could be obtained. The absolute dimensions of the space lattices of the zircon group are indicated in Table XXXI. M. L. Huggins found the structure of zircon resembles that of

TABLE XXXI.—DIMENSIONS OF THE SPACE LATTICES OF THE ZIRCON FAMILY.

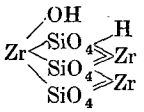
| | Crystal axes in cm. | | | Volume in c.c. atom. | Distance from the O to the M atom in cm. |
|---|---|---|---|---|---|
| | *a* | *c* | *a* : *c* | | |
| Zircon, $ZrO_2SiO_2$ . | $9{\cdot}20\times10^{-8}$ | $5{\cdot}87\times10^{-8}$ | 1 : 0·639 | $4{\cdot}97\times10^{-22}$ | Zr $2{\cdot}71\times10^{-8}$<br>Si |
| Cassiterite, $(SnO_2)_2$ | 9·35 | 6·29 | 1 : 0·673 | 5·50 | 2·08 |
| Rutile, $(TiO_2)_2$ . | 9·05 | 5·83 | 1 : 0·644 | 4·77 | 1·99 |
| Xenotime, $YPO_4$ . | 9·60 | 5·94 | 1 : 0·618 | 5·49 | 1·23 |

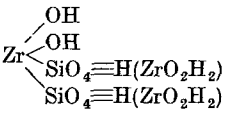
rutile; and A. Johnsen discussed the structure and symmetry of this family of minerals.

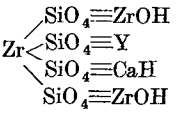
Considerable amounts of ferric oxide are present in some zircons; thus, G. A. König found 9·2 per cent. in a zircon from Pike's Peak, Colorado, and this gave for the formula $Zr_{10}Fe_2Si_{10}O_{43}$. Ferric oxide is present in all natural zircons —may be in solid soln. or as an iron zirconate. Similarly the cerium and yttrium, often present, may be there as a solid soln. of silicate or zirconate of these elements. Anderbergite may be regarded as having a composition:

$$\begin{matrix}ZrOH{\equiv}SiO_4\\ZrOH{\equiv}SiO_4\end{matrix}\!\!>\!Zr\!<\!\begin{matrix}SiO_4{\equiv}Y\\SiO_4{\equiv}CaH\end{matrix}+4H_2O$$

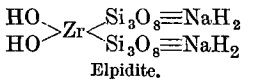
Alvite may be regarded as a mixture of two compounds, $Zr(SiO_4)_4(ZrOH)_4$ plus $Zr(SiO_4)_4(BeOH)_{12}$. According to this hypothesis, these minerals are salts of a dodecabasic *zirconatosilicic acid*, $H_{12}ZrSi_4O_{12}$. The water present in many zircons may represent zircon altered by hydration. The dehydration experiments of F. Zambonini fit very well with the assumption that hydrated zircon is simply zircon with variable amounts of dissolved water. F. W. Clarke, on the other hand, assumes that the water is intrinsically associated with the molecule. Thus, he regards malacone as the first hydration derivative; and the analyses of some cyrtolites correspond with a still further stage, namely, $(HO)_2Zr\{H(ZrO_2H_2)\}_2$, in which part of the $ZrO_2H_2$ may be replaced by other bases. Thus, anderbergite has a composition corresponding with:

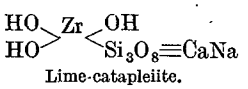

Malacone.

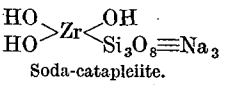

Cyrtolite.


Anderbergite.

The minerals elpidite, lime-catapleiite, and soda-catapleiite represent more advanced stages in the hydration and replacement of zircon ; thus :


Elpidite.


Lime-catapleiite.


Soda-catapleiite.

On the other hand, F. Zambonini regards the water in these minerals as extrinsic and not intrinsic or constitutional ; and he regards elpidite as a metadisilicate, $Na_2ZrSi_6O_{15}.3H_2O$, and catapleiite, $Na_2ZrSi_3O_9.2H_2O$, that is, $O{=}Zr{=}Si_3O_8{=}Na_2 + 2H_2O$.

Zircon is common in nearly all kinds of igneous rocks, particularly the more siliceous ones like granite, syenite, diorite, etc. H. Thürach,[25] W. C. Brögger, T. L. Watson and F. L. Hess, etc., have discussed this subject. It seems to be one of the earliest minerals to crystallize from cooling rock magmas. Instead of zircon, complex silicates like the zircon pyroxenes may be formed. Zircon has been repeatedly obtained synthetically. A. Daubrée, H. St. C. Deville, and H. Caron made it by heating zirconia in a current of silicon tetrachloride. H. St. C. Deville also made it by heating a mixture of zirconia and quartz in the same gas. The first stage of reaction is supposed to involve the formation of zirconium fluoride, which reacts with quartz regenerating silicon tetrafluoride. A small quantity of this gas produces an indefinitely large amount of zircon. P. Hautefeuille and A. Perrey obtained zircon by heating a mixture of silica, zirconia, and lithium molybdate to 800° ; and S. Stevanovic employed a similar process. W. E. Gürtler used sodium metaborate as *agent minéralisateur*. K. von Chrustschoff heated a mixture of gelatinous silica and gelatinous zirconia in a steel bomb at a temp. approaching redness. C. Friedel and E. Sarasin used a somewhat similar process

Small crystals of zircon are not uncommon in granites, basalts, syenites, diorites, and many crystalline or igneous siliceous rocks. It is rarely found in basic igneous rocks like the gabbros and peridotites. Well-shaped crystals are also found among the heavier grains of sands, etc., derived from the disintegration of these rocks. Crystals of zircon are common in auriferous and gem-sands, particularly those of Southern India, Ceylon, and Brazil. Zircon is mined in North Carolina, where in the Henderson county it is extracted from a decomposed granite.

The **colour** of zircon has attracted some attention. The crystals may be transparent or opaque, and colourless or coloured pale yellow, pale grey, orange-yellow, yellowish-green, brownish-yellow, reddish-brown, or red. Some thin sections are violet-blue. The colours are sometimes distributed zonally. F. Sandberger [26] attributed the red colour of hyacinths to the presence of a small quantity of cuprous oxide. This is improbable. W. Hermann showed that oxide of iron is the probable colouring agent of zircon ; and that in green zircons he found chromium and manganese oxides are present. T. Wolff, F. Sandberger, and G. vom Rath observed that rose and flesh-coloured crystals become paler when exposed to light ; and G. F. Richter, and L. Michel noted that the hyacinth-red variety becomes brownish-red when exposed to light—rapidly in sunlight, slowly in diffuse daylight ; when kept in darkness, the original colour is partially restored. C. Doelter observed but little change in the colour when exposed to the arc-light, but in ultra-violet light, the colour becomes paler. T. Wolff, K. Simon, F. Sandberger, and G. vom Rath found that, when heated, the colour is weakened. B. R. Geijer also observed that the colour is destroyed by heat ; C. A. S. Hofmann obtained similar results, and W. Henneberg showed that thermoluminescence accompanies the decolorization by heat, and the effect is not dependent on the colour. G. A. Kenngott found that by heat

reddish-brown crystals became brownish-yellow and remained transparent. H. Traube found that yellow and red crystals were decolorized by heat, and the colour was not restored on cooling. C. Doelter found that the temp. at which decolorization occurs in air is about 700°. E. Newbery and H. Lupton found that some Tasmanian hyacinths became nearly colourless when heated in a hard glass tube, and quite colourless in the Bunsen flame; some French specimens remained yellow after 5 mins.' heating in the blowpipe flame. The colour was restored quickly with the Tasmanian specimens, and slowly with the French specimens, on exposure to radium rays. All the crystals which had been recoloured by radium lost their colour at a temp. lower than was originally required to decolorize the natural crystals. G. Spezia concluded that the coloration is not produced by organic matter, and that the colour changes are not simply produced by raising the temp., but that the colour of zircon is produced by the state of oxidation of the iron—varying when heated in oxidizing or in reducing atm. K. von Kraatz-Koschlau and L. Wöhler said that when iron is present, it is not uniformly distributed and cannot therefore be the cause of the uniform coloration of these minerals; and they showed that the loss in weight which occurs on heating corresponds with the loss of organic matter. G. Spezia emphasized the fact that heating the decolorized mineral in an oxidizing atm. restores the colour; and when this is again heated in a non-reducing atm., it is not decolorized. Again, some crystals are not decolorized if heated in a non-reducing medium. He thinks that when organic matter is present, it affects the coloration by iron as a reducing agent, but does not colour the mineral *per se*. S. Stevanovic confirmed G. Spezia's observations, and concluded that there are two tinctorial agents in the hyacinth—one is a volatile organic substance which exerts a reducing action so that crystals containing only this agent remain after its removal. The other agent is non-volatile, can be reduced and oxidized, and is possibly a compound of iron. From his experiments on the action of radium rays, C. Doelter concluded that it is unlikely that an organic substance is the cause of the coloration; rather is it more probably a colloidal substance which is not stable when heated.

The euhedral **crystals** of zircon are commonly short prisms, Fig. 187, but frequently long prisms are found. Large crystals weighing nearly 6 kgrms. have been found at Renfrew, Ontario. Anhedral crystals are not common in igneous rocks, showing that the zircon must have been one of the earliest crystals to separate in the magma; it is also common as inclusions in other minerals. The larger crystals sometimes contain inclusions of other minerals—possibly apatite and glass. F. Rutley[27] explained the raising of the sp. gr. by calcination as an effect of the expulsion of the liquid (water) and gas inclusions. The crystal belong to the ditetragonaldipyramidal class of the tetragonal system, and, according to A. T. Kupffer, have the axial ratio $a:c=1:0{\cdot}640373$. The crystals were examined by J. B. L. Romé de l'Isle, R. J. Haüy, and F. Mohs, etc. Numerous other observations have been made on the form of the crystals. The angle (111) : (110) with *zircon*, $ZrSiO_4$, is 47° 50′; with *rutile*, $TiTiO_4$, 47° 40′; and with cassiterite, $SnSnO_4$, 46° 27′. This resemblance is taken to indicate that if these minerals are not strictly isomorphous, they are at least analogous in form and composition. **Twinning** is rare. The composition plane is (101). The geniculated twins resemble those of rutile and cassiterite. They are not found with crystals in igneous rocks. Large twinned crystals come from

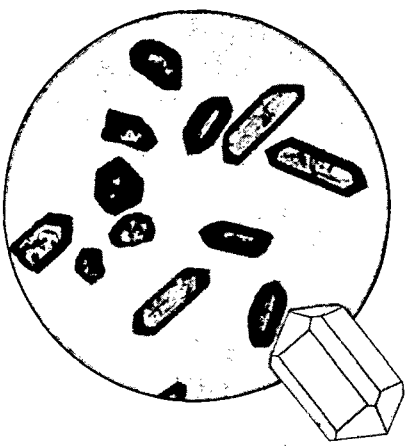


FIG. 187.—Crystals of Zircon.

St. Jerome, Quebec. The **cleavage** parallel to 110 is imperfect and that parallel to (111) is less distinct. H. Traube studied the **corrosion figures** with molten potassium hydrofluoride; and C. Doelter and E. Hussak, etching with fused basalt. G. Grattarola found the **optic axial angles** $2E=19°\ 44'\ 10''$, and $2V=10°\ 1'\ 28''$. The **X-radiogram** of zircon has been discussed in connection with the space-lattice—*vide supra*.

The **specific gravity** of zircon has attracted some attention. C. A. S. Hofmann [28] made a collection of the determinations which had been made. W. Henneberg, and L. F. Svanberg noted that the sp. gr. was augmented by calcination. A. Damour emphasized the fact that the sp. gr. of different zircons ranges from 4·043–4·674; and he noted that the sp. gr. is increased by calcination without change in the chemical composition. He concluded that the zircon exists in different allotropic states. A. H. Church made a similar observation. H. de Sénarmont, and A. des Cloizeaux then showed that the refractive indices of light and heavy zircons are different. R. Köchlin tried to establish a relation between the sp. gr. and colour.

R. Köchlin found green zircons have a sp. gr. between 4·04 and 4·29; pale green, 4·09 and 4·16; yellowish-green, 4·21 and 4·39; dark yellow-green, 4·22 and 4·23; dark green, 4·08; brownish-green, 4·20 and 4·27; greenish-yellow, 4·27; greenish-brown, 4·50 and 4·70; yellow, 4·38 and 4·61; yellowish-orange, 4·69; orange, 4·40; reddish-yellow, 4·53; brownish-yellow, 4·59; reddish-yellow, 4·68; red, 4·57–4·64; dark red, 4·70; brownish-red, 4·61; yellowish-brown, 4·46 and 4·70; reddish-brown, 4·60 and 4·69; bluish, 4·44 and 56; pale violet, 4·68; brownish-violet, 4·66; and colourless, 4·74.

R. Köchlin assumed that zircon exists in two forms, and that intermediate forms with a sp. gr. 4·35–4·55 are isomorphous mixtures of the heavy and light varieties. As L. J. Spencer has emphasized, a low sp. gr. is not alone sufficient to establish the existence of a special modification. S. Stevanovic inferred that there are three related forms of zircon, with properties indicated in Table XXXII. This hypothesis cannot be regarded as established until the equilibrium conditions of the alleged allotropes have been elucidated. On calcination, **β-zircon** passes into **α-zircon**; but **γ-zircon** does not change on calcination, and hence S. Stevanovic assumed that an unknown element closely related to zirconium is present. This has not been confirmed by the fractionation of zirconium.

TABLE XXXII.—PROPERTIES OF THE DIFFERENT FORMS OF ZIRCON.

| —— | Sp. gr. | Index of refraction Na-light. | Birefringence. | Axial angles. | Hardness. |
|---|---|---|---|---|---|
| α-zircon . . | 4·7 | $\epsilon=1·98$; $\omega=1·93$ | Strong | Uniaxial | 7–8 |
| β-zircon . . | 4·3 | Not exactly known | Strong | Biaxial | — |
| γ-zircon . . | 4·0 | 1·81 | Feeble | Unixial | Below 7 |

R. Köchlin showed that the **hardness** of zircon varies with the sp. gr. The samples with a sp. gr. below 4·3 are softer than quartz, while those with a higher sp. gr. are harder. Normal zircon, for instance, with a sp. gr. 4·7, has a hardness between 7 and 8. E. Madelung and R. Fuchs gave $3·01\times10^{-12}$ dynes per sq. cm. for the coeff. of **compressibility**. F. Pfaff [29] gave for the coeff. of **thermal expansion**, $0·0_56264$ in the direction of the *c*-axis, and $0·0_4110540$ in the direction of the *a*-axis; and H. Fizeau gave $0·0_5443$ parallel to the *c*-axis and $0·0_5233$ in a direction perpendicular to the *c*-axis. H. V. Regnault gave 0·14558 for the **specific heat** of zircon between 24° and 99°; and H. Kopp, 0·132 between 16° and 47°. Zircon cannot be fused before the blowpipe, and R. Cusack did not succeed in fusing the mineral. E. D. Clarke, and A. Damour melted zircon to a white enamel in the oxyhydrogen blowpipe flame; and by heating it in a flame fed with warm oxygen, G. Spezia fused zircon to a white enamel. A. Brun gave about 1900° for

the **melting point** of zircon, and A. L. Fletcher found cyrtolite does not flow freely at 1560°. C. Matignon observed that natural crystalline zircon did not melt at 2126°, but at 1800°, dissociation could be observed, and at 1900°, dense white fumes of silica appeared; the residue melted at 2600°; zirkite did not melt at 1950°. E. W. Washburn and E. E. Libman found the m.p. of natural zircon to be near 2550°, and a mixture of zirconia and silica in equi-molar proportions melts at the same temp. The portion of the m.p. curve so far determined is indicated in Fig. 188. There is a eutectic between zirconium dioxide and zircon melting in the neighbourhood of 2300°. The observed data are:

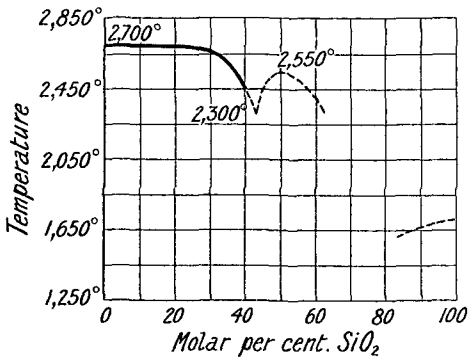



FIG. 188.—Melting Points of Binary Mixtures of Zirconia and Silica.

| $ZrO_2 : SiO_2$ . | 1 : 0 | 3 : 1 | 2 : 1 | 3 : 2 | 1 : 1 | 2 : 3 | 1 : 2 | 1 : 3 |
|---|---|---|---|---|---|---|---|---|
| Melts at. . | 2720° | 2685° | 2650° | 2460° | 2550° | 2420° | 2420° | 2420° |

The **indices of refraction** of zircon of sp. gr. 4·654 are given by S. Stevanovic [30] $\omega=1{\cdot}91778$, and $\epsilon=1{\cdot}97298$ for wave-length 6563; $\omega=1{\cdot}93015$, and $\epsilon=1{\cdot}98320$ for wave-length 5166; and $\omega=1{\cdot}94279$, and $\epsilon=1{\cdot}99612$ for wave-length 4862. D. Brewster gave for normal Singalese zircon, $\omega=1{\cdot}961$, and $\epsilon=2{\cdot}015$; A. des Cloizeaux gave $\omega=1{\cdot}85$, $\epsilon=1{\cdot}86$; H. de Sénarmont, for one of sp. gr. 4·636, $\omega=1{\cdot}92$ and $\epsilon=1{\cdot}97$ for red light; M. Sanger, $\omega=1{\cdot}9239$ and $\epsilon=1{\cdot}9682$, and for a sample from Miask, $\omega=1{\cdot}9313$, and $\epsilon=1{\cdot}9931$ for Na-light. For doubly refracting olive-green beccarite, sp. gr. 4·654, G. Kalb gave for the blue zircon of Siam, $\omega=1{\cdot}9180$, $\epsilon=1{\cdot}9769$, and $\epsilon-\omega=0{\cdot}0589$ for Li-light; $\omega=1{\cdot}9255$, $\epsilon=1{\cdot}9847$, and $\epsilon-\omega=0{\cdot}0592$ for Na-light; and $\omega=1{\cdot}9326$, $\epsilon=1{\cdot}9920$, and $\epsilon-\omega=0{\cdot}0594$ for Tl-light. G. Grattarola gave $\alpha=1{\cdot}9272$, $\beta=1{\cdot}9277$, and $\gamma=1{\cdot}9820$. A. Damour proved that the index of refraction decreases with the sp. gr. of zircon. S. Stevanovic found that with Na- and Li-rays respectively, the index of refraction of natural zircon was 1·8163 and 1·8259; after a mild calcination, 1·8067 and 1·8125; and after a strong calcination, 1·7872 and 1·7914. The **birefringence** of zircon is strong, $\epsilon-\omega=0{\cdot}062$. R. Köchlin found that a zircon of sp. gr. 4·44 with a zonal structure had different double refractions in different parts ranging from 0·022–0·038. J. Babinet, A. Breithaupt, and A. Madelung showed that zircon crystals may be **optically anomalous** in that a basal section rarely gives a normal uniaxial figure, for the black cross is usually broken into a number of lemniscate or hyperbolic brushes. P. A. von Sachsen-Coburg assumed that the effect is due to polysynthetic twinning. H. Rosenbusch said that the microscopic zircons do not show the effect. E. Mallard accordingly argued that the crystals are really mimetic twins of monoclinic individuals, but R. Brauns said that the effect is due to mechanical strains. W. Klein produced the effect by irregular heating. A. des Cloizeaux found that the effect of raising the temp. from 14°–186° was not appreciable. A. Madelung found that beccarite is made biaxial by heat.

H. Becquerel [31] measured the **absorption spectrum** of uraniferous zircon, and obtained the results illustrated by Fig. 189. According to A. H. Church and C. A. MacMunn, the absorption spectrum of Singalese zircon has dark bands with the strongest absorptions where $\lambda=689{\cdot}5$, 683·5, 661, 653, 622·5, 616, 589, 562, 538, 515, and 484. V. von Agafanoff found that plates of zircon are transparent or ultra-violet light as far as the cadmium lines 7, 8, and 9. W. W. Coblentz showed that with ultra-red light there are absorption bands at $2{\cdot}1\mu$, $3{\cdot}1\mu$, $3{\cdot}6\mu$, and complete opacity beyond $5\mu$. T. Liebisch and H. Rubens studied the reflecting power

of zircon for the long infra-red rays. According to W. Haidinger, the **pleochroism** of zircon is usually feeble. Brown Singalese crystals had $\omega$ reddish-brown, and $\epsilon$, green. Observations were also made by E. Hussak, and G. H. F. Ulrich.

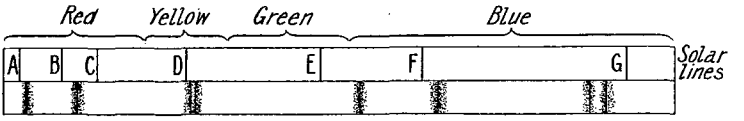



FIG. 189.—The Absorption Spectrum of Zircon.

R. J. Strutt [32] studied the **radioactivity** of the zircon minerals and found malacone, alvite, and cyrtolite exhibited the strongest radioactivity, and these minerals contain thorium. He found Raade-Moss alvite with 4·95 per cent. thoria possessed had a radioactivity 1·81 in millionths per cent. of that of radium bromide; Carolinian zircon, 0·307 per cent. thoria, 0·30; Virginian zircon, 0·217 per cent. thoria, 0·52; Llano cyrtolite, 5·05 per cent. thoria, 8·98; and Hitterö malacone, 1·15 per cent. thoria, 1·40. He also found the radioactivity of Ural zircon to be $865 \times 10^{-12}$ grm. radium; Carolinia zircon, $658 \times 10^{-12}$; Brevig zircon, $139 \times 10^{-12}$; and Kimberley zircon, $74{\cdot}8 \times 10^{-12}$. Observations were made by C. Gockel, and C. Doelter and co-workers. A. C. Cumming found that when radioactive malacone is digested with hydrochloric acid, the radioactive substance passes into soln. and the residue is no longer radioactive. He found no uranium present. E. S. Kitchin and W. C. Winterson also made some observations on this subject. A. Piutti examined the relation between the radioactivity, helium content, and sp. gr. of a number of zircons. R. J. Strutt found 12 c.c. of helium occluded per 100 grms. of Hitterö malacone. The small circular coloured spots known as pleochroic haloes were studied by J. Joly and co-workers, and O. Mügge.

The bleaching action of light and heat on coloured zircons has been previously discussed. K. Simon [33] found that the temp. needed for decolorization depends to some extent on the size of the fragments. The presence of oxygen retards the decolorization; the colour is more or less restored by exposure to sunlight or to **radium radiations.** According to C. Doelter, dark brown and red zircons do not change when exposed to radium radiations; but the paler zircons have their colour intensified. Zircons decolorized by heat have their original colour restored by exposure to radium radiations, although, as W. Hermann showed, the intensity of the colour may not be so great. Observations were also made by K. Simon, S. Lind and D. C. Bardwell, and R. Brauns. The latter showed that a colourless zircon was coloured by a conc. preparation of radium, but not by a dil. one. M. Weber discussed the **pleochroic halo** developed in a zircon crystal in contact with a cordierite crystal. E. Newbery and H. Lupton showed that all specimens of zircon, heated or unheated, showed a greenish luminescence when exposed to radium. The colour of the unheated ones was not changed, but the heated ones all regained their colour to a greater or less extent; they also found that **cathode rays** restored the colour of a decolorized crystal, and the mineral glowed with a blue light; R. Brauns, and C. Doelter showed that **ultra-violet light** weakened the colour of decolorized zircon whose colour had been restored by exposure to radium rays; but the colour of natural crystals was weakened in ultra-violet light. E. Newbery and H. Lupton found that the colour of a crystal which has been obtained by exposing decolorized crystals to radium rays, is discharged by heat at a lower temp. than was needed for the original crystal. W. Henneberg observed the **thermoluminescence** of zircon during decolorization; the non-luminescent varieties are not decolorized by heat; and G. Spezia believed that there is some connection between the thermoluminescence and the colour. A. H. Church said that the glow with a green zircon was orange; and D. Hahn, green. The subject was studied by F. P. Venable. K. Keilhack observed that zircon phosphoresced when exposed to the **X-rays.** E. Newbery

and H. Lupton observed blue and violet phosphorescence with radium radiations and with cathode rays. E. Bichat examined the action of the so-called **N-rays.**

Zircon has a poor **electrical conductivity.** W. Schmidt [34] found that the **dielectric constant** of a crystal from Ceylon was 12·6 parallel to the principal axis, and 12·8 perpendicular thereto. E. T. Wherry found zircon showed no evidence of the rectification required by a radio-detector. L. Grätz studied the dielectric capacity, and B. Bavink, the **magnetic properties** of zircon.

Zircon is not attacked by acids; but when very finely powdered, it is attacked a little by sulphuric acid. For the action of chlorine, and of carbonyl chloride—*vide* zirconium tetrachloride. It is broken down by fusion with alkali hydroxides, and, according to J. C. G. de Marignac,[35] by alkali carbonates, and hydrosulphates. R. Hornberger, and H. Traube found zircon is attacked by fusion with potassium fluoride, or hydrofluoride; and C. Baskerville decomposed it by heating it to 450° in a stream of carbonyl chloride. For the hydration of zircon by weathering, etc., *vide supra.*

T. H. Lee [36] described a zirconium silicate from the Caldas region, Minas Garaes, Brazil, which he named *orvillite*—after Orville A. Derby—it had a composition $8ZrO_2.6SiO_2.5H_2O$, and is soluble in a mixture of hydrofluoric and hydrochloric acids. It is possibly more or less altered zircon.

R. Schwarz and A. Haacke [37] found that the m.p. of pure lithium orthosilicate, 1249°, is lowered by the addition of zirconium orthosilicate in proportion to the conc. of the latter, up to 30 mol. per cent. $ZrSiO_4$, at which composition a pure eutectic is formed, m.p. 1021°. As the proportion of zirconium orthosilicate is still further increased, the m.p. again rises to a maximum at 1152°, the m.p. of **octolithium trizirconium pentorthosilicate,** $3ZrSiO_4,2Li_4SiO_4$. Further increasing the proportion of zirconium orthosilicate, the m.p. falls as far as 70 mol. per cent. $ZrSiO_4$, to rise again subsequently, but experiments could not be continued beyond this point, as the mixtures could not be fused in the furnace used. The two silicates do not form mixed crystals. The mixtures containing 50 mol. per cent. or more of lithium orthosilicate are readily attacked by cold water, the others by boiling water. Those containing a high proportion of zirconium orthosilicate resemble extremely hard porcelain. The sp. gr. increases from 2·28($Li_4SiO_4$) to a maximum 4·024 for the binary compound, falls slightly, and again rises to 4·51($ZrSiO_4$). The mol. wt. of zirconium silicate, calculated from the depression of the f.p. of lithium silicate, corresponds with the simple mol. $ZrSiO_4$.

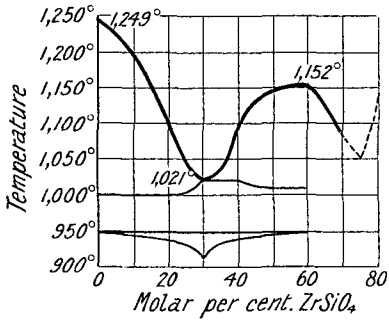



FIG. 190. — Freezing-point Curves of Zirconium and Lithium Orthosilicates.

M. E. Chevreul,[38] and P. Berthier fused mixtures of zircon and potassium hydroxide, and after washing the cold mass, obtained white residues which, according to A. Knop, are *Kieselsäurefreie;* but D. E. Melliss fused a mixture of zircon and four times its weight of potassium carbonate for 2 hrs. in a platinum crucible; extracted the mass with water; and obtained a microcrystalline powder with a composition $K_2O.ZrO_2.2SiO_2$, **potassium disilicozirconate,** $K_2ZrSi_2O_7$, with a sp. gr. 2·79. It was decomposed by hydrochloric acid. L. Ouvrard melted a similar mixture for 15 mins. at a bright red-heat, and obtained rhombic prisms with the composition $K_2O.ZrO_2.SiO_2$, or **potassium silicozirconate,** $K_2ZrSiO_5$. L Ouvrard added that when the fusion is continued for 1½ hrs., only crystalline zirconia is obtained. The crystals were examined by G. Flink. They are attacked by hydrofluoric acid, and ammonium hydrofluoride. W. Gibbs fused zircon with sodium carbonate as

indicated above; boiled the cold cake with a conc. soln. of sodium carbonate, washed the residue with luke-warm water, and obtained a white powder corresponding with **sodium silicozirconate,** $Na_2O.ZrO_2.SiO_2$, or $Na_2ZrSiO_5$. L. Bourgeois included some silica with the zircon and sodium carbonate, and after 24 hrs.' fusion at a red heat, extracted the cold cake with dil. acid, and obtained rhombic prisms with a strong double refraction. They were decomposed by hot water; and with hydrochloric acid, there is a separation of gelatinous silica. T. Scheerer said that sodium zirconate (*q.v.*), not silicozirconate, is obtained in this way. D. E. Melliss boiled with water the cold cake, obtained by fusing a mixture of zircon with 4 times its weight of sodium carbonate, until no more soluble matters were removed. The microscopic hexagonal plates had the composition $Na_2O.8ZrO_2.SiO_2.11H_2O$. The sp. gr. was 3·53. The salt lost water at an incipient red heat; and it was decomposed by sulphuric acid.

P. Berthier fused mixtures of zircon, quartz, and marble in various proportions contained in a carbon crucible. When the proportions of zircon : quartz : marble were 1 : 2·34 : 3·33, a transparent glass, surrounded by a stony crust, was produced; with 1 : 1·01 : 3·33, the mass was pulverulent and baked together; 1 : 2·67 : 2·22 was vitrified and porcelanic; 1 : 3·34 : 2·22 was glassy; 1 : 1·67 : 2·22, merely softened; 1 : 1 : 1·11 was semivitreous; 1 : 0·33 : 1·11 was opaque with a shiny fracture; and 1 : 0·16 : 1·11 was white and stony. Mixtures with the lime less than one-third were decomposed by acids. The evidence does not justify the statement that *calcium silicozirconates*, $CaZrSiO_5$, analogous to titanite, $CaTiSiO_5$, were formed. A number of minerals are assumed to be closely related with the *silicozirconates—e.g. zirkelite*, $(Ca,Fe)O.2(Zr,Ti,Th)O_2$, *vide* zirconates; *uhligite*, $3Ca(Zr,Ti)_2O_5.Al_2TiO_5$, *vide* zirconates; *rosenbuschite*, $6CaSiO_3.2Na_2ZrO_2F_2.TiSiO_3.TiO_3$, *vide* rare earths; *lavenite*, $R(Si,Zr)O_3.Zr(SiO_3)_2.R.Ta_2O_6$; *hainite*, $R(Si,Zr)O_3.Zr(SiO_3)_2.RTa_2O_6$; *wöhlerite*, $12R(Si,Zr)O_3.R(Cb_2O_3.R(Cb_2O_5)$; *hiortdahlite*, $4Ca(Si,Zr)O_3.Na_2ZrO_2F_2$; and *eudialyte* and *eucolite*, $Na_{13}(Ca,Fe)_6Cl(Si,Zr)_{20}O_{52}$.

G. Lindström, and G. Nordenskjöld [39] described crystals of a mineral found near Nagssarsuk, Greenland, to which they applied the term **elpidite**—from ἐλπίς, hope. Analyses by G. Lindström show that the white or reddish-coloured mineral has 20–21 per cent. of zirconia and corresponds with $Na_2O.ZrO_2.6SiO_2.3H_2O$. G. Flink regarded elpidite as a transformation product of a mixed mineral, $Na_2Si_2O_5.Zr(Si_2O_5)_2$. P. Groth represented it by the formula $H_6Na_2ZrSi_6O_{18}$; and F. W. Clarke, by $Zr(OH)_2(Si_3O_8{\equiv}NaH_2)_2$; **sodium hexahydroxyzirconato-dimesotrisilicate**—*vide infra*. From his dehydration curves, F. Zambonini inferred that neither water of crystallization nor constitutional water is present; but that the water is simply dissolved. He found the percentage loss of water from elpidite at different temp. to be:

| | 65° | 115° | 175° | 205° | 250° | 262° |
|---|---|---|---|---|---|---|
| Loss . . . | 0·86 | 4·03 | 6·60 | 7·99 | 8·88 | 9·17 per cent. |

Dehydration is nearly complete at 262°, for the total loss is 9·80°. At 115° in moist air, a part of the expelled water is resorbed; and at 250°, the percentage amount of water resorbed is:

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Hours . . . | 16 | 70 | 135 | 183 | 303 | 375 | 447 | 573 |
| Resorption . . | 1·60 | 1·74 | 2·18 | 2·30 | 2·49 | 2·69 | 2·77 | 2·73 |

G. Flink found that the rhombic crystals have the axial ratios $a:b:c = 0·5101:1:0·9781$. The (110) cleavage is masked. The sp. gr. of the white mineral is 2·524, that of the red is 2·594; and the hardness is nearly 7. According to G. Flink, the optic axial $2V = 75°\ 12'$, while O. B. Böggild gave $2V_a = 89°\ 40'$. G. Flink gave for the indices of refraction $\alpha = 1·5600$, $\beta = 1·5650$, and $\gamma = 1·5739$, and the birefringence $\gamma - \alpha = 0·0139$ for yellow light.

P. C. Weibye and H. Sjögren described a mineral from the islands of Langesund fiord, Norway, which was named **catapleiite**—from καταπλεῖον, satiated—in allusion

to its always being accompanied by a number of rare minerals. Analyses were reported by P. C. Weibye and H. Sjögren, M. Weibull, C. F. Rammelsberg, W. C. Brögger, G. Forsberg, P. T. Cleve, and G. Flink. There are two kinds, one kind is calcareous, and the other almost free from lime.

| | $SiO_2$ | $ZrO_2$ | CaO | $Na_2O$ | $H_2O$ |
|---|---|---|---|---|---|
| Lime-catapleiite . | 39·78–46·83 | 29·33–40·12 | 3·45–5·82 | 8·10–10·83 | 8·86–9·35 |
| Soda-catapleiite . | 41·27–44·04 | 30·80–32·60 | 0·81–0·93 | 14·94–15·05 | 9·24–9·31 |

G. von Hevesy and V. T. Jantzen found about 0·2 per cent. of hafnium in catapleiite. P. C. Weibye and H. Sjögren represented the mineral by $ZrO_2.2SiO_2+Na_2SiO_3+2H_2O$; C. F. Rammelsberg, by $Na_{10}Ca_4Zr_9Si_{27}O_{81}.18H_2O$; C. W. Blomstrand, by $R_4Zr_4(O_2.SiO)_{12}.8H_2O$; W. C. Brögger, $H_2SiO_3.Na_2SiO_3.(ZrO_2H_2)SiO_3$; G. Flink, by $Na_2SiO_3.H_4Zr(SiO_4)_2$; and P. Groth, by $Na_2(SiO_2H_2)_2Si_2O_7$, with some silica replaced by zirconium. F. W. Clarke represented the mineral as **sodium calcium trihydroxyzirconato-metasilicate,** $Zr(OH)_3NaCaSi_3O_8$—*vide infra*. F. Zambonini regards the water of catapleiite as dissolved, being present neither as water of crystallization nor as constitutional water; corresponding with the tendency of zirconium to form complex salts as indicated by the work of R. Ruer and co-workers, A. Rosenheim and A. Frank, and W. Mandl. F. Zambonini considers soda-catapleiite to be the sodium salt of the acid $H_2(ZrSi_3O_9)$, with approximately 2 mols of dissolved water—*vide infra*. M. Weibull, W. C. Brögger, and F. Zambonini studied the dehydration of catapleiite, and the last-named found the percentage loss in a moist stream of air at different temp. to be:

| | 110° | 175° | 218° | 270° | 290° | 325° | 375° | 420°–425° |
|---|---|---|---|---|---|---|---|---|
| Loss . | 0·22 | 0·70 | 1·80 | 3·83 | 6·19 | 7·17 | 7·90 | 8·33 per cent. |

when the total loss is 9·73 per cent. It was found that there is a resorption of water at 270° such that

| | | | | | |
|---|---|---|---|---|---|
| Hours . . | 24 | 48 | 144 | 264 | 306 |
| Resorption . . | 1·53 | 1·60 | 1·71 | 1·83 | 1·77 |

The colour of catapleiite may be light yellow to yellowish-brown, greyish-blue, and violet. The crystals are usually thin, tabular, hexagonal prisms with replaced edges. According to W. C. Brögger, at ordinary temp. the crystals are pseudo-hexagonal and monoclinic—if hexagonal, H. Dauber gave the axial ratio $a:c=1:1·3593$, and W. C. Brögger, $1:1·3605$; while the latter gave for the axial ratios of the monoclinic crystals $a:b:c=1·7329:1:1·3618$, and $\beta=90°\ 11\frac{1}{2}'$. Above 140°, the crystals are hexagonal. G. Flink found the thick crystals of one type become uniaxial at 120°, crystals of another above 200°, and crystals of a third type, at 10°–20°. H. Steinmetz found a transition point at 35°, accompanied by a very small change in vol. O. B. Böggild found that in one type the change begins at 110° and is complete at 130°; in another, it begins at 160° and is complete at 230°; in another, at 30°–40°; in another, at 10°–20°; and in another, the change is partially complete at ordinary temp. Twinning is common—the twinning planes are $(10\bar{1}1)$, $(30\bar{3}2)$, $(33\bar{6}2)$, and $10\bar{1}0)$. The $(10\bar{1}0)$ cleavage is perfect, and the $(10\bar{1}1)$ and $(10\bar{1}2)$ cleavages are imperfect. W. C. Brögger gave for the optic axial angle of soda catapleiite $2E=60°$; G. Flink, 30°; and O. B. Böggild, 41° 3′ with Na-light; W. F. Foshag gave $2V=0°–25°$. H. Sjögren gave for the sp. gr. of lime-catapleiite 2·79–2·81; and G. Flink, for soda-catapleiite 2·743. The values of 2 types at different temp. was found by O. B. Böggild to be:

| 17° | 30° | 40° | 50° | 60° | 70° |
|---|---|---|---|---|---|
| 2·764 | 2·763 | 2·764 | 2·763 | 2·762 | 2·761 |
| 2·751 | 2·745 | 2·740 | 2·739 | 2·739 | 2·739 |

The sp. gr. of the first type does not change very much with temp. since only at 160° does the mineral become uniaxial. The hardness is about 6. O. B. Böggild gave for the indices of refraction $\alpha=1·5905$, $\beta=1·5921$, and $\gamma=1·6269$, and for the

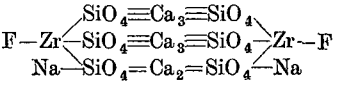
birefringence $\gamma-\alpha=0{\cdot}0364$—with Na-light; W. F. Foshag gave $\alpha=1{\cdot}591$–$1{\cdot}593$; $\beta=1{\cdot}592$–$1{\cdot}593$; and $\gamma=1{\cdot}627$–$1{\cdot}628$. The crystals are optically positive. W. C. Brögger found that when soda-catapleiite is heated, zircon is formed: $Na_2ZrSi_3O_9.2H_2O \rightarrow ZrSiO_4+Na_2Si_2O_5+2H_2O$, and he has found pseudomorphs of zircon after catapleiite. The mineral decomposes when treated with hydrochloric acid, and gelatinous silica separates.

The gem-stone varieties of zircon include *eudialyte* and *eucolite* discussed in connection with the rare earths (*q.v.*). These two minerals are sometimes regarded as mixtures of metasilicates with the oxychloride, $ZrOCl_2$, but F. W. Clarke [40] considers them to be variable mixtures of **zirconium sodium calcium chlorotriorthosilicate,** $Zr(SiO_4{\equiv}CaNa)_3Cl$, and **zirconium sodium calcium chlorotrimesotrisilicate,** $Zr(Si_3O_6{\equiv}CaNa)_3Cl$, in which hydroxyl may partly replace the chlorine; and iron and manganese, the calcium. J. E. Teschemacher referred to a mineral which he called **azorite,** occurring in San Miguel, Azores. It was shown by A. Ben-Saude, J. D. Dana, A. Schrauf, O. Mügge, L. L. Hubbard, A. Osann, and P. do Canto e Castro to be a colourless or pale green variety of zircon. The mineral obtained by G. Grattarola and O. Beccari from Point de Galles, Ceylon, and accordingly named **beccarite,** is an olive-green zircon with silica 30·3 per cent.; zirconia, 62·2; alumina, 2·5; and calcium oxide, 3·6. C. U. Shepard found minute brown crystals of a variety of zircon at Haddam, Connecticut, which he called **calyptolite.** T. Wada reported a greenish or brown radioactive zirconium silicate containing 34·89, $SiO_2$; 28·27, $UO_2$; 16·50, $ThO_2$; 7·0, $Ta_2O_5$; 4·10, $Cb_2O_5$; 1·59, $CeO_2$; 1·60, $Fe_2O_3$; 1·71, CaO; 0·57, MgO; 3·12, $H_2O$, from Naëgi, Mino, Japan, and he called it **naëgite.** The tabular or prismatic crystals belong to the tetragonal system. The sp. gr. is 4·09; the hardness, 7·5. The composition deviates much from the orthosilicate formula. G. Hevesy and V. T. Jantzen found 7 per cent. of hafnia in Japanese naëgite. A. Breithaupt applied the term **ostranite** to a mineral from Stokö, Langesund fiord, Norway. It was shown by G. A. Kenngott, G. Forchhammer, and W. C. Brögger to be a weathered variety of zircon. N. von Kokscharoff referred to a mineral from Tomsk, Russia, which was called **engelhardite,** and shown by P. von Jeremejeff to be a variety of zircon.

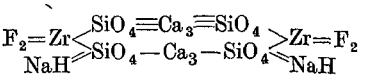
W. C. Brögger [41] called a mineral from the island of Läven in the Langesund fiord, Norway, **lävenite,** although at first it was considered to be mosandrite. It has been also reported from the island Klein-Arö, and Arö; F. Graeff found it in Serra de Tingua and other parts of Brazil; G. Gürich, in Los Islands, West Africa; and A. Osann, in San Miguel, Azores. Analyses were made by P. T. Cleve, and, according to W. C. Brögger, the results correspond with $6\{(Mn,Fe)(Ca,Na_2)Si_2O_6\}.2\frac{1}{2}ZrSi_2O_6.2\{Na_4Zr_2F_4O_4.1\frac{1}{2}(Na_2,H_2)_2(Zr,Ti)_2O_6\}$; P. Groth gave $(Mn,Ca,Fe).(SiO_3)_2.(ZrOF)Na$. The minerals lävenite, guarinite, rosenbuschite, hiörtdahlite, and wöhlerite are sometimes grouped as *zircon-pyroxenes*, and W. C. Brögger considered that just as the pyroxenes are regarded as metasilicates so are the zircon-pyroxenes regarded as metazirconates. The analyses are not clearly interpreted by these formulæ which represent the mineral as a **sodium calcium fluozirconatosilicate.** The colour of lävenite may be pale yellow, almost colourless, or dark yellow, merging into dark brown. The prismatic or tabular crystals belong to the monoclinic system, and have the axial ratios $a:b:c=1{\cdot}0963:1:0{\cdot}71509$, and $\beta=69°\ 42\frac{1}{2}'$. Twins about the (100)-plane are common; and they are also twinned lamellæ. The (100) cleavage is nearly perfect. The optic axial angles with Na-light are $2H_a=90°\ 16'$; $2H_0=116°\ 7'$; $2V=79°\ 46'$. The sp. gr. is 3·51–3·55, and the hardness 6. W. C. Brögger gave for the index of refraction $\beta=1{\cdot}750$. The birefringence is strong; A. Michel-Lévy and A. Lacroix gave $\gamma-\alpha=0{\cdot}03$. The optical character is negative. The crystals are strongly pleochroic. The mineral is incompletely decomposed by the ordinary acids.

G. Guiscardi [42] described a mineral which was found in cavities in the sanadine bombs of Mont Somma, as a variety of titanite. It was called **guarinite**—after C. G. Guarini. According to F. Zambonini and G. T. Prior, G. Guiscardi must have mistaken titanium for zirconium, since guarinite is really the same as that found by W. C. Brögger on one of the Arö Islands, Norway, and called **hiörtdahlite**—after T. Hiörtdahl. This makes these minerals approximate $(Na,Ca)(Si,Zr)O_3$, **sodium calcium zirconatometasilicate.** W. C. Brögger gave $4Ca(Si,Zr)O_3.Na_2ZrO_2F_2$. O. Rebuffat found 1·25 per cent. of yttria, and 3·45 per cent. of ceria earths; and,

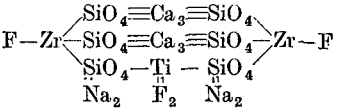
according to F. Zambonini and G. T. Prior, he mistook zirconia for alumina or titania. F. Zambonini and G. T. Prior regard the mineral as a mixed salt of calcium metasilicate and sodium zirconate with some calcium fluoride, $3CaSiO_3.Ca(F,OH)NaZrO_3$. F. W. Clarke represents guarinite by the formula :



and hiörtdahlite a 1 : 1 mixture of this with the hydroxyl being

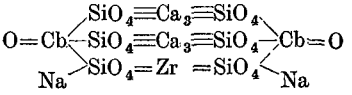


in part replaced by fluorine. The mineral *rosenbuschite—vide* rare earths—**sodium calcium titanium zirconatosilicate,** is assumed to be built on the same plan as guarinite, namely :



The colour is pale yellow to brown. The crystals of hiörtdahlite were stated by W. C. Brögger to be triclinic with axial ratios $a : b : c = 0{\cdot}99835 : 1 : 0{\cdot}35123$, and $\alpha = 89° 22\frac{1}{2}'$, $\beta = 90° 36\frac{5}{6}'$, and $\gamma = 90° 5\frac{5}{6}'$. G. Guiscardi, and V. von Lang said that the crystals of guarinite are rhombic, with axial ratios $a : b : c = 0{\cdot}9892 : 1 : 0{\cdot}3712$ ; F. Zambonini gave $0{\cdot}99268 : 1 : 0{\cdot}37008$ ; this would make the zirconatosilicate dimorphous. The optic axial angle $2V = 90°$ nearly. W. C. Brögger gave 3·267 for the sp. gr. of hiörtdahlite ; G. Guiscardi gave 3·487 for guarinite, and F. Zambonini, 2·9–3·3. The hardness of hiörtdahlite is given as 5–5·6, and that of guarinite as 6. The index of refraction of guarinite is, according to H. Rosenbusch, $\beta = 1{\cdot}68$–$1{\cdot}71$ ; F. Zambonini gave for the birefringence $\gamma - \beta = 0{\cdot}0047$ ; $\beta - \alpha = 0{\cdot}0048$ ; $\gamma - \alpha = 0{\cdot}0095$. He also found the mineral pleochroic. The optical properties agree closely with those of danburite.

T. Scheerer[43] found citron-yellow crystals of a mineral on several islands in the Langesund fiord, Norway. The mineral was named **wöhlerite**—after F. Wöhler. Analyses of the mineral were made by T. Scheerer, R. Hermann, C. F. Rammelsberg, P. T. Cleve, etc. The results correspond with calcium zirconatocolumbatosilicate, $12Ca(Si,Zr)O_3.CaCb_2O_6$, with part of the calcium replaced by sodium ; some iron and manganese are present ; and, according to W. C. Brögger, with the $CaZrO_3$ replaced in part by $CaZr(O_2F_2)$, some ceria earths may also be present. P. Groth gave $Ca_{10}Na_5Si_{10}Zr_3Cb_2O_{42}F_3$. F. W. Clarke represents the composition as a mixed salt having one mol of the same type as that of rosenbuschite with Zr in place of Ti along with 4 mols of **sodium calcium zirconium columbatosilicate ;**



G. Hevesy and V. T. Jantzen found 0·7 per cent. of hafnia in wöhlenite from Langesund. The prismatic or tabular crystals were at first thought to be rhombic by P. C. Weibye, A. des Cloizeaux, H. Dauber, J. D. Dana, and G. A. Kenngott. Later, A. des Cloizeaux, W. C. Brögger, C. F. Rammelsberg, showed that the mineral is monoclinic. The axial ratios are $a : b : c = 1{\cdot}0536 : 1 : 0{\cdot}70878$, and $\beta = 71° 3'$. The colour is various shades of yellow, brown, and grey. Twins on the 100-plane are often found. The 010-cleavage is distinct. The sp. gr. is 3·41-

3·44, and the hardness 5·5–6. W. C. Brögger found the optic axial angles $2H_a = 91° 18'$ for Na-light, $2H_0 = 121° 42'$, and $2V = 78° 37'$. Measurements were also made by A. des Cloizeaux, and A. Michel-Lévy and A. Lacroix. Observations with red, blue and green light were also made. The refractive index $\beta = 1·67–1·74$. Raising the temp. to 75° was found by A. des Cloizeaux to make no perceptible change in the optic axial angle. G. P. Tschernik gave $\gamma - \alpha = 0·023$; $\gamma - \beta = 0·014$; and $\beta - \alpha = 0·014$; and the optical character is negative. The crystals are pleochroic. G. Krüss and L. F. Nilson studied the absorption spectra. The mineral dissolves in hot conc. hydrochloric acid with the separation of silica and columbium pentoxide.

J. J. Berzelius [44] obtained a black mineral from Fredriksvarn, Norway, and he called it **polymignite**—from μίγνυμι, a mixture—in allusion to its complex composition. Analyses were reported by W. C. Brögger, J. J. Berzelius, and G. P. Tschernik. Its composition approximates **calcium cerium silicozircatotantalate,** $5RTiO_3.5RZrO_3.R(TaO_3)_2$, where R denotes iron, calcium, and the cerium metals, and the tantalum, Ta, includes some columbium, Cb. The slender prismatic crystals are often striated. They were examined by G. Rose, M. L. Frankenheim, and W. C. Brögger. They belong to the rhombic system and have the axial ratios $a : b : c = 0·71213 : 1 : 0·51207$. The (100) and (010) faces show traces of cleavage. The sp. gr. is 4·77, and the hardness 6·5.

The **thorium silicates** are represented by thorite or orangite, yttrialite, and mackintoshite discussed in connection with the occurrence of thorium, and the complex uranium silicates. The complex **rare earth silicates** are discussed in connection with the occurrence of the rare earths; and for **scandium orthodisilicate,** or thortveitite, *vide* scandium; and **yttrium orthodisilicate,** or thalenite, *vide* rare earths.


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## § 49. The Chromium Silicates

St. M. Godon [1] evaporated an aq. soln. of chromic acid with silicic acid, and obtained a yellow insoluble powder ; G. A. Quesneville said that chromic acid dissolves a little hydrated silica, and deposits it again on evaporation, and all the chromic acid can be washed from the residue. F. Angel obtained a chromium silicate as a greyish-green hydrogel by mixing soln. of chromic chloride and sodium silicate. The dehydration curve is a continuous function of the temp. The composition approximates to that of **dichromium hexahydro-triorthosilicate,** $H_{12}Cr_4Si_6O_{24}.H_4SiO_4$, or $2H_6Cr_2(SiO_4)_3.H_4SiO_4$. H. Kämmerer obtained a green amorphous clay from Okhansk, Siberia, and he called it *wolchonskoite*—after M. Wolschonsky. Analyses were reported by C. M. Kersten, P. Krotoff, F. Angel, and N. von Kokscharoff. It contains from 17·93 to 18·85 per cent. $Cr_2O_3$ ; 10·43 to 17·85 per cent. $Fe_2O_3$ ; 3·50 to 6·47 per cent. $Al_2O_3$ ; 36·84 to 37·01 per cent. $SiO_2$ ; and 21·84 to 22·46 per cent. $H_2O$. E. T. Wherry and G. V. Brown gave $Cr_2O_3.2SiO_2.2H_2O$, or $H_4Cr_2Si_2O_9$, **dichromodisilicic acid,** $(HO)_4Al_2(O.SiO)_2O$. According to F. Angel, the composition approximates $(H_2,Mg,Fe,Ca)_3(Cr,Fe,Al)_2(SiO_4)_3$. About 11·08 per cent. of moisture is lost by wolchonskoite when dried to a constant weight at 100° in the presence of conc. sulphuric acid. There is a terrace in the dehydration curve between 160° and 190°. F. Angel considers the water given off below 160° to be absorbed, that over 190°, to be constitutional. At 190°, the colour of the mineral begins to change, and at 280°–300° it becomes a brownish-black. The sp. gr. is 2·2–2·3. F. Angel gave 2·337. The hardness is 2–2½. E. T. Wherry and G. V. Brown gave 1·585 for the index of refraction, $\beta$. The mineral is decomposed by hot hydrochloric acid, with the separation of gelatinous silica ; about half the chromium is dissolved.

J. E. Wolff, A. Duflos, and J. Zellner analyzed green clays—*chrome ochres*—from Unst, Shetlands, and Mortenberg, Sweden, etc. These ochres appear to be clays containing chromic and ferric oxides in place of some of the alumina. The *selwynite* of G. H. F. Ulrich—after A. C. Selwyn—from Heathcote, Victoria, contains 4·56 per cent. MgO ; 7·61 per cent. $Cr_2O_3$ ; 33·23 per cent. $Al_2O_3$ ; 47·15 per cent. $SiO_2$ ; and 6·23 per cent. $H_2O$. A chromiferous allophane was found by S. A. W. von Herder at Rudniak, Serbia, and Volterra, Tuscany. He called it *miloschite*—after Prince Miloschi—A. Breithaupt called it *Serbian*. It was analyzed by C. M. Kersten, and E. Bechi. It contains 3·61–8·11 per cent. $Cr_2O_3$ in place of the alumina of allophane. Its sp. gr. is 2·131, and its hardness 1½–2. E. T. Wherry and G. V. Brown represented its formula $(Al,Cr)_2O_3.2SiO_2.2H_2O$, and gave for the indices of refraction $\alpha=1·552$, $\beta=1·552$, and $\gamma=1·559$. It is presumed to be monoclinic. S. M. Losanitsch described a green mineral from Rudniak, Serbia, which he called *alexandrolite* ; its composition approximated $(Al,Cr)_2O_3.2SiO_2.2H_2O$, its sp. gr. was 2·131, and hardness 1½–2. He also obtained a siliceous chromiferous clay from Avala, Serbia, which he called *avalite*—but it is probably a mixture. H. Laspeyres applied the term *cosmochlore* to a chromiferous mineral in the Toluca meteoritic iron ; P. Groth called it *cosmochromite*. The emerald-green crystals are probably monoclinic. The birefringence

is high, the extinction oblique, and there are distinct cleavages parallel to (100) and (010), and less distinct prismatic cleavages. The analysis approximates to $(Ca,Mg,Fe)_2Al_3Cr_3Si_{10}O_{44}$ or $(R'''O)_3R''_{11}(SiO_4)_9$. The hardness is 5–6.

A chromium epidote from Tawmaw, Upper Burma, called **tawmawite,** carrying 11·16 per cent. of chromic oxide, was described by A. W. G. Bleeck.[2] The *calcium aluminium ferric chromium silicate* is deep green in colour and strongly pleochroic. H. Hess [3] found a chromiferous garnet lining cavities in the chrome iron ore of the Ural, and it has been reported from other localities. He named it *uwarowite, ouvarovite, owarowite,* or *ouvaroffite*—after Count Ouvaroo, Owarow, or Ouvaroff. An impure variety occurring with the chromite of Monterey Co., Cal., was called *trautwivite* by E. Goldsmith. Analyses of ouvaroffite were made by A. Komonen, H. Erdmann, A. Damour, T. S. Hunt, L. Aars-Anderson, A. Borgström, and L. Colomba. The results computed by C. F. Rammelsberg agree with the formula **calcium dichromic triorthosilicate,** $Ca_3Cr_2(SiO_4)_3$, plus isomorphous $Ca_3Al_2(SiO_4)_3$ and $Ca_3Fe_2(SiO_4)_3$. The general properties agree with those of the other garnets—*vide* grossular. The sp. gr. is 3·4184 and the hardness 5–7. W. E. Ford gave for the index of refraction 1·870—*vide* Table XXIX. Z. Weyberg[4] fused a mixture of silica, chromic oxide, sodium carbonate, and a large excess of sodium chloride, and after washing, he obtained a crystalline powder of the composition $2Na_2O.3Cr_2O_3.6SiO_2$. The dark green crystals are rhombic and pleochroic. By using a mixture of sodium metasilicate, chromic hydroxide, and an excess of sodium chloride, rhombic crystals of the composition $5Na_2O.2Cr_2O_3.11SiO_2$ were obtained; and with a mixture of ammonium dichromate, sodium metasilicate and sodium chloride, tridymite-like crystals of the composition $3Na_2O.2Cr_2O_3.95SiO_2$. The products with chromic oxide are thus quite different from those with alumina, or ferric oxide. S. J. Thugutt reported that a kind of *chromatosodalite,* $4(Na_2O.Al_2O_3.2SiO_2)Na_2CrO_4.5H_2O$, or *sodium aluminium chromatosilicate,* is formed as a pale yellow amorphous powder when kaolinite, sodium hydroxide and chromate, and water are heated in an autoclave at 176°–206°.


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## § 50. Molybdenum, Tungsten, and Uranium Silicates—Heteropolyacids

In 1826, J. J. Berzelius [1] showed that molybdic and phosphoric acids unite and together act the part of a mixed acid in ammonium phosphomolybdate. The observations of J. C. G. de Marignac, reported in his memoir *Recherches sur les*

*tungstates, les fluotungstates et les silicotungstates* (1862), established the character of these complex acids. This memoir can be regarded as the starting-point of the chemistry of these compounds. Other *complex inorganic acids*, as W. Gibbs called them, were afterwards discussed by A. Laurent, L. Svanberg and H. Struve, F. Margueritte, E. Zettnoff, A. Nutzinger, V. Eggertz, C. Scheibler, A. Lipowitz, H. Debray, F. L. Sonnenschein, M. Sprenger, G. A. Barbieri, D. Klein, F. Mauro, H. Copaux, F. Parmentier, W. Knop, E. H. Jenkins, R. W. Atkinson, R. Finkener, M. Seligsohn, J. Lefort, F. Kehrmann and co-workers, M. Fremery, C. Friedheim, A. Miolati, P. Pfeiffer, etc. A. Rosenheim called the complex acids containing more than one mol. of acid anhydride, **polyacids**—*e.g.* the pyrosulphuric acid, $H_2S_2O_7$, or $H_2[O(SO_3)_2]$; pyrophosphoric acid, $H_4P_2O_7$, or $H_4[O(PO_3)_2]$; tetrachromic acid, $H_2Cr_4O_{13}$, or $H_2[O(CrO_3)_4]$; metatungstic acid, $H_2W_4O_{13}$, or $H_2[O(WO_3)_4]$; etc. In these, the acid radicles are of the same kind, and they are called **iso-polyacids** in contradistinction to the **heteropolyacids** in which the radicles are different—*e.g.* phosphotungstic acid, $H_7[P(W_2O_7)_6]$; silicotungstic acid, $H_8[Si(W_2O_7)_6]$; silicomolybdic acid, $H_8[Si(Mo_2O_7)_6]$; etc. There are two classes of heteropolyacids and salts. In the so-called (i) *wirkliche Heteropolysäuren*, the anion contains only anionagenic constituents, while in the so-called (ii) *Metallkomplexsäuren*, the anion contains amphoteric oxides like chromic oxide, ferric oxide, and alumina.

The formation of the polyacidic anions depends on the electroaffinity of the complex, and R. Abegg and G. Bodländer showed that the tendency to form complexes generally increases with decreasing electroaffinity. Consequently, the oxygenous anions and amphoteric oxides with a feeble electroaffinity form heteropolyanions. A. Rosenheim has shown that the oxides of the elements I.—H, Cu, Au; II.—Be; III.—B, Al; IV.—C, Si, Ti, Zr, Ce, Th, Sn; V.—N, V, Cb, Ta, P, As, Sb; VI.—Cr, Mo, W, U, S, Se, Te; VII.—Mn, 1; and VIII.—Fe, Co, Ni, Rh, Os, Ir, Pt, exhibit a tendency to form heteropolyacids. Hydrogen forms with its amphoteric oxide, water, hydrogen dioxide and the per-salts and per-acids. Many electronegative anions—perchlorate, chlorate, bromate, etc.—have a tendency to form polyanions. The anions $PO'''_4$, $PO''_3$, $HPO''_3$, $H_2PO'_2$, $AsO_4''$, and $AsO'''_3$ form polyanions. $SO_3$ and $SeO_3$ occur frequently in heteropolyanions, while $SO_4$ and $SeO_4$ rarely if ever form such anions. Silicic acid exhibits a marked tendency to form heteropolyacids, and a great number of native silicates—particularly the complex aluminium silicates, are possibly heteropolysilicic acids. There is also a series of silicomolybdates, and a series of silicotungstates.

M. Delafontaine [2] did not succeed in making a silicomolybdate by boiling sodium molybdate with water and silicic acid; but, by other processes, F. Parmentier, W. Asch, and H. Copaux obtained several silicododecamolybdates, and two hydrosilicododecamolybdic acids. W. Asch unsuccessfully tried to make silicomolybdic acids with a smaller proportion of molybdic oxide than is represented by the ratio $MoO_3 : SiO_2 = 12 : 1$, by treating a soln. of sodium metasilicate with smaller proportions of molybdic acid. The product was a mixture of tetrasodium silicododecamolybdate, $2Na_2O.SiO_2.12MoO_3Aq.$, and other molybdates.

F. Parmentier obtained **hydrosilicododecamolybdic acid,** $(SiO_2.4H_2O)12MoO_3.22H_2O$, by the action of dil. hydrochloric acid on **octomercurous silicododecamolybdate,** $4Hg_2O.SiO_2.12MoO_3$, or $Hg_8[Si(Mo_2O_7)_6]$. The mercury salt was made by pouring a soln. of ammonium silicomolybdate into one of mercurous nitrate or adding mercuric molybdate to a soln. of a silicate in nitric acid. The precipitate was washed many times with dil. mercurous nitrate, and dried on a porous tile; it should not be dried by pressure between filter paper owing to the ready reduction of the salt by organic matters. The mercurous salt forms small yellow crystals, which act on polarized light. The salt is decomposed by water, blackened by alkalies, and decomposed by ammonium hydrosulphide precipitating silica and mercuric sulphide. E. Drechsel obtained the acid by extracting the alkali salt with ether. Hydrosilicododecamolybdic acid forms yellow octahedral crystals belonging to the cubic system. According to E. Braüer, the composition of the

acid obtained by crystallization from aq. soln. is $H_8Si(Mo_2O_7)_6.28H_2O$. A soln. of the acid in hot conc. nitric acid furnishes on cooling small yellow plates of $H_8Si(Mo_2O_7)_6.14H_2O$. A. Miolati represented the octobasic acid by the formula $H_8[Si(Mo_2O_7)_6].nH_2O$; and A. Rosenheim showed that the composition of the silver and mercury salts agrees with the octobasicity of the acid. The crystals melt between 45° and 55° in their water of crystallization, and decompose at 100°. The complex acid is sparingly soluble in water and dil. acids. An excess of alkali carbonate and ammonia decomposes the complex acid with the separation of silica. When treated with bases, crystalline salts are formed. Unlike phosphomolybdic acid, potassium hydroxide does not produce an insoluble salt, but with cæsium and rubidium salts, sparingly soluble salts are formed. W. Asch made **octosilver silicododecamolybdate,** $4Ag_2O.SiO_2.12MoO_3.15H_2O$, or $Ag_8[Si(Mo_2O_7)_6].15H_2O$, by pouring a conc. soln. of silver nitrate into one of sodium silicomolybdate. The yellow amorphous precipitate soon becomes crystalline. A. Rosenheim and J. Pinsker prepared the guanidine salt. E. Brauer found the hydrogen ion conc. of a 0·015*N*-soln. to be $[H^{\cdot}]=4{\cdot}3\times10^{-3}$. Two hydrated **hydrosilicododecamolybdic acids** have been reported, but E. Braüer considers that both acids are really the octobasic acid just described. W. Asch obtained crystals of $(2H_2O.SiO_2).12MoO_3.30H_2O$ by adding tetrasodium silicododecamolybdate, $2Na_2O.SiO_2.12MoO_3.21H_2O$, in the cold to a large excess of dil. sulphuric acid (1 : 5), shaking the soln. in a separating funnel with an excess of ether. Three layers are formed; the bottom layer is a soln. of the free acid in ether; the top layer is aq. ether; and the intermediate layer is a soln. of sodium sulphate in ether and water. The bottom layer is run off, and mixed with much water; the ether is evaporated and the aq. soln. conc. at about 45°. Large crystals of the acid are formed. W. Asch found the sp. gr. of aq. soln. of the free acid of normality *N*, at 10° and 40°, to be

| *N* | . | . | . | 0·4 | 0·2 | 0·1 | 0·05 | 0·025 | 0·0125 | 0·00625 | 0·003125 |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 10° | . | . | . | 1·1447 | 1·0736 | 1·0384 | 1·0205 | 1·0116 | 1·0069 | 1·0049 | 1·0035 |
| 40° | . | . | . | 1·1341 | 1·0647 | 1·0303 | 1·0125 | 1·0038 | 0·9992 | 0·9963 | 0·9960 |

and the mol. conductivities of soln. with a gram-eq. of the acid in *v* litres of water,

| *v* | . | . | . | 2·5 | 5 | 20 | 80 | 160 | 320 | 640 | 1280 |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 10° | . | . | . | 215·9 | 230·7 | 257·6 | 272·75 | 282·05 | 286·40 | 290·90 | 295·22 |
| 40° | . | . | . | 327·6 | 360·1 | 402·0 | 426·00 | 439·75 | 453·62 | 461·98 | 482·60 |

The acid is decomposed by alkalies; but with chlorides or sulphates in theoretical proportions two series of salts are produced, $2R_2O.SiO_2.12MoO_3.Aq.$, and $1{\cdot}5R_2O.SiO_2.12MoO_3.Aq$. Aniline, pyridine, and other organic bases give a yellow crystalline precipitate.

H. Copaux obtained crystals of $(2H_2O.SiO_2)12MoO_3.31H_2O$ by mixing a dil. soln. of sodium silicomolybdate with five times the amount of sulphuric acid, and adding ether. The yellow oil which collects at the bottom of the flask is treated with an excess of water and evaporated at 20°–30° for crystals. The same acid was made by mixing hot soln. of ammonium molybdate and sodium silicate in proportions required for $SiO : 12MoO_3$, and adding five times the quantity of sulphuric acid. The mixture was treated with ether, etc., as in the previous case. The two acids are probably the same. The yellow octahedral crystals are often opaque and have superficial efflorescence. They belong to the tetragonal system and have the axial ratio $a : c=1 : 1{\cdot}007$. They are isomorphous with the corresponding silicotungstic acid. When treated with nitric acid at 35°, a triclinic hydrate with 15 mols. of water is formed.

According to W. Knop, by saturating potassium silicate with nitric acid, and adding ammonium molybdate, a yellow colour is produced, and in the presence of much ammonium chloride, an orange precipitate is formed. E. Richters found that the precipitation is accelerated by warming the soln. to 60°. The precipitate dissolves in aq. ammonia and flocculent silicic acid is slowly formed; but in the presence of much ammonium chloride, the separation of silica is incomplete.

F. Parmentier prepared **tetrammonium silicododecamolybdate,** $2(NH_4)_2O.SiO_2.12MoO_3.nH_2O$, or $(NH_4)_4H_4[Si(Mo_2O_7)_6].nH_2O$, by mixing nitric acid soln. of ammonium molybdate and alkali silicate. The yellow liquid furnishes a crystalline precipitate. The octahedral crystals can be purified by dissolving them in water, and precipitating by the addition of an ammonium salt. W. Gibbs reported the formation of yellow crystals of $(NH_4)_2O.SiO_2.12MoO_3.5H_2O$ by mixing soln. of ammonium molybdate and hydrofluosilicic acid. A. Rosenheim and J. Pinsker prepared the guanidine salt.

H. Copaux made **tetralithium silicododecamolybdate,** $2Li_2O.SiO_2.12MoO_3.29H_2O$, or $Li_4H_4[Si(Mo_2O_7)_6].27H_2O$, by evaporating a mixed soln. of the acid and a lithium salt in the cold. The octahedral crystals are singly refracting and belong to the cubic system; they are sparingly soluble in cold water. Five mols. of water are retained at 105°, and 6 mols. when dried in the cold over baryta. F. Parmentier made a **tetrasodium silicododecamolybdate,** $2Na_2O.SiO_2.12MoO_3.nH_2O$, or $Na_4H_4[Si(Mo_2O_7)_6].nH_2O$, by the same method as that employed for the ammonium salt. H. Copaux obtained a salt with $n=14$ by heating under press. for 7–8 hrs. at 150°, a mixture of sodium silicate and molybdic acid, and evaporating the pale yellow liquid at 40°. The yellow triclinic crystals have the axial ratios $a:b:c=1{\cdot}633:1:0{\cdot}544$, and $\alpha=90°\ 37'$, $\beta=94°\ 21'$, and $\gamma=83°\ 30'$. They are stable in air. If the evaporation be conducted at ordinary temp., the triclinic crystals have $n=22$. They deliquesce strongly on exposure to air. W. Asch obtained the salt with $n=21$ by gradually saturating a boiling aq. soln. of sodium metasilicate with molybdic acid. The gelatinous silica first formed dissolves when more molybdic acid is added. The soln. evaporated at 45°, furnishes a syrupy liquid which deposits large yellow monoclinic crystals. The loss of water at different temp. is eq. to 17·59 mols at 100°; 17·85 mols at 140°–145°; 20·15 mols at 225°–235°; 20·97 mols at 230°–235°; and 21 mols at 260°–265°. The mol. wt. of the salt by the lowering of the f.p. by R. Löwenherz's method is 1912, without taking the water into consideration. When treated with chlorides, nitrates, or sulphates, the corresponding silicomolybdates are formed; and with organic bases—like aniline, pyridine, or quinoline—yellow powders, sparingly soluble in water, are formed. The salt is decomposed by sodium carbonate, forming silica, carbon dioxide, and sodium molybdate. F. Parmentier prepared **tetrapotassium silicododecamolybdate,** $2K_2O.SiO_2.12MoO_3.nH_2O$, or $K_4H_4[Si(Mo_2O_7)_6].nH_2O$, by the process employed for the ammonium salt. W. Asch made yellow hexagonal prisms with $n=16$ by treating the sodium salt with the calculated quantity of potassium chloride. The crystals effloresce in air and lose their lustre. When heated to 100°, 14·58 mols of water are lost; at 160°, 15·32 mols; at 215°–240°, 15·50 mols; and at 260°–265°, 16 mols. The sp. gr. of aq. soln. of normality $N$, at 10° and at 40°, are:

| $N$ | 0·4 | 0·2 | 0·1 | 0·05 | 0·025 | 0·0125 | 0·00625 | 0·003125 |
|---|---|---|---|---|---|---|---|---|
| 10° | 1·1550 | 1·0771 | 1·0423 | 1·0797 | 1·008 | 1·0046 | 1·00196 | 1·009 |
| 40° | 1·1482 | 1·0724 | 1·0344 | 1·0098 | 0·9993 | 0·9967 | 0·9942 | 0·9920 |

The mol. conductivities at 10° and 40° for soln. with a gram-eq. of the salt in $v$ litres of water are:

| $v$ | 2·5 | 5 | 10 | 20 | 80 | 160 | 320 | 640 |
|---|---|---|---|---|---|---|---|---|
| 10° | 61·05 | 68·65 | 72·73 | 78·24 | 91·50 | 98·59 | 104·12 | 114·20 |
| 40° | 110·96 | 124·10 | 132·55 | 141·60 | 168·98 | 184·15 | 204·05 | 238·62 |

H. Copaux obtained a potassium salt with $n=18$, by evaporating the soln. at 40°. The hexagonal crystals have a strong negative double refraction, and the axial ratio is $a:c=1:0{\cdot}6809$. They effloresce in air, and slowly decompose. At ordinary temp. over baryta, 16 mols of water are given off; and at 105°, 17 mols of water are given off. H. Copaux also made **rubidium silicododecamolybdate** in a similar manner. He found that the silicomolybdates are usually isomorphous with the corresponding silicotungstates, which they also closely resemble in degree

of hydration and solubility; the mercurous, thallium, rubidium, and ammonium salts of the two series being very sparingly soluble, whilst the alkaloid silicomolybdates are as insoluble as the corresponding silicotungstates. The potassium salts of silicomolybdic and of silicotungstic acids containing $18H_2O$ form hexagonal crystals closely resembling those of quartz, and they are dextro-rotatory, whilst their soln. are optically inactive; lævo-rotatory crystals of these salts can also be obtained from soln. containing traces of alkali impurity; dextropotassium silicomolybdate crystals have $[a]_D=+17{\cdot}0$–$17{\cdot}4°$ and the lævo-crystals $[a]_D=-17{\cdot}1°$.

W. Asch, and H. Copaux made tribasic salts of the alkali silicomolybdates. Thus, W. Asch made **trisodium pentahydrosilicododecamolybdate,** $1\frac{1}{2}Na_2O.\frac{1}{2}H_2O.SiO_2.12MoO_3.16\frac{1}{2}H_2O$, or $Na_3H_5[Si(Mo_2O_7)_6].nH_2O$, by treating a mol of the normal sodium salt with 6 mols of hydrochloric acid; and H. Copaux, by cooling a mixed soln. of normal sodium silicomolybdate and silicomolybdic acid, concentrated at 35°. The monoclinic tabular crystals have the axial ratios $a:b:c=1{\cdot}341:1:0{\cdot}999$, and $\beta=100°\ 38'$. The crystals are stable in air. According to W. Asch, the crystals lose 13·15 mols of water at 100°–110°; 13·36 mols at 140°–145°; 15·5 mols at 225°–235°; 16·5 at 230°–235°; and 16·99 at 260°–265°. The corresponding **tripotassium pentahydrosilicododecamolybdate,** $1\frac{1}{2}K_2O.\frac{1}{2}H_2O.SiO_2.12MoO_3.13\frac{1}{2}H_2O$, $K_3H_5[Si(Mo_2O_7)_6].nH_2O$, was made by W. Asch by mixing a mol of the normal potassium salt with 6 mols of hydrochloric acid; by evaporating equimolar soln. of the acid and the normal potassium salt at 45°–50°; or by treating a mol of the acid with 2 mols of potassium nitrate. H. Copaux also made this salt and found the yellow monoclinic plates have the axial ratios $a:b:c=1{\cdot}200:1:0{\cdot}860$, and $\beta=102°\ 21'$. According to W. Asch, the salt loses 12·16 mols of water at 80°–100°; 12·9 mols at 160°; 13·02 mols at 215°; and 14·02 mols at 260°–265°. The salt is stable only in the presence of an excess of acid; and in contact with water the crystals become turbid and then dissolve completely.

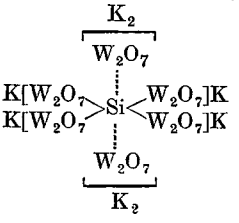
W. Asch made **tetrasilver tetrahydrosilicododecamolybdate,** $2Ag_2O.SiO_2.12MoO_3.12H_2O$, or $Ag_4H_4[Si(Mo_2O_7)_6].12H_2O$, by mixing dil. soln. containing 4 mols of silver nitrate and a mol of sodium silicododecamolybdate. The soln. is evaporated at 45°–50°, and filtered. It furnishes yellow glassy crystals. The salt is decomposed by water with the separation of silica; it is soluble in aq. ammonia; and with hydrochloric acid, it forms silver chloride. F. Parmentier also made tetrasilver silicododecamolybdate. According to W. Asch, if dil. soln. of 3 mols of silver nitrate and a mol of potassium hemihydrosilicododecamolybdate are mixed and concentrated by evaporation, ruby-red crystals of **trisilver pentahydrosilicododecamolybdate,** $1\frac{1}{2}Ag_2O.\frac{1}{2}H_2O.SiO_2.12MoO_3.11H_2O$, $Ag_3H_5[Si(Mo_2O_7)_6].9H_2O$, are formed. On standing, the crystals become insoluble in water. H. Copaux made **silver potassium silicododecamolybdate,** $1\frac{1}{2}Ag_2O.\frac{1}{2}K_2O.SiO_2.12MoO_3.7H_2O$, $Ag_3KH_4[Si(Mo_2O_7)_6].5H_2O$, by the evaporation and crystallization of a soln. containing potassium silicododecamolybdate, silicomolybdic acid, and silver nitrate. The amount of water of crystallization depends on the temperature at which the soln. is evaporated: at 18°–20°, red, triclinic crystals containing $7H_2O$ are deposited; and at 12°–14°, yellow, triclinic crystals containing $15H_2O$. Yellow, crystalline crusts with $11H_2O$ were also formed. The red colour of one of these hydrates is unusual for a silicomolybdate, which are characteristically yellow in colour.

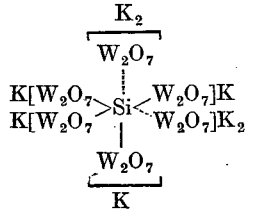
W. Asch treated a soln. of tetrasodium silicododecamolybdate with a calcium salt and obtained **calcium silicododecamolybdate,** $2CaO.SiO_2.12MoO_3.24H_2O$, or $Ca_2H_4[Si(Mo_2O_7)_6].22H_2O$, and H. Copaux made crystals of a similar salt with $26H_2O$ by evaporating a mixed soln. of a calcium salt and the complex acid at 20°. The uniaxial crystals are positive and feebly doubly refracting. They effloresce superficially on exposure to air. By evaporating the soln. at 10°, a salt with $31H_2O$ is formed in regular octahedra. H. Copaux made trigonal crystals of **strontium silicododecamolybdate,** $2SrO.SiO_2.12MoO_3.26H_2O$, or $Sr_2H_4[Si(Mo_2O_7)_6].24H_2O$, by the spontaneous evaporation of a mixed soln. of the complex acid and a strontium salt in the cold or at 30°–35°. The trigonal crystals have the axial

ratio $a:c=1:2{\cdot}639$, and $\alpha=56°\ 44'$. The uniaxial crystals are negative and feebly doubly refracting. They effloresce superficially on exposure to air. H. Copaux made six-sided monoclinic prisms of **barium silicododecamolybdate,** $2BaO.SiO_2.12MoO_3.16H_2O$, or $Ba_2H_4[Si(Mo_2O_7)_6].14H_2O$, by evaporating a mixed soln. of the complex acid and a barium salt at 50°. The crystals have the axial ratios $a:b:c=1{\cdot}811:1:1{\cdot}554$, and $\beta=104°\ 15'$. If the soln. be evaporated at 30°–32°, trigonal crystals, with $22H_2O$, and the axial ratio $a:c=1:1{\cdot}2865$, and $\alpha=88°\ 4'$, are formed. The uniaxial crystals are negative and strongly doubly refracting. They effloresce on exposure to air. They dissolve in four times their weight of cold water. By evaporating the soln. at 20°, H. Copaux obtained a salt with $29H_2O$ in regular octahedral crystals. W. Asch made yellow crystals of a similar salt with $24H_2O$ by double decomposition of a barium salt with the sodium silicododecamolybdate. The salt is soluble in water; and the crystals lose water on exposure to air.

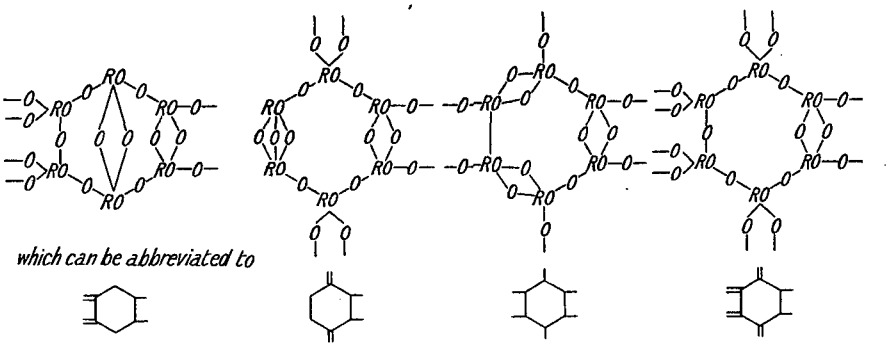
W. Asch made yellow crystals of **magnesium silicododecamolybdate,** $2MgO.SiO_2.12MoO_3.30H_2O$, or $Mg_2H_4[Si(Mo_2O_7)_6].28H_2O$, by double decomposition with the sodium complex salt and a magnesium salt. H. Copaux made the magnesium salt with $31H_2O$ by evaporating a soln. of the acid with a magnesium salt at 15°–35°. The yellow octahedral crystals belong to the cubic system. They readily effloresce on exposure, and are sparingly soluble in water. H. Copaux also made yellow cubic octahedral crystals of **zinc silicododecamolybdate,** $2ZnO.SiO_2.12MoO_3.31H_2O$, $Zn_2H_4[Si(Mo_2O_7)_6].29H_2O$, by evaporation at 15°–35°. They effloresce on exposure to air, and are very soluble. Greenish-yellow triclinic crystals of **cadmium silicododecamolybdate,** $2CdO.SiO_2.12MoO_3.22H_2O$, or $Cd_2H_4[Si(Mo_2O_7)_5].20H_2O$, were made in a similar way. The axial ratios are $a:b:c=0{\cdot}440:1:0{\cdot}383$, and $\alpha=88°\ 43'$, $\beta=91°\ 14'$, and $\gamma=84°\ 42'$. They are stable in air, and readily soluble in water. H. Copaux also made yellow, isotropic, octahedral crystals, **aluminium silicododecamolybdate,** $2Al_2O_3.3(SiO_2.12MoO_3).93H_2O$, or $Al_4\{H_4[Si(Mo_2O_7)_6]\}_3.87H_2O$, by evaporating in the presence of quicklime, at 15°–35°, a soln. of 3 mols of silicomolybdic acid and 4 mols of aluminium chloride. S. J. Thugutt made **sodium aluminium silicomolybdate,** $4(Na_2O.2SiO_2).Na_2MoO_4.7H_2O$, or *molybdato-sodalite*, by heating kaolinite, sodium hydroxide, sodium molybdate, and water for 78 hrs. at 195°–215°. F. Parmentier made **thallous silicododecamolybdate,** $2Tl_2O.SiO_2.12MoO_3.10H_2O$, or $Tl_4H_4[Si(Mo_2O_7)_6].8H_2O$, as a yellow crystalline powder, by double decomposition of ammonium silicomolybdate or silicomolybdic acid with a soln. of a thallous salt. H. Copaux made **chromium silicododecamolybdate,** $2Cr_2O_3.3(SiO_2.12MoO_3).93H_2O$, and **ferric silicododecamolybdate,** $2Fe_2O_3.3(SiO_2.12MoO_3).93H_2O$, by a process similar to that employed for the aluminium salt.

A number of complex compounds of silicic and tungstic acids has been studied principally by J. C. G. de Marignac,[3] G. Wyrouboff, and H. Copaux. There appear to be three hydrates of **hydrosilicododecatungstic acid,** and an isomeric form. The *octocosihydrate*, $H_8[Si(W_2O_7)_6].28H_2O$, crystallizes at ordinary temp. below 28·5° from aq. soln.; above 28·5°, rhombic crystals of the *docosihydrate*, $H_8[Si(W_2O_7)_6].22H_2O$, appear. Conc. aq. soln. of the acid when treated with fuming hydrochloric acid give thin prisms of the *pentadecahydrate*, $H_8[Si(W_2O_7)_6].15H_2O$. An isomeric form, an *icosihydrate*, $H_8[Si(W_2O_7)_6].20H_2O$, has also been obtained in triclinic crystals. The isomeric forms are symbolized . . .

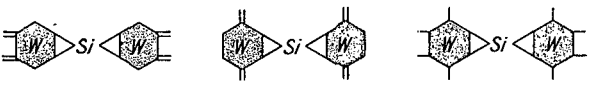


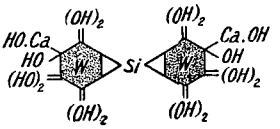
W. and D. Asch's hexite-pentite hypothesis applies better to the deca- and dodeca-tungstic and -molybdic acids than to the aluminosilicic acids. In this theory it is assumed that the dodecamolybdic and dodecatungstic acids and salts are compounded of hexite rings :



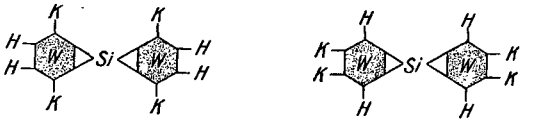

where R represents the sexivalent radicle W or Mo. This makes a series of three possible salts of the type : $4H_2O.SiO_2.12WO_3$, and with nuclei :



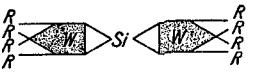
The calcium salt, $2CaO.8H_2O.SiO_2.12WO_3.nH_2O$, which retains 8 mols of water at 100°, can be represented



Likewise the dimorphous potassium salt, $2K_2O.2H_2O.SiO_2.12WO_2.7H_2O$, can be represented



The decatungstic acids and salts are represented in an analogous manner by means of pentite rings. Thus, $4R_2O.SiO_2.10WO_3$ becomes



J. C. G. de Marignac reported **isohydro-silicododecatungstic acid,** $SiO_2.12WO_3.24H_2O$, or $(SiO_2.4H_2O).12WO_3.20H_2O$, *i.e.* $H_8SiW_{12}O_{42}.20H_2O$, or $H_8[Si(W_2O_7)_6].20H_2O$, to be formed by evaporating an aq. soln. of silicotungstic acid to dryness, digesting the residue with water, and again evaporating the aq. extract to a syrupy liquid which then furnishes fine crystals. H. Copaux represented the composition of the acid by $(SiO_2.2H_2O).12WO_3.22H_2O$.

H. Copaux prepared this acid by dissolving sodium tungstate in 7–8 times its weight of water, and gradually adding 20 per cent. sulphuric acid until the soln. reacts feebly

acid to litmus. An aq. soln. of the calculated quantity of sodium silicate is then added, and the soln. again acidified with sulphuric acid. The mixture is evaporated on the water-bath, until oily drops separate when treated with sulphuric acid and ether. The crystals obtained on cooling are a mixture of the required acid with a higher hydrated acid. The two are separated by converting them into their potassium salts. According to H. Copaux, the former gives $2K_2O.SiO_2.12WO_3.18H_2O$, the latter $2K_2O.SiO_2.12WO_3.9H_2O$; the former salt furnishes colourless hexagonal crystals which deliquesce in air; the latter salt furnishes yellow rhombic crystals which do not deliquesce in air. Hence by exposing the mixed salts to air at 40°, the more deliquescent salt is readily removed. The salts are converted to the acids by treatment with a mixture of ether and sulphuric acid.

G. Wyrouboff also prepared this acid by a similar process. E. Drechsel prepared a silicododecatungstic acid by the action of a soln. of sodium tungstate on gelatinous silicic acid. The proportion of contained water was not determined. The crystals of the hydro-silicododecatungstic acid are triclinic pinacoids, which, according to J. C. G. de Marignac, and P. Groth, have the axial ratios and angles $a:b:c=0{\cdot}5829:1:0{\cdot}8534$, and $\alpha=93°\ 23'$; $\beta=122°\ 20'$; and $\gamma=84°\ 1'$. J. D. Klein discussed the isomorphism of silicotungstic and borotungstic acids. The crystals were studied by W. Muthmann, and F. Zambonini. According to H. Copaux, the humidity of the air determines whether the acid is stable or efflorescent. The acid partially melts in its water of crystallization below 100°; and at 200°, it loses all but two mols of water, forming a fine powder which is readily soluble in water with the development of heat. After heating to 300°, the acid is soluble in water, and on evaporation furnishes the original acid, but if heated to dull redness, the acid is decomposed. The acid is soluble in ether. When the aq. soln. is heated in a sealed tube to 150°, it alters more quickly than does the potassium salt; and the dry crystals also change when kept for some time. F. Bourion stated that at 150°–280°, chlorine mixed with the vap. of sulphur chloride, $SCl_2$, removes all the tungsten from the acid. According to J. C. G. de Marignac, when the acid is melted with sodium carbonate, 17·77 per cent. of carbon dioxide is given off; and the acid also readily unites with 2 and 4 mols of base to form salts. J. D. Klein prepared the two series of salts.

G. Wyrouboff, and A. Bertrand prepared complexes of the silicododecatungstic acids with the alkaloids, A, $4A.SiO_2.12WO_3.nH_2O$, by treating a cold conc. soln. of the alkaloid with a 5 per cent. soln. of silicotungstic acid. The use of silicotungstic acid as a test for alkaloids, etc., has been discussed by J. C. G. de Marignac, F. Kehrmann, and B. Flürscheim. M. Javillier studied the silicotungstates of conicine, spartien, and atropine.

J. C. G. de Marignac prepared normal **octammonium isosilicododecatungstate,** $4(NH_4)_2O.SiO_2.12WO_3.16H_2O$, or $(NH_4)_8[Si(W_2O_7)_6].16H_2O$, by evaporating a soln. of the acid in aq. ammonia; and also by boiling a soln. of normal ammonium decatungstate for a long time, filtering off the precipitated silica, and cooling the soln. The white amorphous mass is readily soluble in hot water. He also made **tetrammonium isotetrahydrosilicododecatungstate,** $2(NH_4)_2O.2H_2O.SiO_2.12WO_3.6H_2O$, *i.e.* $(NH_4)_4H_4[Si(W_2O_7)_6].6H_2O$, by boiling a hydrochloric acid soln. of the preceding salt or of one of the silicododecatungstates, and cooling the soln. It is soluble in hot water and when boiled with an excess of aq. ammonia furnishes ammonium hydrotungstate. G. Wyrouboff regards this as the normal salt, and J. C. G. de Marignac's normal salt as a basic salt. J. C. G. de Marignac found that when a soln. of one mol of $SiO_2.12WO_3.24H_2O$ is treated with 4 mols of sodium carbonate it furnishes a syrupy mass, but if 6 mols of the carbonate are used, trigonal crystals of **tetrasodium isotetrahydrosilicododecatungstate,** $2Na_2O.2H_2O.SiO_2.12WO_3.10H_2O$, or $Na_4H_4[Si(W_2O_7)_6].10H_2O$, are formed. The crystals have the axial ratio $a:c=1:1{\cdot}3277$, and $\alpha=86°\ 50'$; they are stable in air, lose 8 mols of water at 100°; and when fused with sodium carbonate, give off 11 mols of carbon dioxide. H. S. van Klooster found that fused sodium tungstate and silicate are almost immiscible below 1100°. J. C. G. de Marignac prepared badly-formed, rhombic crystals of normal **octopotassium isosilicododecatungstate,**

$4K_2O.SiO_2.12WO_3.20H_2O$; they lose 15 mols of water at 100°, and when melted with sodium carbonate give off 9 mols of carbon dioxide.

J. C. G. de Marignac obtained the octocosihydrate, $H_8[Si(W_2O_7)_8].28H_2O$, which he represented **hydrosilicododecatungstic acid,** $SiO_2.12WO_3.32H_2O$, by treating the mercurous salt with hydrochloric acid, and removing traces of mercury from the filtrate by hydrogen sulphide. The filtrate was conc. by evaporation, and allowed to crystallize. This hydrate crystallizes from aq. soln. at temp. below 28·5°. H. Copaux represented the acid by $(SiO_2.2H_2O).12WO_3.31H_2O$, and made it by the action of a soln. of sodium tungstate on freshly precipitated gelatinous silicic acid; and by the action of hydrated tungstic acid on a soln. of sodium silicate.

H. Copaux prepared the acid as follows: Gelatinous silicic acid is made by adding conc. nitric acid to a dil. soln. of sodium silicate until litmus is reddened. The silicic acid is treated with a soln. of sodium tungstate in five times its weight of water. The mixture is diluted so that the weight of liquid is about eight times that of tungstic oxide employed. The soln. is strongly acidified with acetic acid, and heated to its b.p.; when hydrochloric acid produces no precipitate, the soln. is cooled, and treated with a mixture of ether and 33 per cent. of sulphuric acid until the turbidity persists when stirred. The mixture forms three layers—the lowest layer is a compound of ether with the 24 and 32 hydrated silicotungstic acids. The two acids are separated by fractional crystallization of the potassium salts. The salt of the higher hydrate furnishes the first crop of hexagonal prismatic crystals, the lower hydrate forms rhombic crystals. The potassium salt is converted into the acid by treatment with sulphuric acid and ether as before.

According to J. C. G. de Marignac, the octocosihydrate forms colourless tetragonal crystals, but they sometimes have a yellow tinge. The axial ratios are $a:c = 1:1·0117$. According to G. Wyrouboff, the crystals of the acid have an extremely feeble positive double refraction. They effloresce rapidly in air. The crystals begin to melt in their water of crystallization at 36°, and at 53°, fusion is complete; at 100°, 25 mols of water are given off, and no more is lost at 150°; between 150° and 220°, 6 mols of water are given off; and the remaining water is evolved at 250°. The product so obtained dissolves in water with the evolution of much heat, and when the soln. is evaporated, it gives the original acid; but if heated over 350°, the orange-yellow product is insoluble in water. When melted with sodium carbonate, 16·70 per cent. or 13 mols of carbon dioxide are expelled. At 18°, 100 parts of water dissolve 96 parts of the acid, and the soln. has a sp. gr. 2·843. The acid is readily soluble in absolute alcohol; if an excess of ether be added to the alcoholic soln., two liquids are formed, the lower layer is a syrupy soln. of the acid in ether. Anhydrous ether dissolves the acid and the crystals. E. Brauer found that the acid is not readily hydrolyzed, and the conc. of the hydrogen ion is $[H^·]=2·9\times10^{-3}$. G. Wyrouboff regarded the acid as tetrabasic, $H_4SiW_{12}O_{40}.31H_2O$; J. C. G. de Marignac, A. Rosenheim, and H. Copaux regarded it as octobasic. Silicododecatungstic acid is used on account of the colour reactions it gives with alkaloids, and many organic bases, a subject discussed by E. O. North and G. D. Beal.

J. C. G. de Marignac prepared the docosihydrate, $SiO_2.12WO_3.26H_2O$, or $(SiO_2.4H_2O).12WO_3.22H_2O$, *i.e.* $H_8[Si(W_2O_7)_6].22H_2O$, by partially melting hydro-silicododecatungstic acid in its water of crystallization and allowing the decanted liquid to crystallize slowly; by crystallizing an aq. soln. of the acid above 28·5°; by evaporating a soln. of the octocosihydrate acidified with sulphuric or hydrochloric acid. The trigonal crystals have the axial ratios $a:c=1:1·2360$ and $\alpha=88°\ 47'$. G. Wyrouboff found the crystals of hexacosihydro-silicododecatungstic acid to be physically and chemically isomorphous with tetracosihydrated silicotungstates of lithium, and the alkaline earths. The crystals of the acid have a strong negative double refraction. The crystals do not effloresce in air, but they lose 18 mols of water at 100°. With fused sodium carbonate, 17·38 per cent. of carbon dioxide is given off. G. Wyrouboff regarded the acid as tetrabasic,

$H_4SiW_{12}O_{40}.24H_2O$ ; J. C. G. de Marignac, A. Rosenheim, and H. Copaux regarded it as octobasic.

G. Wyrouboff, and E. O. North and G. D. Beal prepared non-crystalline **ammonium silicododecatungstate,** $2(NH_4)_2O.SiO_2.12WO_3.8H_2O$, or $(NH_4)_4H_4[Si(W_2O_7)_6].6H_2O$ ; and also $(NH_4)_4W_{12}SiO_{40}.4NH_4OH.14H_2O$, but no acid salt was made. The rhombohedral crystals of **tetralithium silicododecatungstate,** $2Li_2O.SiO_2.12WO_3.24H_2O$, or $Li_4H_4[Si(W_2O_7)_6].12H_2O$, were found by G. Wyrouboff to have the axial ratios $a:c=1:1{\cdot}6186$. With soln. at 40°–45°, triclinic crystals of $2Li_2O.SiO_2.12WO_3.14H_2O$ having the axial ratios $1{\cdot}1642:1:0{\cdot}9681$ and $\alpha=90°$, $\beta=94°\ 20'$, and $\gamma=86°\ 26'$ were formed. The crystals resemble those of $2Na_2O.SiO_2.12WO_3.13H_2O$. The triclinic crystals are feebly doubly refracting, and rapidly become turbid without loss of weight. The salt loses 8 mols of water at 105°. G. Wyrouboff also made trigonal crystals of a higher hydrate, $Li_4H_4[Si(W_2O_7)_6].22H_2O$, with the axial ratio $a:c=1:1{\cdot}3096$, and a strong negative double refraction. The crystals were studied by W. Muthmann, and F. Zambonini. The salt loses 1·9 mols of water at 105°. G. Wyrouboff also made **dilithium silicododecatungstate,** $Li_2O.SiO_2.12WO_3.24H_2O$, or $Li_2H_6[Si(W_2O_7)_6].21H_2O$, from a mixture of 20 grms. of the previous hydrate, and 10 grms. of silicotungstic acid.

J. C. G. de Marignac prepared normal **octosodium silicododecatungstate,** $4Na_2O.SiO_2.12WO_3.7H_2O$, or $Na_8[Si(W_2O_7)_6].7H_2O$, by boiling acid sodium tungstate with water and gelatinous silica. The liquid, on evaporation, furnishes needle-like crystals ; 100 parts of the salt dried at 100° have the composition just indicated, and 100 parts of water at 19° dissolve 476·2 parts of the salt, and the soln. has a sp. gr. 3·05. By treating this salt with hydrochloric acid at different temp., acid salts are produced ; with an excess of hydrochloric acid, and at 40°–50°, triclinic pinacoidal crystals of *henahydrated* **tetrasodium dihydrosilicododecatungstate,** $2Na_2O.2H_2O.SiO_2.12WO_3.11H_2O$, or $Na_4H_4[Si(W_2O_7)_6].11H_2O$, are produced. The tabular crystals have the axial ratios $a:b:c=1{\cdot}0932:1:0{\cdot}9102$, and $\alpha=88°\ 52'$ ; $\beta=95°\ 18'$ ; and $\gamma=86°\ 37'$. The crystals are strongly doubly refracting ; stable in air ; they lose 7 mols of water at 100° ; and expel 11 mols of carbon dioxide from fused carbonate. The hydrochloric acid soln. at 35°, furnishes the *dodecahydrated salt* in triclinic pinacoidal crystals with axial ratios $a:b:c=1{\cdot}6083:1:0{\cdot}5542$, and $\alpha=90°\ 52'$, $\beta=95°\ 22'$, and $\gamma=83°\ 34'$. The double refraction is negative. The crystals are stable in air. They lose 9 mols of water at 105°. The dehydrated salt dissolves completely in water. At ordinary temp., the hydrochloric acid soln. furnishes the *octodecahydrated salt* which occurs in dimorphous, triclinic, pinacoidal crystals, with a strong double refraction. The *α-salt* has the axial ratios and angles $a:b:c=1{\cdot}0320:1:0{\cdot}9092$, and $\alpha=94°\ 2'$ ; $\beta=93°\ 32'$ ; and $\gamma=88°\ 21'$, while the *β-salt* has $a:b:c=0{\cdot}8056:1:1{\cdot}1221$, and $\alpha=93°\ 14'$ ; $\beta=103°\ 39'$ ; and $\gamma=88°\ 3'$. Both forms effloresce rapidly in air. During the evaporation of the aq. soln., crystals of the henahydrate first appear, then crystals of the *β*-salt, and finally crystals of the *α*-salt, for the metastable *β*-salt passes into the *α*-form. Both varieties of the octodecahydrate rapidly pass into the henahydrate. At 100°, the octodecahydrate loses 14 mols of water, and at a red heat all the water is lost. When fused with sodium carbonate, 11 mols of carbon dioxide are given off. If a soln. of the octodecahydrate be treated with sulphuric acid, or with silicotungstic acid, and evaporated, at 25°–30°, J. C. G. de Marignac, and C. Wyrouboff found that crystals of **disodium hexahydro-silicododecatungstate,** $Na_2O.3H_2O.SiO_2.12WO_3.14H_2O$, or $Na_2H_6[Si(W_2O_7)_6].14H_2O$, are formed in positive, doubly-refracting, triclinic pinacoids with axial ratios $a:b:c=1{\cdot}0748:1:0{\cdot}9521$, and $\alpha=89°\ 6'$, $\beta=95°\ 50'$, and $\gamma=85°\ 17'$. When the aq. soln. is evaporated, silicotungstic acid is first formed, and the conc. mother liquid deposits crystals of the original salt. J. C. G. de Marignac, and G. Wyrouboff obtained triclinic crystals of **sodium nitratosilicododecatungstate,** $4NaNO_3.3(2Na_2O.2H_2O.SiO_2.12WO_3.13H_2O)$, with axial ratios $a:b:c=1{\cdot}0057:1:0{\cdot}8642$, and $\alpha=89°\ 35'$, $\beta=90°\ 20'$, and

$\gamma=91°\ 6'$. The mixed crystals lose 30 mols of water at 100°, and drive 31 mols of carbon dioxide from fused sodium carbonate.

J. C. G. de Marignac prepared the normal salt **octopotassium silicododeca-tungstate,** $4K_2O.SiO_2.12WO_3.14H_2O$, or $K_4H_4[Si(W_2O_7)_6].12H_2O$, which F. Kehrmann represented by the formula $7K_2O.2SiO_2.20WO_3.nH_2O$. It was obtained by boiling a soln. of acid potassium tungstate with gelatinous silicic acid, until a few drops of hydrochloric acid produced no turbidity. On cooling, a crust of crystals appeared, and the salt was purified by recrystallization from water. It is also obtained by treating the acid salt with potassium carbonate. The imperfectly formed crystals appear to be cubic, but they are doubly refracting. The salt loses 4 mols of water at 100°; and drives 9 mols of carbon dioxide from fused sodium carbonate. 100 parts of water at 18° dissolve 10 parts of the salt, and at 100°, 33·3 parts of salt. Three acid salts have been reported. J. C. G. de Marignac made **tripotassium pentahydro-silicododecatungstate,** $3K_2O.5H_2O.2(SiO_2.12WO_3).25H_2O$, say, $K_3H_5[Si(W_2O_7)_6].12H_2O$, by concentrating and cooling a soln. of the tetrapotassium salt with an excess of sulphuric acid; the first crop of crystals is an acid silicotungstate, the second crop is mainly hexagonal crystals of the tetrapotassium salt, and the mother liquid furnishes monoclinic prisms of the tripotassium salt. G. Wyrouboff crystallized the salt from the sulphuric acid soln. between 30° and 40°. The axial ratios of the crystals are $a:b:c=1·2148:1:0·8499$, and $\beta=102°\ 16'$. The double refraction is negative. The crystals are stable in air; lose 27 mols of water at 100°; and give 23 mols of carbon dioxide when fused with sodium carbonate. The salt is decomposed by water so that the concentration of the aq. soln. first gives crystals of the tetrapotassium salt, then crystals of the tripotassium salt, and finally rhombohedral crystals of silicotungstic acid contaminated with potassium. E. O. North and C. D. Beal analyzed potassium silicododecatungstate.

G. Wyrouboff obtained rectangular plates of **tetrapotassium tetrahydro-silico-dodecatungstate,** $2K_2O.2H_2O.SiO_2.12WO_3.13H_2O$, or $K_4H_4[Si(W_2O_7)_6].13H_2O$, by evaporation of the soln. acidified with nitric acid at a temp. exceeding 30°, or at ordinary temp. in the presence of conc. nitric acid. The monoclinic prisms have axial ratios $a:b:c=1·4715:1:1·9939$, and $\beta=102°\ 54'$. The double refraction is feebly negative. If the normal octopotassium salt is treated with hydrochloric acid, and the soln. evaporated, J. C. G. de Marignac found that colourless hexagonal crystals of the *octodecahydrate*, $2K_2O.2H_2O.SiO_2.12WO_3.16H_2O$, are formed, with the axial ratio $a:c=1:0·8585$. G. Wyrouboff, and C. Soret noted the crystals exhibit circular polarization, 14·4° with the *D*-line. The crystals effloresce on exposure to air, and lose 17 mols of water at 100°. All the water can be expelled at higher temp., and the dehydrated salt dissolves readily in water. With molten sodium carbonate, 11 mols of carbon dioxide are given off. 100 parts of water at 20° dissolve 33·3 parts of salt. J. C. G. de Marignac also prepared two varieties of the hydrate $2K_2O.2H_2O.SiO_2.12WO_3.7H_2O$. It is not clear if the alleged varieties contain the same quantities of water of crystallization. The rhombic bipyramids have axial ratios $a:b:c=0·8243:1:1·3311$. The one form occurs in short thick prisms, the other in six-sided plates. Both varieties lose about 7 mols of water at 100°; and about 11 mols of carbon dioxide are given off when fused with sodium carbonate. Both forms are very soluble in hot water, and less so in cold water. According to H. Copaux, when heated with water in a sealed tube at 150°, an isomeric derivative of $SiO_2.12WO_3.32H_2O$ is formed.

R. Godeffroy made normal **octorubidium silicododecatungstate,** $4Rb_2O.SiO_2.12WO_3.nH_2O$, or $Rb_8[Si(W_2O_7)_6].nH_2O$, as a white precipitate by adding rubidium chloride to a soln. of the acid. Crystals are obtained by evaporating the aq. soln. 100 parts of water at 20° dissolve about 0·67 part of the salt, and at 100°, about 5 parts of the salt; it dissolves sparingly in acidulated water, and readily in ammoniacal water. It is not soluble in alcohol. G. Wyrouboff also made the normal salt and an acid salt—$2RbOH.SiO_2.12WO_3.5H_2O$, and

$3Rb_2O.H_2O.2(SiO_2.12WO_3).22H_2O$. By mixing a mol of silicododecatungstic acid with 2 mols of rubidium carbonate, he obtained a white gelatinous precipitate which was washed by decantation, and dried in air. The white powder has the composition **trirubidium hydrosilicododecatungstate,** $3Rb_2O.H_2O.2(SiO_2.12WO_3).22H_2O$, say, $Rb_3H_5[Si(W_2O_7)_6].9H_2O$; it loses 15 mols of water at 105°. When treated with nitric acid, and washed with water, it furnishes **dirubidium silicododecatungstate,** $Rb_2O.H_2O.SiO_2.12WO_3.5H_2O$, or $Rb_2H_4[Si(W_2O_7)_6].4H_2O$, which loses 5 mols of water at 105°. R. Godeffroy also made **octocæsium silicododecatungstate,** $4Cs_2O.SiO_2.12WO_3.nH_2O$, or $Cs_4H_4[Si(W_2O_7)_6].nH_2O$, like the corresponding rubidium salt. 100 parts of water at 20° dissolve 0·005 part of the white crystalline powder and about 0·5 part at 100°. It is not soluble in alcohol or acidulated water, but it dissolves in ammoniacal water.

G. Wyrouboff prepared crystals of **cupric silicododecatungstate,** $2CuO.SiO_2.12WO_3.29H_2O$, or $Cu_2H_4[Si(W_2O_7)_6].27H_2O$; rhombohedral crystals of $2CuO.SiO_2.12WO_3.27H_2O$ with $a:c=1:2·6706$, which are stable below 10°; between 10° and 40° the pentacosihydrate is formed; and over 40°, the tetradecahydrate. The crystals of the dodecahydrate are isomorphous with the corresponding strontium salt, and have the axial ratios $a:b:c=1·4602:1:1·0283$, and $\gamma=84°\ 14'$. The crystals were studied by W. Muthmann, and F. Zambonini. J. C. G. de Marignac made **octosilver silicododecatungstate,** $4Ag_2O.SiO_2.12WO_3.3H_2O$, or $Ag_8[Si(W_2O_7)_6].3H_2O$, as a pale yellow precipitate, by treating an aq. soln. of the ammonium salt with silver nitrate. It loses its water below a red heat and becomes dark violet. The salt decomposes at a bright red heat. It is not perceptibly soluble in cold water. The wash-water is opalescent, and it clears on boiling. J. C. G. de Marignac prepared **tetrasilver tetrahydrosilicododecatungstate,** $2Ag_2O.2H_2O.SiO_2.12WO_3.7H_2O$, or $Ag_4H_4[Si(W_2O_7)_6].7H_2O$, by evaporating a soln. of silver carbonate in the dil. acid. The salt is sparingly soluble in water, but soluble in dil. nitric acid; hydrochloric acid gives a precipitate of silver chloride. G. Wyrouboff found the salt to lose 4 mols of water at 105°.

J. C. G. de Marignac obtained ill-defined crystals of normal calcium silicododecatungstate by dissolving calcium carbonate in the warm acid. Three hydrates of the acid salt of **calcium tetrahydrosilicododecatungstate,** $2CaO.2H_2O.SiO_2.12WO_3.nH_2O$, have been obtained by crystallization from a conc. soln. of calcium carbonate in hydrosilicotungstic acid. G. Wyrouboff obtained the hexadecahydrate, $2CaO.SiO_2.12WO_3.18H_2O$, or $Ca_2H_4[Si(W_2O_7)_6].16H_2O$, at 30° from soln. strongly acidified with nitric acid. The six-sided plates are triclinic with axial ratios $a:b:c=1·4228:1:—$, and $\alpha=87°\ 40'$, $\beta=90°\ 30'$, and $\gamma=81°\ 6'$. The crystals were studied by W. Muthmann, and F. Zambonini. The salt loses 10 mols of water at 105°. The docosihydrate was obtained at 45° or at ordinary temp. from soln. acidified with nitric acid. The trigonal crystals have the axial ratio $a:c=1:1·2523$, and $\alpha=89°\ 8'$. J. C. G. de Marignac said that this salt is isomorphous with rhombohedral silicododecatungstic acid and with the corresponding barium salt; it loses 16 mols of water at 100°; and drives 11 mols of carbon dioxide from molten sodium carbonate. The salt loses 17 mols of water at 105°. The pentacosihydrate forms trigonal crystals with $a:c=1:2·6419$, and $\alpha=56°\ 42'$. It loses 19 mols of water at 105°. J. C. G. de Marignac made triclinic crystals of the icosihydrate, $Ca_2H_4[Si(W_2O_7)_6].20H_2O$, which became moist, but did not deliquesce, in air. The prismatic crystals had the axial ratios $a:b:c=0·4461:1:0·5121$, and $\alpha=86°\ 52'$, $\beta=119°\ 38'$, and $\gamma=96°\ 2'$. The salt is very soluble in water; it loses 13 mols of water at 100°; and expels 11 mols of carbon dioxide from fused sodium carbonate. Triclinic crystals of another salt, the composition of which is doubtful, but approximates to $5CaO.3H_2O.2(SiO_2.12WO_3).47H_2O$, had axial ratios $a:b:c=0·5917:1:0·8627$, and $\alpha=101°\ 6'$, $\beta=102°\ 34'$, and $\gamma=99°\ 24'$. It lost 39 mols of water at 100°.

G. Wyrouboff obtained what are presumably mixed crystals of **calcium nitratosilicododecatungstate,** $Ca(NO_3)_2.2CaO.SiO_2.12WO_3.15H_2O$, with calcium nitrate by crystallization

at 30° from soln. strongly acidified with nitric acid. The monoclinic prisms have axial ratios $a:b:c=0{\cdot}9036:1:1{\cdot}1820$, and $\beta=94°\ 52'$. The mixed salt loses 8 mols of water at 105°, and all at 250°. He also obtained a triclinic tridecahydrate. Both salts are decomposed by water.

G. Wyrouboff prepared four hydrates of **strontium tetrahydrosilicododecatungstate,** $2SrO.2H_2O.SiO_2.12WO_3.nH_2O$, from soln. of strontium carbonate in the silicododecatungstate. The tetradecahydrate separates from aq. soln. over 50°. The monoclinic crystals are isomorphous with those of the barium salt. They lose 9 mols of water at 105°. A nitric acid soln. at 30° deposits first the henicosihydrate and then a pentadecahydrate. The latter forms monoclinic six-sided plates with axial ratios $a:b:c=1{\cdot}3001:1:1{\cdot}0058$, and $\beta=96°\ 46'$. The double refraction is negative. They lose 10 mols of water at 105°. The henicosihydrate forms triclinic six-sided prisms with axial ratios $a:b:c=1{\cdot}0212:1:0{\cdot}5947$, and $\alpha=92°\ 46'$, $\beta=91°\ 16'$, and $\gamma=95°\ 18'$. The crystals rapidly become turbid on exposure to air, without loss of weight. They lose water at 105°. The henicosihydrate is stable between 30° and 40°; the pentadecahydrate between 40° and 50°; and the tetradecahydrate, over 50°. The pentacosihydrate is formed below 30° in effloresceing trigonal crystals with $a:c=1:2{\cdot}5933$, and $\alpha=57°\ 30'$. The crystals were studied by W. Muthmann, and F. Zambonini. They have a feeble double refraction. The crystals lose 19 mols of water at 105°. G. Wyrouboff also suspected that a docosihydrate can be produced.

J. C. G. de Marignac made **barium silicododecatungstate,** $4BaO.SiO_2.12WO_3.27H_2O$, by adding baryta-water to hydro-silicododecatungstic acid, $SiO_2.12WO_3.24H_2O$, until more than 2 mols of barium hydroxide have been added. The product forms a sticky mass, almost insoluble in cold water, and sparingly soluble in hot. When the hot soln. is cooled, it redeposits a viscid mass. If kept for many days in contact with cold water, or for a short time in contact with hot water, a white powder is formed which loses 19 mols of water at 100°, and drives 9 mols of carbon dioxide from fused sodium carbonate. According to J. C. G. de Marignac, when an excess of barium chloride is poured into the aq. acid, a sticky mass is precipitated which dries in air to a hard glass of barium silicododecatungstate, $4BaO.SiO_2.10WO_3.22H_2O$. It loses 15 mols of water at 100°. If barium carbonate be dissolved in an aq. soln. of the acid until a precipitate of normal barium silicotungstate begins to appear, on evaporation, and cooling, the filtered soln. furnishes prismatic crystals of dodecahydrated **barium tetrahydrosilicododecatungstate,** $2BaO.2H_2O.SiO_2.12WO_3.12H_2O$. G. Wyrouboff regards this as the normal salt, and he obtained it by evaporating the soln. above 30°. According to J. C. G. de Marignac, the monoclinic prisms have the axial ratios $a:b:c=1{\cdot}7987:1:1{\cdot}5440$, and $\beta=103°\ 53'$. The crystals were studied by W. Muthmann, and F. Zambonini. The crystals are isomorphous with the strontium salt, and exhibit a strongly negative double refraction. The salt loses 8 mols of water at 100°, and drives 11 mols of carbon dioxide from fused sodium carbonate. If the tetradecahydrate, $2BaO.2H_2O.SiO_2.12WO_3.14H_2O$, be allowed to stand in contact with its mother liquor, rhombohedral crystals of the docosihydrate appear. The axial ratio $a:c=1:1{\cdot}3407$, and $\alpha=86°\ 26'$. The crystals have a strongly negative double refraction; they gradually effloresce in air; and lose 16 mols of water at 100°. H. Copaux said that 100 parts of cold water dissolve 70 parts of the salt; and G. Wyrouboff that at 15°, 100 parts of water dissolve 25 parts of the salt. He studied the isomorphism of barium silicododecatungstate and silicododecamolybdate.

G. Wyrouboff evaporated a mixed soln. of the barium and potassium salts and obtained monoclinic prisms of what he regarded as **barium potassium silicododecatungstate,** $K_2O.BaO.SiO_2.12WO_3.17H_2O$. The axial ratios are $a:b:c=0{\cdot}6471:1:0{\cdot}6056$, and $\beta=98°\ 45'$, and the crystals have a positive double refraction. The crystals are stable in air and lose 14 mols of water at 105°. Rhombic crystals of barium sodium silicododecatungstate, $Na_2O.BaO.SiO_2.12WO_3.28H_2O$, were prepared by adding barium chloride to a hot soln. of the acid sodium salt, and cooling. The axial ratios are $a:b:c=0{\cdot}9551:1:0{\cdot}9833$. If barium nitrate be used in place of the chloride, triclinic crystals

containing barium nitrate are formed, and these decompose when treated with water. Barium sodium silicododecatungstate loses 21 mols of water at 100°, and drives 9 mols of carbon dioxide from fused sodium carbonate. Long washing with water extracts sodium silicododecatungstate and leaves the normal barium salt behind; this, with hydrochloric acid, forms barium tetrahydrosilicododecatungstate.

G. Wyrouboff prepared trigonal crystals of heptacosihydrated **beryllium silicododecatungstate,** $2BeO.SiO_2.12WO_3.29H_2O$, or $Be_2H_4[Si(W_2O_7)_6].27H_2O$, by evaporating a soln. of beryllia in the acid $SiO_2.12WO_3.32H_2O$ over 45°, or at 30° in the presence of nitric acid. The axial ratio is $a:c=1:2{\cdot}4282$, and $\alpha=57°\ 56'$. The crystals lose 10·44 per cent. of water at 105°. Octahedral crystals of the enneacosihydrate are deposited if the soln. be evaporated below 45°. The crystals are singly refractive, and they belong to the cubic system. They lose 11·51 per cent. of water at 105°. G. Wyrouboff also reported crystals of $4BeO.3(SiO_2.12WO_3).45H_2O$, by evaporating the nitric acid soln. at 30°. The crystals were studied by W. Muthmann, and F. Zambonini. The doubly refracting crystals do not effloresce in air although they become superficially matt; they lose water at 105°. J. C. G. de Marignac made normal **magnesium silicododecatungstate** in a manner similar to that for the corresponding calcium salt. The crystals were studied by W. Muthmann, and F. Zambonini. J. C. G. de Marignac, and G. Wyrouboff also made acid salts, **magnesium tetrahydrosilicododecatungstate,** $2MgO.2H_2O.SiO_2.12WO_3.nH_2O$, with $n=16$ and 25. The hexadecahydrate is obtained by conc. of a soln. of magnesia in the acid. It forms triclinic crystals with axial ratios $a:b:c=0{\cdot}4062:1:0{\cdot}3959$, and $\alpha=86°\ 50'$, $\beta=90°\ 23'$, and $\gamma=90°\ 10'$. The double refraction is strongly negative. The crystals do not effloresce in air; they lose 10 mols of water at 100°; and drive 13 mols of carbon dioxide from fused sodium carbonate. The pentacosihydrate is formed under 20°; and the trigonal crystals have the axial ratio $a:c=1:2{\cdot}6600$, and $\alpha=56°\ 44'$. The crystals have a negative double refraction; they do not effloresce in air.

G. Wyrouboff prepared **zinc silicododecatungstate,** $2ZnO.SiO_2.12WO_3.nH_2O$, or $Zn_2H_4[Si(W_2O_7)_6].(n-2)H_2O$, by evaporating a soln. of zinc oxide in silicododecatungstic acid. If crystallization occurs above 25°, the hexadecahydrate appears; if between atm. temp. and 25°, the pentacosihydrate; and if about 10°, the heptacosihydrate. The hexadecahydrate occurs in triclinic prisms with axial ratios $a:b:c=0{\cdot}4034:1:0{\cdot}3911$, and $\alpha=86°\ 6'$, $\beta=91°\ 26'$, and $\gamma=91°\ 5'$. At 105°, 10 mols of water are evolved. The pentacosihydrate forms trigonal crystals with the axial ratio $a:c=1:6279$ and $\alpha=56°\ 64'$. The crystals were studied by W. Muthmann, and F. Zambonini. The salt loses 21 mols of water at 105°. The heptacosihydrate forms basic rhombohedra, and loses 21 mols of water at 105°. All the hydrates effloresce readily on exposure to air. G. Wyrouboff likewise prepared **cadmium silicododecatungstate,** $2CdO.SiO_2.12WO_3.23H_2O$, or $Cd_2H_4[Si(W_2O_7)_6].21H_2O$, by evaporating a soln. of cadmium oxide in the hydrosilicododecatungstic acid acidified with nitric acid. The triclinic prisms have the axial ratios and angles $a:b:c=0{\cdot}3784:1:0{\cdot}3207$, and $\alpha=88°\ 7'$, $\beta=96°\ 9'$, and $\gamma=89°\ 31'$. The crystals were studied by W. Muthmann, and F. Zambonini. The salt does not effloresce on exposure to air; but it loses 15 mols of water at 100°. The pentacosihydrate is obtained by evaporating the soln., free from nitric acid, below 35°. The efflorescent trigonal crystals have the axial ratio $a:c=1:2{\cdot}6123$, and $\alpha=57°\ 10'$. They lose 20 mols of water at 105°. If the aq. soln. be evaporated with a large excess of nitric acid at 35°–40°, basic prisms, probably triclinic, of $4CdO.3(SiO_2.12WO_3).44H_2O$, are formed. They lose 22 mols of water at 105°.

J. C. G. de Marignac, and G. Wyrouboff prepared rhomboidal plates of pentahydrated **mercurous silicododecatungstate,** $4Hg_2O.SiO_2.12WO_3.5H_2O$, by adding mercurous nitrate to a soln. of the acid $SiO_2.12WO_3.33H_2O$. The salt becomes anhydrous at 100°. G. Wyrouboff said that if the mercurous salt is precipitated at a very low temp., a higher hydrate is obtained. The pentahydrate is

insoluble in dil. nitric acid, but it dissolves slowly in the conc. acid, forming the acid mercuric salt. The anhydrous salt is insoluble in water, sparingly soluble in dil. nitric acid, and is decomposed by hydrochloric acid, forming mercurous chloride and silicododecatungstic acid. When fused with sodium carbonate, about 13 mols of carbon dioxide are evolved.

G. Wyrouboff made **mercuric silicododecatungstate,** $2HgO.SiO_2.12WO_3.15H_2O$, or $Hg_2H_4[Si(W_2O_7)_6].13H_2O$, by dissolving 2 mols of mercuric oxide in an aq. soln. of hydrosilicotungstic acid, and evaporating at 25°; also by the action of conc. nitric acid on the mercurous salt, and evaporating at 25°. The crystals forming triclinic prisms have the axial ratios $a:b:c=0{\cdot}9848:1:1{\cdot}0191$, and angles $\alpha=97°\ 40'$, $\beta=94°\ 22'$, and $\gamma=90°\ 40'$. The salt loses 10 mols of water at 105°, and the remainder at 250°; at a red heat, the mercury is volatilized. The salt is sparingly soluble in water, the aq. soln. decomposes when boiled, and precipitates what G. Wyrouboff regarded as a basic salt, but J. C. G. de Marignac would regard it as the normal salt: $4HgO.SiO_2.12WO_3.nH_2O$.

According to J. C. G. de Marignac, the evaporation of a soln. of gelatinous alumina in hydrosilicododecatungstic acid gives non-deliquescent triclinic crystals of **aluminium silicododecatungstate,** $2(Al_2O_3.6H_2O).3(SiO_2.12WO_3).75H_2O$. The axial ratios are $a:b:c=1{\cdot}509:1:1{\cdot}790$, and $\alpha=96°\ 44'$, $\beta=121°\ 57'$, and $\gamma=75°\ 44'$. The crystals lose 51 mols of water at 100°, and drive 39 mols of carbon dioxide from fused sodium carbonate. G. Wyrouboff prepared triclinic crystals of aluminium silicododecatungstate, $2Al_2O_3.3(SiO_2.12WO_3).60H_2O$, by evaporating a nitric acid soln. of gelatinous alumina in hydrosilicododecatungstic acid at 35°. The axial ratios $a:b:c=0{\cdot}8563:1:1{\cdot}0658$, and $\alpha=87'\ 44'$, $\beta=105°\ 11'$, and $\gamma=91°\ 48'$. The crystals are stable in air, and lose 37 mols of water at 105°. If the aq. soln. be evaporated at 35°, or at 18°–20° in the presence of nitric acid, trigonal crystals of the 81-hydrate are deposited. The axial ratio is $a:c=1:2{\cdot}6653$, and $\alpha=56°\ 19'$. The crystals were studied by W. Muthmann, and F. Zambonini. They effloresce on exposure to air, and lose 60 mols of water at 105°. According to J. C. G. de Marignac, if the aq. soln. be evaporated at ordinary temp., the 93-hydrate is formed in regular octahedral crystals which effloresce readily on exposure to air. They lose 66 mols of water at 100°, and when fused with sodium carbonate give off 39 mols of carbon dioxide. If a cold soln. of the higher hydrate be rendered turbid by the addition of ammonia, the soln. becomes clear when warmed, and when the excess of ammonia has been expelled, the soln. on cooling deposits octahedral crystals of **ammonium aluminium silicododecatungstate,** $9(NH_4)_2O.2Al_2O_3.3(SiO_2.12WO_3).75H_2O$. They lose 66 mols of water at 100°, and expel 39 mols of carbon dioxide from fused sodium carbonate. G. Wyrouboff prepared **gallium silicododecatungstate,** $2Ga_2O_3.3(SiO_2.12WO_3)$ with 60, 87, and $93H_2O$. The 60-hydrate has axial ratios $a:b:c=0{\cdot}9057:1:1{\cdot}1585$ and $\gamma=74°\ 20'$, and those of the 87-hydrate $a:c=1:2{\cdot}6346$. The crystals were studied by W. Muthmann, and F. Zambonini. G. Wyrouboff made **thallium silicododecatungstate,** $2TlOH.SiO_2\ 12WO_3.9H_2O$. He also prepared normal 26-hydrated **cerium, lanthanum, and praseodymium silicododecatungstates,** with the general formula $2MO.SiO_2.12WO_3.26H_2O$. These salts are isomorphous with the hydrated calcium and strontium silicododecatungstates. The acid salts $3M(OH)_2.2(SiO_2.12WO_3).36H_2O$ were also prepared. He also made normal 26- and 27-hydrated **neodymium, samarium, and gadolinium silicododecatungstates** with the general formulæ $2MO.SiO_2.12WO_3.26H_2O$, and $2MO.SiO_2.12WO_3.27H_2O$, or $MO_4(SiW_{12}O_{40})_3.81H_2O$, and in addition 30-hydrated gadolinium salt $2GdO.SiO_2.12WO_3.30H_2O$, as well as the acid salt $3M(OH_2).2(SiO_2.12H_2O).36H_2O$. The 26-hydrated **yttrium, terbium, and ytterbium silicododecatungstates** with the general formula $2MO.SiO_2.12WO_3.26H_2O$, and the corresponding acid salts $3M(OH)_2.2(SiO_2.12WO_3).49H_2O$, and acid **erbium silicododecatungstate,** $3Er(OH)_2.2(SiO_2.12WO_3)$ with 49 and $51H_2O$, were also made. The crystals were studied by W. Muthmann, and F. Zambonini. G. Wyrouboff prepared two **thorium silicododecatungstates,**

$2ThO.SiO_2.12WO_3$ with 27 and $30H_2O$, and the acid salt $2ThO.4H_2O.2(SiO_2.12WO_3).45H_2O$. The crystals were studied by W. Muthmann, and F. Zambonini.

G. Wyrouboff dissolved chromic oxide in a soln. of the acid $SiO_2.12WO_3.33H_2O$, and obtained three hydrates of **chromium silicododecatungstate,** $2Cr_2O_3.3(SiO_2.12WO_3).nH_2O$. If the crystallization occurs at 30° from soln. containing nitric acid, monoclinic prisms of the 60-hydrate are obtained with axial ratios $a:b:c=0{\cdot}8658:1:1{\cdot}0798$, and $\beta=106°\,16'$. The crystals were studied by W. Muthmann, and F. Zambonini. The crystals are stable in air, and lose water at 105°. Trigonal crystals of the 87-hydrate separate at 25°. The axial ratio is $a:c=1:2{\cdot}5354$, and $\alpha=56°\,29'$; the crystals have a negative double refraction, and lose 60 mols of water at 105°. If the crystallization occurs below 25°, octahedral, singly refracting crystals of the 93-hydrate are formed; they lose 66 mols of water at 105°. According to G. Wyrouboff, if uranyl nitrate be added to a soln. of silicododecatungstic acid, and the soln. be evaporated to drive off the nitric acid, a yellow mass of isotropic octahedral crystals is formed. Quite a number of more or less ill-defined **uranium silicododecatungstates** were reported to be formed by varying the proportions of acid to base. Thus, with the mol. ratio $UO_3:(SiO_2.12WO_3):H_2O$, G. Wyrouboff obtained 6 : 3 : 91; 5 : 3 : 90; 3 : 3 : 88; 2 : 3 : 87; 5 : 9 : 264; 3 : 6 : 177; 4 : 9 : 267; as well as a number of others whose composition was not determined. G. Wyrouboff prepared crystals of **lead silicododecatungstate,** $2PbO.SiO_2.12WO_3.21H_2O$, with axial ratios $a:b:c=1{\cdot}7963:1:1{\cdot}1203$ and $\gamma=81°\,35'$; as well as crystals of $4PbO.SiO_2.12WO_3.20H_2O$. G. Wyrouboff prepared rhombohedral crystals of **manganese silicododecatungstate,** $2MnO.SiO_2.12WO_3.27H_2O$, with axial ratios $a:c=1:2{\cdot}6549$, and crystals of the 18-hydrate with axial ratios $a:b:c=0{\cdot}4018:1:0{\cdot}4088$. The crystals were studied by W. Muthmann, and F. Zambonini. Similarly, 18- and 27-hydrated **cobalt silicododecatungstates** with axial ratios respectively $a:b:c=0{\cdot}4067:1:0{\cdot}4055$, and $a:c=1:2{\cdot}6760$; and of 18- and 27-hydrated **nickel silicododecatungstates,** with $a:b:c=0{\cdot}40451:1:0{\cdot}4166$, and $a:c=1:2{\cdot}6392$, were obtained. The crystals of the cobalt and nickel salts were studied by W. Muthmann, and F. Zambonini. G. Wyrouboff made yellow crystals of **ferric silicododecatungstate,** $2Fe_2O_3.3(SiO_2.12WO_3).93H_2O$, and of $2Fe_2O_3.3(SiO_2.12WO_3).60H_2O$, with axial ratios $a:b:c=0{\cdot}8465:1:1{\cdot}0897$, and $\gamma=73°\,20'$.

J. C. G. de Marignac prepared what he regarded as octobasic **heptahydrosilicododecatungstic acid,** $SiO_2.10WO_3.7H_2O$, or $(SiO_2.4H_2O).10WO_3.3H_2O$, *i.e.* $H_8SiW_{10}O_{36}.3H_2O$, by treating the mercurous salt with hydrochloric acid. The aq. soln. should be evaporated in vacuo in the cold. H. Copaux also prepared the acid by treating the ammonium salt with ether and sulphuric acid. The acid obtained by the evaporation of the aq. soln. is a clear glass with a faint yellow tinge. It does not change when heated to 100°, but it cracks and crazes when exposed to air, probably owing to the absorption of moisture. When fused with sodium carbonate, 11 mols of carbon dioxide are given off. The acid is soluble in water, and gelatinous silica sometimes separates from the soln. on evaporation. The aq. soln. is not rendered turbid when salts of barium, calcium, magnesium, aluminium, or lead are added; silver nitrate gives a yellow precipitate insoluble in water, and easily soluble in nitric acid; and mercurous nitrate gives a similar precipitate slightly soluble in nitric acid. Salts other than the ammonium salt have not been obtained of a high degree of purity, but are usually contaminated with salts of the silicododecatungstic acids. J. C. G. de Marignac believed that the acid forms two series of salts—one with two and the other with four mols of base. A. Pinagel could not prepare *silicoenneatungstic acid,* $SiO_2.9WO_3.nH_2O$.

J. C. G. de Marignac prepared normal **octammonium silicododecatungstate,** $4(NH_4)_2O.SiO_2.10WO_3.8H_2O$, or $(NH_4)_8SiW_{10}O_{36}.8H_2O$, or $(NH_4)_8[Si(W_2O_7)_5O].8H_2O$, by boiling a soln. of ammonium hydrotungstate with gelatinous silica, and evaporating the filtered soln.—the salt crystallizes out on cooling. H. Copaux made it by boiling a soln. of silicododecatungstic acid with an excess of ammonia,

until the silica first precipitated has nearly all dissolved. The strongly ammoniaca liquid is filtered and allowed to cool when rhombic bipyramidal prisms separate The crystals have axial ratios $a:b:c=0{\cdot}5890:1:0{\cdot}4774$. At 100°, the crystals lose 2·63 mols of water. According to J. C. G. de Marignac, 100 parts of water at 18° dissolve 22·2 parts of the salt, hot water dissolves much more. The soln. is neutral; loses ammonia when boiled; and deposits silica when boiled for a long time or when treated with an acid. The warm soln. takes up calcium carbonate or gelatinous alumina without depositing silica, but some ammonia is given off, and when the soln. is conc. it forms a sticky mass, which congeals to a clear colourless glass. J. C. G. de Marignac, and A. Pinagel also made **hexammonium silicodecatungstate,** $3(NH_4)_2O.SiO_2.10WO_3.10H_2O$—the former, by boiling a soln. of the normal salt for a long time, and adding water from time to time to replace that lost by evaporation. The monoclinic prisms have axial ratios $a:b:c=0{\cdot}688:1:-$ and $\beta=114°\ 48'$. At 100°, the salt loses 8 mols of water. A soln. of potassium carbonate in silicodecatungstic acid furnished *potassium silicodecatungstate*, $4K_2O.SiO_2.10WO_3.17H_2O$; or else, according to F. Kehrmann, $K_7[Si(W_2O_7)_5OH].11H_2O$. J. C. G. de Marignac did not succeed in making a definite *sodium silicodecatungstate*; by treating a mol of the acid with 2 or 4 mols of sodium carbonate, the soln. furnished a gum-like mass. A soln. of calcium carbonate in silicodecatungstic acid gives on evaporation a gum-like mass, *calcium silicodecatungstate*. G. Wyrouboff obtained an amorphous precipitate of *barium silicodecatungstate*, $4BaO.SiO_2.10WO_3.22H_2O$, by adding a barium salt to a soln. of sodium silicodecatungstate. According to J. C. G. de Marignac, when silicodecatungstic acid is mixed with four mols of potassium carbonate, and evaporated at a suitable temp., the first crop consists of the normal silicodecatungstate, then needles of what is regarded as a mixed salt, and finally rhombohedral plates of heptadecahydrated **octopotassium silicodecatungstate,** $4K_2O.SiO_2.10WO_3.17H_2O$. When fused with sodium carbonate, 7 mols of carbon dioxide are evolved. C. Friedheim and W. H. Henderson also made the tetracosihydrate. J. C. G. de Marignac found that if an aq. soln. of the acid be mixed with two mols of potassium carbonate, the first crop of crystals is a mixture of silicodecatungstates, and the final crop is mainly **tetrapotassium tetrahydro-silicodecatungstate,** $2K_2O.2H_2O.SiO_2.10WO_3.8H_2O$. The crystals lose 7 mols of water at 100°; and when fused with sodium carbonate, 9 mols of carbon dioxide are given off.

A series of potassium salts of white *silicohenatungstic acid* intermediate between silicodeca- and silicododeca-tungstic acid were obtained by J. C. G. de Marignac. For example, tetradecahydrated **octopotassium silicohenatungstate,** $4K_2O.SiO_2.11WO_3.14H_2O$, crystallizes in rhombic bipyramidal needles with axial ratios $a:b:c=0{\cdot}8875:1:0{\cdot}4123$. It loses 8 mols of water at 100°, and when fused with sodium carbonate, expels 8 mols of carbon dioxide. A. Pinagel made a 13-hydrate by passing steam into water with potassium paratungstate, $3K_2O.7WO_3.8H_2O$, in suspension and gradually adding gelatinous silicic acid. When hydrochloric acid produces no turbidity the filtered soln. is evaporated for crystallization. J. C. G. de Marignac prepared **tetrapotassium tetrahydrosilicohenatungstate,** $2K_2O.2H_2O.SiO_2.11WO_3.10H_2O$. The yellowish triclinic pinacoidal crystals have axial ratios $a:b:c=1{\cdot}810:1:1{\cdot}709$, and $\alpha=96°\ 31'$, $\beta=123°\ 38'$, and $\gamma=99°\ 38'$. It loses 8 mols of water at 100° and when fused with sodium carbonate it gives off 10 mols of carbon dioxide.

O. Kallauner and J. Hruda [4] studied the fusibility of binary mixtures of uranium oxide and clay. L. Bourgeois failed to make a uranium silicate by heating mixtures of uranium oxide and silica. A. Bornträger mixed a soln. of a uranyl salt (1 : 10) with an equal vol. of a dil. soln. of water-glass of sp. gr. 1·38, and obtained a crystalline precipitate of **uranyl silicate,** $UO_3.7SiO_2$. A calcium uranium silicate under the name *uranotile* was described by E. Boricky. It occurs at Wölsendorf, Bavaria; Kupferberg, Silesia; and at Neustädtel, Saxony, in fibrous masses, or in minute, acicular, lemon-yellow or orange-yellow crystals, which, according to P. Pjatnitzky, belong to the triclinic system and have the axial ratios $a:b:c=0{\cdot}6257:1:0{\cdot}5943$, and $\alpha=87°\ 41'$, $\beta=85°\ 18'$, and $\gamma=96°\ 31'$. The

crystals were described by V. von Zepharovich and A. Schrauf. A mineral described by M. Websky as *uranophane* is considered to be an impure uranotile. Its crystals are said to be rhombic. Analyses by R. Grundmann, M. Websky, C. Winkler, F. A. Genth, H. B. von Foullon, and E. Boricky agree with $CaO.3UO_3.3SiO_2.9H_2O$; or with $CaO.2UO_3.2SiO_2.6H_2O$; P. Groth represented it by $CaU_2.Si_2O_{11}.5H_2O$; and F. W. Clarke regarded it as hexahydrated **calcium uranyl orthodisilicate,** $Ca(UO_2)_2Si_2O_7.6H_2O$; and T. L. Watson, $CaO.2UO_3.3SiO_2.7H_2O$. M. Websky gave for the composition of uranophane, $5(K_2,Ca,Mg)O.2Al_2O_3.6UO_3.10SiO_2.28H_2O$, **calcium uranyl aluminium silicate.** The sp. gr. of uranotile was given as 3·8–3·9, and that of uranophane as 2·65. The hardness is less than 3. A. Schoep applied the name *sklodoskite*—after Mme. Curie-Sklodowska—to a radioactive mineral with the composition of **magnesium uranyl orthodisilicate,** $Mg(UO_2)_2Si_2O_7.7H_2O$. The rhombic prisms are lemon-yellow with the indices of refraction $\alpha=1{\cdot}613$, $\beta=1{\cdot}635$, and $\gamma=1{\cdot}657$. The sp. gr. is 3·54. The pleochroism is yellow, pale yellow, and colourless.

The mineral *mackintoshite*, discussed in connection with the rare earths, may, according to F. W. Clarke, be regarded as a **thorium uranyl silicate,** $UO_2.2ThO_2.3SiO_2.3H_2O$; and *thorogummite*, discussed in the same place, as a hydrated derivative.

A. Schoep [5] described some fine-grained crystal aggregates from Kasolo, Belgian Congo, with the composition $12UO_3.5SiO_2.14H_2O$; he called the mineral **soddite.** The crystals are rhombic; the sp. gr. is 4·627 at 17°; and the hardness 3–4. He also described canary-yellow, felted, needle-like crystals occurring on a mass of soddite from Chinkolobwe, Belgian Congo. The crystals have a lower birefringence than soddite, and the optical properties are different. He suggested the name **chinkolobareite,** and regarded it as a dimorphous form of soddite.

A. I. Walcker [6] stated that a soln. of sodium silicate gives a precipitate with a soln. of stannic chloride, but not with one of stannous chloride; J. M. Ordway obtained similar results, and found that the gelatinous precipitate contained very variable proportions of alkali, stannic oxide, and silica. A. Breithaupt, F. Hessenberg, A. E. Nordenskjöld and A. Gadolin, and G. Bischof applied the term *stannite* to what they regarded as a **stannic silicate,** but A. des Cloizeaux, and G. Tschermak regard it as a mixture of quartz and cassiterite, and F. Geinitz, J. R. Blum, J. H. Collins, R. Pearce, and R. P. Greg and W. G. Lettsom, a pseudomorph of cassiterite after felspar.

A. Hutchinson found that a rare mineral from Roscommon Cliff, St. Just, Cornwall, which he called **stokesite**—after G. G. Stokes—corresponded with **calcium silicostannate,** $CaO.SnO_2.3SiO_2.2H_2O$, which F. Zambonini would write $O{=}Sn{=}Si_3O_8{=}Ca{+}2H_2O$, analogous with his formula for catapleiite, $O{=}Zr{=}Si_3O_8{=}Na_2{+}2H_2O$. A. Hutchinson considers it to be a salt of tetrasilicic acid, $H_4Ca(Si,Sn)_4.O_{11}$. On F. W. Clarke's system, the formula would be $(HO)_3Sn(Si_3O_8{\equiv}HCa)$. The colourless crystals belong to the rhombic system, and A. Hutchinson gave for the axial ratios $a:b:c=0{\cdot}3462:1:0{\cdot}8437$. The (110) cleavage is perfect; (010) less so. The sp. gr. is 3·185, and the hardness 6. The optic axial angle $2V=69\frac{1}{2}°$; the index of refraction, $\beta=1{\cdot}6125$; and the birefringence, $\gamma-\alpha=0{\cdot}01$—Na-light. L. Bourgeois found that crystals with the composition $CaO.SiO_2.SnO_2$ are produced when three parts of silica and four parts of stannic oxide are heated with an excess of calcium chloride to bright redness for about eight hours, and the cooled mass extracted with water. If the time of fusion has been short, the residue is a mixture of tridymite and cassiterite, but if the reaction has proceeded further the residue consists of calcium silicostannate, whilst if the heating has been too far prolonged, the products are calcium disilicate and calcium stannate. The monoclinic prisms, analogous to titanite, have a lower birefringence than titanite. The sp. gr. is 4·34. The crystals are not attacked by acids, alkali-lye, or potassium hydrosulphate. They are less fusible than titanite.

T. W. Hogg [7] observed that a mixture of lead monoxide and silica at a red-heat

unite to form a silicate. The temp. of formation is lower than the fusion temp. of the mixture. Fused lead oxide is a powerful solvent for silica and silicates, and, as shown by E. Biewend, the soln. usually congeals to a glass. These glasses are of industrial importance as the base of many glasses and pottery glazes. Various formulæ are used in the industries, but the formulæ are not intended to represent compounds, but rather the mol. proportions of the components of the glass. The glassy frit sold as "lead bisilicate," for instance, contains lead oxide and silica in the porportions $PbO : SiO_2 = 1 : 2$. One of the "heaviest flint glasses" has about 78 per cent. of PbO, and approximates closely to the proportions required for a metasilicate. Such glasses may crystallize when cooled slowly, and one, obtained in this way, was regarded as lead metasilicate, $PbSiO_3$, by L. Bourgeois. Crystalline masses have also been found under the fusion hearth of lead roasting furnaces undergoing repair. Analyses of glasses containing such crystals were reported by L. Elsner, E. S. Dana and S. L. Penfield, H. A. Wheeler, etc. M. Faraday investigated a number of lead glasses, J. J. Berzelius said that lead silicate is formed when lead fluosilicate is heated with ammonia. W. E. B. Blenkinsop and F. M. Lyte heated basic lead sulphate or lead oxychloride and silica. A. C. Becquerel found that a lead silicate is formed on the boundary walls of the collodion membrane separating lead nitrate and potassium silicate soln. B. Huick electrolyzed a 1–2 per cent. soln. of a mixture of 95 per cent. sodium acetate and 5 per cent. of sodium silicate between lead electrodes, and obtained a lead silicate. W. Mostowitsch, and S. Hilpert and co-workers made glasses with $PbO : SiO_2 = 6 : 1$, 5 : 1, 4 : 1, 3 : 1, 5 : 2, and 4 : 3; but there is nothing to show that the products were chemical individuals—most probably not so.

J. W. Mellor and co-workers measured the softening temp. of a series of these glasses and found an abrupt drop from the m.p. of lead oxide, 877°, to 540° with mixtures containing one per cent. of silica, and raising the silica up to 12 per cent. lowered the softening temp. 8° more, Fig. 192. Mixtures with these proportions of silica were inclined to devitrify. Mixtures with from 12–30 per cent. of silica softened between 532° and 543°; and subsequent additions of silica raised the softening temp. rapidly; and, owing to the volatilization of lead oxide, the course of the curve was not followed much further. W. Mostowitsch obtained values for the m.p. nearly 200° higher than these data. S. Hilpert with P. Weiller, and with R. Nachen obtained the results indicated in Fig. 191. There is a maximum at 770° corresponding with the m.p. of the metasilicate, and higher proportions of silica gave mixtures which formed glasses; and silicates with over 34 per cent. of silica by weight melted over 1000°, and formed turbid masses on cooling. There is a maximum at 740° corresponding with lead orthosilicate, $Pb_2SiO_4$, and a eutectic between the orthosilicate and lead oxide at 717°; there are two eutectics close between the ortho- and the meta-silicates, and the intermediate maximum at 690° corresponds with the lead orthodisilicate, $Pb_3Si_2O_7$, or lead pyrosilicate. H. C. Cooper and co-workers also examined the heating curves of the lead silicates and found evidence of the formation of lead orthosilicate, m.p. 746°; lead metasilicate, m.p. 766°; and an intermediate eutectic, m.p. 717°. They further obtained evidence of the formation of the pyrosilicate, and showed that the crystals obtained from the lead smelters contain this silicate mixed isomorphously with other silicates. S. Hilpert and R. Nachen measured the velocity of crystallization, and the crystallizing power in terms of the number of nuclei formed in a given time per unit area at different temp. They say that there is inconclusive evidence of the existence of a basic

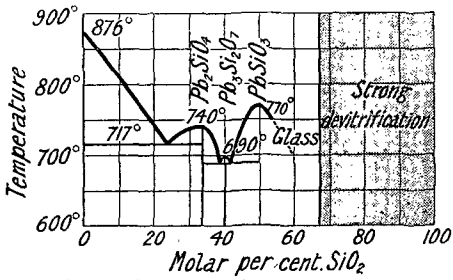



FIG. 191.—Freezing-point Curves of Binary Mixtures of Lead Oxide and Silica.

silicate, $3PbO.SiO_2$, or $PbO.Pb_2SiO_4$, *lead oxyorthosilicate.* H. C. Cooper and co-workers showed that when quickly cooled, all fusions containing less than 80 equivalents per cent. of lead oxide give clear, coloured glasses. When slowly cooled, all fusions containing more than 60 eq. per cent. of lead oxide crystallize completely; those which are richer in silica crystallize only in part, but if the resulting solid is finely powdered and heated for several hours to a temp. which is 10°–100° lower than the m.p., a sintered, crystalline mass is obtained. J. W. Mellor and co-workers found the temp. at which the lead silicate glasses became so soft that the corners of angular fragments were rounded. The results are plotted in Fig. 192.

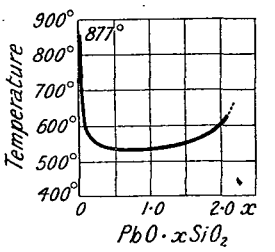



FIG. 192.—Softening Temperatures of Lead Silicate Glasses.

S. Hilpert and P. Weiller showed that the sp. vol. of the lead silicates were always greater than corresponded with the mixture rule. They found for the sp. gr.

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| $SiO_2$ per cent. . . | 8·6 | 13·0 | 17·8 | 20·28 | 24·09 | 27·56 | 32·54 | 33·38 |
| Sp. gr. . . . . | 8·124 | 7·005 | 6·45 | 6·14 | 5·74 | 5·28 | 4·87 | 4·73 |

The refractive indices of glasses rich in lead oxide are very high. S. Hilpert and P. Weiller's results are indicated in Table XXXIII. The glasses all showed a complete absorption of the violet and ultra-violet rays. The orthosilicate glass is dark yellow, and the metasilicate light yellow. The colour darkens with rise of

TABLE XXXIII.—INDICES OF REFRACTION OF LEAD SILICATE GLASSES.

| Per cent. PbO in glass. | Red H-line. | Orange Hg-line. | Na-line. | Yellow Hg-line. | Green Hg-line. | Blue Hg-line. | Violet Hg-line. |
|---|---|---|---|---|---|---|---|
| 87·00 | 2·058 | — | 2·078 | 2·083 | 2·095 | 2·174 | — |
| 84·00 | — | 2·025 | 2·028 | 2·038 | 2·048 | 2·104 | 2·112 |
| 82·20 | — | — | 1·979 | 1·986 | — | 2·048 | — |
| 79·72 | — | — | 1·960 | — | — | — | — |
| 75·91 | — | 1·922 | 1·930 | — | 1·935 | 1·965 | — |
| 72·41 | — | — | 1·864 | 1·866 | — | 1·897 | — |
| 29·00 | — | — | 1·773 | 1·779 | 1·785 | 1·811 | 1·824 |

temp. The yellow colour may largely be an effect of traces of silver or iron in the lead oxide. L. Elsner discussed the colour of the lead silicate glasses. The solubility of lead oxide in fused lead silicate glass increases with the rise of temp., and K. Beck assumes that the yellow colour of the lead silicate glasses rich in bases is really due to a thermolytic dissociation, $PbO.nSiO_2 \rightleftharpoons PbO + nSiO_2$. From his study of the electrical properties of flint glass, G. L. Addenbrooke inferred that the glass is really a soln. of silica in lead metasilicate, and not a mere mixture of lead and silicon oxides. According to M. Berthelot, the lead silicate glasses are decomposed by exposure to the radiations from a radium salt, and coloured black, or if the lead silicate glass has had its colour bleached by a little manganese oxide, it may be coloured violet. The volatilization of lead oxide from lead silicates was discussed by W. Thomason, S. Hilpert, F. O. Doeltz and C. A. Graumann, and M. Stoermer. The loss in mgrm. per sq. cm. per hour was found by O. Andersen to be as follows:

| PbO . . . . | 85 | 78·7 | 75 | 70 | 65 | 60 per cent. |
|---|---|---|---|---|---|---|
| 900° . . . . | 1 | 1 | — | — | — | — |
| 1000° . . . . | 8 | 2 | 1 | 1 | — | — |
| 1100° . . . . | 13 | 4 | 2 | 2 | 1 | 1 |
| 1200° . . . . | 37 | 11 | 8 | 7 | 5 | 4 |
| 1300° . . . . | 100 | 40 | 30 | 23 | 16 | 13 |
| 1400° . . . . | 318 | 131 | 91 | 60 | 46 | 33 |

S. Hilpert and P. Weiller found that the highly "leaded" glasses are attacked by exposure to air; M. Faraday found the addition of potash rendered the glass stable in air. According to W. Mostowitsch, and S. Hilpert and P. Weiller, the basic glasses up to and including the metasilicate easily dissolve in mineral acids and acetic acid with the separation of silica; the glasses with increasing proportions are less readily attacked, so that the $PbO.2SiO_2$ glass is attacked only by hydrofluoric acid. K. Beck said that lead metasilicate is readily decomposed by a 4 per cent. soln. of acetic acid, or a one per cent. soln. of nitric acid at 25°; the higher silicates are less readily attacked, and this the more the higher the proportion of silica. W. Balters also tested the solubility of the glasses in acetic acid. According to P. Bartel, the solubility of the lead glasses in 4 per cent. acetic acid decreases with increasing proportions of silica up to $PbO.2{\cdot}5SiO_2$; increases up to $PbO.3{\cdot}75SiO_2$; and finally decreases again. The resistance to attack is favoured by additions of calcium, barium, magnesium, zinc, or aluminium oxide. K. Beck and co-workers found that borax and boric acid decrease the resistance to attack, and alumina makes the glass more resistant. Owing to the toxic character of lead compounds used in glazes, and the slight solvent action of the mucous fluids, the Government prescribes certain restrictions in the use of lead compounds in pottery manufacture. A ground frit which does not give up more than 5 per cent. of lead oxide when shaken for an hour with 1000 times its weight of 0·25 per cent. hydrochloric acid is considered innocuous. W. Jackson and E. M. Rich showed that the amount dissolved under these conditions is determined by the fineness of grinding. The controversy which ensued is an admirable illustration of the influence of desire and temperament on the judgment. K. Beck found that alkali-lye forms alkali silicate and plumbate. The glasses richer in lead than the metasilicate are reduced by hydrogen at 240°; while the reduction of metasilicate and more siliceous glasses begins only above 300°. W. Mostowitsch observed that the lead silicates are reduced by hydrogen at 290°–300°, forming a mixture which may contain lead suboxide, $Pb_2O$; at 410°, the reduced lead collects in globules. C. Simmonds said that while hydrogen reduces the orthosilicate to silica and metallic lead, the metasilicates and more acid silicates furnish *silicites* (*q.v.*). Carbon monoxide, and hydrocarbons also reduce lead silicates to the metal. L. Kahlenberg and W. J. Trautman observed no reaction between silicon and lead metasilicate. J. Percy found that lead silicate is partially decomposed by lead sulphide, furnishing metallic lead; and E. Grieshammer noted the solubility of galena in molten glass.

The range of stability of **lead orthosilicate,** $Pb_2SiO_4$, is indicated in Fig. 191; the crystals are readily obtained by annealing the orthosilicate glass. Crystals of lead orthosilicate, were first made by H. C. Cooper and co-workers; and have not been observed in nature. The interference figure of the crystals is negative and biaxial. The index of refraction, and birefringence are high. S. Hilpert and co-workers found 7·005 for the sp. gr. of the glass and for the m.p., 740°; H. C. Cooper and co-workers gave 746° for the m.p., and 2·07 for the index of refraction of the orthosilicate glass. For the action of acids, etc., *vide supra.*

As indicated above, crystals of **lead metasilicate,** $PbSiO_3$, were prepared in the laboratory by L. Bourgeois before they were discovered in nature. The conditions under which they are formed are indicated in Fig. 187. They are conveniently prepared by annealing the glass. C. Palache and H. E. Merwin found a snow-white mineral at Alamos, Mexico, which they called **alamosite**, and the analysis corresponded with lead metasilicate. It forms radiated fibrous aggregates with a more or less pronounced spheroidal form. Isolated fibres are colourless and transparent, and are elongated in the direction of the axis of symmetry. The monoclinic crystals resemble those of wollastonite and have the axial ratios $a:b:c=1{\cdot}375:1:0{\cdot}924$, and $\beta=84°\,10'$; but whether or not the two minerals are isomorphous has not been established owing to appreciable difference in the lengths of the $a$-axis, and in the cleavages. S. Hilpert and P. Weiller found the artificial crystals are biaxial and rhombic or monoclinic. The cleavage of the

mineral parallel to (011) is perfect. The sp. gr. of the mineral is 6·488, and the hardness $4\frac{1}{2}$. S. Hilpert and P. Weiller gave 5·93 for the sp. gr. of the artificial silicate glass, and 6·36 for the crystals. K. Schulz gave 0·07886 for the sp. ht. of the glass; and 0·07807 for the crystals between 20° and 100°. The rate of crystallization of the metasilicate was found by S. Hilpert and R. Nacken to be slower than that of the orthosilicate; it is greatest at about 100° below the m.p. H. E. Merwin found that the optical axial angle $2V=65°$ for Na-light; and the indices of refraction $\alpha=1·947$, $\beta=1·961$, and $\gamma=1·968$. P. Weiller gave for the glass 1·96. The birefringence is strong, the optical character is negative. H. C. Cooper and co-workers gave 766° for the m.p. of the metasilicate; and S. Hilpert and co-workers, 766°. The mineral dissolves in nitric acid with the separation of gelatinous silica. For the action of acids, etc., on the metasilicate, *vide supra*. It has been shown that C. Simmonds's experiment from which he inferred that lead metasilicate is reduced by hydrogen to lead metasilicate admits of another interpretation, and consequently also his argument that one oxygen of lead metasilicate is attached to lead and to another oxygen atom and not to silicon $>Si<^{O.Pb}_{O.O}$ is inconclusive and probably wrong. R. Schwarz and G. A. Mathis made lead metasilicate, $PbSiO_3.H_2O$, by the action of a lead salt on water-glass, and they made **lead hemiamminometasilicate,** $PbSiO_3.\frac{1}{2}NH_3.H_2O$, by the action of ammonia on the metasilicate.

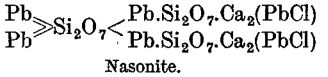
A. Sjögren and C. H. Lundström reported that white masses of a mineral with a curved lamellar structure were scattered through the iron ore along with calcite, garnet, tephroite, and galena near Pajsberg, Sweden, and the mineral was called **barysilite.** Analyses reported by A. Sjögren and C. H. Lundström, H. Sjögren, and R. Mauzelius correspond with *lead pyrosilicate*, or **lead orthodisilicate**, $Pb_3Si_2O_7$, where a small proportion of the lead may be replaced by manganese, magnesium, or calcium. P. Groth said that barysilite can be regarded as the normal salt of hexabasic disilicic acid, $H_6Si_2O_7$; or as a basic salt of metadisilicic acid, $(Pb_3O_2)Si_2O_5$. G. Cesaro regarded the water as constitutional, and assumed the silicate to be derived from $H_{10}Si_3O_{11}$. The compound was made by H. C. Cooper and co-workers, and by S. Hilpert and R. Nacken, Fig. 191. Impure crystals were also reported by E. S. Dana and S. L. Penfield, and by H. A. Wheeler occurring below the hearth of an old lead furnace. The crystals of barysilite are uniaxial and probably trigonal with the axial ratio $a:c=1:0·4863$. H. C. Cooper and co-workers said the artificial prismatic crystals belong to the dihexagonal bipyramidal class, and have the axial ratio $a:c=1:1·0246$; E. S. Dana and S. L. Penfield gave $1:1·032$. The index of refraction and the birefringence are high; and the interference figure positive and uniaxial. The crystals are pleochroic. The basal cleavage of the mineral is distinct, the prismatic cleavage less so. The sp. gr. is 6·11–6·55, H. Sjögren gave 6·72; the hardness is 3. S. Hilpert and R. Nacken found the m.p. to be 690°, as indicated in Fig. 191. The crystals may tarnish on exposure to air by the oxidation of the manganese. The mineral dissolves in nitric or hydrochloric acid with gelatinization of the silicic acid; and in the case of hydrochloric acid, with the separation of lead chloride.

C. J. Peddle [8] studied the properties of the glasses in the ternary and quaternary systems: $SiO_2$–PbO–$K_2O$ or $Na_2O$; and $SiO_2$–PbO–$K_2O$–$Na_2O$—*vide* glass. Many glasses approximate in composition, $(K,Na)_2O.PbO.6SiO_2$. J. N. von Fuchs said that a soln. of water-glass takes up lead oxide and forms a gelatinous mass which dries in air to a product resembling opal. V. Merz made the alkali-lead-glass by melting a mixture of water-glass and red-lead. A. Gray and J. J. Dobbie gave 3·591 for the sp. gr. of a glass, $2K_2O.5PbO.17SiO_2$, and 3·495 for $2K_2O.5PbO.22SiO_2$; and W. Beetz gave 4·71 for a heavy flint glass. E. Zschimmer and H. Schulz measured the hardness of these glasses. P. Suboff gave 0·1234 for the sp. ht.; W. Beetz, 0·04313 for the thermal conductivity of heavy flint glass; A. Winkelmann, 7·44 for the dielectric constant, and A. Gray and J. J. Dobbie,

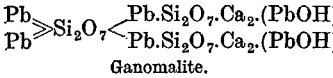
7·991 at 14° for the first of the above-mentioned glasses, and 7·966 for the second at 15°, and 7·630 at 120°. W. Beetz, and T. Gray measured the electrical conductivity, and A. Gray and J. J. Dobbie gave $35000\times10^{10}$ for the sp. resistance of the first of the above glasses up to 135°, and $18000\times10^{10}$ for the second up to 130°—see the glasses for the refractive indices. M. Stoemer found that no change occurs when the glass is heated in an oxidizing atm., but in a reducing atm., lead is volatilized, and the silicate is reduced. O. Anderson did not find sufficient volatilization of lead at 900°–1400° to affect the refractive index. C. Simmonds studied the reduction of lead silicates heated in hydrogen. According to E. Grieshammer, sulphur is not absorbed by the molten glass; and hydrogen sulphide attacks the glass at ordinary temp., and this the more, the greater the proportion of lead oxide. When powdered flint glass is mixed with sodium dioxide, zinc sulphide, and some potassium persulphate, J. H. Walton and H. A. Scholz found that it is decomposed when the mixture is ignited by magnesium wire as in the thermite process. T. E. Thorpe and C. Simmonds, and K. Beck and co-workers studied the action of acids—*vide supra*; and O. Inwald, the effect of phosphates. K. Beck and co-workers found the addition of 5 per cent. of borax makes lead monosilicate melt at 450°; the disilicate, at 510°; the trisilicate, at 600°; and the tetrasilicate, at 590°.

W. E. Ford and W. M. Bradley found colourless transparent crystals of a mineral from Franklin, New Jersey, which they called *margarosanite*. R. Mauzelius obtained a similar mineral near Langsban, Sweden. Analyses corresponded with **lead dicalcium trimetasilicate,** $PbCa_2(SiO_3)_3$, associated with a little manganese—approximately 1·14 per cent. MnO. The lamellar masses consist of triclinic crystals which, according to R. Mauzelius, have the axial ratios $a:b:c=0{\cdot}84419:1:1{\cdot}2838$, and $\alpha=74°\ 37'$, $\beta=129°\ 29'$, and $\gamma=101°\ 5'$. W. E. Ford and W. M. Bradley found that the plates have two good cleavages making an angle of 78°, and they are nearly perpendicular to the lamellar cleavage. The sp. gr. is 3·991, R. Mauzelius reported 4·39. The hardness is $2\frac{1}{2}$–3. W. E. Ford and W. M. Bradley gave for the refractive indices $\alpha=1{\cdot}730$, and $\gamma=1{\cdot}795$. The mineral is decomposed by nitric acid with the separation of gelatinous silicic acid.

A. E. Nordenskjöld[9] found prismatic grey or colourless crystals or granular masses of a plumbiferous mineral at Langban, Sweden, and in other localities; and he named it *ganomalite*—from $\gamma\acute{\alpha}\nu\omega\mu\alpha$, lustre. Analyses by J. Wiborgh, and G. Lindström corresponded with $Pb_3Si_2O_7.(Ca,Mn)SiO_4$. F. W. Clarke, following S. L. Penfield and C. H. Warren, represents it and nasonite as being related as indicated by the following schemes:



Nasonite.



Ganomalite.

This makes the mineral **hexaplumbic tetracalcium dihydroxytriorthosilicate.** G. Cesaro made some observations on the constitution. The tetragonal crystals of ganomalite have the axial ratio $a:c=1:0{\cdot}707$ (nearly). The (101) and (001) cleavages are distinct. G. Lindström gave 5·74 for the sp. gr., and A. E. Nordenskjöld, 4·98. The double refraction is strong, and the optical character positive. Ganomalite is readily soluble in nitric acid with the separation of gelatinous silica.

G. Flink[10] described irregular, foliated, pale-green masses of a mineral which was found at Langban, Sweden, and he called it *molybdophyllite*—from $\mu\acute{o}\lambda\upsilon\beta\delta os$, lead; and $\phi\acute{\upsilon}\lambda\lambda o\nu$, leaf—in allusion to its structure. The analyses corresponded with $PbMgSiO_4.H_2O$, **hydrated magnesium lead orthosilicate;** or, as F. W. Clarke suggested, $(PbOH)(MgOH)SiO_3$, *magnesium lead dihydroxymetasilicate.* G. Aminoff gave for the formula $(R''OH)_2SiO_3$. The crystals are hexagonal. G. Aminoff gives for the axial ratio $a:c=1:0{\cdot}549$, the perfect basal cleavage resembles that of mica. The thin flakes are somewhat flexible. The etching figures resemble those

of the members of the hexagonal system. G. Aminoff showed that the X-radiogram corresponds with the trigonal symmetry with $a:c$ about 1 : 0·549. The indices of refraction are $\omega$=1·8148, and $\epsilon$=1·7611 for Na-light. The birefringence is $\omega-\epsilon$=0·0537 ; and the optical character, negative. The sp. gr. is 4·717, and the hardness is 3–4. G. Aminoff discussed the relation between the crystals of friedelite and molybdophyllite. P. A. van der Meulen reported yellow, transparent, acicular crystals of *zinc lead oxydisilicate*, $5(Pb,Zn)O.2SiO_2$, of sp. gr. 6·153, in the glassy material from furnace flues.

S. L. Penfield and C. H. Warren found a white mineral in granular, cleavable masses at Franklin Furnace, New Jersey ; they called it *nasonite*—after F. L. Nason. Analyses correspond with $Pb_4(PbCl)_2Ca_4(Si_2O_7)_3$. F. W. Clarke's view of the composition is indicated in connection with ganomalite. This makes the mineral **hexaplumbic tetracalcium dichlorotriorthosilicate,** the crystals are probably tetragonal. The basal and prismatic cleavages are imperfect. The birefringence is strong and negative. The sp. gr. is 5·425, and the hardness 4. G. Lindström [11] found a massive mineral associated with the lead ore of Langban, Sweden ; it was named *melanotecite*—from μέλας, black ; and τηκεῖν, to melt—in allusion to its relation with hyalotecite. The analyses are summarized by $Pb_2Fe_2Si_2O_9$, corresponding with the formula of the isomorphous kentrolite. P. Groth represented the composition **lead diferryl orthodisilicate,** $Pb_2(FeO)_2Si_2O_7$. C. H. Warren gave $Pb_3Fe_4Si_3O_{15}$, which F. W. Clarke wrote $Fe\{SiO_4(FeO)Pb\}_3$. The colour of the mineral is dark green to black. H. G. Nordenskjöld gave for the axial ratios of the rhombic mineral $a:b:c$=0·6216 : 1 : 0·9041. G. Lindström found that the massive mineral is cleavable in two directions ; the sp. gr. is 5·73, and the hardness 6½. It is strongly pleochroic. H. G. Nordenskjöld measured the absorption spectrum. The mineral is decomposed by nitric acid.

A. Fouqué and A. Michel-Lévy [12] prepared a *lead-felspar*, or **lead dialuminodiorthosilicate,** $PbAl_2(SiO_4)_2$, or $Pb(AlSiO_4)_2$—*vide* felspar. K. Beck and co-workers found that 5 per cent. of alumina raises the softening temp. of the lead silicate glasses—the monosilicate to 595°, the disilicate to 660°, and the trisilicate to 700°. The attack by dil. acids is at the same time reduced. J. Szilasi prepared *lead ultramarine blue* by heating green sodium-ultramarine and a soln. of lead nitrate under press. L. Wunder made it by heating soln. of lead nitrate and ultramarine blue containing a small proportion of silica in a wrought-iron bomb at 160°. He made *lead-ultramarine-red* by heating ultramarine-red with a conc. soln. of lead nitrate in a wrought-iron tube at 160° ; and *lead-ultramarine-violet*, by treating ultramarine-violet in a similar manner.

A. Damour,[13] and G. vom Rath described crystals of a dark brown mineral from Southern Chile, and the mineral was called *kentrolite*—from κέντρον, a spike. Analyses were made by A. Damour, G. Flink, and D. Lovisato. The results can be represented by the formula, $Pb_2Mn_2Si_2O_9$ ; but if the contained manganese is quadrivalent, $Pb_2MnSi_2O_9$ ; on account of the isomorphism of this mineral and melanotecite, the former is preferred. P. Groth represented the compound as **lead dimanganyl orthodisilicate,** $Pb_2(MnO)_2Si_2O_7$. The crystals are often grouped in sheaf-like forms resembling stibite. The mineral also occurs massive. According to G. vom Rath, the rhombic crystals have the axial ratios $a:b:c$=0·6334 : 1 : 0·8830. M. Websky drew attention to the close agreement of the angles of kentrolite with those of descloizite. The cleavage is prismatic and distinct. The prismatic planes are often horizontally striated. The sp. gr. is 6·19, and the hardness 5. The surface of kentrolite is often black owing to surface oxidation. The mineral dissolves in sulphuric acid with the separation of silica and manganese oxide ; and in hydrochloric acid with the evolution of chlorine.

A. E. Nordenskjöld [14] found a massive and coarsely crystalline, white or grey, mineral associated with the felspar at Langban, Sweden. It was named *hyalotecite* —ὕαλος, glass ; and τήκειν, to melt. Analyses by A. E. Nordenskjöld, and A. Lindström corresponded with the formula $R_4BFSi_6O_{17}$, where R represents

Ba, Ca, and Pb. F. W. Clarke represents its composition by two possible formulæ:

$$Si_2O_5\begin{cases}R-Si_2O_5-R-BO_2\\R-Si_2O_5-R-F\end{cases}\qquad O=B\begin{cases}R\\R\\Si_3O_8\end{cases}\begin{matrix}>R\\<Si_3O_8>R\\<R-F\end{matrix}$$

The latter agrees with **lead barium calcium fluoboryl diorthotrisilicate ;** and P. Groth represents it as a metasilicate, $HR_4B(SiO_3)_6$, with F replacing some of the hydroxyl. G. Cesaro made some observations on this subject. According to A. des Cloizeaux, the cleavage is easy in two directions at an angle approximately 90°, and less easy in a third direction in the same zone. The crystals are optically biaxial and positive. The optic axial angle $2H$=98°–99° for the red ray. The sp. gr. is 3·81, and the hardness 5–5½.

S. L. Penfield and H. W. Foote [15] found a unique mineral at Franklin Furnace, New Jersey, which they called *roeblingite*—after W. A. Roebling. It occurs in white aggregates of prismatic crystals and massive. The composition corresponds with a mixture of $5CaH_2SiO_4+2PbOCa(SO_4)$, or *calcium lead sulphatohydrosilicate.* The sp. gr. is 3·433, and the hardness 3·25. It readily dissolves in dil. acid, yielding gelatinous silica on evaporation. The *wilkeite*, $3Ca_3(PO_4)_2.CaCO_3.3Ca_2\{(SiO_4)(SO_4)\}$, of A. S. Eakle and A. F. Rogers is probably a mixture. The hexagonal prism has its axial ratio $a:c=1:0·73$; the hardness is 5; the sp. gr. 3·234 at 25°; the index of refraction 1·640; and the birefringence, *c.* 0·004.

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## § 51. The Manganese Silicates

W. A. Lampadius,[1] P. Berthier, and N. G. Sefström tested the fusibility of various mixtures of manganese oxide and silica—$MnO : SiO_2 = 4:1, 2:1, 1:1$, and $1:2$—in their studies on slags. Various mixtures of these two constituents with magnesia, lime, ferrous oxide, and alumina were also tried. R. Rieke measured

the fusibility of mixtures of clay and manganese oxide. S. Avery showed that the manganiferous glasses become strongly coloured when exposed to sunlight, the ultra-violet rays, or radium radiations—*vide* glass. I. Bang prepared a manganese blue by calcining an intimate mixture of manganese oxide, silica, and baryta or soda-lime. According to A. I. Walcker, aq. soln. of manganese sulphate and sodium silicate give a white precipitate which has not been closely examined. For colloidal manganese silicate, *vide* water-glass. F. Dörinckel investigated mixtures of manganous oxide and 20–60 molar per cent. of silica fused in a platinum crucible; mixtures with more manganese oxide attacked the platinum, and those with more silica only fused above the m.p. of platinum. The mixtures are melted a second time to ensure a complete reaction. The resulting curves, Fig. 193, show that a manganous orthosilicate is formed at 1323° between some primary crystals and the liquid; and that with mixtures containing 49–60 molar per cent. of silica, primary crystals rich in silica react with the liquid at 1215° to form manganous metasilicate. The eutectic between these two silicates is at 1190°, with 45 molar per cent. of silica. R. Akerman measured the heats of solidification of a number of manganese calcium silicate slags.

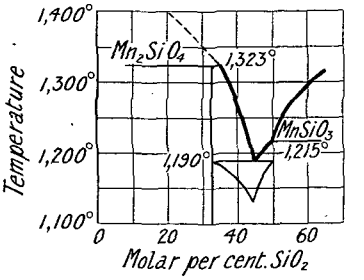



FIG. 193.—Freezing Points of Mixtures of Manganous Oxide and Silica.

A. Breithaupt [2] applied the term **tephroite**—from τέφρος, ash-coloured—to an ash-grey manganous silicate which he examined. Specimens have been found in various other localities. A variety from Langban, Sweden, was called by H. Sjögren *picrotephroite*—πικρός, bitter—in allusion to the magnesian content. Analyses were reported by G. J. Brush, W. G. Mixter, G. C. Stone, A. Damour, L. J. Igelström, J. Wiborgh, F. Pisani, G. Paykull, A. des Cloizeaux, C. F. Rammelsberg, T. Thomson, J. H. L. Vogt, H. Sjögren, and J. C. H. Mingaye and co-workers. In the idealized case, tephroite corresponds with **manganese orthosilicate**, $Mn_2SiO_4$; but there is usually some magnesia present, 1·38–18·60 per cent.; and 0–11·61 per cent. of zinc oxide; as well as a small proportion of ferrous oxide and lime. Usually, tephroite is regarded as a mixture, $nMn_2SiO_4.Mg_2SiO_4$, with $n$ greater than unity. P. Berthier, and L. Bourgeois obtained crystals of tephroite by fusing the component oxides in the right proportions; and A. Gorgeu, by passing hydrogen or carbon dioxide sat. with steam over a heated mixture of manganese chloride and silica; rhodonite is formed unless the action is continued for a long time. The presence of alkali chloride accelerates the formation of tephroite. J. H. L. Vogt, and J. H. Whiteley and A. F. Hallimond found tephroite and rhodonite crystals in some steel converter slags.

Crystals of tephroite are rare; the mineral usually occurs in crystalline masses; the colour is grey, greyish-red, flesh-red, reddish-brown, and rose-red. The colour often darkens on exposure to air. The crystals belong to the rhombic system, and, according to H. Sjögren, have the axial ratios $a:b:c=0{\cdot}46004:1:0{\cdot}59389$; G. Flink gave $0{\cdot}4621:1:0{\cdot}5914$. The crystals are isomorphous with olivine. Observations were also made by A. des Cloizeaux. E. Kittl found that manganese orthosilicate glass has a smaller number of centres of crystallization than other orthosilicates, and unlike them forms radiating groups of crystals. The cleavage is distinct in two directions at right angles to one another. A. des Cloizeaux, and G. Flink gave for the optic axial angles $2H_a=81°\,4'$, $2H_0=112°\,16'$, and $2V_a=76°\,6'$ for the yellow ray; $2H_a=84°\,4'$, and $2E=161°\,48'$ for the red ray; and $2H_a=82°\,59'$ and $2E=156°\,35'$ for the blue ray. The sp. gr. is 3·95–4·15; F. M. Jäger and H. S. van Klooster gave 4·044 at 25°/4° for the sp. gr. The hardness is 6–7. E. Kittl, and F. M. Jäger and H. S. van Klooster, 1290°–1300°, gave 1170°–1200° for the m.p. The last-named found that the index of refraction exceeds 1·739;

the birefringence is strong; and the optical character negative. S. E. Larsen gave for the indices of refraction $\alpha$=1·759–1·767, $\beta$=1·785–1·792, and $\gamma$=1·797–1·805. The crystals are strongly pleochroic. Manganese orthosilicate is decomposed by hydrochloric acid without the evolution of chlorine, but with the separation of gelatinous silicic acid. A. Gorgeu also found that chlorine water, or a soln. of sodium hydrocarbonate, readily attacks this silicate; when melted with manganese chloride and silica with the exclusion of air and water vapour, the metasilicate is formed.

L. J. Igelström [3] applied the term *hydrotephroite* to what appeared to be a hydrated tephroite from Pajsberg, Sweden. The composition approximated *ditritahydrated manganese orthosilicate*, $3(Mn,Mg)_2SiO_4.2H_2O$; the colour was pale red; and the hardness 4. It is decomposed by acids with the separation of gelatinous silica. He also applied the term *epigenite* and *neotesite* to other analogous forms approximating *hydrated manganese orthosilicate*, $(Mn,Mg)_2SiO_4.H_2O$. It is decomposed by acids without the gelatinization of the silica. M. H. Klaproth analyzed another hydrate from Klapperud which had the composition *dihydrated manganese orthosilicate*, $Mn_2SiO_4.2H_2O$. A. H. Phillips described needle-like crystals of a mineral from Franklin, New Jersey, which had a composition corresponding with $(Mg,Mn,Zn)_8Si_3O_{14}.2H_2O$, and which he called *gageite*—after R. B. Gage. Bementite—*vide infra*—can be regarded as *manganese dihydro-orthosilicate*, $MnH_2SiO_4$. S. L. Penfield and C. H. Warren described a pale purple-red mineral from Franklin Furnace, New Jersey, which they called *leucophoenicite*—from λευκός, pale; and φοίνιξ, purple-red. The composition corresponds with $Mn_3(MnOH)_2(SiO_4)_3$, *manganese dihydroxy-triorthosilicate*. It is considered to resemble a humite with all the fluorine replaced by hydroxyl. The crystals are monoclinic. The sp. gr. is 3·848, and the hardness 5½–6. It is slightly pleochroic. It readily dissolves in hydrochloric acid yielding gelatinous silica on evaporation. The water is expelled at a red heat. F. W. Clarke considers both gageite and leucophoenicite to be members of the humite group, and, writing R for Mg, Zn, Mn, uses graphic formulæ of the type:

$$\begin{matrix}ROH\\ROH\end{matrix}\!>\!SiO_4\!<\!\begin{matrix}R\\R\end{matrix}\!>\!SiO_4\!<\!\begin{matrix}R\\R\end{matrix}\!>\!SiO_4\!<\!\begin{matrix}ROH\\ROH\end{matrix}$$

S. L. Penfield and C. H. Warren described some delicate bluish-green, prismatic crystals which they found at Franklin Furnace, New Jersey, to which they applied the name *glaucochroite*—from γλαυκός, blue-green; and χρόα, colour. The composition approximates to an isomorphous mixture of *calcium and manganese orthosilicates*, $(Ca,Mn)_2SiO_4$, with the ratio Ca : Mn=1 : 1. The rhombic crystals have the axial ratios $a:b:c$=0·440 : 1 : 0·566; twinning plane is (011), and the vertical axes cross at 58° 31′. The optic axial angle $2V$=60° 51′. The indices of refraction are $\alpha$=1·679–1·686, $\beta$=1·716–1·722, and $\gamma$=1·729–11·735; and the birefringence $\gamma-\alpha$=0·049. The sp. gr. is 3·407, and the hardness 6. The mineral is soluble in hydrochloric acid.

C. Palache and W. T. Schaller [4] found a bright pink or reddish-brown mineral in monoclinic crystals at Franklin Furnace, New Jersey; they called it **hodgkinsonite.** The analyses correspond with **manganese zinc dihydroxyorthosilicate,** $Ma(ZnOH)_2SiO_4$. The axial ratios are $a:b:c$=1·539 : 1 : 1·1165, and $\beta$=84° 33½′. The mean refractive index is 1·73. The mineral decrepitates when heated, and fuses to a brown enamel; no water is lost at 110°. It is readily soluble in acids with the separation of gelatinous silica. S. G. Gordon made some observations on this mineral.

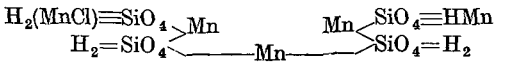
A. Schneider [5] reported small prismatic crystals of a mineral in the manganese mines at Nanzenbach, Germany, which he called **inesite**—from ἶνες, flesh fibres—in allusion to the colour and structure; and G. Flink found some in the mine at Harrtig, Sweden, which he called *rhodotilite*—from ῥόδαν, rose; and τίλος, fibre—and later, he established its identity with inesite. A. Hamberg said that the *manganocalcite* described by A. des Cloizeaux, and P. Groth and J. A. Krenner was an inesite. A. Schneider represented his analyses by $(Mn,Ca)(MaOH)_2Si_3O_8.H_2O$, in agreement with the fact that part of the water persists at 300°. Analyses were also made by A. Hamberg, O. C. Farrington, and C. Flink. G. Flink gave the formula $(Ca,Mn)SiO_3.\frac{1}{2}H_2O$; O. C. Farrington, $H_2(Mn,Ca)_6Si_6O_{19}.3H_2O$;

F. Zambonini, $H_2(Mn,Ca)_2Si_2O_7.\frac{2}{3}H_2O$, **hydrated manganese calcium orthodisilicate**. F. W. Clarke gave $Mn_2.Si_2O_9(Mn.Si_2O_7.MnH_3)_2+2H_2O$, plus $Ca_2.Si_2O_7(Ca.Si_2O_7,H_3)_2+2H_2O$, where $Si_2O_7$ is the sexivalent radicle of orthodisilicic acid. A. Hamberg showed that the amount of moisture varies markedly with the humidity of the air; and F. Zambonini found that 1·98 per cent. of water is lost at 110°, and 5·98 per cent. at 310°. The dehydration curve consists of two parts: the part up to 200° does not correspond with any perceptible change in the mineral, while above that temp. the nature of the mineral is changed. A. Schneider found that 4·54 per cent. of water was lost at 110°; and 0·48 at 200°; 2·23 at 300°; 0·62 at 440°; and 1·35 on ignition—total loss, 9·22 per cent.

The colour of the mineral is rose-red or flesh-red, and on exposure, this coloration disappears. The crystals usually occur in fibrous masses, often radiated and spherulitic. The prismatic crystals, according to R. Schiebe, and A. Schneider, belong to the triclinic system, and have the axial ratios $a:b:c=0{\cdot}975266:1:1{\cdot}32078$, and $\alpha=92°\ 18'\ 12''$, $\beta=132°\ 55'\ 54''$, and $\gamma=93°\ 50'\ 42''$. The cleavage parallel to (010) is perfect, less so when parallel to (100) and still less to $(1\bar{1}0)$. The sp. gr. approximates 3·03, and the hardness 6. F. Ulrich gave 3·03 for the sp. gr.; and $\alpha=1{\cdot}618$, $\beta=1{\cdot}6369$, and $\gamma=1{\cdot}644$ for the indices of refraction. R. Schiebe found the optic axial angle 2G to be 64° for Li-light, 63° 28′ for the Na-light, and 62° 51′ for the Tl-light. The index of refraction is 1·7782. The optical character is negative; the crystals are faintly pleochroic.

D. F. Hewett and E. V. Shannon [6] reported rhombic crystals of a mineral from Costa, Oriente Province, Cuba, and he called it *orientite*. The composition approximates $4CaO.2Mn_2O_3.5SiO_2.4H_2O$, or, with manganese tervalent, $Ca_4Mn_4(SiO_4)_5.4H_2O$. The sp. gr. is 3·05, and the hardness 4·5–5·0. The biaxial crystals have the refractive indices $\alpha=1{\cdot}758$, $\beta=1{\cdot}776$, and $\gamma=1{\cdot}795$. The mineral is not attacked by cold hydrochloric acid, but is readily dissolved by the hot acid with the separation of flocculent silica, and the evolution of chlorine; it is partly decomposed by moderately conc. sulphuric acid; and is almost insoluble in conc. nitric acid.

E. Bertrand [7] found a manganese silicate in the mines at Aderville, Hautes Pyrénées, and he named it **friedelite**—after C. Friedel. Analyses were made by E. Bertrand, A. Gorgeu, C. Palache, H. Lienau, G. Lindström, L. J. Igelström, and A. Hoffmann and F. Slavik. Formulæ have been proposed by C. F. Rammelsberg, E. S. Dana, F. Zambonini, and A. Hoffmann and F. Slavik. P. Groth, and F. W. Clarke gave $H_7Mn_4(MnCl)(SiO_4)_4$, **manganese chloroheptahydrotetrorthosilicate,** or graphically:




which is analogous with the formula for dioptase when MnCl′ is replaced by hydrogen, and manganese by copper. C. Palache gave: $H_9Mn_7(MnCl)(SiO_4)_6$, and $H_{20}Mn_{14}(MnCl)_2Si_{12}O_{49}$; G. Aminoff, $H_2\{R''(OH,Cl)\}(SiO_3)_2$; and F. Zambonini, $H_{16}R''_{11}(MnCl)_2(SiO_4)_{10}$. The rose-red crystals are commonly tabular, and the mineral also occurs massive with a saccharoidal structure and distinct cleavage, passing into compact masses with indistinct cleavage. The crystals belong to the trigonal system with the axial ratio $a:c=1:0{\cdot}5624$; G. Aminoff obtained $1:0{\cdot}532-0{\cdot}562$, and this agreed with the X-radiograms. The faces $(10\bar{1}0)$ and and $(10\bar{1}1)$ are often striated. The (0001) cleavage is perfect; the sp. gr., 3·07; the hardness, 4–5; the double refraction is strong; and the optical character, negative. The mineral dissolves in hydrochloric acid with the separation of gelatinous silicic acid. G. Aminoff discussed the relations between the crystals of molybdophyllite and friedelite.

According to J. F. L. Hausmann,[8] J. Clason and H. Gahn discovered in the iron mines of Bjelkegrura, Sweden, hexagonal prisms of a ferruginous silicate which they

called *pirodmalite*—from πῦρ, fire; and ὀσμή, odour—in allusion to the odour when heated; D. L. G. Karsten altered the term to **pyrosmalite**. R. J. Haüy, and J. A. H. Lucas called it *fer muratê*. Analyses were made by J. Lang, E. Ludwig, F. Wöhler, W. Hisinger, N. Engström, A. Gorgeu, and F. Zambonini; and attempts to deduce a formula were made by C. F. Rammelsberg, E. Ludwig, F. W. Clarke, G. Tschermak, F. Zambonini, and A. Gorgeu. The isomorphism of the mineral with friedelite, and the similarities in the properties of the two minerals show that the constitution and composition are the same except that much of the manganese of friedelite is replaced by ferrous iron. This makes pyrosmalite **manganese ferrous chloroheptahydrotetrorthosilicate,** $H_7(Mn,Fe)_5Cl(SiO_4)_4$. The crystals are thick and prismatic, or else they are tabular. The mineral also occurs massive and foliated. The colour is greenish-black, pale liver-brown, grey, or green. The crystals are often brown externally, and light yellowish-green internally. Observation on the crystals were made by J. F. L. Hausmann, W. Haidinger, G. Flink, R. J. Haüy, and H. J. Brooke. According to A. E. Nordenskjöld, the axial ratio of the trigonal crystals is $a:c=1:0{\cdot}5308$. G. Aminoff found the X-radiogram agreed with the relations of this mineral with friedelite and molybdophyllite. The cleavage parallel to (0001) is perfect, and imperfect parallel to $(10\bar{1}0)$. The sp. gr. is 3·06–3·19, and the hardness 4–4½. E. S. Larsen gave $\omega=1{\cdot}675$, and $\epsilon=1{\cdot}636$. G. Flink also showed that $\omega$ and $\epsilon$ were respectively 1·768 and 1·644 for red light; 1·682 and 1·647 for yellow light; and 1·686 and 1·651 for green light. The double refraction is strong, and the optical character negative. P. E. W. Oeberg gave 0·1978 for the sp. ht. F. Zambonini found that there is a change when the mineral is heated to 200°; and that a large proportion of the water is lost at about 400°. The mineral is decomposed by acids with the separation of gelatinous silica.

J. Jåkob[9] observed a **manganese tetramesosilicate,** $3MnO.4SiO_2.3H_2O$, from Val d'Err, Graubünden. He called it **parsettensite** from the occurrence at Alp Parsettens. The copper-red mineral occurs massive, it is uniaxial, and probably pseudohexagonal. Its sp. gr. is 2·590, and its indices of refraction $\omega=1{\cdot}576$ and $\epsilon=1{\cdot}546$. Part of the water is expelled at 100°, and the remainder at dull redness. In the oxidizing flame it fuses to a brownish-black glass. It is decomposed by hot hydrochloric acid with the separation of silica. A variety of parsettensite with an extra Mn(OH) group was called **errite** after its occurrence at the Val d'Err. Errite is brownish-red, and has the sp. gr. 2·681, and the indices of refraction $\omega=1{\cdot}575$, and $\epsilon=1{\cdot}547$.

G. Flink[10] reported colourless rhombic dodecahedra of a mineral, which he called **harstigite,** among the garnets at a Harstig mine, Pajsberg, Sweden. The analysis approximates $H_7(Ca,Mn)_{12}Cl_3Si_{10}O_{40}$; and F. W. Clarke represents the analysis $H_4Ca_5Mn_2Al_2(SiO_4)_6$, making harstigite **calcium dimanganous dialuminium tetrahydrohexorthosilicate.** The small prismatic crystals belong to the rhombic system, and have the axial ratios $a:b:c=0{\cdot}71479:1:1{\cdot}01495$. No cleavage was reported. The optic axial angles are $2H_a=57°\ 50'$ for red light, 57° 56′ for yellow light, and 58° 8′ for green light; $2V=90°\ 27'$. W. Ramsay gave for the indices of refraction with Na-light, $\alpha=1{\cdot}6782$, and $\gamma=1{\cdot}68308$. The optical character is positive. The sp. gr. is 3·049, and the hardness 5½. The ignited powder readily dissolves in hydrochloric acid with the evolution of chlorine.

In the eighteenth century, there were many references to *Rothbraunstein*, *Rothstein*, and *Rothspath*. A sample of this mineral from Kapnik, Hungary, analyzed by A. von Ruprecht,[11] was called by J. J. N. Huot, *kapnikite;* by D. L. G. Karsten, *Kapnik felspar:* and by A. G. Werner, *manganese-spar*. According to E. F. Germar, C. F. Jasche suggested the term **rhodonite**—from ῥόδον, a rose—in allusion to the beautiful red colour. The term rhodonite was adopted by F. S. Beudant, J. F. L. Hausmann, and most subsequent writers.

R. J. Haüy called the mineral *manganèse oxydé rose silifère;* C. C. von Leonhard, *Kieselmangan;* M. H. Klaproth, *Schwarzbraunsteinerz;* F. S. Beudant, *opsimose*—from

ὄψιμος, late; E. F. Glocker, *manganolite*; and more or less impure or altered varieties have received various names. They were analyzed by A. Schneider, E. Schweizer, etc. P. Berthier called a more or less oxidized form from St. Marcel, Piedmont, *marceline*. from Pesillo, and J. von Jewreinoff's *heterocline*, analyzed by J. J. N. Huot's *pesillite* ly mixtures of a hydrated silicate, silica, and wad. C. F. Jasche, J. J. Berzelius, are proba a green manganiferous earthy silicate from Schebenholze, Harz, and E. F. Germar called nge—in allusion to the change of colour from green to yellowish-*allagite*—from ἀλλαγή, cha; it was analyzed by A. P. J. du Mênil, and shown to contain brown on exposure to air ermar called a rose-red sample *hydropite*—from ὕδρωψ, dropsy; some carbonate. E. F. G variety associated with allagite was called *photicite* or, according and a yellowish carbonated —from φωτίζω, enlightening. Photicite was analyzed by to R. Brandes, *photizite*- A. Damour, T. Thomson, and A. P. J. du Mênil. The grey or A. H. Chester, P. Berthier, *Hornmangan*—and the *tomosite* of C. F. Jasche and E. F. Germar brown *corneous manganese*— ticite. L. J. Igelström called a variety from Pajsberg, Sweden, are of a similar nature to pho idized and hydrated varieties are represented by *klipsteinite*—*pajsbergite*. More or less o hich is an amorphous black or brown mass from Klapperud, after A. von Klipstein—w n Kobell, and J. F. Bahr. H. Fischer showed that the supposed and was described by F. v J. Igelström described *stratopeite*—from *stratum*, and πηός, mineral is a mixture. curring at Pajsberg, Sweden; J. F. Bahr, and A. E. Arppe, a relation by affinity— Wittingi, Finland; and P. T. Cleve, N. and A. E. Nordenskjöld, *wittingite*, occurring at *ptocite*—from νεότοκος, of recent origin—occurring at Gestrikland, and A. Schneider, *ne* other places. J. T. Pardee and co-workers analyzed the neotocite Sweden, and several hington. The three last-named varieties of altered rhodonite appear from Western Was E. T. Wherry discussed the proposal to apply the term neotocite to the to be the same. oidal manganese silicates with the ratio $MnO : SiO_2$ approximating 1 : 1. amorphous or col pplied the term *hydrorhodonite* to a hydrated variety of rhodonite from N. Engström a den. A. Hamberg's *caryopilite*—from κάρυον, walnut; and πῖλος, felt—Langban, Sw Pajsberg, Sweden, and consists of reniform or stalactitic nodules with felted masses of radiating fibres. The composition approximates $4MnO.3SiO_2.3H_2O$, but the material analyzed was impure. J. T. Pardee and co-workers suggested that caryophilite is the same as bementite. According to C. Hintze, through some confusion of cummingtonite, and the rhodonite from Cummington, Mass., analyzed by R. Hermann, C. F. Rammelsberg and others have referred to a *manganese-amphibole* which G. A. Kenngott called *hermannite*; no such amphibole is known.

Analyses of rhodonite were reported by J. J. Berzelius,[12] C. F. Rammelsberg, L. Colomba, J. J. Ebelmen, H. von Foullon, A. Hamberg, D. Fino, F. A. Römer, A. Roccati, L. J. Igelström, M. Weibull, A. H. Chester, J. D. Dana, G. Lindström, L. V. Pirsson, L. Sipocz, R. Hermann, W. Camac, C. U. Shepard, G. vom Rath, H. Hahn, F. Pisani, and F. Fromme. Analyses of the purer samples of rhodonite correspond with **manganese metasilicate,** $MnSiO_3$. A. Brongniart described a greyish-red calciferous manganese metasilicate from Mexico, and called it *bustamite* —after M. Bustamente. A. Breithaupt showed that it belongs to the pyroxene group, and J. F. L. Hausmann demonstrated that it is closely related with rhodonite. Calcareous varieties were analyzed by F. Pisani, G. Lindström, G. vom Rath, J. Fromme, and L. J. Igelström. The formulæ correspond with mixtures $n CaSiO_3.MnSiO_3$. E. S. Larsen and E. V. Shannon represent the composition by $CaMn(SiO_3)_2$, and consider the mineral to be a triclinic pyroxene, *i.e.* a sub-species of rhodonite. It has the optic axial angle $2V=44°$, and the indices of refraction $\alpha=1{\cdot}662$, $\beta=1{\cdot}674$, and $\gamma=1{\cdot}676$.

According to A. S. Ginsberg, the f.p. curve, Fig. 194, of mixtures of *calcium and manganese metasilicates*—the former with a m.p. 1512° and the latter with a m.p. 1218°—shows a minimum at 1184° corresponding with 12·8 molar per cent. of calcium metasilicate. S. Kallenberg gave 1180° for the m.p. of manganese metasilicate; and 1150° for the m.p. of the entectic with 10 per cent. of calcium metasilicate. A. S. Ginsberg infers that wollastonite and rhodonite are isodimorphous, furnishing monoclinic mixed crystals. Wollastonite is triclinic; hence, he inferred that there must be a monoclinic variety of rhodonite. A. S. Ginsberg measured the sp. gr. and hardness of binary mixtures of calcium and manganese metasilicates. E. Kittl found the glass in crystallizing developed 120 nuclei per sq. cm. P. Lebedeff obtained the f.p. curve of mixtures of *manganese and strontium metasilicates*, but found there is a great tendency to form glasses with solid soln. near the m.p. The two silicates are isomorphous. Similarly with mixtures of

*manganese and barium metasilicates.* The f.p. curve has a minimum, but it was not exactly located because of glass formation. He also found that *magnesium and manganese metasilicates*, Fig. 195, form two series of sol'd soln., with a break in the f.p. curve at 1328° and 40 molar per cent. $MgSiO_3$. The m.p. of magnesium metasilicate is 1535°, and of manganese metasilicate 1210°. The optical examination shows that the crystals at the magnesium end of the series have the properties

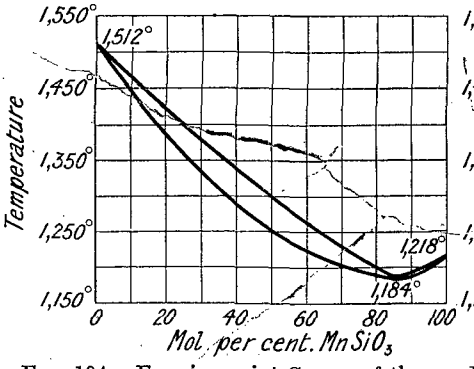



FIG. 194.—Freezing-point Curves of the Binary System: $CaSiO_3$–$MnSiO_3$.

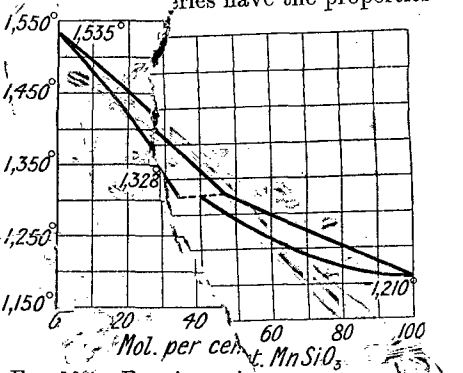



FIG. 195.—Freezing-point Curves of the Binary System: $MgSiO_3$–$MnSiO_3$.

of enstatite, and those at the manganese end the properties of rhodonite, confirming the representation of the system as one of two series of solid soln.

A crystalline and foliated mineral resembling red felspar was mentioned by S. Fowler, T. Thomson, and S. Robinson as a siliceous oxide of manganese. It occurs near Sterling, New Jersey, and was called *fowlerite* by C. U. Shepard. E. F. Glocker showed that it is closely related to rhodonite; and R. Hermann found that it contained zinc, so that C. F. Rammelsberg called the zinciferous rhodonites, fowlerite. C. U. Shepard also called a variety of fowlerite *keatingine*. The iron-black *dyssnite* of T. Thomson was considered to be *manganese sesquisilicate*; J. D. Dana said that it is an altered fowlerite. Analyses of fowlerite were made by C. U. Shepard, C. F. Rammelsberg, W. Camac, and L. V. Pirsson. The formulæ correspond with $m CaSiO_3.nZnSiO_3.MnSiO_3$, which appears to be a mixture of silicates in isomorphous association.

Rhodonite has been reported by F. Wiser,[13] P. von Jeremejeff, E. Tacconi, C. W. C. Fuchs, J. H. Whiteley and A. F. Hallimond, and J. H. L. Vogt in various iron and steel furnace slags. P. Berthier, N. G. Sefström, and L. Bourgeois made rhodonite by fusing a mixture of the constituent oxides. A. S. Ginsberg, and S. Kallenberg employed a similar process, and A. Gorgeu fused a mixture of silica and manganous chloride in an atm. of moist hydrogen or air. Good crystals were obtained in the presence of alkali chloride. According to S. Kallenberg, although the crystalline form of synthetic rhodonite is very similar to that of the naturally occurring rhodonites, it differs from the minerals in the positive character of its double refraction. Synthetic rhodonites containing iron and magnesium silicate are optically similar to the pure manganese silicate, but in the presence of 5 per cent. of calcium silicate the positive double refraction changes to negative. Since the natural rhodonites generally contain calcium silicate in greater proportion than this, the apparent discrepancy in the optical behaviour of synthetic rhodonite and the minerals is readily explained.

Rhodonite occurs in crystals or cleavable masses; and also in compact or granular masses. The colour ranges from a light brownish-red to flesh-red, and rose-pink; it is sometimes greenish or yellowish when impure; and sometimes black on the outside where it has been exposed to air. The fine red rhodonite stone is quarried in the Ural Mountains and used for ornamental purposes. The crystals are often large with rounded edges; commonly tabular, and spear-shaped.

As emphasized by H. Rose,[14] the crystals sometimes resemble pyroxene in habit G. Rose regarded the crystals as monoclinic, but H. Dauber showed tha they are triclinic, and, according to G. Flink, have the axial ratios $a:b:=1{\cdot}07285:1:0{\cdot}62127$, and $\alpha=103°\ 18'\ 7''$, $\beta=108°\ 44'\ 8''$, and $\gamma=81°\ 39'\ 16''$ Observations on the crystals have been made by J. D. Dana, E. S. Larsen an E. V. Shannon, A. des Cloizeaux, F. Tamnau, P. Groth, N. von Kokscharoff, R. P. Greg, H. Sjögren, A. Hamberg, V. Goldschmidt, M. Weibull, L. V. Pirsson, C. Anderson, W. E. Ford and R. D. Crawford, and H. L. Ungemach. C. Hlawatsch called triclinic crystals similar to but not identical with rhodonite, lining the cavities of slags, *vogtite*—after J. H. L. Vogt. The cleavage parallel to (110) is perfect, and that parallel to (001) less perfect. T. L. Walker investigated the corrosion of rhodonite. G. Flink gave for the optic axial angles $2H_a=79°\ 25'$, $2H_0=109°\ 56'$, and $2V_a=75°\ 57'$ for the red Li-ray; $2H_a=79°\ 0'$, $2H_0=108°\ 25'$, and $2V_o=76°\ 12'$ for the yellow Na-ray; and $2H_a=78°\ 38\frac{1}{2}'$, $2H_0=107°\ 13\frac{1}{2}'$, and $2V_a=76°\ 22'$ for the green Tl-ray. A. des Cloizeaux gave for bustamite $2E=68°$ for the red ray and 72° for the green ray. E. Kittl found that the glass during crystallization developed 240 nuclei per sq. cm. The sp. gr. ranges from 3·40 to 3·68. J. Jakob gave 3·416 for the sp. gr. of rhodonite; and A. S. Ginsberg found for various mixtures of calcium and manganese metasilicates, the linear relations:

| $MnSiO_3$ | 0 | 15 | 40 | 60 | 70 | 85 | 90 | 100 per cent. |
|---|---|---|---|---|---|---|---|---|
| Sp. gr | 2·919 | 2·992 | 3·080 | 3·180 | 3·219 | 3·302 | 3·313 | 3·350 |

G. Stein gave 3·44 for the sp. gr. of the artificial crystals of manganese metasilicate, and 3·36 for the sp. gr. of the glass. F. M. Jäger and H. S. van Klooster gave 3·716 for the sp. gr. of manganese metasilicate at 25°/4°. The hardness of rhodonite is 5·5–6·5. A. S. Ginsberg found that with mixtures of calcium and manganese metasilicate, the relative hardness has a maximum for mixtures with 15 per cent. $MnSiO_3$:

| $MnSiO_3$ | 0 | 15 | 40 | 70 | 85 | 100 |
|---|---|---|---|---|---|---|
| Hardness | 0·041 | 0·045 | 0·055 | 0·058 | 0·061 | 0·048 |

C. Doelter gave 1170°–1195°, and 1220°–1240°, for the m.p. of different samples of rhodonite; A. Woloskoff, 1216°; N. V. Kultascheff, 1180°; A. S. Ginsberg, 1219°; S. Smolensky, 1218°; G. Stein, 1470°–1500°; F. M. Jäger and H. S. van Klooster, 1273°; and S. Kallenberg, 1180°. For the m.p. of mixtures of manganese silicate with calcium and magnesium silicates, *vide* Figs. 194 and 195. C. Doelter gave 1140°–1170° for the m.p. of fowlerite. P. E. W. Oeberg found the sp. ht. of rhodonite to be 0·1699; H. le Chatelier gave 5·4 Cals. for the heat of formation; and S. Wologdine, 7·725 Cals. For the heat of crystallization, O. Mulert gave 0·0649 Cals. per gram, or 8·52 Cals. per mol.; and for the heat of soln. of crystalline and glassy manganese silicate in 20 per cent. hydrofluoric acid, he gave respectively 53·07 and 61·59 Cals. per mol. A. Michel-Lévy and A. Lacroix gave for the mean index of refraction, $\beta=1{\cdot}73$; and for the birefringence, $\gamma-\alpha=0{\cdot}010$–$0{\cdot}011$. F. M. Jäger and H. S. van Klooster gave 1·739–1·733 for the index of refraction; and J. Jakob, $\alpha=1{\cdot}721$, and $\gamma=1{\cdot}730$. The optical character is negative. The crystals are pleochroic; this was observed by J. Jakob, G. Flink, A. des Cloizeaux, W. Ramsay, and N. von Kokscharoff.

Rhodonite usually darkens on exposure to air, sometimes becoming nearly black, owing to oxidation. The mineral is slightly acted on by acids, and the calciferous varieties often effervesce owing to the presence of calcium carbonate. The powdered mineral partly dissolves in hydrochloric acid, and the insoluble part is white. According to A. Woloskoff, the f.p. curve of mixtures of manganese metasilicate and sulphide has a eutectic with 6·85 molar per cent. of MnS. The minerals *torrensite*, $MnSiO_3.MnCO_3$; *lacroisite*, $MnSiO_3.5MnCO_3$; *huelvite*, $3Mn_2SiO_4.2MnCO_3$; *vielaurite*, $2Mn_2SiO_4.5MnCO_3$; and *chocolate-stone*, $5Mn_2SiO_4.3Mn_3O_4.2MnCO_3$, are considered by H. Lienau to be different stages in the weathering of rhodonite.

A. Gorgeu found that the metasilicate dissolves in melted manganous chloride and crystallizes out again on cooling; if the fusion be conducted in the vapour of water, the orthosilicate is slowly formed. A. Gautier and L. Hallopeau found that when rhodonite is treated with the vap. of carbon disulphide at a white heat, rhodonite is converted into manganese sulphide, $Mn_3S_4$. G. A. König described a greyish-yellow mineral occurring in the zinc mines of Franklin Furnace, New Jersey. It is called *bementite*—after C. S. Bement. C. Palache said the axial angle is small, and the crystals belong to the rhombic system. Bementite is soft, with a micaceous cleavage, and sp. gr. 2·981. Its analysis corresponds with **hemihydrated manganous metasilicate,** $MnSiO_3.\frac{1}{2}H_2O$. It dissolves in hot hydrochloric acid without the gelatinization of the silica. C. Palache's analysis corresponds with $H_6Mn_5(SiO_4)_4$. P. Groth considers it to be *manganese dihydrorthosilicate*, $MnH_2SiO_4$. J. T. Pardee, E. S. Larsen, and G. Steiger represent their analyses of the mineral by $8MnO.7SiO_2.5H_2O$; they consider caryopilite is of the same mineral species. J. H. Collins described an amber-brown mineral from Penwith, Cornwall, which he called *penwithite*. Its analysis corresponds with **dihydrated manganous metasilicate,** $MnSiO_3.2H_2O$.

G. Flink[15] obtained columnar crystals of a light-red mineral with the habit of pectolite, to which it is related chemically. It was found at Julianchaab, Tutop Agdlerkofia, and Kangerdluarsuk, Greenland. It was examined by C. Winther, O. B. Böggild, and C. Christensen, and named **schizolite**—from $\sigma\chi\acute{\iota}\zeta\omega$, to cleave—in allusion to the marked cleavage. The composition approximates to **sodium calcium manganese hydrotrimetasilicate,** $HNa(Ca,Mn)_2(SiO_3)_3$, where some ferrous iron may replace the calcium, and some titanium, the silicon. The crystals belong to the triclinic system and have the axial ratios $a:b:c = 1{\cdot}10613:1:1{\cdot}98629$, and $\alpha=90°\ 11'$, $\beta=94°\ 45\frac{3}{4}'$, and $\gamma=103°\ 7\frac{1}{4}'$. The cleavages (100) and (001) are both perfect. The optical axial angle $2E=82°\ 40'$. The sp. gr. is 3·048–3·089; and the hardness 5–5½. The mean index of refraction for sodium light is 1·632; and the birefringence on (100) is 0·0271. The crystals are optically positive. A. Breithaupt[16] referred to flesh-red or rose-red radiating fibrous masses of a calcareous manganese carbonate, as manganocalcite; but E. Breussig showed that the mineral from Schemnitz is a mixture of carbonate and silicate. The silicate had a composition corresponding with $H_2Mn_3(SiO_3)_4.H_2O$, **manganese dihydrotetrametasilicate.** He called the mineral **agnolite,** from $\ddot{\alpha}\gamma\nu o\epsilon\omega$, not recognized. The mineral belongs to the triclinic system; the cleavage is parallel to the length of the fibres. The sp. gr. is 3·054–3·067, and the hardness 5. According to F. Ulrich, agnolite is identical with inesite. J. Jakob described **tinzenite** from Val d'Err, Graubünden, as a yellow manganese silicate with the composition $2CaO.Mn_2O_3.Al_2O_3.4SiO_2$, and occurring in monoclinic crystals with the indices of refraction $\alpha=1{\cdot}693$, $\beta=1{\cdot}701$, and $\gamma=1{\cdot}704$; and the optical axial angle $2V=62°\ 43'$.

A. G. Werner[17] applied the term **carpholite** or *karpholite*—from $\kappa\acute{\alpha}\rho\phi o\varsigma$, straw—to straw-yellow crystals of a mineral he obtained in the tin mines of Schlackenwald, Bohemia. Analyses were reported by A. Steinmann, L. de Koninck, K. A. Lossen, F. Stromeyer, and G. A. Kenngott. The analyses correspond with $(Mn,Fe,Mg)O.(Al_2,Fe_2)O_3.2SiO_2.2H_2O$, or, in the idealized case, $H_4CaAl_2Si_2O_{10}$. Carpholite is considered to be isomorphous with lawsonite (*q.v.*), and to have the same constitution, making **manganese dialuminium tetrahydroxydimetasilicate,** $(HO)_4MnAl_2(SiO_3)_2$. P. Groth wrote the constitutional formula $Mn\{Al(OH)_2\}_2(SiO_3)_2$; and F. W. Clarke gave a formula like that for lawsonite with manganese in place of calcium.

A. Michel-Lévy and A. Lacroix said that the crystals belong to the rhombic system like lawsonite; H. Fischer said they belong to the monoclinic system. The crystals were also examined by P. Groth, G. A. Kenngott, O. Mügge, and W. Haidinger. The crystals appear in radiated or stellated tufts and groups of acicular forms. The turning plane is (100). The optic angle is $2V=60°$ approx.

There is a distinct pleochroism. The sp. gr. is 2·876–2·935, and the hardness 5–5½. The birefringence is $\gamma-\alpha=0{\cdot}022$; and the optical character is negative. The water passes off at a red heat. The mineral is not decomposed by hydrochloric acid, and it is decomposed by fusion with alkali carbonates.

In 1797, M. H. Klaproth [18] analyzed a garnet which he designated *granatförmiges Braunsteinerz.* It was obtained from Spessart, Bavaria, and hence F. S. Beudant called it *spessartine,* and it is now known as **spessartite** or *manganese garnet.* Several analyses have been made.[19]

C. F. Rammelsberg [20] deduced the formula $(Ca,Fe,Mn)_3(Al,Fe)_2(SiO_4)_3$; and in the idealized case, spessartite is **manganese dialuminium triorthosilicate,** $Mn_3Al_2(SiO_4)_3$, with isomorphous admixtures of other garnets—*vide* grossular. H. E. Bocke concluded that there is a continuous series of mixed crystals between spessartite and almandine; but there is an extended break in the series between spessartite and pyrope.

Spessartite occurs in granite, quartzite, and some schists. W. Cross reported it in rhyolite rocks. A. Gorgeu obtained spessartite by fusing a mixture of pipe-clay and an excess of manganese chloride. C. Doelter and E. Hussak heated a mixture of alumina and silica in the proper proportions along with an excess of manganese chloride, and obtained tephroite, rhodonite, and manganese garnet. L. Bourgeois also reported the formation of spessartite by fusing a mixture of the constituents; this, however, is doubtful because his product was soluble in acids. He may have made manganese-leucite.

The crystallographic properties are indicated in connection with grossular. The colour is yellow, or reddish-brown. The sp. gr. ranges from 3·77 to 4·27. An increase of ferric oxide in place of alumina raises the sp. gr.; and an increase of calcium in place of manganese lowers the sp. gr.; the hardness varies from 7 to 7½. C. Doelter and E. Hussak found that manganese-garnet decomposes when melted, forming rhodonite, tephroite, anorthite, and a glass—*vide* grossular. R. C. Sabot found the indices of refraction for Li-, Na-, and the Tl-light to be respectively 1·7981–1·8099, 1·7998–1·8145, and 1·8046–1·8195. E. Reymond studied the action of chlorine and of hydrogen chloride on the mineral.

W. Haidinger [21] described a monoclinic mineral from the auriferous sands of Olahpian, Transylvania. It was called **partschite**—after P. Partsch. A. Breithaupt previously mentioned this as an *unbekennten Mineralien.* Its composition approximates to that of spessartite, $(Mn,Fe)_3Al_2(SiO_4)_3$, with which it appears to be isomeric. The axial ratios are $a:b:c=1{\cdot}266:1:0{\cdot}817$. The sp. gr. is 4·006; W. E. Ford gave 4·180. The hardness is 6½–7.

A. Hamberg,[22] obtained foliated or micaceous brown crystals of a mineral from the mine at Harstig, Sweden; he regarded it as a *mangano-zeolite,* and called it *ganophyllite*—from *γάνος,* lustre; *φύλλον,* leaf—in allusion to the high lustre on the cleavage plates. The analyses correspond with $7MnO.Al_2O_3.8SiO_2.6H_2O$, which F. W. Clarke formulated

$$\begin{matrix}Mn\\Mn\\Mn\end{matrix}\!\!>\!SiO_4\!>Al.MnSiO_4.Al<\!SiO_4\!<\!\begin{matrix}Mn\\Mn\\Mn\end{matrix}+7H_2O$$

It is probably a mixture of several silicates. The short prismatic crystals belong to the monoclinic system, and have the axial ratios $a:b:c=0{\cdot}4130:1:1{\cdot}8309$, and $\beta=86°\ 39'$. The basal cleavage, like that of mica, is perfect. The percussion figure is a six-rayed star. The optic axial angle is $2E=41°\ 19'$ and $2V=23°\ 36'$ for the red ray, and $2E=41°\ 53'$ and $2V=23°\ 52'$ for the yellow ray. The indices of refraction are for the red ray, $\alpha=1{\cdot}6941$, $\beta=1{\cdot}7250$, and $\gamma=1{\cdot}7264$; and for the yellow ray, $\alpha=1{\cdot}7046$, $\beta=1{\cdot}7287$, and $\gamma=1{\cdot}7287$; E. S. Larsen and E. V. Shannon gave $\alpha=1{\cdot}563$–$1{\cdot}573$; $\beta=1{\cdot}593$–$1{\cdot}603$; and $\gamma=1{\cdot}593$–$1{\cdot}604$. The optical character is negative. The sp. gr. is 2·84, and the hardness 4–4½.

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## § 52. Iron Silicates

W. A. Lampadius,[1] N. G. Sefström, W. S. Patterson and P. F. Summers, and P. Berthier made a number of observations on the fusibility of ferruginous slags, and artificial products containing $4FeO.SiO_2$, *ferrous orthosilicate*, $2FeO.SiO_2$, or $Fe_2SiO_4$, and ferrous metasilicate, $FeO.SiO_2$, or $FeSiO_3$. They also made *ferric orthosilicate*, $2Fe_2O_3.3SiO_2$, or $Fe_4(SiO_4)_3$, and *ferric metasilicate*, $Fe_2O_3.3SiO_2$, or $Fe_2(SiO_3)_3$, and tested the fusibility of various other combinations, $Fe : CaO : SiO_2 = 1 : 1 : 1, 4 : 2 : 3$, and $1 : 1 : 2$; $Fe_2O_3.3CaO.3SiO_2$; $2FeO.8MgO.5SiO_2$; $3FeO.Al_2O_3.3SiO_2$; and $Fe_2O_3 : Al_2O_3 : SiO_2 = 1 : 1 : 3$,

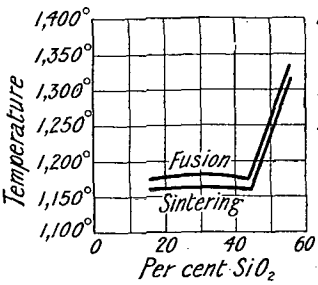



FIG. 196.—Formation Temperatures of Ferrous Silicates.

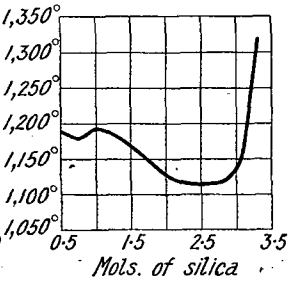



FIG. 197.—Formation Temperatures of $2FeO.CaO.nSiO_2$.

and $1 : 1 : 6$. P. Berthier said that the two ferrous silicates melted easily giving a mass containing rectangular prismatic crystals. The molten silicate readily penetrated a clay crucible. There was no evidence of the formation of the two ferric silicates, and P. Berthier assumed that the ferric oxide was reduced to ferrosic oxide by the gases of the furnace. J. Percy also recorded some observations on these products. J. W. Mellor found that the softening temp. of clay was lowered from 1710°–1160° by the introduction of 28 per cent. of ferric oxide. R. Rieke investigated the fusibility of clay and ferrous oxide in a neutral atm. H. O. Hofman, and H. Steffe measured the temp. of formation of the ferrous silicates and calcium ferrous silicates, and the results by the latter are illustrated on Figs. 196 and 197. The latter diagram refers to the $FeO : CaO = 2 : 1$, in admixture with varying proportions of silica. M. Rüger observed no formation of the ferrous silicates between 900° and 1200°. The results for the system $FeO$–$CaO$–$SiO_2$ were plotted by L. Babu, and H. E. Ashley on a triangular diagram. For colloidal iron silicates, *vide* water-glass. A. W. Thomas and L. Johnson studied the mutual precipitation of ferric hydroxide and silicic acid from colloidal soln.

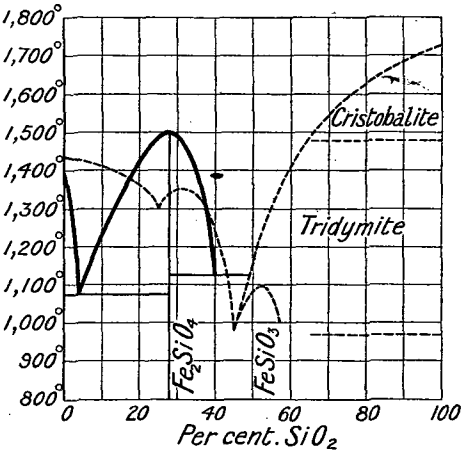



FIG. 198.—Freezing Points of Mixtures of Ferrous Oxide and Silica.

J. H. Whiteley and A. F. Hallimond studied the formation of iron silicates in the slags from acid hearth steel furnaces, and they deduced a possible equilibrum curve for the f.p. of binary mixtures of ferrous oxide and silica. This is shown by dotted lines in Fig. 198. The results observed by O. von Keil and A. Dammann, with mixtures containing up to 40 per cent. silica, are shown by continuous lines in the same diagram—*vide supra*, Fig. 198.

C. G. Gmelin[2] found nodules of a black mineral in the volcanic rocks at Fayal, Azores, and he called it **fayalite.** The same mineral has been found in a few other localities—Slievecarrach, Ireland; the Yellowstone National Park; Cheyenne Mountain, Colorado; Lipari, Iceland; Cerro de las Navajas, Mexico; etc. Analyses were reported by C. G. Gmelin, C. F. Rammelsberg, R. von Fellenberg, T. Thomson, A. E. Delesse, F. A. Gooch, A. Schertel, E. Classen, E. Mitscherlich, J. H. L. Vogt, F. Bothe, B. Kosmann, H. Laspeyres, G. O. Smith, S. Weidman, S. L. Penfield and E. H. Forbes, K. Busz and F. W. Rüsberg, A. Harpf, W. E. Hidden, J. B. Mackintosh, D. Lovisato, M. Kispatic, and J. Söllner. The results show that in the ideal case, the mineral is **ferrous orthosilicate,** $Fe_2SiO_4$. In some cases ferric oxide is present. The so-called *manganese-fayalites* have up to about 9 per cent. of MnO, probably in solid soln. as manganese orthosilicate; those with zinc orthosilicate are called *zinc-fayalites—vide infra.* The occurrence of fayalite in slags and other furnace products has been frequently recorded. Thus, N. Sokoloff found fayalite in roasted siliceous earths, in blast furnace slags, in slags from cupolas, in converter slags, and in slags from copper furnaces. Observations on this subject have been made by F. Mitscherlich, C. W. C. Fuchs, J. J. Nöggerath, C. T. Jackson, W. H. Miller, F. Bothe, M. Dondorff, B. Kosmann, J. J. Ebelmen, A. E. Arnold, C. O. Trechmann, H. Laspeyres, A. W. Stelzner, G. Bellinzona, and J. H. L. Vogt. A. Lacroix observed that a slag was formed during the eruption of Mt. Pelée, Martinique, by the melting together of the andesite walls and the iron contents of a warehouse. The slag contained fayalite, magnetite, and glass. By heating a mixture of ferrous chloride and silica in a current of hydrogen charged with steam, A. Gorgeu obtained crystals of fayalite.

Fayalite occurs in minute crystals of tabular habit, and also massive. The colour is light yellow and transparent, becoming opaque and dark brown to black, and often iridescent on the surface owing to oxidation. The crystals belong to the rhombic system, and, according to S. L. Penfield, have the axial ratios $a:b:c=0{\cdot}4584:1:0{\cdot}5793$; J. Söllner gave $0{\cdot}4600:1:0{\cdot}5811$. Observations on the crystals were made by M. Bauer, and many of those who studied the fayalite in slags. The cleavage (010) is distinct; (100) is less so. H. Michel studied the zonal structure in some artificial crystals of fayalite. J. Söllner found the optic axial angle $2V=51°\ 1'\ 35''$. S. L. Penfield and E. H. Forbes gave $2H=57°\ 27'$ for the Li-ray, 56° 32′ for the Na-ray, and 55° 2′ for the Tl-ray. The reported values for the sp. gr. of fayalite range from 3·90–4·24, and the hardness from $6\frac{1}{2}$–7. According to C. Doelter, the m.p. of fayalite is 1055°–1075°; O. Keil and A. Dammann gave 1500° (Fig. 198). E. Kittl found that the glass developed 220,000 nuclei per sq. cm. in crystallizing. V. Pöschl measured the sp. gr. and m.p. of mixtures of fayalite, $Fe_2SiO_4$, and of forsterite, $Mg_2SiO_4$, and found

| Fayalite | 0 | 10 | 20 | 30 | 40 per cent. |
|---|---|---|---|---|---|
| Sp. gr. | 3·11 | 3·16 | 3·30 | 3·36 | 3·46 |
| M.p. | 1600° | 1330° | 1315° | 1305° | 1290° |
| | — | 1370° | 1360° | 1340° | 1320° |

He also studied the ternary system: forsterite–fayalite–lime olivine. J. Söllner gave for the indices of refraction for the yellow Hg-line, $\alpha=1{\cdot}8044$, $\beta=1{\cdot}8382$, and $\gamma=1{\cdot}8462$; and S. L. Penfield and E. H. Forbes gave $\alpha=1{\cdot}8236$, $\beta=1{\cdot}8642$, and $\gamma=1{\cdot}8736$; and for the strong birefringence $\gamma-\alpha=0{\cdot}050$. The optical character is negative. Fayalite dissolves in hydrochloric acid with the separation of gelatinous silica. This subject was investigated by J. M. Thiele.

J. J. Bernhardi and R. Brandes[3] referred to a compact greenish-yellow mineral with an opal-like appearance which they called *chloropal*—from χλωρός, green; and opal.

The mineral was obtained from Unghwar, Hungary, and was hence called *unghwarite* by E. F. Glocker; P. Berthier called a yellow or greenish-yellow variety with an unctuous feel, **nontronite,** from Nontron, Dordogne, France, where it was found. A. Breithaupt called a

greenish variety with a soft soapy feel, *pinguite*—from *pinguis*, fat—it was analyzed by C. M. Karsten. It was obtained from Wolkenstein, Saxony. J. C. Freiesleben called a liver-brown variety from Halsbrücke, Freiberg, *Fettbol*; and A. Krantz, C. Bergemann, and A. H. Church called a grass-green variety *gramenite*—from *gramen*, grass—it was analyzed by C. Bergemann. A. Knop described a brownish-yellow imperfectly characterized silicate occurring in cavities in the limburgyte of Sadbatch, Kaiserstuhl. It was called *glasurite* in allusion to its occurring in layers glazing the interior of the cavities. He described another leek-green variety occurring under similar conditions as *protonontronite*. J. F. L. Hausmann described a fibrous yellow mineral from Antario Pereira, Mines Graes, Brazil, as *anthosiderite*—*ἄνθος*, flower; and *σίδηρος*, iron. G. H. E. Schnedermann's analysis agrees with the formula $2Fe_2O_3.9SiO_2.2H_2O$; F. W. Clarke gave $Fe_4(Si_3O_8)_3.2H_2O$. F. Zambonini applied the term *müllerite*—after H. Müller—to a massive yellowish-green mineral from Nontron, Dordogne, France, with a lower proportion of water than chloropal or nontronite; otherwise it closely resembles this mineral. Analyses were also reported by C. F. Rammelsberg, and M. Weibull. The formulæ are müllerite, $Fe_2O_3.2SiO_2.2H_2O$; and nontronite, $Fe_2O_3.3SiO_2.5H_2O$. F. W. Clarke suggests that müllerite is **ferric metasilicate**, $Fe_2(SiO_3)_3.2H_2O$. Since the name müllerite had been previously given for another mineral, M. Bauer proposed the term *zamboninite*. F. Katzer described a green granular or scaly earth from Kritz, Bohemia; it was named *hoeferite*—after H. Hoefer. It closely resembles chloropal or nontronite. Its composition approximates $Fe_2O_3.2SiO_2.3H_2O$. F. Katzer said that höferite is *das reinste bis jetzt bekannte naturliche Eisenoxydhydrosilicat*. The sp. gr. is near 2·4, and its hardness 1–3.

Analyses were reported by J. J. Bernhardi and R. Brandes, F. Hiller, T. Thomson, C. von Hauer, P. Berthier, P. A. Dufrénoy, V. A. Jacquelain, E. Biewand, C. M. Karsten, J. H. Collins, H. Mehner, A. Schrauf, A. H. Church, M. Weibull, F. von Kobell, A. Liversidge, E. F. Smith, L. N. Chapell, H. Müller, H. Stadlinger, C. von John, F. Kovar, E. Weinschenk, G. Steiger, etc. The results are not very concordant. The silica ranges from 36·90–48·59; the ferric oxide from 11·04–36·44, and the alumina from 0·75–25·95; water from 15·71–25·41 per cent. along with a little ferrous oxide, magnesia, and lime. The mineral appears to be related to kaolinite, with ferric oxide in place of alumina. F. W. Clarke gave for chloropal $Fe_2(SiO_4)_3H_6$. Idealized nontronite, according to E. Weinschenk, and E. T. Wherry and G. V. Brown, has the composition $Fe_2O_3.2SiO_2.2H_2O$; although usually the actual composition is often nearer F. von Kobell's $Fe_2O_3.3SiO_2.2H_2O$, which resembles that of müllerite—*vide infra*. T. E. Thorpe gave for nontronite $Fe_2O_3.3SiO_2.5H_2O$; and A. Bergeat, $2Fe_2O_3.9SiO_2.4H_2O$. These minerals range in composition between ferric kaolinite and a ferric halloysite. A. Lacroix described a mineral, *faratsihite*, $(Al,Fe)_2O_3.2SiO_2.2H_2O$, from Faratsiho, Madagascar, with refractive indices rather higher than those of kaolinite. Chloropal is an earthy mineral, or compact-like opal; it has a light green colour which becomes dark chestnut brown when the water is expelled. There is no evidence of crystallization. The sp. gr. varies from 1·727–2·105; and the hardness $2\frac{1}{2}$–$3\frac{1}{2}$. E. T. Wherry and G. V. Brown gave for the refractive indices $\alpha=1{\cdot}595$, $\beta=1{\cdot}595$, and $\gamma=1{\cdot}620$. It is partly decomposed by hydrochloric acid. C. Simmonds found that chloropal is completely reduced by heating it to redness in hydrogen. J. W. Mellor found the heating curve gave a terrace at about 150°, and he inferred that nontronite probably breaks down at that temp. into free silica, free ferric oxide, and water; G. Tammann and C. F. Grevemeyer also came to the same conclusion, and added that nontronite became yellow at 100°, brownish at 450°, brown at 800°, and reddish-brown at 800°–900°. It lost 78 per cent. of its water at 100°, none at 100°–200°, and the remaining water was lost continuously between 300° and 600°. Ten per cent. sulphuric acid dissolved out 0·01 per cent. of iron at 20°, and 1·73 per cent. in the mineral calcined at 1000°. H. von Wartenberg represented the action of chlorine on the heated mineral by $3Fe_2SiO_4+3Cl_2=Fe_4(SiO_4)_3+2FeCl_3$.

J. E. Spurr [4] classed a mineral as glauconite which C. K. Leith, and H. N. Winchell, and F. W. C arke found to be free from potassium and the chemical composition to approximate o $FeSiO_3.nH_2O$. The colloidal mineral was called *greenalite*. C. R. van Hise and C. K. Leith showed that a similar product is obtained by reactions between soln. of ferrous salts and the hydrogel of silicic acid. A little ferric iron is present in both the natural and artificial products. A black or dark brown compact earthy mineral found in various

parts of Norway and other countries was called *hisingerite*—after W. Hisinger—by J. J. Berzelius.[5] It was analyzed by P. T. Cleve, A. F. Thoreld, C. F. Rammelsberg, F. W. Clarke, G. M. Schwartz, M. Weibull, P. Sustschinsky, A. H. Church, A. Nikolajeff, and L. J. Iwanoff. The formula approximates to $H_4Fe_2Si_2O_9.2H_2O$, or $Fe_2O_3.2SiO_2.4H_2O$; E. S. Simpson represented it $Fe_2O_3.2SiO_2.2H_2O$ + adsorbed water. The index of refraction is 1·49–1·53. A variety occurring at Degerö, Finland, was called *degerõite* by H. J. Holmberg; a variety from Wilmington, Delaware, was called *canbyite* by A. C. Hawkins and E. V. Shannon—half the water being lost at 110°, the analysis was summarized by $H_2Fe'''_2Si_2O_9.2H_2O$; the indices of refraction were $\alpha=1{\cdot}562$, $\beta=1{\cdot}580$, and $\gamma=1{\cdot}582$, but marked variations were observed; the optic axial angle was small and the optical character negative; a dark green or black variety with rather less water than hisingerite, was called *skotiolite*—from σκότιος, dark—by A. E. Arppe. A non-homogeneous earth containing about 15·5 per cent. MnO, and occurring at Vestra Silfberg, Sweden, was called *manganhisingerite* by M. Weibull. An earthy mineral from the gilling mine, Södermanland, Sweden, was called *gillingite* by W. Hisinger. It was analyzed by C. F. Rammelsberg. A variety from Bodenmais, Bavaria, *thraulite*—from θραυλός, fragile—by F. von Kobell; another variety from the same locality was called *jollyte*—after G. Jolly—by F. von Kobell. J. P. Cooke called a reddish-black earth from Mineral Hill, Pennsylvania, *melanosiderite*—from μέλας, black; and σίδηρος, iron. The analysis agrees with $Fe_3SiO_4.6H_2O$. F. A. Genth suggested that melanosiderite is a variety of limonite with colloidal silica or silicic acid as an impurity. J. Krenner described a massive black earth occurring at Avasthal, Hungary; and he called it *avasite*. The composition approximates $5Fe_2O_3.2SiO_2.9H_2O$, and it is probably limonite admixed with silicic acid.

A. Scacchi[6] described a mineral resembling olivine which he found in the Vesuvian lavas of 1831, near Capa di Sabataniello. Analyses show that it contains *calcium and ferrous orthosilicates* in isomorphous association $(Ca,Fe)_2SiO_4$. The crystals were examined by E. Scacchi. E. Kittl found the glass in crystallizing developed 240 nuclei per sq. cm. Analyses were made by H. Struve, S. L. Penfield, W. G. Mixter, and C. H. Warren. S. L. Penfield and E. H. Forbes gave for the optic axial angles $2H=76°\ 59'$ for Li-light, 76° for Na-light, and 75° 46′ for Tl-light. The sp. gr. is 3·91, and the hardness 6–7. The lime-iron-olivine of J. H. L. Vogt has a similar composition. The rhombic crystals have the axial ratios $a:b:c=0{\cdot}43663:1:0{\cdot}57832$. The colour ranges from colourless to pale brown. W. T. Schaller reported on a sample of a red mica-like mineral which he called *gillespite*—after F. Gillespie, who found it near Dry Delta, Alaska. Its composition approximates **barium ferrous tritertetrasilicate,** $BaFe''Si_4O_{10}$; its sp. gr. is 3·33; its hardness 4; it is optically uniaxial; its birefringence is low; and it is strongly pleochroic. C. T. Jackson found crystals of a manganous variety, $(Ca,Fe,Mn)_2SiO_4$, in some blast-furnace slags. The *hyalo-siderite* of F. A. Walchner[7] is a mixture of *magnesium and ferrous orthosilicates* in isomorphous association, and approximately $(Mg,Fe)_2SiO_4$ with Mg : Fe = 2 : 1; likewise also the mineral named by G. J. Brush,[8] *hortonolite*—after S. R. Horton—from the iron-mine at Monroe, New York. Observations by G. J. Brush, and J. M. Blake show that the mineral is intermediate in composition between olivine and fayalite, for the ratio Mg : Fe is nearly 1 : 1. The rhombic crystals are yellow or yellowish-green, and have the axial ratios $a:b:c=0{\cdot}46630:1:0{\cdot}5803$. The optic axial angle $2H_a=83°–86°$; the sp. gr. is 3·91; and the hardness 6–7. G. T. Prior found the silicate $(Mg,Fe)_2SiO_4$ with Mg : Fe = 3 : 1 in the meteorites of Barote, India, and Witterkrantz, South Africa.

K. Hofmann-Degen obtained a kind of olivine in cavities in the slag at the Clausthal-silver works. The composition approximates $(Fe,Ca)_2SiO_4$ with about 2 per cent. of the magnesium silicate, and 5 per cent. of calcium orthosilicates. The axial ratios are $a:b:c=0{\cdot}4371:1:0{\cdot}5768$, and refractive indices for Na-light, $\alpha=1{\cdot}6958$, $\beta=1{\cdot}7340$, $\gamma=1{\cdot}7430$.

J. W. Döbereiner[9] applied the term *knebelite*—after M. von Knebel—to a mineral which, according to J. F. L. Hausmann, and G. A. Kenngott, was derived from the granite of Ilmeneau. It has been observed in other localities. The *iron-knebelite* or *igelströmite* of M. Weibull was obtained from Norrbärke, Dalekarlia. Analyses were reported by J. W. Döbereiner, A. des Cloizeaux, M. Weibull, A. Erdmann, and F. Kossmat and C. von John. The results show that the dominant

constituents are *manganous and ferrous orthosilicates* in isomorphous association, $(Mn,Fe)_2SiO_4$. K. Busz and E. W. Rüsberg found knebelite in furnace slags. According to M. Weibull, the black rhombic crystals have the axial ratios $a : b : c = 0{\cdot}467 : 1 : -$. The crystals are pleochroic. A. des Cloizeaux gave $2E = 115°–120°$ for the optic axial angle. The sp. gr. is 3·93–4·17, and the hardness 6–7. P. E. W. Oeberg gave 0·1665 for the sp. ht.

W. T. Roepper[10] described an iron-manganese-zinc-chrysolite occurring at Sterling Hill, and at Franklin Furnace, New Jersey. J. D. Dana called it *roepperite;* and G. A. Kenngott, *sterlingite* (actually *stirlingite*). The analysis by W. T. Roepper corresponds with a mixture of *ferrous, manganous, zinc, and magnesium orthosilicates* in isomorphous association. The colour when fresh is pale yellow, but it darkens on exposure to air, becoming green and black. The crystals belong to the rhombic system. The (001) and (010) cleavages are distinct; (100) is splintery. The sp. gr. is 3·95–4·08, and the hardness 5½–6. The crystals are slightly negative, and they are decomposed by acids with the separation of gelatinous silicic acid. E. Kittl found the glass $FeMnSiO_4$ developed 10 nuclei per sq. cm. W. Stelzner observed foliated aggregates of tabular crystals of a *zinc-fayalite* in the zinc-furnace slags of Freiberg. The analysis corresponds with an isomorphous mixture of *ferrous and zinc orthosilicates*, $(Zn,Fe)_2SiO_4$.

According to A. Cronstedt,[11] a cross made of two brown six-sided crystals of a mineral, called *lapis crucifer*, or *Basler Tauffstein* (baptismal-stone) was worn as an amulet at baptisms in Basel in the eighteenth century. According to G. F. Kunz, to-day the *lapis crucifer* is worn as a charm in Brittany and other places. C. P. G. de Robien called the mineral *pierre de croix;* A. Cronstedt, and J. G. Wallerius, *basaltes crystallisatus;* J. B. L. Romé de l'Isle, *schorl cruciforme;* J. C. Delamétherie, *staurolite;* H. B. de Saussure, *granatite;* and R. J. Haüy, *staurotide*. The term **staurolite**—from *σταυρός*, a cross—is now generally employed. M. F. Heddle described a reddish-yellow mineral from Milltown, Scotland, as *xantholite*—from *ξανθός*, yellow—but A. Lacroix showed that this mineral is staurolite mixed with some mica. T. Thomson called it *crucite;* and G. A. Kenngott altered the term to *crucilite*.

Analyses were made by H. V. Collet-Descotils,[12] L. N. Vauquelin, M. H. Klaproth, and many others. C. W. Paykull analyzed a sample from the dolomite of Nordmark, Wermland, Sweden, and found 11·61 per cent. of $Mn_3O_4$, and it was called *manganese-staurolite* or *nordmarkite;* while F. A. Genth found a sample from Georgia with 7·13 per cent. of zinc oxide, and it was called *zinc-staurolite*. From his study of the analyses, C. F. Rammelsberg assumed that the mineral was a mixture of a salt of the silicic acid, $H_8SiO_6$, and a bivalent base, and a salt of the silicic acid, $H_{24}Si_3O_{18}$, and a tervalent base. S. L. Penfield and J. H. Pratt deduced the formula $HAl_5FeSi_2O_{13}$, or **aluminium ferroxytetraluminyldiorthosilicate,** $(FeOH)(AlO)_4Al(SiO_4)_2$. P. Groth gave $(AlOH)(AlO)_4Fe(SiO_4)_2$; and W. Friedl, $(Fe,Mg)_6Al_6(AlO)_{18}(OH)_4(SiO_4)_{11}$. F. W. Clarke represents andalusite by the formula $(Al{\equiv}SiO_4)_2 : Al.SiO_4{\equiv}(AlO)_3$, and for the staurolite he gives $Fe : [(SiO_4 : Fe)—Al=\{SiO_4 : (AlO)_3\}]_2$, in which some Fe″ can be replaced by $(FeOH)_2$.

Staurolite is found in many metamorphic schists—*e.g.* muscovite or paragonitic schist—and in some gneisses or slates. It is often associated with garnet, sillimanite, cyanite, and tourmaline. H. St. C. Deville and H. Caron[13] obtained what they called staurolite, by the action of silicon tetrafluoride on a heated mixture of alumina and quartz; but H. St. C. Deville showed that the product really had the composition of sillimanite. P. Hautefeuille and J. Margottet also said they obtained in their work on the synthesis of phosphates a substance resembling staurolite. In neither case is the evidence sufficient to establish the claim that staurolite has been synthesized.

The colour of staurolite may be reddish-brown, yellowish-brown, or brownish-black. The crystals commonly have inclusions—quartz, garnet, cyanite, mica,

tourmaline, magnetite, rutile, carbonaceous matters, etc. The quartz inclusions, said A. von Lasaulx,[14] may amount to 30–40 per cent. of the total weight of the crystals. This is sufficient to account for the great variations—amounting to 27–51 per cent.—in the proportion of silica reported in the analyses. The carbonaceous matters may be regularly arranged, producing a tessellated appearance when viewed in cross-section, and recalling the effect observed with andalusite. This subject has been studied by S. L. Penfield and J. H. Pratt, A. Lacroix, S. Webber, and C. T. Jackson. Euhedral crystals occur in short prisms, crystals also occur with rounded edges but seldom in anhedral grains. W. Phillips gave measurements from which A. des Cloizeaux calculated for the axial ratios of the rhombic crystals, $a:b:c=0{\cdot}4734:1:0{\cdot}6828$. Observations on the crystals were made by M. J. Ackner, G. Primics, C. F. Peters, N. von Kokscharoff, J. R. Blum, E. J. Chapman, G. A. Kenngott, A. des Cloizeaux, B. Studer, A. von Lasaulx, P. Termier, O. Luedecke, G. Gürich, E. S. Dana, C. F. Rammelsberg, F. A. Genth, V. von Zepharovich, P. Groth, and Comte de Limur. The crystals commonly occur as cruciform twins; when the twinning plane is (032), the twins cross nearly at right angles; when it is (232), the twins cross at nearly 60°; and in the rarer case, when it is (230), the *b*-axes make an angle of 70° 45½′. Sometimes the twinning does not affect the outward form of the crystals, and the optical properties alone show that twinning has taken place. Trillings sometimes occur. The cleavage parallel to (010) is distinct but interrupted; traces occur parallel to (110). A. Michel-Lévy and A. Lacroix gave for the optic axial angles with red light, $2H_a=113°\ 10'$, and $2V_a=88°\ 46'$; F. Hörner gave $2V=82°\ 2'$–$89°\ 45'$. A. des Cloizeaux gave $2H_0=117°\ 52'$, and $2V_0=91°\ 39'$. The last-named found that by raising the temp., the optic axial angles are perceptibly diminished. The sp. gr. of staurolite ranges from 3·4–3·8; F. Hörner, using E. Clerici's liquids, obtained 3·753–3·778; and C. F. Rammelsberg, 3·654–3·660. The hardness is 7 or over 7. R. Cusack, gave 1115° for the m.p.; and A. L. Fletcher, 1165°. G. Spezia made some observations on this subject. The indices of refraction are high. A. Michel-Lévy and A. Lacroix gave for red-light $\alpha=1{\cdot}736$, $\beta=1{\cdot}741$, $\gamma=1{\cdot}7466$; W. H. Miller gave $\beta=1{\cdot}7526$; A. des Cloizeaux, 1·749; and F. Hörner, $\alpha=1{\cdot}7344$–$1{\cdot}7640$; $\beta=1{\cdot}7399$–$1{\cdot}7660$; and $\gamma=1{\cdot}7033$–$1{\cdot}7733$. The birefringence is low. A. des Cloizeaux gave $\gamma-\alpha=0{\cdot}010$, and $\gamma-\beta=0{\cdot}003$. The optical character is positive. The pleochroism is distinct and was studied by H. Rosenbusch.

Staurolite is imperfectly decomposed by sulphuric acid. Staurolite alters into muscovite. C. Simmonds found that staurolite does not show any definite reduction by hydrogen at a red heat. The alteration of staurolite in nature has been discussed by J. R. Blum,[15] A. Pichler, H. Rosenbusch, and C. R. van Hise. According to F. W. Clarke, the alleged alteration of staurolite into steatite is questionable. J. Lemberg studied the action of soln. of sodium silicate at 200° for 586 hrs.—part was transformed into analcite, and part into a hydrated sodium silicate.

Pliny in his *Historia naturalis* (**37**. 25) refers to various kinds of carbunculi; and added that the Alabandic stones from Orthosia, Caria (Asia Minor), were cut and polished at Alabanda. The stone from Alabanda appears to be the common, *syrian, oriental* or *precious garnet*, and, in the Middle Ages, the name Albanda came to be applied to a costly stone—the garnet, ruby, topaz, and hyacinth. The term was corrupted and appears in various forms in the writings of the Middle Ages—*alamandina, alavandina*, and *almandina*; U. F. B. Brückmann,[16] indeed, attempted to derive the term from Allemands. D. L. G. Kartsen applied the term **almandine** to the ferrous-garnet, and J. J. Berzelius, *Fahlun Granet*.

Numerous analyses have been reported; [17] and from them C. F. Rammelsberg,[18] and J. Uhlig deduced the formula $(Fe,Mg)_3(Fe,Al)_2(SiO_4)_3$. In the idealized case almandine is regarded as **ferrous dialuminium triorthosilicate,** $Fe_3Al_2(SiO_4)_3$, and the presence of magnesium and ferric-iron are supposed to be due to isomorphous admixture with magnesia-garnet and a ferric-garnet—*vide* grossular. Almandine occurs in granitic rocks, gneisses, etc.

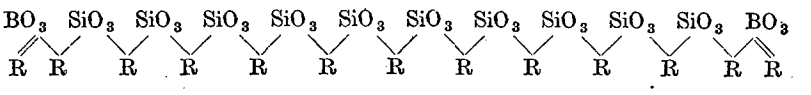
The properties of the crystals have also been discussed in connection with grossular. Almandine is coloured various shades of red, brownish-red, and rarely black. The sp. gr. ranges from 4·1–4·3. M. Seebach found the sp. gr. of a sample crystallized and fused were respectively 4·04, and 3·09 at ordinary temp.; another sample gave respectively 4·025 and 3·240. W. E. Ford gave 4·250 for the sp. gr., and P. J. Holmquist, 4·039–4·201; and for the hardness on the (111)-face, 1058 (quartz on the (0001)-face, 1000); on the (110)-face, 1159; and on the (100)-face, 1246. The hardness is 7–7½ on Mohs' scale. J. Joly gave for the m.p. 1175°; R. Cusack, 1265°; A. L. Fletcher, 1313°–1318°; A. Brun, 1070°; and C. Doelter, 1110°–1215°. There is no true m.p. because, as C. Doelter and E. Hussak showed, the mineral decomposes when it is melted—*vide* grossular. A. des Cloizeaux found 1·7716 for the index of refraction. H. Rosenbusch gave for Li-, Na-, and Tl-light respectively 1·8022–1·8052, 1·8078–1·8107, and 1·8125–1·8159; C. Schmidt, 1·7958, 1·8017, and 1·8062; A. Brun, 1·787–1·795, 1·791–1·800, and 1·805; and M. Seebach, 1·7722–1·7883; 1·7778–1·7936, and 1·7858–1·7866. W. E. Ford gave 1·830. The alterations which almandine undergoes in nature have been discussed by J. R. Blum,[19] J. Roth, E. Helland, C. W. Paijkull, and H. G. T. Wachtmeister. The action of chlorine and hydrogen chloride on the heated mineral was studied by E. Reymond.

J. B. L. Romé de l'Isle [20] referred to *une espèce de schorl violet* from St. Cristophe, Dauphiny; A. G. Werner called a variety from Thum, Saxony, *Thumerstein*, a name later changed to *thumite*; J. F. Blumenbach called it *Glasschörl*: J. C. Delamétherie, *yanolite*—from *ἰάνθον*, violet; A. Estner, *Afterschörl*; M. H. Klaproth, *Glasstein*; and R. J. Haüy, **axinite**—from *ἀξίνη*, an axe—in allusion to the broad acute-edged form of the crystals.

Analyses were made by M. H. Klaproth,[21] L. N. Vauquelin, W. Hisinger, and many others. C. F. Rammelsberg attempted to deduce a formula and obtained $H_4R''_8R'''_8Si_{11}O_{44}$, supposed to be a complex, containing $H_4SiO_4+4R''_2SiO_4+2R'''_4Si_3O_8$. Empirical formulæ were also proposed by J. E. Whitfield O. Luedecke, W. E. Ford, P. Jannasch and J. Locke, etc. H. Sjögren gave $R''_4(SiO_3)_5 : Al.BO_3$; and P. Groth, $(Ca,Mn,Fe,Mg,H_2)_7B_2(Al,Fe)_4(SiO_4)_8$. G. Cesaro regarded axinite as a combination of diortho-and meta-silicates or else a basic triple metasilicate with $B_2O$ replacing some silicon. W. T. Schaller concluded that axinite is really an isomorphous mixture of two components: *ferro-axinite*, $Al_2BHCa_2Fe(SiO_4)_4$, and *mangano-axinite*, $Al_2BHCa_2Mn(SiO_4)_4$. If the boron be basic and eq. to aluminium, these two axinites are to be regarded respectively as *calcium dialuminium ferrous boratotetrorthosilicate*, and *calcium dialuminium manganous boratotetrorthosilicate*; but if the boron be acidic, as it usually is, F. W. Clarke considers it to be a mixed ortho- and tri-silicate:

$$\left.\begin{matrix}Ca_2{=}SiO_4\\ Fe{=}Si_3O_8\end{matrix}\right\rangle Al{-}BO_3{=}AlOH$$

T. L. Walker and A. L. Parsons' analyses correspond with $13RO.B_2O_3.10SiO_2$, thus making axinite a *calcium ferrous manganese aluminium boratosilicate*:




Axinite occurs in cavities in granite and diabase—*e.g.* Striegau, Silesia, and Mt. Monzoni, Tyrol. It is probably formed as a contact mineral in the presence of calcium aluminosilicates. The mineral has not been synthesized. C. Doelter [22] found that if melted and slowly cooled, crystals resembling augite are formed. It might possibly be obtained in a dry melt if the right *agent minéralisateur* were present; and possibly also in a hydrothermal way.

Axinite occurs crystalline and massive in lamellæ or granules. The colour is

clove-brown, plum-blue, pearl-grey, honey-yellow, greenish-yellow, and peach-blossom-red. K. von Kraatz-Koschlau and L. Wöhler[23] could not satisfy themselves that manganese is the cause of the colour. The euhedral crystals are usually broad and acute-edged, and rarely prismatic. The anhedral crystals are lamellar or granular. The crystals belong to the triclinic system; according to A. Schrauf, the axial ratios are $a:b:c=1{\cdot}5542:1:0{\cdot}86415$, and $\alpha=96°\ 57'$, $\beta=98°\ 52'$, and $\gamma=103°\ 2'$; and, according to A. Schmidt, $a:b:c=1{\cdot}14936:1:0{\cdot}86501$, and $\alpha=96°\ 57'\ 52''$, $\beta=98°\ 53'\ 39''$, and $\gamma=102°\ 51'\ 55''$. Observations were made by V. Goldschmidt, G. vom Rath, A. des Cloizeaux, O. Luedecke, M. Websky, F. C. Neumann, C. F. Naumann, F. A. Quenstedt, A. Lévy, R. H. Solby, B. W. Frazier, H. Buttgenbach, W. H. Miller, F. Hessenberg, J. D. Dana, W. T. Schaller, H. Sjögren, A. Offret and F. Gonnard, E. T. Wherry, K. Zimanyi, G. Aminoff, E. M. Poitevin, and A. Franck. The cleavages parallel to (010), (001), and $(1\bar{3}0)$ are distinct; the cleavage parallel to $(1\bar{1}1)$ less so; and the cleavages parallel to $(1\bar{1}0)$ and (021) are in traces. Some faces are often striated. A. des Cloizeaux found the optic axial angles somewhat variable even in sections of the same crystal. He found, for red-light, $2H=71°\ 38'$ to $87°\ 49'$; $2V=71°\ 38'$ to $74°\ 17'$; and $2E=153°\ 46'$ to $158°\ 13'$; while for blue-light, $2H=83°\ 28'$ to $87°\ 47'$; $2V=71°\ 39'$; and $2E=159°\ 49'$ to $172°\ 10'$. A. Krejci gave $2V=c.\ 70°$. The change with variations of temp. between 21° and 171° was found to be very slight; J. Beckenkamp also found only about half a minute variation in the axial angles between 20° and 200°.

The sp. gr. of axinite, according to C. F. Rammelsberg, is 3·294, and after fusion, 2·812; W. Haidinger gave 3·271; A. Krejci, 3·22; and E. Grill, 3·314. W. T. Schaller found the sp. gr. varied with the proportion of contained manganese—per cent. MnO—

| | | | | | | |
|---|---|---|---|---|---|---|
| MnO . | 1·06 | 2·99 | 9·59 | 10·71 | 13·41 | 13·69 |
| Sp. gr. . | 3·268 | 3·287 | 3·299 | 3·302 | 3·306 | 3·358 |

Iron oxide probably also has a great influence. R. Cusack gave 995° for the m.p. of axinite, but added that the mineral probably changes before it fuses. A. L. Fletcher gave 1045°. C. Doelter found axinite is decomposed by fusion—*vide supra*. The indices of refraction are moderately high. A. des Cloizeaux found $\alpha=1{\cdot}6720$, $\beta=1{\cdot}16779$, and $\gamma=1{\cdot}6810$ for red-light, and $\alpha=1{\cdot}6850$, $\beta=1{\cdot}6918$, and $\gamma=1{\cdot}6954$ for blue-light. The birefringence is low, $\gamma-\alpha=0{\cdot}0090$ for red light and 0·0104 for blue-light. A. Krejci gave $\alpha=1{\cdot}678$; $\beta=1{\cdot}685$; and $\gamma=1{\cdot}688$. The pleochroism of the crystals is well marked; it was studied by D. Brewster, W. Haidinger, A. des Cloizeaux, O. Luedecke, H. Rosenbusch, and A. Bertin. The pyroelectricity of the crystals was studied by R. J. Haüy, A. Lévy, C. P. Brard, P. Riess and G. Rose, W. G. Hankel, and G. Friedel and A. de Gramont. Axinite also becomes electrified by friction. G. A. Kenngott found that the powdered and moistened mineral has a strong alkaline reaction; after calcination, the reaction is not so marked. Acids scarcely affect axinite; but after fusion, the mineral is decomposed by hydrochloric acid with the separation of gelatinous silicic acid.

E. L. Gruner[24] found asbestos-like or lamellar-fibres of brown mineral, which he called *pyroxene ferrugineux*, in the metamorphic schists of Collobrières, Dept. du Var. It was named by G. A. Kenngott, **grunerite.** Analyses of grunerite from this and other localities by E. L. Gruner, S. Kreutz, and A. C. Lane and F. Sharpless show that its composition corresponds with **ferrous metasilicate,** $FeSiO_3$, plus a few impurities. C. F. Rammelsberg showed that chemically, and A. des Cloizeaux that optically, grunerite is related to amphibolic hornblende. E. V. Shannon obtained the iron end-member of the anthophyllitic series of mixed crystals, $(Mg,Fe)SiO_3$. He called it *iron-anthophyllite.* It occurs impure in the Cœur d'Alene district, Idaho. The colour of the mineral is white or pale brown. The plane of twinning is (100). The cleavage resembles that of hornblende. A. Lacroix found the optic axial angle to be $2E=95°$. The extinction angle, according to A. Michel-Lévy and A. Lacroix,

is 11°–15°. E. L. Gruner gave 3·713 for the sp. gr. For the synthesis of the metasilicate, *vide supra*. H. le Chatelier gave for the heat of formation $FeO+SiO_2=FeSiO_3+5$ Cals.; and $FeCO_3+SiO_2=CO_2+FeSiO_3-7·6$ Cals. S. Wologdine gave $(FeO,SiO_2)=5·905$ Cals. The index of refraction and birefringence were stated by A. C. Lane and F. Sharpless to be high, for the mean index of refraction is 1·7, and $\gamma-\alpha$ exceeds 0·030; A. Lacroix gave $\gamma-\alpha=0·056$. The rhombic crystals of iron-anthophyllite have a positive elongation, and the indices of refraction $\alpha=1·668$, and $\gamma=1·685$. Grunerite is pleochroic.

T. G. Bonney [25] found a mineral resembling hornblende occurring in groups of prismatic crystals in the granite and syenite of the Island of Socotra, Indian Ocean. It has been reported by A. Harker, T. G. Bonney, G. A. Koenig, etc., in other localities. A. Sauer named it *riebeckite*—after E. Riebeck. W. C. Smith found implements made of riebeckite among relics of ancient dwellers near Jebel Katul, Soudan. Analyses were made by A. Sauer, G. A. Koenig, E. Grill, J. Orcel, C. Palache and C. H. Warren, and H. Rosenbusch. The mineral was studied by B. Gossner, A. Vendl, S. Kreutz, M. G. Murgoci, and V. de Souza-Brandao. In the idealized form it is supposed to be **sodium ferric dimetasilicate,** $NaFe(SiO_3)_2$, mixed with ferrous metasilicate and possibly some microcline. It approximates $2NaFe(SiO_3)_2.FeSiO_3$. Riebeckite is the amphibole representative of the pyroxene acmite or ægirite. Z. Weyberg fused a mixture of silicic acid, ferric hydroxide, sodium carbonate, and a large excess of sodium chloride, and obtained crystals of sodium ferric dimetasilicate, $NaFe(SiO_3)_2$. The black prismatic crystals of riebeckite belong to the monoclinic system. The prismatic cleavage (110) is perfect. The sp. gr. is 3·33–3·49, and the hardness $5\frac{1}{2}$–6. C. Palache and C. H. Warren gave 1·693 for the index of refraction with Na-light; the birefringence is feeble $\alpha-\gamma=0·0051$ for the blue ray and 0·003 for the red ray. The optical character is negative. The mineral is strongly pleochroic. F. W. Clarke and G. Steiger found that the mineral is decomposed when heated with ammonium chloride.

M. H. Klaproth [26] referred to a *Blau-eisenstein* from Griqualand, S. W. Africa, and J. F. L. Hausmann called it *crocidolite*—from κρόκις, woof—in allusion to its fibrous structure. E. T. Wherry and E. V. Shannon called the blue pleochroic amphiboles, *glaucamphiboles*, and described a semi-magnesian crocidolite with the composition $Na_2O.MgO.FeO.Fe_2O_3.6SiO_2.H_2O$. M. F. Heddle called an earthy variety from the gneiss and granite of Abriachan, Scotland, *abriachanite*. Analyses were made by M. H. Klaproth, F. Stromeyer, C. Doelter, A. Renard and C. Klement, A. H. Chester and F. J. Cairns, and A. E. Delesse. It is regarded as a fibrous variety of riebeckite, and its composition averages $NaFe(SiO_3)_2.FeSiO_3$—*vide* glaucophane. Crocidolite occurs in long asbestiform fibres. The optical properties correspond with the monoclinic system; the cleavage is prismatic; the sp. gr. 3·20–3·30; and the hardness 4. The optic axial angle $2E=95°$. A. Lacroix found the birefringence $\gamma-\alpha=0·025$, and the optical character negative. G. Hepburn described a brownish-yellow alteration product which he called *griqualandite*; it was analyzed by A. Renard and C. Klement, C. F. Rammelsberg, and F. Wibel and F. Neelsen. By the infiltration of siliceous matters, the South African mineral forms a yellowish-brown compact rock with a fibrous structure, and a chatoyant lustre, and is popularly known as *tiger's eye*, or *cat's-eye*. H. von Foullon, and A. Bukowsky described an asbestiform variety of glaucophane in which the aluminium has been partly replaced by ferric iron; and it is sometimes classed with abriachanite. It was found in Rhodes Island, and called *rhodusite*. It was analyzed by H. von Foullon, P. Tschirwinsky, W. Isküll, R. Doht and C. Hlawatsch, M. F. Heddle, and W. Jolly and M. Cameron. W. Isküll studied the action of hydrochloric acid on the mineral. W. F. Smeeth, and L. J. Spencer described a soda-ferric-amphibole approximating $2NaFe'''(SiO_3)_2.Mg_3Fe''(SiO_3)_4$ from the Bababudan Hills, Mysore, and hence called *bababudanite*. C. Palache, and G. D. Louderback described a blue mineral occurring in lath-shaped crystals in Berkeley, California. It was called *crossite*—after W. Cross. The mineral is intermediate in composition between riebeckite and glaucophane. The sp. gr. is 3·16. It was strongly pleochroic. B. Gossner studied the chemical composition of this and related minerals.

H. Ström [27] mentioned the occurrence of a crystalline hornblende or schörl at Eker, Norway; and P. Ström regarded it as a definite mineral species which he named *wernerine*—after A. G. Werner. J. J. Berzelius called it **acmite**—from ἀκμὴ, a point—in allusion to the pointed extremities of the crystals. A mineral found by

J. Esmark in the Langesund fiörd, Norway, was named by J. J. Berzelius *ægirine*, and later called **ægirite**—after Ægir, the Icelandic god of the sea. The crystals of acmite were shown by N. B. Möller, and W. Haidinger to belong to the augite group; and the crystals of ægirite were examined by P. Plantamour, L. J. Wallmark, and shown by T. Scheerer, A. Breithaupt, G. A. Kenngott, and M. von. Hornberg to belong to the augite family, and G. Rose suggested that the two minerals belong to one species. C. F. Rammelsberg showed that acmite and ægirine have nearly the same composition. J. D. Dana, and A. des Cloizeaux regarded them as independent species, but G. Tschermak, and C. Doelter showed that the essential characters of ægirite and acmite are identical, but, as W. C. Brögger emphasized, each possesses certain peculiarities which makes it desirable to retain the names representing them as varieties of one species.

Analyses were made by P. Ström, J. J. Berzelius, A. Breithaupt, C. F. Rammelsberg, C. Doelter, F. Pisani, J. Morozewicz, F. Gutzkow, W. Ramsay, J. Machado, C. H. Smith, S. Hillebrand, A. Osann, F. W. Clarke, C. Palache and C. H. Warren, B. J. Harrington, W. A. Silbermüntz, Z. Weyberg, R. Doht and C. Hlawatsch, H. Rosenbusch, and J. Lorenzen. A. Holmes found a specimen with 0·0253 per cent. of uranium, and 0·015 per cent. of lead; and E. S. Larsen and W. F. Hunt found at Rainy Creek, Montana, a vanadiferous ægirite with up to 3·98 per cent. $V_2O_3$. Attempts to represent the composition by formulæ show that idealized acmite contains sodium ferric dimetasilicate, $NaFe'''(SiO_3)_2$, in isomorphous association with ferrous and calcium metasilicates. It is the pyroxene equivalent of the amphibole riebeckite. Various mixture formulæ have been proposed by C. F. Rammelsberg, C. Doelter, J. Lorenzen, J. Machado, J. Morozewicz, S. Hillebrand, and C. Palache and C. H. Warren. Acmite is a mineral of eruptive rocks and is generally accompanied by leucite or nephelite; it is common in elæolitic syenite. M. Vucnik found that when the constituent oxides are fused together, a glass containing crystals of magnetite is formed; and when acmite is fused, it also solidifies into a mixture of magnetite and glass. C. Doelter, however, observed that some acmite is formed by fusing and cooling a mixture of the constituent oxides. H. Bäckström kept a mixture of silica, ferric oxide, and sodium carbonate for 3 days at a dull red-heat, and obtained crystals of acmite; and he also obtained acmite by fusing a leucitic phonolite and very slowly cooling the glass. Z. Weyberg also obtained acmite by fusing a mixture of silica, ferric oxide, and soda with a large excess of sodium chloride. Z. Weyberg also obtained a *chromic-acmite*, or **sodium chromic dimetasilicate,** $NaCr(SiO_3)_2$, by substituting chromic oxide for ferric oxide. J. Morozewicz also observed the formation of acmite in metasilicate magmas containing less than 50 per cent. of silica. P. Niggli obtained a *potash-acmite*, **potassium ferric dimetasilicate,** $KFe(SiO_3)_2$, by the hydrothermal process at 450°.

The long prismatic crystals of acmite are coloured brown, or reddish-brown; ægirite also occurs in long prismatic crystals arranged in tufts or groups, and in fibrous forms usually dark green. V. S. Deleano and E. Dittler found the crystallizing power is not marked, but the speed of crystallization is considerable. The monoclinic crystals of acmite and ægirite were found by W. C. Brögger to have nearly the same axial ratios $a:b:c=1·09957:1:0·60120$, and $\beta=73°\ 10\frac{5}{6}'$. The twinning of ægirite is not common; but acmite is commonly twinned on the (100)-plane. Polysynthetic twinning enclosing twinning lamellæ is also common. The crystals are often vertically striated or channelled; and the prisms may be bent, twisted, or broken. Inclined hemihedrism as with pyroxene is also found. The cleavage parallel to (110) is distinct, that parallel to (010) is less so. The crystals of acmite often show a zonal structure, being green within and brown outside—the green ægirite is strongly pleochroic, while the brown acmite is but feebly pleochroic. The optic axial angles are large. W. C. Brögger gave for ægirite with Na-light, $2E=134°\ 27'$; $2H_a=63°\ 41'$; $2H_0=117°\ 18'$; and $2V_a=63°\ 28'$; W. Ramsay gave $2V=63·13°–66°$. F. Zambonini attributed the isomorphism of diopside and

acmite to the near equality of the at. vol. and sum of the valencies of the groups CaMg and NaFe'''. R. W. G. Wyckoff studied the X-radiograms of acmite. The sp. gr. varies from 3·5–3·6, and the hardness from 6–6½. A. Brun gave for the m.p. of acmite, 970°; C. Doelter, 965°; and V. Schumoff-Deleano and E. Dittler, 960°–1030°. H. Leitmeier gave for ægirite, 940°–950°; and M. Vucnik, 970°–1010°. E. A. Wülfing found the indices of refraction to be $\alpha$=1·7630, $\beta$=1·7990, and $\gamma$=1·8126 for Na-light; W. Ramsay gave $\alpha$=1·777, $\beta$=1·801; and W. F. Hunt, for vanadiferous ægirite, $\alpha$=1·745, $\beta$=1·770, and $\gamma$=1·782. E. A. Wülfing gave for the birefringence $\gamma-\alpha$=0·0496; $\gamma-\beta$=0·0136; and $\beta-\alpha$=0·036. The optical character is negative. Acmite is but slightly affected by acids. W. C. Brögger found acmite altered to analcite, and J. F. Williams, to manganiferous pectolite. F. W. Clarke and G. Steiger found no marked change when ægirite is heated in the vap. of ammonium chloride in a sealed tube.

H Sjögren[28] found a mineral at Langban, Sweden, which had been confused with schafferite, and which he called *urbanite*—after Urban Hjärne; the mineral was also investigated by L. J. Igelström, who called it *lindesite*. The two minerals are very much alike except that the latter has rather more manganese oxide—the highest reported for lindesite is 10·97 per cent. MnO, and for urbanite, 6·71 per cent. Analyses show that it is probably a mixture of acmite and diopside. The colour is chestnut-brown to brownish-black. The monoclinic crystals belong to the pyroxene family, and have the axial ratios $a:b:c$=1·1009 : 1 : 0·6058, and $\beta$=72° 7′. The habit is pyramidal; the cleavage parallel to (110) is distinct. The sp. gr. is 3·52–3·53, and the hardness 5–6. It is strongly pleochroic. It is only slightly attacked by acids. The so-called *ægirine-augites* seem to be intermediate in composition between the augites and ægirite.[29]

In nature, wollastonite is often tinted presumably with ferrous metasilicate. The mineral **hedenbergite** was named by J. J. Berzelius[30] after L. Hedenberg, and was classed by R. J. Haüy among the amphiboles. C. C. von Leonhard regarded it as a ferruginous variety of augite. C. F. Rammelsberg found hedenbergite in slags. Hedenbergite appears to be one end-member of a series of solid soln. of calcium and ferrous metasilicates. The composition in the ideal case approximates **calcium ferrous metasilicate,** $CaFe(SiO_3)_2$; and there are many intermediate members of the series with the general formula $Ca(Fe,Mg)(SiO_3)_2$, between it and diopside, $CaMg(SiO_3)_2$ (*q.v.*). A. Brun gave 1190° for the m.p. of hedenbergite; C. Doelter obtained numbers ranging from 1095°–1135°; and V. Pöschl, 1100°–1140°. Calcium ferrous dimetasilicate is monoclinic; sp. gr. 3·5–3·6; and hardness 5–6. In nature, the mineral is contaminated with a variable proportion of diopside, and other silicates. V. S. Deleano and E. Dittler studied the rate of crystallization of hedenbergite. G. Tammann investigated the action of ferrous aluminate, iron, manganese, and nickel, and also iron sulphide on the fused calcium ferrous dimetasilicate. C. Doelter, H. Wulf, H. Rosenbusch, E. Manasse, T. Wada, D. Lovisato, V. Pöschl, G. vom Rath, K. Busz, H. Sjögren, E. A. Wülfing, and A. H. Phillips discussed complexes which are regarded as solid soln. of hedenbergite and diopside. V. Pöschl measured the sp. gr., the m.p., and the angle of extinction of mixtures of diopside, $CaMg(SiO_3)_2$, and hedenbergite, and found:

| Diopside | 0 | 30 | 40 | 50 | 60 | 70 | 80 | 90 | 100 per cent. |
|---|---|---|---|---|---|---|---|---|---|
| Sp. gr. | 3·53 | 3·26 | 3·16 | 3·01 | 2·98 | 2·96 | 2·90 | 2·87 | 3·03 |
| M.p. | 1100° | 1175° | 1185° | 1210° | 1215° | 1225° | 1235° | 1245° | 1300° |
| | 1140° | 1200° | 1210° | 1225° | 1230° | 1240° | 1250° | 1265° | 1325° |
| Extinction | 50° 30′ | 50° | 49° 20′ | 47° | 45° 20′ | 43° 40′ | 31° | 36° | 32° |

A. Breithaupt called hedenbergite *bolopherite*—from $\beta\acute{o}\lambda os$, earth; $\phi o\rho\acute{\epsilon}\omega$, to carry; and L. J. Igelström called a variety with a stellate radiated structure, *asteroite*. M. Weibull obtained a variety rich in manganese, *manganohedenbergite*, from Vester-Silfberg, Sweden. E. F. Glocker, and B. Sewergin applied the term *lotalite* to a variety of hedenbergite from Lotalia, Finland. The *violan* of A. Breithaupt is a dark violet-blue variety of hedenbergite which occurs in prismatic crystals at St. Marcel, Piedmont. It was analyzed by A. des Cloizeaux, L. Grünhut, and E. Schluttig. L. J. Igelström's *anthochroite*—from $\check{a}\nu\theta os$, flower; and $\chi\rho\acute{o}a$, colour—is a rose-red or violet variety of violan. The manganiferous hedenbergites have been examined by L. L. Fermor, A. K. Coomaraswamy, T. Wada, and

L. J. Igelström. A. N. Winchell reported a *titanohedenbergite* from Pigeon Point, Minnesota, which he called *pigeonite*.

J. Palmgren [31] found *ferroanthophyllite*, $3FeSiO_3+RSiO_3$, in an eulysite rock from Södermanland, and E. V. Shannon found it in the Cœur d'Alene district of Idaho with the composition $(Fe,Ca,H_2,Mn)SiO_3$. He regards ferroanthophyllite as the end-member of the anthophyllite series, and the magnesian end-member is called *magnesioanthophyllite*. The pyroxenic mineral *sobralite*, found by J. Palmgren, associated with ferroanthophyllite, has the composition $4MnSiO_3.2FeSiO_3.CaSiO_3.MgSiO_3$. It is triclinic, with three cleavages. J. M. Sobral found sobralite with the optical axial angle $2V=41°$; the birefringence $\beta-\alpha=0{\cdot}0025$; $\gamma-\beta=0{\cdot}0175$; and $\gamma-\alpha=0{\cdot}0200$; and the optical character negative.

A zinciferous variety, found by W. H. Keating and L. Vanuxem, [32] has been called *jeffersonite*. It is supposed to be a complex of $CaMg(SiO_3)_2$, $CaFe(SiO_3)_2$, $CaMn(SiO_3)_2$, and $CaZn(SiO_3)_2$, or a mixture of the individual metasilicates. Analyses have been reported by R. Hermann, F. Pisani, F. A. Genth, W. A. Waldschmidt, G. J. Brush, W. F. Hillebrand, and F. W. Clarke and E. A. Schneider. C. Doelter synthesized it by crystallization from a mixture of the molten constituents. Its indices of refraction are $\alpha=1{\cdot}668$, $\gamma=1{\cdot}703$; and its birefringence, 0·030. A. des Cloizeaux measured the crystal constants. The sp. gr. is 3·63. V. Pöschl gave 3·53 for the sp. gr. of a sample with 25 per cent. of ferrous oxide; 1140° for the m.p., and 50° 30′ for the optic axial angle. R. Hermann, and G. A. Kenngott likened it to augite; A. Breithaupt regarded it as a pyroxene.

A. Breithaupt [33] applied the term *richterite*—after T. Richter—to a yellow amphibole from Langban, Sweden, with a sp. gr. 2·826; L. J. Igelström, and G. Flink used the same term for a similar mineral, though possibly not the same, from Pajsberg, Sweden, which, according to G. A. Michaelson, had a sp. gr. 3·09. The colour is brown, yellow, or rose-red. Analyses were made by S. Kreutz, N. Engström, G. A. Michaelson, L. J. Igelström, and R. Mauzelius. The crystals were examined by G. Flink, who found the monoclinic crystals had the axial ratios $a:b:c=0{\cdot}5499:1:0{\cdot}2854$, and $\beta=75°\,46'$. It is considered to be a mixed *sodium magnesium manganese metasilicate*, or better, $(Mn,Fe,Mg,Ca,Na_2,K_2)SiO_3$. G. T. Prior, P. Termier, G. M. Murgoci, and A. F. Rogers have discussed riebeckite in rocks. H. Sjögren described a coarsely crystalline columnar aggregate associated with rhodonite at Langban, and known locally as *blue rhodonite*. H. Sjögren called it *astochite*—from ἄστοχος, missing the mark—in allusion to the fact that it was at first regarded as a pyroxene. R. Mauzelius' analysis shows that it is not far from richterite in composition, $(Mn,Fe,Mg,Ca,Na_2,K_2H_2)SiO_3$. The colour, said A. Hamberg, is not sufficient to distinguish it as a separate species from richterite; and H. Sjögren called it *soda-richterite*. The crystals are monoclinic; the cleavage angle is 56° 27′; the colour varies from blue to greyish-violet; and the extinction angle is 15° 40′–17° 15′. The optical character is negative. N. O. Holst described a yellow mineral occurring in fine crystalline needles at Langban, Sweden. It was named *marmairolite*—from μαρμαίρειν, to glisten. Its sp. gr. is 3·07; and its hardness, 5. The composition approximates to that of richterite, and F. J. Wiik suggested that marmairolite is a massive form of that mineral. G. Brocchi [34] found a mineral occurring at Vesuvius and at Capo di Bove in wool-like forms, coloured dark brown. It was named *breislakite*—after S. Breislak. The greenish-grey or greyish-white hair-like crystals in the lava of Cyclops Mt. were named *cyclopeïte* by A. des Cloizeaux. This is not to be confounded with the lime-felspar *cyclopite* of W. S. von Waltershausen. C. F. Rammelsberg emphasized the resemblance of breislakite to hornblende; but E. J. Chapman regarded it as a variety of pyroxene. A. von Lasaulx, however, showed that its optical properties and form are like those of the amphiboles. The pleochroism is well-marked. It is considered to be a variety of richterite.

H. J. Brooke [35] described a mineral from Greenland which he named *arfvedsonite*, or *arfwedsonite*—after J. A. Arfvedson. According to W. Haidinger, it is a ferruginous variety of hornblende. The older analyses of T. Thomson, and J. A. Arfvedson were shown by A. Breithaupt to refer probably to ægirite (*q.v.*). The analyses quoted by C. F. Rammelsberg is also that of ægirite; and A. Lacroix showed that G. A. Koenig's analysis is probably that of riebeckite. Analyses were made by J. Lorenzen, F. Berwerth, S. Bertolio, B. Gossner, and K. Rördam. The results show that the mineral is a *soda-hornblende*, and is a complex mixture. The main constituent may be ferrous metasilicate which is associated with sodium and calcium metasilicates, and possibly also $NaFe(SiO_3)_2$. J. Söllner regards it as a complex of meta-, ortho-, and tri-silicates. The mineral occurs in black prisms or dark green plates, which, according to W. C. Brögger, belong to the monoclinic system, and have the axial ratios $a:b:c=0{\cdot}55687:1:0{\cdot}29781$, and $\beta=73°\,2\frac{1}{4}'$. The twinning plane is (100); the prismatic cleavage (110) is perfect, that parallel to (010) is imperfect. The pleochroism is strongly defined. The optical character is probably positive. The sp. gr. is 3·4–3·5; and the hardness 6. The mineral is not readily attacked by acids. W. C. Brögger described an amphibolic mineral, closely related to arfvedsonite, occurring near Barkevik, Norway, and hence called *barkevikite*. The prismatic crystals are deep velvet-black, and have a perfect prismatic cleavage. Analyses were made by P. Plantamour, C. F. Rammelsberg, and G. Flink. The composition is intermediate between that of hornblende and that of arfvedsonite, and it was studied by B. Gossner. The mineral is strongly pleochroic. The sp. gr. is 3·428. C. Hlawatsch described an

amphibolic mineral from Cevadaes which he named *osannite*—after A. Osann. Its composition is intermediate between that of arfvedsonite and that of riebeckite, and it was studied by B. Gossner. The sp. gr. is 3·4; hardness, 5–6; and birefringence, $\gamma-\alpha=0{\cdot}005$. A. Lacroix described a rhombic, bluish-green mineral which he called *grandidierite* and obtained from Andrahomana, South Madagascar. The composition approximated $2(Na,K,H)_2O.7(Mg,Fe,Ca)O.11(Al,Fe)_2O_3.7SiO_2$, or, according to A. Lacroix and A. de Gramont, $2Na_2O.4FeO.8(Al,Fe,B)_2O_3.5SiO_2$. Its sp. gr. is 2·99; its birefringence is negative; and its indices of refraction $\alpha=1{\cdot}6018$, $\beta=1{\cdot}6360$, and $\gamma=1{\cdot}6385$ for Na-light. The mineral was also described by C. Hlawatsch.

A number of **magnesium ferrous metasilicates,** or magnesium ferrous manganous metasilicates, has been reported. They are probably solid soln. For example, the mineral **cummingtonite** is a magnesian amphibole which, according to A. des Cloizeaux,[36] is monoclinic. It was found by C. Dewey at Cummington, Mass., as a grey to brown fibrous or fibrolamellar mass. It contains about 10·30 per cent. MgO, 32·60 per cent. FeO, and 50–91 per cent. of silica with a little manganese oxide, alumina, and calcium oxide, so that its formula becomes $(Fe,Mg)SiO_3$. The mean refractive index is 1·638; the cleavage angle, 54° 48′.

The term *antholite* was applied by J. D. Dana, and by G. A. Kenngott to certain asbestiform amphiboles. A kind of manganiferous cummingtonite was found by A. Erdmann at Dannemora, Sweden, and hence called *dannemorite*. It was described by J. D. Dana, and G. A. Kenngott, and represented by the formula $(Fe,Mn,Mg)SiO_3$. A variety from Brunsjö which contained much iron and possessed an asbestos-like texture was called by L. J. Igelström *asbeferrite*. Analyses were also made by F. J. Wiik, and A. Erdmann. M. Weibull called a similar mineral from Vester-Silfberget in Delarne, *silfbergite*; and L. J. Igelström, one from Hillängs in Delarne, *hillängsite*.

W. E. Ford and W. M. Bradley [37] described a mineral from Iva, South Carolina, which they called *pyroxmangite*. The analyses approximate to $(Mn,Fe)SiO_3$, **ferrous manganese metasilicate,** with some calcium and aluminium silicate as impurity. The colour ranges from amber to yellowish-brown, reddish-brown, and dark brown. It is regarded as a manganese pyroxene—hence the name. The crystals are triclinic. There are cleavages parallel to the two prism faces, and one is more distinct than the other. The angle between the cleavages is 91° 50′. There is a parting plane (010). The optic axial angle $2V=30°$. The sp. gr. is 3·80, and the hardness $5\frac{1}{2}$–6. The mean index of refraction is 1·755; and the optical character is positive. The mineral is insoluble in acids.

A. Lévy [38] described crystals of a mineral from Arendal, Norway, which he called **babingtonite**—after B. G. Babington. Analyses were reported by C. Palache and F. R. Fraprie, B. K. Emerson, S. Hillebrand, M. Watanabe, A. E. Arppe T. Thomson, F. Zambonini, C. F. Rammelsberg, G. Forbes, M. F. Heddle, C. Jehn, B. Gossner, and H. Klemm. The results correspond with a mixture of **calcium manganous ferrous metasilicates,** $(Ca,Mn,Fe)SiO_3$, mixed with some ferric metasilicate, $Fe_2(SiO_3)_3$. The discussion—by C. F. Rammelsberg, C. Doelter, H. S. Washington and H. E. Merwin, E. Jannetaz, G. Tschermak, C. Palache and F. R. Fraprie, P. Groth, A. Knop, F. Zambonini, and S. Hillebrand—on the nature of babingtonite has turned mainly on the components which make up the mineral. Babingtonite has not been made artificially; although M. Schläpfer and P. Niggli obtained crystals which they assumed to be babingtonite by heating in an autoclave water mixed with lime, alumina, silica, and metal chlorides. The occurrence of babingtonite in converter slags has been reported by R. Groth and H. Scheerer, G. vom Rath, L. Buchrucker, and J. H. L. Vogt.

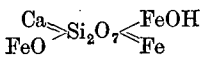
The crystals of babingtonite are small, and as emphasized by W. Haidinger, they resemble black augite or hornblende; and their colour is dark greenish-black. H. Dauber found that the triclinic crystals have the axial ratios $a:b:c=1{\cdot}06906:1:0{\cdot}6384$, and $\alpha=104°\ 21\frac{1}{2}'$, $\beta=108°\ 30\frac{5}{6}'$, and $\gamma=83°\ 34\frac{1}{4}'$. Observations on the crystals were made by A. Lévy, A. des Cloizeaux, W. H. Miller, H. S. Washington and H. E. Merwin, G. vom Rath, E. S. Larsen, M. Watanabe, P. Groth and H. Scheerer, J. H. L. Vogt, and H. Klemm. The cleavage $(1\bar{1}0)$ is

perfect, (110) is less distinct. M. Watanabe gave for the indices of refraction $\alpha=1{\cdot}715$, $\beta=1{\cdot}725$, and $\gamma=1{\cdot}740$; the crystals are biaxial and positive. A. Michel-Lévy and A. Lacroix gave for the optic axial angle $2V=60°–65°$; and the birefringence $\gamma-\alpha=0{\cdot}032$. X-radiograms of babingtonite were reported by R. W. G. Wyckoff. The sp. gr. is 3·35–3·37, and the hardness 5·5–6·0. The crystals are pleochroic. S. Hillebrand studied the nature of the silicic acid which separates when babingtonite is decomposed by hydrochloric acid. O. B. Böggild studied the relationship of babingtonite to schizolite; and, according to H. S. Washington and H. E. Merwin, babingtonite, rhodonite, pyroxmangite, and sobralite form a group of triclinic minerals sufficiently different from the pyroxenes to be regarded as a group by themselves. J. Palmgren described a triclinic pyroxene from Söndermanland, Sweden, with the approximate composition $(Mn,Fe,Ca,Mg)SiO_3$. The sp. gr. is 3·50.

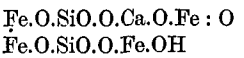
F. Katzer [39] found a reddish-brown amorphous ferruginous manganese silicate in the iron deposits of Vares, Bosnia, and he called it *pöchite*—after F. Pöch. The composition approximates $H_{16}Fe_8Mn_2Si_3O_{29}$. The sp. gr. is 3·695, and the hardness $3\frac{1}{2}$–4. G. Flink [40] described a brown pleochroic mineral from Langban, Sweden, as *ektropite*. The composition approximated $12(Mg,Ca,Mn,Fe)O.8SiO_2.7H_2O$. The monoclinic crystals had the axial ratios $a:b:c=0{\cdot}74:1:0{\cdot}84$, and $\beta=61°\ 5'$. The sp. gr. was 2·46, the hardness 4, and the indices of refraction $\alpha=1{\cdot}62$, $\gamma=1{\cdot}63$.

In 1806, C. H. le Lièvre [41] obtained from the Rio la Marina, and Cape Calamita, Elba, large crystals of a mineral which was called *yenite* or *jenite* in commemoration of the battle of Jena, 1806; J. F. d'Aubuisson called it *lepor*—from *lepus*, un lièvre (a hare); H. Steffens, **ilvaite**—from the Latin name for Elba; and A. G. Werner, *lievrite*, after its discoverer. The German text-books generally employ lievrite, the American text-books, following A. des Cloizeaux, ilvaite. The black mineral found by F. von Kobell near Szurrasko, Hungary, and named *wehrllite*—after A. Wehrll—was considered by C. A. Zipser to be lievrite. It is massive and granular. Both H. Fischer, and V. von Zepharovich showed that wehrlite is a mixture of several minerals.

Analyses of ilvaite were made by L. N. Vauquelin, H. V. Collet-Descotils, F. Stromeyer, F. von Kobell, and many others.[42] C. F. Rammelsberg [43] tried to work out a formula for ilvaite from the analysis and obtained $R''_{12}Fe'''_4Si_9O_{36}$. G. Städeler showed that water is probably an essential constituent; this was confirmed by L. Sipöcz, and C. F. Rammelsberg then gave $H_2R''_6Fe_2Si_4O_{18}$. P. Groth gave $(FeOH)Fe_2Ca(SiO_4)_2$. A. Baschieri regarded the mineral as a salt of diorthosilicic acid, $H_6Si_2O_7$, which he isolated by the hydrochloric acid process; and he gave the accompanying formula. A. Himmelbauer by a similar method obtained metasilicic acid, and he represented the mineral by the accompanying formula.

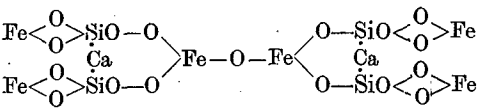


A. Baschieri's formula.



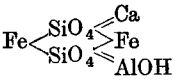
A. Himmelbauer's formula.

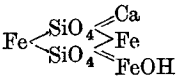
J. E. Reynolds represented his analysis, $6RO.Fe_2O_3.4SiO_2$, by the formula:



F. Zambonini explained the difference in the results by assuming different experimental conditions; and C. Doelter, by assuming a difference in the state of hydration of the mineral owing to the difference in the climates where the samples were obtained; and G. Tschermak assumed that ilvaite, like olivine, contains two different silicic acids, since with conc. hydrochloric acid, metasilicic acid is formed, and with dil. hydrochloric acid, orthosilicic acid is produced. A. Himmelbauer

also suggested that the mineral might be an addition compound of magnetite, $FeO.Fe_2O_3$, and a calcium ferrous silicate. F. W. Clarke used a formula of the same type as those employed for bertrandite, and calamine :




corresponding with **calcium diferrous aluminohydroxydiorthosilicate.** B. Bavink studied the magnetic properties of lievrite. W. Vernadsky studied the constitution and chemical relations of ilvaite. The mineral has not been synthesized. Ilvaite has been found in iron mines ; it appears to have been formed by contact action,[44] say, by the action of silicates on iron oxide—*e.g.* magnetite—which like ilvaite contains both ferrous and ferric oxides. It has also been found in dolomite, limestone, granite, syenite, and porphyry.

Ilvaite commonly occurs in prisms with the prismatic faces striated ; anhedral crystals occur in prismatic or irregularly shaped aggregates ; and it also occurs in compact or columnar masses. The colour is dark greyish-black. The crystals belong to the rhombic system, and A. des Cloizeaux[45] gives for the axial ratios $a : b : c = 0{\cdot}6650 : 1 : 0{\cdot}44268$ ; J. Lorenzen gave 0·674367 : 1 : 0·448449 ; and G. Flink, 0·66195 : 1 : 0·43897. The crystals have been studied by R. J. Haüy, W. H. Miller, F. Hessenberg, G. vom Rath, A. Weisbach, G. Flink, and J. Lorenzen. The cleavages parallel to (010) and to (001) are rather distinct ; those parallel to (100), (110), and to (101) are imperfect or indistinct. O. B. Böggild studied the corrosion figures and optical characters of ilvaite. J. Lorenzen found for the optic axial angle $2E$ approximately 60°. The sp. gr. ranges from 3·9–4·1, and the hardness 5–6. The index of refraction is high ; E. A. Wülfing gave 1·89. The mineral is strongly pleochroic. It is decomposed by hydrochloric acid with the separation of gelatinous silica. C. Simmonds found that ilvaite is partially reduced by hydrogen at a red heat. F. W. Clarke and G. Steiger studied the action of ammonium chloride vap.

P. Hautefeuille[46] heated a mixture of silica, ferric oxide, and potassium vanadate to about 960°, and after washing away the soluble salts obtained small greenish-yellow, transparent crystals, the composition is analogous to that of leucite—*ferric-leucite*, $KFe(SiO_3)_2$, or **potassium ferric dimetasilicate.** The icositetrahedral crystals exhibit anomalies like those of ordinary leucite. The formation of crystals of ferric-leucite requires a somewhat higher temp. than that of ordinary felspar. When a mixture of alumina, ferric oxide, silica, and potassium vanadate is heated, it may happen that only felspar is produced and no leucite, if the temp. be so regulated that the potassium vanadate does not attack the ferric oxide.

The term **glauconite**—from γλαυκός—bluish-green—was applied by G. Keferstein[47] to the green grains of earth in the green-sand of the chalk formation, and in other rocks. The grains are often casts of the shells of rhizopods ; and they have been found in fragments of coral. G. Jenzsch applied the term *chlorophanerite* to a similar earth found in cavities in eruptive rocks. According to J. Murray and A. F. Renard, glauconite is widely disseminated upon the sea-bottom, but most abundantly in comparatively shallow waters, near the mud-line, *i.e.* just beyond the limits of wave and current action where the fine muddy particles commence to make up a considerable portion of the deposits. Analyses have been reported by G. H. Cook, W. B. Clark, A. J. Hoskins, L. W. Collet and G. W. Lee, W. A. Caspari, A. Lacroix, H. Wurtz, K. von Haushofer, P. Berthier, T. S. Hunt, J. Murray and A. F. Renard, M. B. Corse and C. Baskerville, A. Johnsen, J. Morozewicz, L. Cayeux, G. R. Mansfield, N. Sahlbom, A. F. Hallimond, J. W. Mallet, P. N. Chirvinsky, W. van der Marck, D. H. von Dechen, W. Fischer, H. D. Rogers, E. Hitchcock, A. E. Delesse, W. S. von Waltershausen, S. Haughton, C. F. Rammelsberg, A. T. Kupffer, F. Dewalque, E. vom Bamberger, M. F. Heddle, C. W. von

Gümbel, E. Knerr and F. Schönfeld, A. des Cloizeaux, P. Schemjatschensky, W. Smirnoff, G. Steiger, N. Ermola, etc. The composition is exceedingly variable, for glauconite is invariably contaminated with extraneous matters and alteration products. The iron is mainly in the ferric state, and potassium is always present; some aluminium may partly replace iron, and other bases partly replace potassium. The material used by K. Glinka for analysis was freed from impurities by heavy soln., and the analyses correspond with **hydrated potassium ferric dimetasilicate,** $KFe(SiO_3)_2.H_2O$. A. F. Hallimond regarded the glauconite from Lewes, Sussex, as $R_2O.4(R_2O_3.RO).10SiO_2.nH_2O$, in which $Fe_2O_3$ and $Al_2O_3$, and MgO and FeO, are mutually replaceable. Where potash is more or less replaced by soda, A. F. Hallimond applied the term *soda-glauconite*. F. W. Clarke said that the water is probably zeolitic, and not constitutional. According to P. Groth, glauconite may be a chlorite or a serpentine. J. Murray and A. F. Renard thus explain the origin of the glauconite now forming on the sea-bottom.

The shell is first filled with fine silt or mud upon which the organic matter of the dead animal can act. Through intervention of the sulphates contained in the sea water, the iron of the mud is converted into sulphide, which oxidizes later to ferric hydroxide. At the same time, alumina is removed from the sediments by soln. and colloidal silica is liberated. The latter reacts upon the ferric hydroxide in presence of potassium salts extracted from adjacent minerals, and so glauconite is produced. This view is sustained by other evidence, namely, the constant association of the glauconite shells with the débris of rocks in which potassium-bearing minerals, such as orthoclase and muscovite, occur.

L. Cayeux has shown that in sedimentary rocks, the glauconite has been formed subsequent to its consolidation. K. Glinka regards it as a product of the weathering of ferruginous augites and hornblendes. K. Andrée, K. C. Berz, and K. Hummel have discussed this subject. The subject has been discussed by C. W. von Gümbel, D. S. Calderon and co-workers, L. W. Collet, L. F. de Pourtales, and F. W. Clarke. W. A. Caspari described the synthesis of a compound resembling glauconite by the action of mixed soln. of potassium ferric tartrate and potassium silicate at 180°. L. W. Collet and G. W. Lee said that it is formed by the action of alkali silicates on iron sulphide or sulphate.

Glauconite is earthy or granular and massive. It sometimes resembles chlorite very closely, and it may be blackish-green, olive-green, yellowish-green, or greyish-green in colour. L. Cayeux said that the grains are biaxial and doubly refracting with the optic axial angle $2E=30°–40°$—but sometimes nearly zero. The sp. gr. ranges from 2·2–2·6, and the hardness 2–3. D. D. Jackson and J. J. Morgan found that the vap. press. of the alkali is negligibly small below 1350°. When heated, M. W. Travers found that hydrogen and carbon monoxide are given off: $2FeO+H_2O=Fe_2O_3+H_2$; and $2FeO+CO_2=Fe_2O_3+CO$. C. Simmonds showed that it is completely reduced when heated to redness in a current of hydrogen. K. Glinka found a boiling soln. of potassium carbonate dissolves alumina, lime, and ferric oxide, while alkali is taken up. Dil. hydrochloric acid attacks it slowly while the conc. acid soon decomposes it completely. K. Glinka described the passage, by weathering, of glauconite into ferruginous clay; and G. Klemm, the alteration of glauconite into ferrite.

The so-called *green-earth*, or *Grunerde* is related to glauconite; it appears to be the *creta viridis* of Pliny;[48] and it was used as a pigment for painting in the mediæval times under the name *terra di Verona*. J. B. L. Romé de l'Isle, A. Estner, and C. A. S. Hofmann, speak of *la terre verte de Verone* found in cavities in the amygdaloid at Monte Baldo, Verona. The green earth also occurs in other localities, and E. F. Glocker called a variety *seladonite*, or, in French, *céladonite* in allusion to the sea-green colour—from κελάδων, burning; and hence the use of the term for a verdant lover. Several analyses have been reported; they average $(Fe,K_2,H_2,Mg)_3(Al,Fe)_2(SiO_3)_6.1·24H_2O$. It is probably an impure glauconite. The sp. gr. is 2·570–2·595—A. Lacroix gave 2·907, and G. Levi, 2·78. A. Lacroix said that the mineral is pleochroic.

F. Kretschmer [49] described a green earth from Sternberg, Moravia, which he called *viridite*; its composition approximated $4FeO.2SiO_2.3H_2O$. He also described a mineral *mackensite* from the same locality whose composition approximated $Fe_2O_3.SiO_2.2H_2O$, or *ferryl metasilicate*, $(FeO)_2SiO_3.2H_2O$. The *hverlera* of G. Forchhammer is a ferruginous clay from Krisuvig, Iceland; similarly also with the *keffekilite* of F. E. L. Fischer obtained from Krim, Sevastopol. A. Cronstedt referred to the *keffekil tartarorum* as being used as a substitute for soap. The *neurolite* of T. Thomson from Stanstead, Canada; the *rhodalite*—from ῥοδαλός, rose-coloured—of T. Thomson, and J. E. Portlock obtained in Antrim, Ireland; and the *portite* of G. Meneghini and E. Bechi, occurring at Toscana, appear to be ferruginous clays. E. Mallard described a grey clay from Noyant, France, which he named *bravaisite*—after A. Bravais. It consists of a mass of crystalline fibres. Its composition approximates $2(K_2,Mg,Ca)O.2(Al,Fe)_2O_3.9SiO_2.5H_2O$. The sp. gr. is 2·6; the hardness 1–2; double refraction, strong; extinction parallel; optical character negative; and optic axial angle $2E=40°$. G. Starkl regards bravaisite as related with the *Weissererde* of Ann-Capelle, Austria.

M. F. R. d'Andrada [50] described a brown or reddish-brown manganiferous garnet from Drammen and Feiringen, Norway, which he called *allochroite*—from ἄλλος, other; χρόα, colour—the variety to which this name is now applied is apple-green. This garnet is representative of the calcium-ferric-garnets to which J. D. Dana applied the term **andradite**—after M. F. R. d'Andrada.

There are many varieties to which different names have been given, and the so-called *common garnet*, and *black garnet* belong to this group. The bivalent base is almost wholly lime in the mineral topazolite which has the colour of topaz and was described by B. Bonvoisin, and C. A. S. Hofmann. N. von Kokscharoff described a grass-green or emerald-green variety which was called *demantoid* in allusion to its diamond-like lustre. It is used as a gem-stone. A coarse granular variety coloured brownish-yellow or reddish-brown, and possessing a resinous lustre, was called *colophonite* or *kolophonite*—from κολοφάνια, resin—by A. G. Werner, M. F. R. d'Andrada, P. L. Simon, and J. F. L. Hausmann. Colophonite from Arendal is now considered to be a variety of vesuvianite. J. A. H. Lucas called it *grénat résinite*. A similar variety was called *Pechgranat* by D. L. G. Karsten. Some so-called colophonite is vesuvianite. A black garnet of the calcium ferric type was called by A. G. Werner *melanite*—from μέλας, black—although varieties of other than the ferric-garnets may be black. V. Iskyul studied the action of hydrochloric acid on melanite. A. G. Werner, and C. A. S. Hofmann applied the term *pyreneite* to a greyish-black garnet found in the Pyrenees. A green garnet like *allochroite* was called *jelletite*—after A. Jellet—by J. Apjohn; and a massive garnet found by H. Piddington in India and described by W. T. Blanford and H. Söchting was called *calderite*.

The magnesium-calcium ferric garnets include the original *allochroite* of M. F. R. d'Andrada; and the similar mineral called Granat von Langban by E. Rothoff, and *rothoffite* by J. J. Berzelius. T. Thomson's *polyadelphite*—from πολύς, many; ἀδελφός, brother—was named in allusion to its containing many bases. It came from Franklin, New York, and is a brownish-yellow variety of andradite. B. G. Bredberg's variety, from Sala was called by J. D. Dana, *bredbergite*. R. J. Haüy named a variety from Schwarzenberg, Saxony, and Lana, Siberia, *aplome* or *haplome*—from ἁπλόος, simple—in allusion to the fundamental cubic form which is simpler than the dodecahedral form common to the garnets.

Numerous analyses of andradite have been made,[51] and from these C. F. Rammelsberg calculated that the best representative formula for these garnets is $(Ca,Fe)_3(Al,Fe)_2(SiO_4)_3$; or, in the idealized case, $Ca_3Fe_2(SiO_4)_3$, or **calcium diferric triorthosilicate,** or *calcium ferric-garnet*. Some aluminium may replace the ferric-iron, and ferrous iron; magnesium, or manganese may replace the calcium. Presumbably these are carried by $Mg_3Al_2(SiO_4)_3$, $Fe''_3Fe'''_2(SiO_4)_3$, $Mn_3Al_2(SiO_4)_3$, etc., present in isomorphous admixture—*vide* grossular. L. Hezner made some observations on this subject. The analyses of J. Uhlig indicate the presence of some vanadium, cerium, and chromium which he assumed to be present respectively as $Ca_3V_2(SiO_4)_3$, $Ca_3Ce_2(SiO_4)_3$, and $Ca_3Cr_2(SiO_4)_3$. C. Bergemann reported a Norwegian garnet to contain 6·66 per cent. of yttria earths, and he called it *yttria-garnet*. Analyses by C. B. Benedicks, L. Jaczewsky, and M. Websky, indicated about 2·6 per cent. E. T. Wherry applied the at. vol. theory of isomorphism to explain the various replacements in the garnet family.

Andradite is common in granitic rocks, gneisses, etc.; and as an accessory mineral in subsilicate eruptive rocks, the leucitic, and the nephelitic rocks. It

also occurs in serpentines, beds of iron ore, and as a product of contact metamorphism associated with wollastonite and pyroxene in certain volcanic rocks. M. H. Klaproth,[52] A. Mitscherlich, and F. von Kobell reported andradite to be formed by melting vesuvianite, but C. Doelter was unable to verify this; indeed, andradite itself decomposes when it is melted. A. des Cloizeaux', and L. Bourgeois' experiments, also, do not lend support to the validity of these early reports. F. Fouqué and A. Michel-Lévy reported that andradite is formed when nephelite and pyroxene are fused together, and C. Doelter found this to be the case when the fused mass is kept below its m.p. for some time. L. Michel produced andradite and sphene by heating a mixture of ilmenite, silica, and calcium sulphide to 1200°.

The colour of andradite may be greenish-yellow, brownish-yellow, resin-brown, brown, dark brown, and black. The differently coloured varieties have different names—allochroite is green; melanite, black; etc., as indicated above. From his observations on the action of oxidizing and reducing gases on heated garnet, W. Hermann [53] inferred, that iron, chromium, and manganese oxides act as tinctorial agents in garnets. The crystallographic properties are indicated in connection with grossular. The crystals were also examined by A. Bianchi. The sp. gr. ranges from 3·3–4·1. W. E. Ford gave 3·750. A. H. Church, F. von Kobell, G. Magnus, and M. Seebach found a decrease in the sp. gr. of the mineral after it had been fused. The hardness is 6½–7. The m.p. is difficult to determine since, as indicated above, decomposition occurs about that temp.—*vide* grossular. C. Doelter gave for the m.p. of melanite, 925°–950°; and V. S. Deleano and E. Dittler, 950°–1160°. For topazolite, A. Brun gave 1150°. A. Osann gave for the indices of refraction of demantoid with Li-, Na-, and Tl-light respectively 1·8780, 1·8893, and 1·9005; while H. Rosenbusch gave for melanite 1·8467, 1·8566, and 1·8659. W. E. Ford gave 1·895. M. Seebach found a decrease in the index of refraction after melanite had been fused. G. A. Kenngott found that powdered and moistened allochroite reacts alkaline to litmus. Both F. von Kobell, and G. Magnus found that garnets which are not attacked by hydrochloric acid, are decomposed with the separation of gelatinous silica after the mineral has been fused—pyrope and, according to P. Jannasch, other garnets are more or less exceptional. M. Seebach found great differences in the action of hydrochloric acid since demantoid gives up 0·94 per cent. to that acid, while andradite from Dognecea is almost wholly soluble.

A. Meister [54] found what appeared to be hexagonal tabular crystals in the limestone in contact with the nepheline-syenite of southern Yenisei district, near the Angara River, Siberia, and he called the mineral *angaralite*. The black colour is due to carbonaceous impurities; the colour is bronze after heating. The composition corresponds with $2(Ca,Mg)O.5(Al,Fe)_2O_3.6SiO_2$, or idealized, $Mg_2Al_5(AlO)_5(SiO_4)_6$. The uniaxial crystals have the sp. gr. 2·619; the birefringence is below that of quartz; the optical character is positive.

F. Tacconi [55] reported a brownish-red mineral in the limestone of Candoglia, Tocetal, which he called *taramellite*. The composition approximates **barium ferrous ferryl triferric decametasilicate**, $Ba_4Fe''(FeO)Fe'''_3(SiO_3)_{10}$. The sp. gr. is 3·293, the hardness 5½, the optic axial angle $2E=75°\ 40'$; the index of refraction is over 1·74; and the double refraction is small. The mineral is not decomposed by the ordinary mineral acids.

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## § 53. Cobalt and Nickel Silicates

A. Breithaupt[1] applied the term *conarite* to a green mineral from a mine at Röttis, Voigtland. The name is derived from *κόνναρος*, an evergreen tree, and should be *connarite*; not conarite, from *κόναρος*, well fed; nor *comarite*, from *κόμαρος*, a strawberry plant—as suggested by A. des Cloizeaux. Analyses by C. Winkler corresponded with $2NiO.3SiO_2.2H_2O$, or $H_2Ni_2Si_3O_9.H_2O$, **nickel hydrotrimetasilicate;**

F. W. Clarke considers it to be nickel tetrahydro-triorthosilicate, $H_4Ni_2Si_3O_{10}$. The mineral was at first regarded as a phosphate—it contains nearly 2 per cent. $P_2O_5$. According to E. Bertrand, the optical character is negative; and the crystals are probably hexagonal. The sp. gr. ranges from 2·459–2·619, and the hardness is nearly 3. C. Simmonds found the nickel is reduced by heating the mineral to redness in a stream of hydrogen. A. Breithaupt's *röttisite*, from Röttis, Voigtland, is considered to be the gel form of connarite. R. Schwarz and G. A. Mathis made **nickel and cobalt metasilicates,** $NiSiO_3.H_2O$, and $CoSiO_3.2H_2O$, by treating a soln. of water-glass with a salt of the metal. M. Rüger found that a mixture of cobalt oxide and silica in the molar proportions 1 : 2 furnishes a violet mass at 900°; the colouring agent can be washed out by dil. acids, and it is cobalt metasilicate, $CoSiO_3$; ruby-red **cobalt orthosilicate,** $Co_2SiO_4$, was produced by heating a mixture of the constituents in theoretical proportions for 6 hrs. at 100°, cooling quickly and dissolving free silica from the powdered product with potash-lye, and free cobalt oxide with hydrochloric acid. M. Rüger could not make **nickel orthosilicate** or metasilicate by the same process. L. Bourgeois claimed to have made both cobalt and nickel orthosilicates by heating the oxide or chloride and an excess of amorphous silica at a high temp. for several hours. Cobalt orthosilicate is said to be a violet powder consisting of deep violet, non-dichroic crystals resembling peridoite. The sp. gr. is 4·63. It gelatinizes with acids. Nickel orthosilicate is said to be similar, but the colour is greenish-yellow, and the sp. gr. 4·85. Polysilicates could not be made. R. Schwarz and G. A. Mathias made **nickel and cobalt amminometasilicates,** $NiSiO_3.NH_3.H_2O$, and $CoSiO_3.NH_3.H_2O$, by the action of ammonia on the metasilicates. R. Schwarz and H. Bausch prepared a reddish-violet non-crystalline powder of **cobaltic chlorotriamminotetrerosilicate,** $[Co(NH_3)_3Cl(Si_4O_9)]$, by the action of a soln. of sodium metasilicate on cobaltic chloropentamminochloride. When heated to 120°, it yields blue **cobaltic tetrerosilicate,** $CoSi_4O_9$; it does not react with water or cold dil. hydrochloric acid, but the hot acid decomposes it, as does also a soln. of sodium hydroxide. A soln. of cobaltic hexamminochloride reacts with one of sodium metasilicate, forming **cobaltic chlorotetraminotetrerosilicate,** $[Co(NH_3)_4(Si_4O_9)]Cl$, which is freed from water at 105°. When heated, it yields cobaltic tetrerosilicate. They also obtained what they regarded as **cobaltic tetramminotriterosilicatometasilicate,** $[Co(NH_3)_4(Si_3O_7)]_2SiO_3$, by the action of a larger proportion of sodium metasilicate on cobaltic hexamminochloride. By treating cobaltic hexamminotrihydroxide, $[Co(NH_3)_6](OH)_3$, with dioxodisiloxane, $H_2Si_2O_3$, they obtained **cobaltic tetramminotetrerosilicatohydroxide,** $[Co(NH_3)_4(Si_4O_9)]OH$. For the colloidal cobalt silicates, *vide* water-glass.

In the so-called *nickel-gymnite* of F. A. Genth, W. Keller and H. Tiedemann, G. A. Kenngott, and W. J. Taylor, the magnesium of deweylite is in part replaced by nickel. It occurs as a green amorphous incrustation or stalactitic mass of hardness 3–4, and sp. gr. 2·409. It has been reported at Webster, North Carolina; Texas, Pa.; Michipicoten, Lake Superior; Saasthal, Valais. Analyses by F. A. Genth, T. S. Hunt, J. A. Bachmann, P. H. Walker, and F. P. Dunnington correspond approximately with $2NiO.2MgO.3SiO_2.6H_2O$, or **magnesium nickel tetrahydrotriorthosilicate,** $H_4Ni_2Mg_2(SiO_4)_3$. F. W. Clarke considers the mineral to be *nickel magnesium orthotrisilicate*, $Mg_2Ni_2Si_3O_{10}.6H_2O$. J. D. Dana called it *genthite* after F. A. Genth.

A nickeliferous mineral from New Caledonia was described and in some cases analyzed by J. Garnier, A. Liversidge, E. Bertrand, G. vom Rath, P. C. W. Typke, A. des Cloizeaux, C. A. Münster, E. Glasser, V. Thiollière, T. S. Hunt, F. Zambonini, R. Helmhacker, J. H. L. Vogt, W. L. Austin, etc. A similar mineral was obtained by M. Meissonnier, from Malaga, Spain; and W. Hood, F. W. Clarke, H. J. Biddle, etc., have likewise described samples from Oregon, and North Carolina. The composition is variable, but it is idealized into **magnesium nickel metasilicate,** $(Mg,Ni)SiO_3.nH_2O$, or *magnesium nickel dihydro-orthosilicate*, $H_2(Ni,Mg)SiO_4.nH_2O$. P. Kraft discussed the formation of nickel magnesium silicate gels by the weathering

of magnesian rocks in the presence of nickeliferous rocks. M. Rüger, by the method indicated above, found that **zinc cobalt orthosilicate,** $CoZnSiO_4$, could be obtained. If *stannic oxide* be added to the mixtures before calcination the products are mixtures of cobalt meta- or ortho-silicate with stannic oxide. Varieties of *smalt* were obtained by fusing mixtures of cobalt oxide, silica, and stannous oxide, barium oxide, or alkali oxides.

A. Liversidge attempted to distinguish a dark green unctuous variety which he called *noumeaite, noumeite,* or *numeite,* after Noumea, New Caledonia; and a pale green variety which adheres to the tongue and which he called *garnierite.* The term *garnierite* was employed by J. D. Dana. The sp. gr. ranges from 2·20–2·87, and the hardness is 3–4. F. Zambonini found that under a pressure of 6 mm., and over 90 per cent. sulphuric acid, the losses after the 1st, 5th, and 32nd hour were respectively 4·57, 6·98, and 7·61 per cent. The partially dehydrated mineral reabsorbs water to within 4 per cent. of its original value. When heated, water is lost:

| | 69°–70° | 108°–110° | 146° | 238° | 291° | 367° | 420°–425° | 480° |
|---|---|---|---|---|---|---|---|---|
| Loss . . | 5·98 | 7·24 | 7·79 | 8·62 | 9·08 | 9·85 | 10·60 | 11·98 |

The grey colour of the mineral appears deeper at 146°, at 238° the colour is dirty green, and at 480°, dark grey. A. de Gramont studied the spectrum. C. Simmonds found that the nickel is reduced by heating the mineral to redness in a stream of hydrogen. F. Cornu suggested the colloidal origin of garnierite, and F. Zambonini found that the contained water may be replaced by alcohol and other substances. E. Dittler observed that garnierite adsorbs aniline dyes.

In 1788, M. H. Klaproth referred to a green nickeliferous magnesium silicate called *chrysophrase earth,* which was later called *pimelite* by D. L. G. Karsten—from πιμελή, fatness. It was also analyzed or described by C. F. Rammelsberg, W. Baer, H. Fischer, A. Breithaupt, and E. Bertrand. C. Schmidt described a pimelite which E. F. Glocker found to be different, and he called it *alipite*—from ἀλιπης, not greasy. R. Hermann also described a nickeliferous magnesium silicate from Refdansk, Urals, and hence he called it *refdanskite.* It was analyzed by N. Besborodko. G. A. Koenig obtained a hydrated *zinc nickel silicate* from Franklin, New Jersey. He called it *saulesite*—after A. B. de Saules. It contained 38·22 per cent. NiO; 31·02 per cent., $SiO_2$; 4 per cent., ZnO; 9·44 per cent. of water lost at 100°, and 7·14 per cent. lost between 100° and 600°.


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## § 54. Silicon Fluorides

Normal **silicon tetrafluoride,** or **tetrafluorosilane,** $SiF_4$, was discovered by C. W. Scheele,[1] in 1771, during his experiments on the action of sulphuric acid on fluorspar. He found that the volatile acid is totally different from every other in dissolving silica from glass, etc., and carrying it off in the form of vap. When the attempt was made to collect the gas over water in the pneumatic trough, pure silica was deposited as the gas came in contact with the water. F. C. Achard, A. G. Monnet, and M. Boulanger raised objections to this work (**2**. 17, 2), but, in 1780, C. W. Scheele completely established the validity of his former observations. J. C. Wiegleb, J. C. F. Meyer, C. F. Bucholz, and G. Wenzel also showed that the silica in the gas was derived from the glass retort, and that the gas is obtained by heating a mixture of silica sand, fluorspar, and sulphuric acid. Further, the quantity of silica given up by the gas in contact with water is equal to the quantity lost by the silica in the retort. In 1775, J. Priestley repeated C. W. Scheele's experiments, and collected the gas in a dry vessel over mercury. He also made observations on the chemical properties of this gas. The nature of the gas was established by the work of J. L. Gay Lussac and L. J. Thénard, J. Davy, and J. J. Berzelius.

While the nature of silicon tetrafluoride was being established, the remarkable effect obtained by passing the gas into water was noted. J. Priestley, for example, said that the water contains an acid, and added:

> By a repetition of the process, the acid liquor may be procured of a very considerable degree of strength. There seems, however, to be a limit to its strength; for the acid is exceedingly volatile, as is evident from its pungent smell; so that I thought that I gained nothing by repeating the process more than eight or ten times; because it was impossible to transfer the water from one vessel to another, but more acid would be lost by evaporation than would be acquired by another impregnation with the acid air.

The acid is the so-called **hydrofluosilicic acid,** $H_2SiF_6$, and the salts **fluosilicates,** *silicofluorides*, or *silicifluorides*. The nature of the acid was made clear by J. J. Berzelius. The salts were particularly investigated by C. W. Scheele, J. J. Berzelius, and F. Stolba, and their isomorphous relationship with the fluotitanates, fluozirconates, and fluostannates established by J. C. G. de Marignac.

In addition to silicon tetrafluoride, H. St. C. Deville,[2] and L. Troost and P. Hautefeuille reported the formation of a lower fluoride, **silicon subfluoride,** when the gaseous tetrafluoride is passed over silicon heated to the softening point of glass and then suddenly cooled. He also obtained, at the beginning of the reaction between silicon tetrafluoride and aluminium, a small quantity of a volatile fluid which wetted glass with difficulty, and was thought to be a subfluoride. L. Troost and P. Hautefeuille, by sparking silicon tetrafluoride between silicon electrodes, obtained the subfluoride accompanied by a white sublimate of what they regarded as a subfluoride. The need for abrupt cooling is due to the decomposition which occurs at a dull red-heat. The white powder is decomposed with the evolution of hydrogen when treated with aq. ammonia, or potash-lye; water at 0° transforms it into hydroxide; it reduces permanganate and chromate soln., but does not reduce auric chloride or selenious acid. A. Jaquerod and M. Tourpaian found that when silicon tetrafluoride is passed over glass-wool at a red heat, the weight of the normal litre increases from 4·693–4·820 grms., and they explain this by assuming that a subfluoride is formed. The evidence for the existence of the subfluoride is not unimpeachable; and its composition is unknown.

**The preparation of silicon tetrafluoride.**—Carbon tetrafluoride can be made

by the direct union of the elements, and H. Moissan[3] obtained silicon tetrafluoride by the action of fluorine on crystalline or amorphous silicon, or on silica contained in a fluorspar tube. E. Vigouroux said that the reaction between fluorine and silicon is attended by incandescence. G. S. Newth also obtained the gas by the action of dry hydrogen fluoride on crystalline silicon. H. Moissan and F. Siemens found that the gas is formed when the soluble modification of silicon is digested in hydrofluoric acid. The gas is also formed when hydrofluoric acid acts on silica or a silicate; thus, the anhydrous acid becomes heated when in contact with glass. and boils up with the evolution of silicon tetrafluoride. The process of etching glass with hydrofluoric acid depends on the formation of silicon tetrafluoride when the dil. acid or the vap. is allowed to act on glass. G. Gore made the gas by heating potassium hydrofluoride with an excess of silica and sulphuric acid: $2KHF_2+SiO_2+2H_2SO_4=2KHSO_4+2H_2O+SiF_4$.

The early workers—*vide supra*—obtained silicon tetrafluoride from a mixture of fluorspar, powdered glass or sand, and sulphuric acid. This is also a common way of preparing the gas. The mixture is heated in a dry glass flask fitted with a safety-funnel containing mercury. Water must be carefully excluded since otherwise the gas is decomposed; consequently, an excess of sulphuric acid is employed to absorb the water formed during the reaction: $CaF_2+H_2SO_4=2HF+CaSO_4$; and $4HF+SiO_2=2H_2O+SiF_4$. This process was recommended by J. J. Berzelius, W. Hempel, etc. According to J. J. Berzelius, if the glass which comes in contact with the silicon tetrafluoride has the slightest trace of adsorbed moisture, it becomes clouded by an opaque deposit of silica which adheres tenaciously to the glass. The gas can be collected over mercury.

A thoroughly dried mixture of 4 parts of fluorspar and 2–3 parts of sand or powdered glass is put in a dried flask, and 5 parts of sulphuric acid are added. The whole is well mixed by shaking the flask, which should not be more than half filled. Heat is gradually applied, and the gaseous product collected over mercury. If passed into water as in the preparation of hydrofluosilicic acid, if the delivery tube is narrow, it soon becomes choked with silica. There are several methods of overcoming this difficulty. L. J. Thénard made the end of the delivery tube dip under mercury. Care, of course, is necessary to prevent water getting in the tube above the mercury. J. J. Berzelius, A. Maus, and L. Gmelin devised methods of passing the gas into water without choking the delivery tube; but none is so good as the mercury process.

H. Moissan recommended purifying the gas by passing it through a tube containing pieces of glass or glass-wool, and heated to redness. By cooling the gas to −60°, the hydrogen fluoride is condensed; and that impurity can be removed by passing the contaminated gas through a tower packed with sodium fluoride. The gas can be condensed by cooling in liquid air, and purified by fractional distillation. As indicated above, A. Jaquerod and M. Tourpaian said that the treatment recommended by H. Moissan decomposes some of the gas. C. Truchot prepared the gas of a high degree of purity by strongly heating barium fluosilicate—30–40 grms. of the salt gave between two and three litres of gas.

L. Troost and P. Hautefeuille obtained silicon tetrafluoride by passing boron trifluoride rapidly through a porcelain tube at a red heat; H. Moissan found arsenic trifluoride likewise reacts with glass at a dull red-heat; and A. Simon obtained the gas by the action of carbon tetrafluoride or phosphorus trifluoride on silica, or a silicide of iron and manganese. H. St. C. Deville noted that a little gas is formed when steam is passed over a mixture of fluorspar and sand at a red heat; and C. M. Tessié du Motay, by heating a mixture of fluorspar, silica or clay, and carbon. In the latter case, the gas is accompanied by carbon monoxide. S. S. Svendsen represented the reaction between calcium fluoride and silica: $2CaF_2+3SiO_2=SiF_4+2CaSiO_3$; and $2CaF_2+SiO_2=SiF_4+2CaO$. If water vap. be present, the reaction may furnish hydrogen fluoride: $3CaF_2+SiO_2+3H_2O=6HF+CaSiO_3+2CaO$, or hydrofluosilicic acid, $3CaF_2+SiO_2+H_2O=H_2SiF_6+3CaO$, according to the proportion of water used. H. Moissan noted that silicon tetrachloride is not attacked by fluorine in the cold, yet at 40°, the fluorine burns

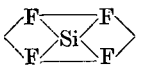
with a pale flame, forming silicon tetrafluoride; and arsenic trifluoride reacts in the cold with silicon tetrachloride, forming silicon tetrafluoride and arsenic trichloride. O. Ruff and K. Albert likewise found that antimony trifluoride reacts with silico-chloroform, $SiHCl_3$, forming silicon tetrafluoride; and E. Berger prepared silicon tetrafluoride from a mixture of lead fluoride, calcium silicate, and alkali nitrate.

**The physical properties of silicon tetrafluoride.**—This compound at ordinary temp. is a colourless, pungent, fuming gas. J. Dalton gave for the **density** of the gas, 4·17; J. Davy, 3·5735; J. B. A. Dumas, 3·60; and C. Truchot, 3·6 when the theoretical value, air unity, is 3·619. A. F. O. Germann and H. S. Booth found 4·6840 grms. for the **weight of a normal litre** at 0° and 760 mm.; and A. Jaquerod and M. Tourpaian 4·693 grms.—*vide supra*—they estimate the coeff. of **compressibility** to be 0·000069, and the **coefficient of expansion** under constant press. between 0° and 18·17° to be $\alpha$=0·003754; and between 0° and 30°, and a constant press. of 726 mm., $\alpha$=0·003752. M. Faraday said that at −105·5° the gas liquefied under a press. of about 9 atm. to form a clear, transparent, colourless, mobile liquid; but it did not solidify at any temp. to which it could be subjected; he added that if the gas confined in a sealed tube be cooled to 0° by a little ice, a liquid appears, but by cooling with a mixture of ice and salt there is a greater condensation of the gas—the press. approximating 30 atm. According to H. Moissan, at −97° and under atm. press., silicon tetrafluoride forms a white amorphous solid, K. Olschewsky said −102°, and that by raising the temp. the solid vaporizes without passing into the liquid state. H. Moissan found that under a press. of 2 atm., the **melting point** was −77°; the resulting colourless mobile liquid had a **boiling point** of −65° under a press. of 1810 mm. O. Ruff and K. Albert gave −90° for the **sublimation temperature** at 759 mm. press. H. Moissan gave −1·5° for the **critical temperature,** and 50 atm. for the **critical pressure.** A. Guntz, H. Hammerl, and M. Berthelot found that the **heat of formation** from crystalline silicon and gaseous fluorine is 239·8 Cals.; and E. Baur calculated 219·6 Cals. F. Fischer and K. Thiele found that the heat of soln. of silica is greater than that of boric acid in hydrofluoric acid. W. Herz gave 2·89 for the **chemical constant.** B. H. Wilsdon studied the energy involved in the motion of the electrons during the dissociation of silicon tetrafluoride.

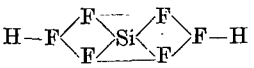
According to A. Dufour, J. Chautard, E. Demarçay, etc., the **spectrum** of the electrical discharge in a tube containing the gas is banded. C. Porlezza studied the regularities in the band spectrum of silicon tetrafluoride. The **Zeeman effect** has been studied by H. M. Reese, etc. J. Chautard showed that new lines appear when the discharge tube is placed in a magnetic field, and A. Cotton showed that the lines persist after the magnetic field is withdrawn; hence they are probably due to chemical action since the glass is attacked. The magnetic spectrum consists of diffuse rays accompanied at the red end by a background of varying intensity, the latter being often resolved into more or less widely-spaced channels. The lines may be separated into three principal groups, of which the frequencies in each group obey Deslandres' formula $N=A-(Bm+C)^2$, *vide* **4.** 25, 3. In the first two groups, the Zeeman effect is abnormal, and in the third group normal. H. Buff and A. W. Hofmann electrically heated an iron or platinum wire in an atm. of silicon tetrafluoride, but the amount of gas decomposed was scarcely perceptible; on the other hand, W. R. Hodgkinson and F. K. Lowndes similarly heated a platinum wire to its m.p. and obtained crystals of silicon at the bottom of the containing vessel. M. Berthelot, and H. Moissan found that the electrical discharge did not decompose the gas after an hour's action, but J. M. Seguin found that with the spectroscope the electric discharge furnishes a blue fluorine line—*vide supra.* L. Troost and P. Hautefeuille found that sparks from an induction coil between carbon electrodes decomposed the gas, while the silicon deposit which collected was thought to be a subfluoride—*vide supra.* If the tetrafluoride vap. be passed over heated silicon, a ring of crystalline silicon is formed in the part

of the porcelain tube just below a red heat; and similarly with the voltaic arc between silicon electrodes in an atm. of silicon fluoride, the flame has a violet glow and a brilliant envelope containing finely divided silicon, which is gradually deposited on the inner surface of the vessel. When the distance between the poles is as large as possible, the light shows a most brilliant violet colour—*vide* hexachlorodisilane. W. J. Pope gave 11·51 for the **refraction equivalent** of the $SiF_6$-radicle.

**The chemical properties of silicon tetrafluoride.**—The composition of silicon tetrafluoride can be represented graphically on the assumptions that silicon is quadrivalent, and fluorine univalent $F_2=Si=F_2$, or, if fluorine be tervalent, the compositions of silicon tetrafluoride and of hydrofluosilicic acid, $H_2SiF_6$, can be represented by the formulæ:



Silicon tetrafluoride.



Hydrofluosilicic acid.

J. Davy said that the gas reddens litmus even when carefully dried. Most of the metalloids are without action on silicon tetrafluoride, but when heated with the metals, the gas is decomposed. J. Davy did not detect any sign of chemical change when a mixture of silicon tetrafluoride and **hydrogen** is exposed to sunlight; but J. M. Seguin found that there is a reaction if the mixture be sparked. H. Moissan observed no reaction by sparking a mixture of equal vols. of **oxygen** and silicon tetrafluoride. The gas is not combustible, and it does not support the combustion of a taper or burning wood. The gas forms a white cloud when exposed to ordinary moist air; and the crystalline product, when washed free from acid with warm water, and dried at 130°, has, according to H. H. Landolt, the composition $HSi_2O_4F$; *i.e.* $HF.2SiO_2$, or **hydrofluomesodisilicic acid,** HO.SiO.O.SiO.F. When this product is heated by the gas-blowpipe it loses silicon tetrafluoride, water, and an acid gas. The residue appears to be silica associated with 3·06 per cent. of fluorine and corresponding with $HF.8SiO_2$—*vide infra* the alkali oxyfluosilicates. On the assumption that the hydrofluomesodisilicic acid contains some free silica, H. Schiff and E. Bechi represent the reaction: $8HSi_2O_4F+SiO_2=2H_2O+2HF+SiF_4+2HSi_8O_{16}F$. The hydrofluomesodisilicic acid volatilizes completely when heated with ammonium fluoride. J. J. Berzelius discussed the possibility of the existence of $4HF.SiO_2$. **Water** absorbs and decomposes a large quantity of gas with the production of hydrofluosilicic acid, $H_2SiF_6$, and hydrated silica: $3SiF_4+2H_2O=SiO_2+2H_2SiF_6$. C. T. Barfoed, and K. Daniel discussed the reaction from the point of view of analytical chemistry. In 24 hrs., said J. J. Berzelius, 100 parts of water absorb 140·6 parts of the gas; the absorption at first is rapid, but as the liquid becomes thickened by the precipitated silica, the absorption is much slower. According to J. Davy, one vol. of water absorbs 265 vols. of gaseous silicon tetrafluoride. The precipitated silicic acid, said J. J. Berzelius, is somewhat soluble in water, and consequently one-fourth, not one-third, of the silicon of the gas appears in the precipitate. When the precipitate is thoroughly washed, it is quite free from fluorine. Consequently, there is a marked difference in the products of the reaction between silicon tetrafluoride with an excess of water, and with a limited supply of water vap. According to A. Daubrée, water-vap. at a red heat decomposes silicon tetrafluoride, forming crystalline silica. According to A. Guntz, $2H_2O+SiF_4 \rightleftharpoons SiO_2+4HF-25·8$ Cals., and this reaction can occur only when the temp. is high enough to prevent the secondary formation of hydrofluosilicic acid which develops sufficient heat to compensate for this absorption. According to L. Troost and P. Hautefeuille, steam above 150° is not decomposed by silicon tetrafluoride. E. Baur has shown that the condition of equilibrium of the gas phase corresponds with $C_{SiF_4}C^2_{H_2O}/C^4_{HF}=163\times10^7$ at 104°, and $5·4\times10^7$ at 270°. The equilibrium point

of the reaction favours the decomposition of the silicon tetrafluoride with rise of temp. Hence the formation of silicon tetrafluoride and water from silicic and hydrofluoric acid is accompanied by an evolution of heat, and from the equation $d(\log K)/dT=q/RT^2$, the heat evolution is calculated to be $SiO_2+4HF=SiF_4+2H_2O$ =8·945 Cals., which is about one-third the value 25·8 calculated from the thermochemical data.

Conc. aq. **hydrofluoric acid** was found by F. Kessler to absorb silicon tetrafluoride to form hydrofluosilicic acid; but **hydrogen fluoride,** according to C. Truchot, does not unite with silicon tetrafluoride at temp. down to −30°. J. Davy found that **iodine** can be sublimed in the gas without chemical change. J. Davy did not observe any reaction by heating **sulphur** in an atm. of silicon tetrafluoride; and H. Schiff and E. Bechi found that when the gas is heated with **hydrogen sulphide** there is no chemical change.

J. Davy did not observe any decomposition of silicon tetrafluoride when **carbon** is heated in the gas. According to W. Knop, absolute **alcohol,** or alcohol with 8 per cent. of water readily absorbs silicon tetrafluoride without the separation of silicic acid, and a strongly acid fluid of sp. gr. 1·044 is formed. When exposed to air, the liquid called by W. Knop *Kieselfluoralcohol,* gives off silicon tetrafluoride, and when distilled, the same gas is given off and some silicic acid first separates, and afterwards a siliciferous alcohol distils over. W. Knop also found ethylorthosilicate and hydrofluosilicic acid among the products of the action of silicon tetrafluoride on alcohol. When the Kieselfluoralcohol is mixed with a little water it gelatinizes, but with much water it forms a clear soln. Aq. ammonia precipitates silicic acid, and on addition of aq. alcohol produces a compound of the composition $(NH_4)_5Si_3F_{17}$—*vide infra.* Many organic compounds, *e.g.* aniline, *o*- and *p*-toluidine, dimethylamine, dimethylaniline, *p*=chloraniline, quinoline, acetone, etc.—unite with silicon tetrafluoride, forming additive products.

According to J. Davy, dry **ammonia** reacts with dry silicon tetrafluoride forming white *silicon diamminotetrafluoride,* $SiF_4.2NH_3$—*vide infra.* A. Hileman showed that when the gas is passed into aq. ammonia, ammonium fluoride and silicic acid are formed. Silicon fluoride was found by J. J. Berzelius to unite with **nitric oxide, nitrogen trioxide, tetroxide, and pentoxide.** F. Kuhlmann showed that nitric acid absorbs silicon tetrafluoride copiously, forming a fuming liquid from which water or alkalies precipitate silicic acid. J. Davy said that the gas is not decomposed by heated **phosphorus.** A. Besson found that at −22° under a press. of 50 atm. two vols. of **phosphine** unite with 3 vols. of silicon tetrafluoride, forming white crystals of *silicon phosphinotetrafluoride,* $3SiF_4.2PH_3$. J. Davy found that the gas is absorbed by **antimonic oxide.**

According to J. L. Gay Lussac and L. J. Thénard, and J. J. Berzelius, at ordinary temp., **potassium** has a slight action on silicon tetrafluoride; when the metal is heated in the gas it becomes white; then darkens, becoming black; then it takes fire, burning with a dark red flame, absorbing a quantity of the gas equal in vol. to that of the hydrogen which would be evolved had the metal been treated by water. The resulting hard porous mass which remains is a mixture of potassium fluoride, potassium fluosilicate, and silicon. The behaviour of **sodium** is similar. J. Davy observed that the gas was not changed by molten **zinc.** H. St. C. Deville passed silicon tetrafluoride over heated **aluminium** and obtained a mixture of aluminium fluoride and silicon. A. F. O. Germann and H. S. Booth found that the gas had no action on **mercury.** J. J. Berzelius said that when the gas is passed through a layer of white-hot **iron** turnings, very little is absorbed, for the iron becomes covered with a thin layer of silicon and iron fluoride; E. Frémy said that when the gas is heated in the presence of iron or **platinum,** the metals are transformed into silicides, and H. Moissan said that at a red heat the gas is decomposed with the liberation of some free fluorine.

According to J. Davy, aq. soln. of the bases act like water, precipitating one-third of the silica and forming a fluosilicate of the metal, or they simply precipitate

the silica and form a fluoride of the metal. Many of the alkalies, alkaline earths, and anhydrous metallic oxides absorb silicon fluorides with the evolution of heat, sometimes with incandescence, forming a mixture of the metal fluoride and silica. According to C. Truchot, when the gas is treated with **lithium hydroxide** the alkali fluoride is formed; similar results were obtained by J. Davy, and C. Truchot with **sodium hydroxide**: $SiF_4+4NaOH=SiO_2+2H_2O+4NaF$, but with **potassium hydroxide,** the fluosilicate was formed: $3SiF_4+4KOH=SiO_2+2H_2O+2K_2SiF_6$. According to J. Davy, **calcium oxide** becomes red hot when immersed in the gas, and the reaction is probably eq. to $2CaO+SiF_4=2CaF_2+SiO_2$. If **calcium hydroxide** be present, heat is necessary to start the reaction. J. Davy also found that **barium oxide** absorbs the gas, and the product gives off the gas when treated with sulphuric acid; according to J. B. A. Dumas, if the baryta be heated in the gas, the mass becomes incandescent, and the reaction approximates to $SiF_4+4BaO=2BaF_2+Ba_2SiO_4$. J. Davy found that silicon tetrafluoride combines with **magnesium oxide** without ignition, and the gas is also absorbed by **manganese,** and **mercuric oxides;** and copiously by **ferric oxide.** The gas is expelled with sulphuric acid. He also found that **aluminium oxide** absorbs the gas. The action of silicon tetrafluoride on heated alumina enabled A. Daubrée to synthesize topaz, and other minerals. The reaction has been investigated by H. St. C. Deville, and A. Reich. The gas is said to be *un minéralisateur par excellence.* L. Troost and P. Hautefeuille found that red-hot alumina, and **zirconium oxide** are rapidly attacked by silicon tetrafluoride. Silicon tetrafluoride, said J. J. Berzelius, is not absorbed by **boric oxide,** but it is absorbed by **boric acid,** forming a white powder which does not fume. When the product is treated with water, part is dissolved, forming a soln. of hydrofluoboric acid, $HBF_4$. A. Hileman found that when a conc. aq. soln. of **potassium chloride** is treated with silicon tetrafluoride, potassium fluosilicate and hydrochloric acid are formed. J. J. Berzelius observed that no action occurs when the anhydrous **alkali carbonates** and **alkali borates** are treated with the gas. J. Davy showed that the gas is not affected by fused **potassium chlorate,** or by heated **calcium chloride.** L. Troost and P. Hautefeuille found that at a red heat **porcelain** is slowly attacked by silicon tetrafluoride; and H. Rose, that **glass** is slowly attacked at ordinary temp.—possibly owing to a film of moisture on the glass—because A. F. O. Germann and H. S. Booth could detect no action.

According to O. Ruff and C. Albert,[4] silicochloroform does not react when heated with lead and silver fluorides; with antimony and arsenic trifluorides in a sealed tube the reaction is of the type: $3SiHCl_3+4SbF_3=3SiF_4+2Sb+2SbCl_3+3HCl$; but with tin and titanium tetrafluorides, the reaction is of the type: $3SnF_4+4SiHCl_3=4SiHF_3+3SnCl_4$. The product, **silicofluoroform,** or **trifluosilane,** $SiHF_3$, is best obtained by heating molar proportions of silicochloroform and titanium tetrafluoride in a closed copper vessel or glass tube for 18 hrs. at 100°–120°. The vessel is then cooled in liquid air and allowed to become warm slowly, the gases evolved being condensed by means of liquid air. Silicofluoroform boils at −80·2° under 758·5 mm. press., and melts at about −110°. It slowly decomposes in a sealed glass tube, even at the ordinary temp., according to the equation $4SiHF_3=2H_2+3SiF_4+Si$, the decomposition being greatly accelerated by heat. It burns in air with a very pale blue flame, the temp. of ignition being higher than that of silicochloroform: $12SiHF_3+6O_2=3SiF_4+3SiO_2+4H_2SiF_6+2H_2SiO_3$. Water and sodium hydroxide decompose it thus: $2SiHF_3+4H_2O=Si(OH)_4+H_2SiF_6+2H_2$. Alcohol forms ethyl orthosilicate, $Si(OEt)_4$; ether forms ethyl silico-orthoformate, $SiH(OEt)_3$, and ethyl fluoride. Toluene dissolves its own vol. of silicofluoroform.


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## § 55. Hydrofluosilicic Acid and its Salts

The observations of J. Priestley[1] and others on the preparation of hydrofluosilicic acid, $H_2SiF_6$, have been previously indicated. The acid is known only in soln., for all attempts to make the anhydrous acid either by concentrating the aq. soln., or by the direct union of hydrogen fluoride and silicon tetrafluoride, have proved abortive. J. Priestley showed that in the former case, the acid volatilizes, after a certain conc. has been obtained. Although F. Kessler was able to prepare hydrofluosilicic acid by the action of silicon tetrafluoride on a conc. aq. soln. of hydrofluoric acid, C. Truchot observed no sign of combination in the absence of water. J. J. Berzelius obtained the acid by the action of cold dil. hydrofluoric acid on powdered quartz. The silica dissolves quietly at first, but afterwards, if the quartz be in excess, and the acid conc., silicon tetrafluoride is evolved. J. J. Berzelius' method of passing silicon tetrafluoride into water for the preparation

of hydrofluosilicic acid has already been indicated. The mixture of aq. acid and gelatinous silicic acid is separated by straining or filtration. The resulting liquid, said J. J. Berzelius, is a dil. soln. of hydrofluosilicic acid with a little silicic acid in soln. The preparation of hydrofluosilicic acid by this process was discussed by F. Stolba, W. Hempel, A. Ziegler, A. W. Hoffmann, and C. M. Tessié du Motay and E. Karcher. F. Stolba also used cryolite in place of fluorspar. A. Ziegler found the absorption of the gas is favoured by warming the water to 60°–70°. F. Stolba showed that if the sulphuric acid contains arsenic, the hydrofluosilicic acid will be contaminated with arsenious fluoride.

E. Fleischer treated a mixture of silica and cryolite with a boiling soln. of barium hydroxide, and obtained barium fluosilicate. The product was boiled with a soln. of calcium sulphate acidified with hydrofluoric acid; the soln. of calcium fluosilicate was mixed with an equal vol. or more of alcohol, and filtered from the precipitated barium sulphate; the calculated quantity of sulphuric acid was added, the calcium sulphate filtered off, and an alcoholic soln. of hydrofluosilicic acid obtained. E. Baur and A. Glässner obtained a soln. of the acid of a high degree of purity by treating purified and dry barium fluosilicate with conc. sulphuric acid in a platinum retort. A. F. Meyerhoffer used calcium fluoride. F. A. Hoppen obtained hydrofluosilicic acid as a by-product in the purification of graphite by hydrofluoric acid. For the preparation of hydrofluosilicic acid by the joint action of silica, calcium fluoride, and steam by S. S. Svendsen's process, *vide* silicon tetrafluoride. F. Halla purified the acid by the following process:

Commercial hydrofluosilicic acid may be purified by removing the arsenic with hydrogen sulphide, and the excess of gas with a current of air; precipitating the iron with potassium ferrocyanide; treating the soln. with copper sulphate, filtering, removing the excess of copper with hydrogen sulphide, and the excess of the latter with air; adding lead fluosilicate to precipitate sulphuric and hydrofluoric acids, and removing the lead in a similar way to the copper. Addition of barium hydroxide to remove the hydrofluoric and sulphuric acids is not so good, as it causes a small amount of the hydrofluosilicic acid to hydrolyze.

A dil. soln. of hydrofluosilicic acid can be conc. by evaporation at a low temp., but the process cannot be carried very far because the soln. at 40° can be evaporated completely without residue. According to J. J. Berzelius, conc. hydrofluosilicic acid exposed to the air at ordinary temp. absorbs moisture until the conc. has acquired a definite value, and a very dil. acid, on the contrary, gives off water in air until it attains the same conc. The most conc. acid J. J. Berzelius could prepare contained 42·85 per cent. of water and corresponded with $H_2SiF_6+6H_2O$. The phenomenon thus resembles to some extent the distillation of acids of constant composition. The hydrofluosilicic acid vaporizes with the steam, but at the same time the acid is partly dissociated into hydrogen fluoride and silicon tetrafluoride. According to E. Baur, at a press. of 720 mm., an acid containing 13·3 per cent. of hydrofluosilicic acid gives a vap., the composition of which is exactly expressed by the formula $H_2SiF_6$. The distillate from more conc. acids contains silicic acid, whilst dil. acids yield a distillate containing hydrogen fluoride; further, conc. acids dissolve silicic acid when evaporated with it, whereas dil. soln. deposit this acid on evaporation. An acid containing 30·2 per cent. of hydrofluosilicic acid boils at 108·5° under 7·20 mm. press. E. Baur and A. Glässner measured the vap. density of hydrofluosilicic acid at 23°, 31·5°, and 42° at press. between 650 and 1350 mm. of mercury. Under these conditions, the mol. wt. is between 80 and 83, showing that more than half of the acid is dissociated, and at 100°, probably more than two-thirds is dissociated. C. A. Jacobsen holds that the vap. density of hydrogen fluoride agrees with the formulæ $H_2F_2$ and $H_3F_3$, and on this assumption believed that the hydrofluosilicic acid was completely dissociated. He also showed that hydrofluosilicic acid like carbonic and sulphurous acids cannot exist in the state of vap. E. Baur studied the equilibrium con-

ditions between silicon tetrafluoride, hydrogen fluoride, water, and silicic acid—*vide supra*, silicon tetrafluoride.

Hydrofluosilicic acid has a very sour taste resembling that of hydrochloric acid, and, like that acid, it irritates the skin, and reddens litmus. According to C. Truchot, on cooling to −20° a soln. of silicon tetrafluoride in hydrofluoric acid containing one eq. of water, crystals of the **monohydrate,** $H_2SiF_6.H_2O$, are formed; on exposure to air, the crystals fume strongly and decompose. F. Kessler passed silicon tetrafluoride into conc. hydrofluoric acid and found no deposition of silica or absorption of excess of gas, but noted a deposition of acicular crystals in the delivery tube. The crystals were free from hydrogen fluoride, for their aq. soln. after precipitation by an excess of potassium chloride did not corrode glass; and they were free from excess of silica because the potassium fluosilicate so formed, after washing with dil. alcohol, left no trace of silica in the evaporated wash-waters. The composition of the crystals approximated to that of the **dihydrate,** $H_2SiF_6.2H_2O$. The crystals were very deliquescent; fumed strongly in air; melted at 19°; and at a higher temp. they decomposed with ebullition. C. Truchot could not make the dihydrate, but on cooling at 0° a soln. of silicon tetrafluoride in 4–6 eq. of water, he obtained fuming crystals of the **tetrahydrate,** $H_2SiF_6.4H_2O$. The sp. gr. was 1·7; and they readily melted to form a syrupy liquid. When heated in vacuo, they decomposed into silicon tetrafluoride, hydrogen fluoride, and water.

The sp. gr., $S$, of aq. soln. of hydrofluosilicic acid, determined by F. Stolba, are shown in Table XXXIV; and the results can be represented by the formula $S=1+0{\cdot}004n+\{n(n-3)+2\}\times10^{-5}$, where $n$ represents half the percentage amount of contained $H_2SiF_6$, at 17·5°/17·5°. For the heat of formation, C. Truchot

TABLE XXXIV.—SPECIFIC GRAVITIES OF HYDROFLUOSILICIC ACID AT 17·5°/17·5°.

| Per cent. $H_2SiF_6$. | Specific gravities. | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | 0 | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |
| 0 | — | 1·0080 | 1·0161 | 1·0242 | 1·0324 | 1·0407 | 1·0491 | 1·0576 | 1·0661 | 1·0747 |
| 10 | 1·0834 | 1·0922 | 1·1011 | 1·1100 | 1·1190 | 1·1281 | 1·1373 | 1·1466 | 1·1559 | 1·1653 |
| 20 | 1·1748 | 1·1844 | 1·1941 | 1·2038 | 1·2136 | 1·2235 | 1·2335 | 1·2436 | 1·2537 | 1·2639 |
| 30 | 1·2742 | 1·2846 | 1·2951 | 1·3056 | 1·3162 | — | — | — | — | — |

gave $Si_{cryst.}+6F+2H+Aq.=H_2SiF_6.aq.+375{\cdot}1$ Cals.; A. Guntz gave 374·3 Cals.; H. Hammerl, $3SiF_4+2H_2O+Aq.=2H_2SiF_6.aq.+SiO_2.aq.+67$ Cals.; C. Truchot, $SiF_4+2HF+Aq.=H_2SiF_6.aq.+33{\cdot}9$ Cals. J. Thomsen gave for the heat of neutralization $H_2SiF_6.aq.+NaOH.aq.=\ldots+13{\cdot}3$ Cals.; $\frac{1}{2}H_2SiF_6.aq.+NaOH.aq.=\ldots+13{\cdot}3$ Cals.; and $H_2SiF_6.aq.+2NaOH.aq.=\ldots+26{\cdot}6$ Cals.—*vide infra*, alkali fluosilicates. C. Truchot gave for the heat of dissolution of tetrahydrate, +8·0 Cals. W. Ostwald found the eq. conductivity, $\lambda$, at 25° for soln. with an eq. of the acid per $v$ litres, to be

| $v$ | 2 | 8 | 32 | 64 | 128 | 256 | 512 | 1024 | 2048 | 4096 |
|---|---|---|---|---|---|---|---|---|---|---|
| $\lambda$ | 216 | 281 | 324 | 342 | 358 | 377 | 415 | 495 | 652 | 847 |

The increase in the conductivity above $v=256$ is due to the hydrolysis of hydrofluosilicic acid into silicic and hydrofluoric acids. S. Arrhenius discussed the ionization of the acid in soln. W. Ramsay and F. L. Usher examined the effect of radium radiations on hydrofluosilicic acid, and claimed to have degraded silicon to carbon. This has not been verified.

According to J. Davy, if hydrogen chloride be passed into hydrofluosilicic acid, water is taken from the compound, and silicon fluoride is formed. A. Hileman found that when the acid is boiled with potassium iodide and iodate, iodine is set

free. J. Davy, and F. Stolba found that sulphuric acid behaves like hydrogen chloride gas; and that boric acid precipitates gelatinous silica from hydrofluosilicic acid, and forms hydrofluoboric acid, $HBF_4$. According to J. Davy, and J. J. Berzelius, an excess of aq. ammonia, sodium hydroxide, or other salifiable base precipitates the whole of the silica, and forms a fluoride, and A. Hileman represented the reaction: $H_2SiF_6+6KOH=6KF+Si(OH)_4+2H_2O$. A soln. of an alkali hydroxide or carbonate decomposes the fluosilicates, forming a fluoride and silicate. Consequently, when hydrofluosilicic acid is titrated with a soln. of sodium hydroxide with litmus as indicator, there are two transition points. The first corresponds with the neutralization of the original acid: $H_2SiF_6+2NaOH=Na_2SiF_6+2H_2O$; and the second with the decomposition of the fluosilicate: $Na_2SiF_6+4NaOH=6NaF+Si(OH)_4$. Litmus shows the permanent excess of alkali after the completion of the second reaction, for silicic acid does not behave as an acid to litmus under these conditions. The reaction was studied by C. A. Jacobson, J. Katz, and J. G. Dinwiddie. C. R. Wagner and W. H. Ross showed that the reaction, $H_2SiF_6+6NaOH=6NaF+H_2SiO_3+3H_2O$, occupies an appreciable time; and L. J. Hudleston and H. Bassett inferred that the reactions involved are (i) $SiF_4+3H_2O=H_2SiO_3+4HF$; (ii) $SiF_4+2HF=H_2SiF_6$; and (iii) $3SiF_4+3H_2O=2H_2SiF_6+H_2SiO_3$. The reactions are reversible because hydrofluosilicic acid is formed equally by the action of silicon tetrafluoride on water and of hydrofluoric acid on silica; and hydrofluosilicic acid with sufficient alkali yields sodium fluoride and silicic acid as end-products. The proportion of hydrofluoric acid in the aq. soln. was found by E. Baur, and C. A. Jacobson to be negligibly small. For the second of the above reactions, L. J. Hudleston and H. Bassett found $[SiF_4][HF]^2=K[H_2SiF_6]$, where $K=4\times10^{-5}$. They also showed that silicic acid can exist in soln. with an active mass proportional to its conc., to the extent of at least 0·003 mol. per litre at 15°. J. Katz found that pyridine fixes the acid without decomposition. A. von Berkel showed that with a soln. of calcium hydroxide, calcium fluoride, fluosilicate, and silicate, and hydrated silica are formed. According to J. J. Berzelius, ammonium, potassium, and sodium salts produce a transparent precipitate which is scarcely perceptible at first; and barium salts gave a white crystalline precipitate which becomes visible after a few seconds. For the action of hydrofluosilicic acid, *vide* **2**. 20, 28. E. Guerry and E. Toussaint discussed the action of ammonium salts in the presence of citric acid; and A. Gawalowsky, the action of soln. of chromium salts.

W. T. Gibbs found that silicate minerals are more rapidly opened up by hydrofluoric acid if a trace of hydrofluosilicic acid be present. The reports of the action of hydrofluosilicic acid on glass, by J. J. Berzelius, and J. Davy, indicate that the acid cannot be preserved in glass bottles, but, added H. Rose, the acid slowly dissolves some alkali, lime, and ferric oxide from the glass, and precipitate these substances when alcohol is added. J. J. Berzelius also said a mixture of the acid with half its vol. of alcohol, does not attack glass. If the acid be evaporated on glass, the surface is corroded because, added J. J. Berzelius, silicon tetrafluoride is at first evolved, and the hydrofluoric acid in the residual liquor becomes more and more conc., which subsequently also evaporates. Hence, the acid attacks glass when evaporated on its surface. When evaporated over sulphuric acid in vacuo, it corrodes the glass receiver, because after the silicon fluoride has been given off, hydrofluoric acid remains to be evaporated. The work of E. Baur and A. Gaässner, indicated above, explains the facts more clearly, for a soln. which will dissolve silica will also corrode glass, and a soln. containing hydrofluosilicic acid but no hydrofluoric acid does not etch glass. H. St. C. Deville found that hydrofluosilicic acid has a considerable solvent action on alumina forming what he regarded as a soln. of *hydrofluoaluminic acid*. A similar soln., free from silica, was obtained by treating china clay with hydrofluosilicic acid (*q.v.*). He added:

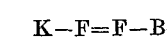
When dil. hydrofluosilicic is placed in contact with ignited alumina, aluminium fluosilicate is first formed. Then, when an excess of alumina is added, and the digestion prolonged, the fluosilicate is decomposed, silica is deposited, and hydrated soluble aluminium fluoride is formed.

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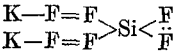
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## § 56. The Fluosilicates

The salts of hydrofluosilicic acid are called *silicofluorides*, or, in harmony with the commonly recognized name for the acid, **fluosilicates.** In general, the fluosilicates are made by dissolving the oxides, hydroxides, or carbonates in the acid; by the action of silicon tetrafluoride on the metal fluorides—solid or in soln.; by dissolving the fluoride and silica in aq. hydrofluoric acid; and in some cases by dissolving the metal in the acid. An excess of acid must always be present or the salts may be hydrolyzed. The fluosilicates usually form characteristic crystals, some are useful for identifying certain metals under the microscope. The low solubilities of the salts of potassium, sodium, and barium are noteworthy. The salts decompose with the evolution of silicon tetrafluoride when heated, and leave the metal fluoride as a residue. When a fluosilicate is warmed with sulphuric acid, hydrofluosilicic acid is given off. Nitric or hydrochloric acid partially decomposes the fluosilicates, and some of the chlorides and nitrates are partially decomposed by hydrofluosilicic acid. The reaction is therefore reversible. The fluosilicates are isomorphous with the corresponding fluotitanates, fluozirconates, and fluostannates. Graphic formulæ for the fluoborates and fluosilicates are usually based on the tervalency of fluorine:



Potassium fluoborate.



Potassium fluosilicate.

According to A. Werner's *Neuere Anschauungen auf dem Gebiete der anorganischen Chemie* (Braunschweig, 68, 1905), hydrofluosilicic acid is a complex acid analogous to hydrofluoboric acid, hydrochloroplatinic acid, and other halogeno-acids. The silicon is considered to be the central atom with a co-ordination number 6, thus furnishing the acid $[SiF_6]H_2$.

F. Kessler [1] recommended hardening the surface of calcareous stones by means of the fluosilicates of the metals—*e.g.* magnesium, aluminium, or lead—which form an insoluble oxide. Carbon dioxide is given off, and calcium fluoride, silica, and alumina or lead carbonate, or magnesium fluoride, may be formed. The fluosilicates have also been recommended as antiseptics by G. Heinzelmann, G. Jacquemin, A. Cobenzl, F. J. Homeyer, etc. E. Prior described the antiseptic properties of hydrofluosilicic acid under the trade-name *keramyl;* and H. Schnegg showed that the acid is also the active constituent in the disinfectant with the trade-name *montanin*. According to A. Cobenzl, the sodium, potassium, and ammonium fluosilicates are used in rat-poisons.

J. Davy [2] found that one vol. of silicon tetrafluoride unites with 2 vols. of ammonia, forming a white powder—**silicon diamminotetrafluoride,** $Si(NH_3)_2F_4$. It is decomposed by water into ammonium fluosilicate and silicic acid; and by hydrogen chloride into ammonium chloride and silicon tetrafluoride.

W. Knop mixed alcoholic soln. of hydrofluosilicic acid and ammonia, and obtained a gelatinous mass which when dried had the composition *ammonium heptadecafluosilicate,* $5NH_4F.3SiF_4$, but there is nothing to show whether a mixture or compound is involved. J. C. G. de Marignac mixed normal ammonium fluosilicate with an excess of ammonium fluoride and obtained tetragonal crystals of the composition $3NH_4F.SiF_4$, or *ammonium heptafluosilicate,* $(NH_4)_3SiF_7$, which volatilize when heated and without melting; when treated with a soln. of ammonium carbonate, there is a period of quiescence after which bubbles of carbon dioxide are formed, and silicic acid is precipitated. H. Baker prepared the same salt.

A. Scacchi reported the occurrence of ammonium fluosilicate which he called *cryptohalite,* along with ammonium chloride in a Vesuvian fumarole. J. L. Gay Lussac and L. J. Thénard, J. Davy and J. J. Berzelius, etc., made **ammonium fluosilicate,** $(NH_4)_2SiF_6$, by neutralizing a soln. of hydrofluosilicic acid with dil. aq. ammonia; a little silicic acid is usually precipitated at first; and if an excess of ammonia is used, still more silicic acid is precipitated. F. Stolba neutralized one-third of the required amount of hydrofluosilicic acid with ammonia, and after mixing that product with the remaining two-thirds of acid, evaporated the filtered soln. for crystallization. J. J. Berzelius made this salt by heating an intimate mixture of ammonium chloride and sodium or potassium fluosilicate in a glass vessel until the required compound sublimes. F. Stolba made it by dissolving iron in hydrofluosilicic acid, treating the conc. soln. with ammonium chloride, and, on cooling the liquid, crystals of ammonium fluosilicate separated. According to J. Davy, if an aq. soln. of the salt be evaporated spontaneously, large, transparent, four-sided prisms are formed, or, according to J. J. Berzelius, six-sided prisms containing water of crystallization; but this is an error, they are anhydrous. According to A. Priess, the crystals are isodimorphous with those of the potassium salt. J. C. G. de Marignac obtained octahedral crystals of the cubic salt, and B. Gossner obtained them by evaporating the aq. soln. above 13°, while below 5°, the aq. soln. furnishes the hexagonal form. If the temp. approaches 12° both forms appear. J. C. G. de Marignac first obtained both the hexagonal and the cubic crystals side by side from a soln. containing an excess of hydrofluoric acid and ammonium fluoride. According to B. Gossner, the axial ratio of the hexagonal crystals is $a : c = 1 : 1{\cdot}6552$. The symmetry deduced from the corrosion figures is that of the dihexagonal bipyramidal class. R. M. Bozorth showed that the X-radiogram of ammonium fluosilicate is analogous with those of ammonium chloroplatinate, and ammonium and potassium chlorostannates, being like that of calcium fluoride type with each fluorine replaced by an $NH_4$-group, and each calcium atom by a fluosilicate group having six fluorine atoms equidistant from the silicon atom in the directions of the axes of the crystal. The length of unit cube containing four mols. is 8·38 A.; the shortest distances between the centres of the atoms of silicon and fluorine is 1·72 A. The sp. gr. of the cubic crystals is 1·970, according to H. Töpsöe and C. Christiansen, and 2·011, according to B. Gossner; F. Stolba gave 1·9469 at 14°, and for the sublimed salt 1·9966 at 17·5°. B. Gossner found the

sp. gr. of the hexagonal crystals to be 2·152. J. J. Berzelius said that the salt decrepitates slightly when heated, and sublimes to form a solid crystalline mass without fusion or decomposition. The index of refraction of the cubic crystals, according to H. Töpsöe and C. Christiansen, is 1·3682 for the *C*-line, 1·3696 for the *D*-line, and 1·3723 for the *F*-line. The double refraction of the hexagonal crystals is feeble and negative. C. Truchot found for the heat of formation, $H_2SiF_6$ (one mol. in 10 litres of water)+$6NH_4O$ (one mol. in 4 litres of water)=$6NH_4F_{soln.}$ +$Si(OH)_4$+56·2 Cals; $H_2SiF_{6soln.}+2NH_4O_{soln.}=(NH_4)_2SiF_{6soln.}$+27·2 Cals.; $H_2SiF_6+2NH_{3gas}=(NH_4)_2SiF_{6solid}$+66·8 Cals.; $SiF_{4gas}+2NH_4F_{soln.}=(NH_4)_2SiF_{6soln.}$ +34·2 Cals; $SiF_{4gas}+2NH_4F_{solid}=(NH_4)_2SiF_{6solid}$+36·6 Cals.; and for the heat of soln. of a mol of $(NH_4)_2SiF_6$ in 1200 mols. of water at 7°, 8·4 Cals. J. Davy, and J. J. Berzelius said that the salt is very soluble in water, but does not deliquesce in air. According to F. Stolba, 100 parts of water at 17·5° dissolve 18·6 parts of the salt, and the soln. has a sp. gr. 1·0961; 100 parts of boiling water dissolve 55·5 parts of salt; and one part of salt dissolves in 45·5 parts of 31 per cent. alcohol. J. Davy said that the salt has a strong saline taste and reddens moist litmus. When the soln. is boiled in glass vessels some silica is dissolved and precipitated when the soln. is diluted. The salt is decomposed by sulphuric acid with the evolution of silicon tetrafluoride and hydrofluoric acid; hydrogen chloride has a less energetic action; and hydrochloric acid does not affect the salt. A soln. of potassium hydroxide liberates ammonia and forms potassium fluosilicate, but does not precipitate silica; J. Davy said sodium hydroxide acts similarly, but J. L. Gay Lussac and L. J. Thénard said that all the silica is precipitated. J. Davy found that ammonia forms ammonium fluoride and precipitates all the silica, while J. J. Berzelius, and J. L. Gay Lussac and L. J. Thénard found a portion of the silica remains in soln. F. J. Faktor studied the antiseptic qualities of the salt.

E. Ebler and E. Schott[3] precipitated small crystals of **hydrazine fluosilicate,** $N_2H_4.H_2SiF_6$, by adding alcohol to a mixture of equi-molar proportions of a 50 per cent. aq. soln. of hydrazine hydrate and 20 per cent. hydrofluosilicic acid. The salt melts with decomposition at 186°; it is readily soluble in water and sparingly soluble in methyl or ethyl alcohol; and when heated in vacuo, it yields silicon tetrafluoride and hydrazine dihydrofluoride. They also made crystals of **hydroxylamine fluosilicate,** $(NH_2OH)_2H_2SiF_6.2H_2O$, adding 16 per cent. aq. hydrofluosilicic acid to a 25 per cent. aq. soln. of hydroxylamine and allowing the mixture to evaporate. The salt crystallizes from boiling methyl alcohol in scales, and is almost insoluble in alcohol, but dissolves readily in water.

J. J. Berzelius[4] first prepared lithium fluosilicate by evaporating an aq. soln. of the salt obtained by the action of the acid on an aq. soln. of a lithium salt. F. Stolba evaporated a soln. of lithium carbonate or acetate in a small excess of hydrofluosilicic acid, and obtained crystals of **dihydrated lithium fluosilicate,** $Li_2SiF_6.2H_2O$; and C. Truchot obtained the same salt by the action of silicon tetrafluoride on water having lithium fluoride in suspension. The potassium salt was found by A. Cossa in the fumaroles of the Vulcano crater in one of the Lipari Islands, and he called the mineral *hieratite*—from Hiera, the Greek name of the crater. J. J. Berzelius noted that a detonation occurs when a mixture of silicon and potassium hydrofluoride is heated. He also said that molten sodium or potassium fluoride dissolves silica, but does not give off silicon tetrafluoride when heated to a high temp. Gebrüder Siemens made the alkali fluosilicates by mixing the alkali chloride and silica into a thin paste with water, and adding hydrofluoric acid. H. Howard patented the preparation of alkali fluosilicate from phosphatic rocks by treating the sulphuric acid soln. with a quantity of an alkali soln. insufficient to convert the phosphoric acid in soln. into the mono-alkali salt, and the resulting precipitate of alkali fluosilicate separated. The product is decomposed by water with the separation of silica. H. Schiff and E. Bechi obtained a glassy mass which they suggested contained *potassium oxyfluosilicate*, $2KF.SiO_2$, or $KF.SiO_2$

He also said that a mixture of potassium fluoride and potassium silicate, $K_2Si_2O_5$, forms a fusible mass. C. W. Scheele made **potassium fluosilicate,** $K_2SiF_6$, and **sodium fluosilicate,** $Na_2SiF_6$, by crystallization from a mixture of hydrofluosilicic acid and an aq. soln. of a potassium or sodium salt. According to J. J. Berzelius, the alkali salt separates very slowly from the soln., and it is at first scarcely visible; afterwards, it produces prismatic colours in the liquid, and is finally deposited as a transparent, gelatinous, iridescent mass, which dries on the filter to a white powder. The evaporation of the sat. aq. soln. furnishes small six-sided prisms, or rhombohedral crystals. G. Cesaro observed that crystals of the hexagonal sodium salt were developed by the prolonged action of hydrofluosilicic acid on glass; and K. Kraut observed tetragonal (perhaps hexagonal) doubly refracting crystals of the potassium salt as a by-product in the preparation of perchloric acid by the hydrofluosilicic acid process. J. J. Berzelius observed that when sodium hydrofluoride, $NaHF_2$, is digested with silicic acid, sodium fluosilicate and fluoride are formed. Here is reaction between an acid and an acid salt which produces a salt with an alkaline reaction. The fluorine compounds generated during the manufacture of fertilizers are not always allowed to escape as injurious fumes from the chimney of the factory, but they are directed through a series of wooden chambers where they are exposed to a spray of water which converts the fluosilicon compounds into hydrofluosilicic acid. This is then converted into sodium fluosilicate.

F. Stolba obtained potassium fluosilicate by adding sodium fluosilicate to an aq. soln. of a potassium salt. He also found potassium fluoride is decomposed when heated with hydrofluosilicic acid; that sodium fluosilicate is formed when hydrofluosilicic acid is treated with sodium chloride; and that silicic acid does not react with a boiling soln. of potassium fluoborate, but when a soln. of potash water-glass is mixed with hydrochloric acid and potassium fluoborate, potassium fluosilicate is incompletely precipitated. C. Truchot obtained potassium fluosilicate by the action of silicon tetrafluoride on a soln. of potassium fluoride. A. F. Meyerhofer made it from a mixture of potassium fluoride, silica, and hydrochloric acid with or without calcium fluoride; from potassium chloride, calcium fluoride, silica, and hydrochloric acid; from potassium chloride, silicon tetrafluoride, calcium fluoride, and a small proportion of acid; or from potassium silicate, calcium fluoride, and hydrochloric acid. R. Bunsen made **rubidium fluosilicate,** $Rb_2SiF_6$, as an opalescent powder by adding a hydrofluosilicic acid to a soln. of a rubidium salt; and F. Stolba, by treating an aq. soln. of rubidium alum with cupric fluosilicate, and washing the product by decantation. K. Preis obtained **cæsium fluosilicate,** $Cs_2SiF_6$, in octahedral crystals, by mixing an aq. soln. of cæsium chloride with cupric fluosilicate, and adding alcohol; or in cubic crystals, by evaporating an aq. soln. of the salt.

Dihydrated lithium fluosilicate furnishes short prismatic crystals belonging to the monoclinic system which, according to J. C. G. de Marignac, have the axial ratios $a : b : c = 1{\cdot}235 : 1 : 2{\cdot}160$. The crystals of the sodium salt were stated by J. C. G. de Marignac, G. Cesaro, E. Bertrand, and F. Stolba to belong to the hexagonal system; and the first named gave for the axial ratio $a : c = 1 : 0{\cdot}5635$. According to K. Preis, J. C. G. de Marignac, and B. Gossner, the crystals of the potassium salt are dimorphous—cubic and hexagonal. K. Preiss reported that the hexagonal crystals were found, together with calcium sulphate, as a deposit in a large basin containing phosphoric acid of sp. gr. 1·161 prepared from phosphorites in the chemical works at Pečky, Bohemia. Small, regular crystals of the same compound were found, together with the hexagonal form, with the axial ratio $a : c = 1 : 0{\cdot}8898$—B. Gossner gave $1 : 1{\cdot}6006$. According to K. Preis, the potassium and ammonium salts are isodimorphous. The cubic form is obtained in octahedra by slowly cooling a hot aq. soln. of the salt; as already mentioned, it also occurs in nature as the mineral *hieratite*. The cubic crystals were obtained by J. J. Berzelius; and B. Gossner obtained them in thin plates by drying the soln. at about 10°. F. Stolba obtained cubic crystals of rubidium fluosilicate having octahedral

and dodecahedral faces. B. Gossner said that the rubidium salt, like the potassium salt, occurs in two forms; the hexagonal form being obtained by drying a soln. at about 16°. K. Preis obtained octahedral crystals of the cæsium salt belonging to the cubic system. H. Töpsöe gave 2·44 for the sp. gr. of lithium fluosilicate, and F. Stolba, 2·33 at 12° for the hydrate, and 2·88 at 12° for the anhydrous salt. He also gave 2·7547 at 17·5° for the sodium salt. B. Gossner gave 2·746 for the sp. gr. of the cubic crystals of the potassium salt, and 3·081 for the hexagonal crystals. F. Stolba gave 2·665 for the sp. gr. of the cubic potassium salt at 17·5°, and 3·338 for the rubidium salt at 20°. K. Preis gave 3·3756 for the sp. gr. of the cæsium salt at 17°. F. Stolba and J. C. G. de Marignac observed that dihydrated lithium fluosilicate loses water when heated in air, and it becomes anhydrous at 100°. F. Stolba found that below red heat, the lithium salt gives off silicon tetrafluoride; or, if steam be present, hydrofluosilicic acid. J. J. Berzelius saw that both the sodium and potassium salts fuse at a red heat, and decompose at a higher temp., the former more readily than the latter. The evolution of silicon tetrafluoride is attended by the boiling of the fused mass, which becomes more and more refractory, until, after a prolonged ignition, there remains potassium fluoride holding some silica in soln. According to F. Bothe, the decomposition into silicon tetrafluoride and alkali fluoride is incomplete. The heats of formation estimated by C. Truchot are: $SiF_{4gas}+2LiF_{soln.}=Li_2SiF_{6soln.}+27$ Cals.; $SiF_{4gas}+2LiF_{solid}=Li_2SiF_{6solid}+25{\cdot}16$ Cals.; $SiF_{4gas}+2NaF_{soln.}=Na_2SiF_{6solid}+36{\cdot}6$ Cals.; $SiF_{4gas}+2NaF_{solid}=Na_2SiF_{6solid}+25{\cdot}4$ Cals.; $H_2SiF_{6soln.}+2LiOH_{soln.}=Li_2SiF_{6soln.}+28{\cdot}6$ Cals.; $H_2SiF_{6soln.}+6NaOH_{soln.}=6NaF_{solid}+Si(OH)_{4solid}+Aq+66$ Cals.; A. Guntz gave $H_2SiF_{6soln.}+2NaOH=Na_2SiF_{6solid}+31{\cdot}6$ Cals.; J. Thomsen found that the heat of neutralization of hydrofluosilicic acid by sodium hydroxide is nearly the same as that of hydrochloric acid. C. Truchot found $SiF_{6gas}+2KF_{soln.}=K_2SiF_{6solid}+22{\cdot}8$ Cals.; $SiF_{4gas}+2KF_{solid}=K_2SiF_{6solid}+26{\cdot}4$ Cals.; $H_2SiF_{6soln.}+2KOH_{soln.}=K_2SiF_{6solid}+22$ Cals.; $3SiF_{4gas}+4KOH_{soln.}=2K_2SiF_{6solid}+Si(OH)_{4solid}+82{\cdot}9$ Cals. The heat of soln. of anhydrous lithium fluosilicate is +1·840 Cals. G. Cesaro gave for the indices of refraction of dihydrated lithium fluosilicate $\omega=1{\cdot}300$ and $\epsilon=1{\cdot}296$. For sodium fluosilicate, L. Raiteri gave 1·3112 for $\lambda=677$; 1·3125 for $\lambda=589$; 1·3132 for $\lambda=535$; and 1·3146 for $\lambda=458$; and for potassium fluosilicate, 1·339 for $\lambda=677$. B. Gossner found the cubic form of potassium and rubidium fluosilicates singly refracting, and the hexagonal form had a feeble negative double refraction. The electrolysis of fused potassium fluosilicate was found by F. Ullik to give amorphous silicon.

H. Behrens and P. D. C. Kley recommended the ready formation of crystals of sodium and potassium fluosilicates as microchemical tests for the alkalies in question. J. C. G. de Marignac found the solubility of the dihydrated lithium fluosilicate in 100 parts of water at 17° to be 75 parts; and C. Truchot, 52·6 parts. J. J. Berzelius said that the sodium salt is much more soluble in water, particularly hot water, than the potassium salt; and F. Stolba found 100 parts of water at 17·5° dissolve 0·70 part of salt, and 2·46 parts in boiling water; supersaturation readily occurs. It will be observed that the fluosilicates of cæsium, rubidium, potassium, sodium, and barium are but sparingly soluble in water, the others are fairly soluble:

| $Cs_2SiF_6$ | $Rb_2SiF_6$ | $K_2SiF_6$ | $Na_2SiF_6$ | $Li_2SiF_6$ | $(NH_4)_2SiF_6$ |
|---|---|---|---|---|---|
| 0·60 | 0·16 | 0·12 | 0·65 | 73 | 18·6 |

J. J. Berzelius said that an excess of acid does not increase the solubility of the sodium salt; and C. Truchot that this salt is not soluble in a soln. of sodium fluoride. F. Stolba also found the solubility is much reduced in the presence of sodium chloride. C. W. Scheele, and J. L. Gay Lussac and L. J. Thénard said that potassium fluosilicate is sparingly soluble in cold water, but is more freely dissolved by hot water. F. Stolba found that 100 parts of water dissolve 0·12 part of the potassium salt at 17·5°, and 0·95 part in boiling water. The presence of potassium chloride, sulphate, or nitrate lowers the solubility, and this the more the greater the pro-

portion of foreign salt. Aq. soln. of ammonium chloride and hydrochloric acid augment the solubility of potassium fluosilicate. F. Stolba found that 100 parts of water dissolve about 0·16 part of rubidium fluosilicate at 20°, and 1·37 parts in boiling water. He added that the salt is more soluble in acidulated water. K. Preis found that 100 parts of water dissolve 0·60 part of cæsium fluosilicate, and more is dissolved by boiling water. F. Stolba said lithium fluosilicate is soluble in aq. alcohol; 100 parts of 46 per cent. alcohol dissolve 4 parts of the dihydrated fluosilicate, and 100 parts of 79 per cent. alcohol, 0·4 part. M. Pierrat found for solubility in

| | | | | | |
|---|---|---|---|---|---|
| Alcohol . | 94·7 | 42·4 | 27·3 | 15·9 | 8·7 | 0 per cent. |
| Salt . . | 0·0096 | 0·05 | 0·09 | 0·21 | 0·46 | 0·9 grm. per litre |

H. Rose said that alcohol precipitates sodium or potassium fluosilicate completely from its aq. soln.; and K. Preis, that cæsium fluosilicate is not soluble in alcohol. M. Pierrat measured the electrical conductivity of aq. soln. of the potassium salt.

The aq. soln. of lithium fluosilicate has an acid reaction. According to J. J. Berzelius, potassium fluosilicate is decomposed by treatment with cold potassium hydroxide or carbonate; but when boiled with the latter, carbon dioxide is evolved and the salt is decomposed with the deposition of gelatinous silica and the formation of potassium fluoride. F. Stolba showed that the reaction: $K_2SiF_6+4KOH=6KF+Si(OH)_4$ is quantitative and can be used for the volumetric determination of the alkali hydroxide, or the alkali fluosilicate, or even hydrofluosilicic acid. The process has been discussed by L. Schucht, and S. Kohn. If an acid be added to the mixture of potassium fluoride and silicic acid, the potassium fluosilicate is regenerated. C. W. Scheele found that every trace of lime can be removed from a soln. of calcium hydroxide by treatment with potassium fluosilicate, and F. Stolba showed that when a soln. of the potassium salt is boiled with calcium carbonate the reaction is symbolized: $K_2SiF_6+2CaCO_3=2KF+2CaF_2+SiO_2+2CO_2$, and if an excess of the alkali salt be present, some potassium carbonate is formed. When a soln. of potassium fluosilicate is boiled with an eq. amount of magnesium oxide, the reaction is symbolized: $K_2SiF_6+2MgO=2KF+2MgF_2+SiO_2$, and if an excess of magnesia is used, some potassium hydroxide is formed. J. J. Berzelius found that with sulphuric acid, potassium fluosilicate furnishes silicon tetrafluoride, and hydrogen fluoride. An aq. soln. of boric acid precipitates silica, but the reaction is far from complete. J. J. Berzelius said that when heated with potassium, silicon and potassium fluorides are formed; and with iron at a white heat, potassium and iron fluorides and iron silicide are formed; while, according to H. N. Warren, with aluminium in the presence of potassium chloride and carbonate at a white heat, graphitic silicon is formed. M. A. Razukin studied the reversible adsorption of sodium fluosilicate by charcoal, colloidal silica, and alumina; and he measured the electrical conductivity of aq. soln. of the salt. R. T. Thomson, and A. W. M. Rob son examined the antiseptic properties of sodium fluosilicate; and S. Marcovitch, its use as an insecticide.

J. J. Berzelius [5] prepared **cuprous fluosilicate,** $Cu_2SiF_6$, by the action of hydrofluosilicic acid on cuprous oxide. F. Stolba obtained this compound when hydrofluosilicic acid is heated in a copper vessel in the preparation of cupric fluosilicate—*vide infra*. According to J. J. Berzelius, the product resembles red cuprous fluoride, and when exposed to moist air it is decomposed, forming cupric fluoride and cuprous hydroxide, and finally cupric oxyfluoride. When strongly heated, it fuses, and gives off silicon tetrafluoride. J. J. Berzelius also found that when a soln. of cupric oxide in hydrofluosilicic acid is evaporated spontaneously in air, transparent octahedra and six-sided prisms of **hexahydrated cupric fluosilicate,** $CuSiF_6.6H_2O$, are formed; or, according to J. C. G. de Marignac, by cooling a fairly conc. soln. F. Stolba gradually added cupric carbonate to hydrofluosilicic acid, heated in a copper vessel; the soln. was conc. a little, and filtered so as to remove the separated silica; the filtrate was evaporated almost to dryness; and washed with a little

water. The product was dissolved in water and evaporated at 10°–22° in a platinum dish, or in a glass or porcelain dish coated with paraffin wax. W. Knop and W. Wolf passed silicon tetrafluoride into 98 per cent. alcohol, carrying in suspension precipitated cupric hydroxide. The product was washed a few times with alcohol. If the cupric hydroxide be in excess, an insoluble green basic salt is formed. F. Stolba, and L. Balbiano boiled a mol of barium fluosilicate with a soln. containing a mol of cupric sulphate, and in about 15 mins. added a little more barium fluosilicate to make up for that which is entangled with the precipitated barium sulphate. The filtrate was then evaporated as previously indicated for crystallization. A. G. Betts made cupric fluosilicate by treating finely divided copper with ferric fluosilicate, or with hydrofluosilicic acid and lead peroxide.

The deep blue octahedral or prismatic crystals were found by J. C. G. de Marignac to belong to the trigonal system, and to have the axial ratio $a : c = 1 : 0{\cdot}5395$, and $\alpha = 110° 34'$. H. Töpsöe and C. Christiansen gave 2·207 for the sp. gr.; B. Gossner gave 2·222; and F. Stolba, 2·1576 at 19°/19°. J. A. Groshans made some observations on the density of this salt. H. Töpsöe and C. Christiansen found the indices of refraction $\omega = 1{\cdot}4074$ and $\epsilon = 1{\cdot}4062$ for the *C*-line; $\omega = 1{\cdot}4092$ and $\epsilon = 1{\cdot}4080$ for the *D*-line; and $\omega = 1{\cdot}4138$ and $\epsilon = 1{\cdot}4124$ for the *F*-line. The double refraction is feeble and negative. J. J. Berzelius observed that the crystals effloresce on exposure to air, becoming light blue and opaque and forming the tetrahydrate by the loss of 2 mols of water. F. Stolba showed that in moist air, the crystals are deliquescent; and when heated to 100°, the salt gradually loses 14·5 per cent. of water in 24 hrs.; at 125°, the salt loses 56·3 per cent. of water and silicon tetrafluoride in 4 hrs., and the residue is no longer completely soluble in water. J. C. G. de Marignac found that after calcination, 29·25 per cent. remains probably as oxyfluoride. L. Balbiano found that the hexahydrate loses 2 mols of water at 90° or in vacuo over sulphuric acid, and is decomposed at 130°–140°: $CuSiF_6.6H_2O = SiF_4 + HF + 5H_2O + Cu(OH)F$. J. J. Berzelius said that the fluosilicate is readily soluble in water, and F. Stolba found that 100 parts of water dissolve 233·6 parts of salt at 17°. At 20°, 100 parts of 62 per cent. alcohol dissolve 5·56 parts of salt; 100 parts of 85 per cent. alcohol, 0·667 part of salt; and 100 parts of 92 per cent. alcohol, 0·162 part of salt. F. Stolba measured the sp. gr. of soln. of cupric fluosilicate. *When the sat. soln. in dil. alcohol is warmed, or mixed with conc.* alcohol, a heavy, blue, oily liquid separates; and when shaken with an excess of conc. alcohol, a light blue salt approximating $CuSiF_6.5\frac{1}{2}H_2O$ separates. J. Schröder said that cupric fluosilicate is insoluble in pyridine. W. Knop and W. Wolf found that when the aq. soln. is treated with zinc or iron, metallic copper is first deposited and hydrogen then appears owing to the decomposition of the silicon tetrafluoride. S. H. C. Briggs showed that with cupric chromate, a soln. is obtained which, on evaporation, gives a mixture of the fluosilicate and oxychromate. As just indicated, **tetrahydrated cupric fluosilicate,** $CuSiF_6.4H_2O$, is formed by driving two mols of water from the hexahydrate; or, according to J. C. G. de Marignac, by evaporating the aq. soln. at 50°. The monoclinic prismatic crystals have the axial ratios $a : b : c = 0{\cdot}7604 : 1 : 0{\cdot}5519$, and $\beta = 105° 37°$. They are isomorphous with the tetrahydrated cupric fluostannate. According to L. Balbiano, the tetrahydrate absorbs ammonia, but no ammino-derivative of hydrofluosilicic acid is formed. On treating the bright blue product of the reaction with water, a blue mass is left undissolved, consisting of silica and cupric diamminohydroxyfluoride; the latter is soluble in dil. ammonia, and on heating this soln., cupric oxyfluoride is deposited. The action of ammonia on the fluosilicate is therefore: $CuSiF_6.4H_2O + 7NH_3 = CuF.OH.2NH_3 + 5NH_4F + SiO_2 + H_2O$. T. E. Thorpe and J. W Rodger found that when a soln. of copper sulphate is added to a soln. of the compound of ammonia and thiophosphoryl fluoride, the filtrate from the copper sulphide deposits crystals of **copper phosphatofluosilicate,** $Cu_3(PO_4)_2.CuSiF_6$.

According to J. J. Berzelius,[6] the evaporation of a soln. of silver oxide in hydrofluosilicic acid yields crystals of tetrahydrated **silver fluosilicate,** $Ag_2SiF_6.4H_2O$.

S. Kern obtained the salt as a greyish-white precipitate on adding silver nitrate to hydrofluosilicic acid. J. C. G. de Marignac said that the crystals are rectangular octahedra which melt below 100°, and at the same time lose water with decomposition. J. J. Berzelius said that the crystals deliquesce on exposure to air; and when a soln. of the salt is treated with aq. ammonia, a light yellow, basic salt is precipitated which passes into silver silicate when treated with an excess of ammonia. M. Löb and W. Nernst measured the electrical conductivity of the aq. soln.; and K. Eisenreich found that on electrolysis, rather more silver is deposited than corresponds with the electrochemical eq. H. Hetsch examined the bactericidal action of the salt which has the commercial name *isotachiol*. A number of calcium fluosilicates or calcium aluminium fluosilicates has been reported: for instance, the *zeophyllite* of A. Pelikan,[7] and F. Cornu; with the composition $H_4Ca_4Si_3O_{11}F$; apophyllite, cuspidin, lepidolite, etc. There is the product approximating $CaO.3SiO_2.6CaF_2$, obtained by H. St. C. Deville by heating calcium oxide in a stream of silicon tetrafluoride; and the products obtained in the attempt to synthesize the fluoriferous silicate minerals (*q.v.*). J. J. Berzelius made the normal salt by digesting levigated fluorspar and finely divided silica in hydrofluoric acid, or, according to F. Stolba, in hydrochloric acid. J. J. Berzelius also obtained the salt by saturating hydrofluosilicic acid with calcium carbonate, and evaporating the filtered soln. for crystallization. F. Stolba preferred to use about two-thirds this quantity of carbonate so that some free acid is present; otherwise the calcium fluosilicate is unstable. E. Fleischer obtained calcium fluosilicate from cryolite—*vide supra*, hydrofluosilicic acid. The four-sided, obliquely truncated crystals, as J. J. Berzelius described them, are those of **dihydrated calcium fluosilicate**, $CaSiF_6.2H_2O$. J. J. Berzelius, and F. Stolba made **dihydrated strontium fluosilicate**, $SrSiF_6.2H_2O$, in a similar manner. J. L. Gay Lussac and L. J. Thénard made **barium fluosilicate**, $BaSiF_6$, as a precipitate by mixing hydrofluosilicic acid and barium chloride. At first the soln. remains clear, but small crystals are soon deposited. F. Stolba used a similar process. J. J. Berzelius found that nearly all the barium is precipitated. If the soln. are mixed at a boiling heat, the crystals are somewhat larger, but they are still microscopic. According to E. Fleischer, barium acetate or butyrate precipitates a mixture of barium fluoride and fluosilicate from hydrofluosilicic acid. A mixture of silica and barium fluoride is transformed by hydrobromic acid into barium fluosilicate, and conversely, hydrobromic acid and barium fluosilicate furnish hydrofluosilicic acid. E. Fleischer made barium fluosilicate from cryolite—*vide supra*, hydrofluosilicic acid.

J. J. Berzelius described the crystals of the barium salt as prisms with acute summits, and those of the dihydrated strontium salt as "rhombic prisms with dihedral summits resting on the two acute lateral edges." K. Haushofer said that the crystals of the barium salt are rhombohedral; and H. Behrens uses the crystals in his microchemical test. J. C. G. de Marignac said that the dihydrated strontium salt shows monoclinic prisms with axial ratios $a:b:c=1{\cdot}179:1:1{\cdot}232$ and $\beta=110°\,22'$, and he added that the crystals of the dihydrated calcium salt are probably similar. K. Haushofer said the six-sided plates of dihydrated calcium fluosilicate are probably isomorphous with the dihydrated strontium salt. F. Fouqué and A. Michel-Lévy made some observations on the crystals. H. Töpsöe gave 2·252 for the sp. gr. of the hydrated calcium salt; F. Stolba, 2·99 at 17·5° for the hydrated salt; and 4·277 at 21° for the anhydrous barium salt. When heated, these fluosilicates lose their combined water and become opaque, and, as shown by J. J. Berzelius, C. Truchot, and others, on calcination silicon tetrafluoride is evolved and the fluoride remains. Calcium fluosilicate is partly dissolved and partly decomposed by water, forming a precipitate of silicic acid and calcium fluoride, and a soln. of hydrofluosilicic acid. As J. J. Berzelius showed, the salt is soluble in hydrofluosilicic acid without decomposition, and the soln., on evaporation, yields crystals of the original salt. L. Schucht and W. Möller showed that some colloidal calcium fluoride and silicic acid remain in the liquid when calcium fluosilicate is decomposed

by water. J. J. Berzelius noted that strontium fluosilicate is also partially decomposed by water, forming a basic salt, and a liquid containing an excess of acid. F. Stolba said that cold water dissolves the salt completely but not without decomposition, and, added J. C. G. de Marignac, the soln. when heated furnishes some strontium fluoride. J. J. Berzelius said that barium fluosilicate is very sparingly soluble in cold water, but dissolves more freely in hot water. C. R. Fresenius found that at ordinary temp., 100 parts of water dissolve 0·0263 part of salt. F. Stolba found that 100 parts of water dissolve 0·0268 part of salt at 17·5°; 0·0302 part at 21°; and 0·0351 part at the boiling temp. J. J. Berzelius said that hydrochloric acid dissolves calcium fluosilicate without decomposition, but when the soln. is evaporated, hydrofluosilicic acid is given off, and calcium chloride is formed; and when the soln. is treated with aq. ammonia, calcium fluoride and silica are precipitated, while ammonium chloride and fluoride remain in soln. C. F. Rammelsberg said that the precipitate might be a fluoxysilicate, $3CaF_2.SiO_2$ J. J. Berzelius said that strontium fluosilicate is readily soluble in acidulated water without decomposition, and, added C. R. Fresenius, hydrochloric acid augments the solubility of strontium fluosilicate, and that hydrofluosilicic acid does not interfere. J. J. Berzelius said that hydrochloric acid does not increase the solubility of barium fluosilicate, but this is not right, since C. R. Fresenius found that 100 parts of water acidulated with hydrochloric acid dissolve 0·136 part of barium fluosilicate at ordinary temp., and some barium chloride is formed; and F. Stolba, that 100 parts of 4·25 per cent. hydrochloric acid at 22° dissolve 0·205 part of barium fluosilicate. C. R. Fresenius said that the solubility of barium fluosilicate is increased in the presence of nitric acid, and F. Stolba found that 100 parts of 8 per cent. nitric acid dissolve 0·368 part of salt at 22°. E. Fleischer said that calcium fluosilicate readily dissolves in 60 per cent. alcohol; and C. R. Fresenius, that the strontium salt is soluble in alcohol, and this the more the less conc. the alcohol. The latter also said that the barium salt is almost insoluble in alcohol, so that the properties have been employed in the separation of barium and strontium. G. Tammann found that 100 parts of 50 per cent. alcohol dissolve 0·00256 part of barium fluosilicate, and, added C. R. Fresenius, the presence of hydrochloric acid diminishes the solubility, so that the addition of hydrofluosilicic acid precipitates some barium fluosilicate from an alcoholic or acidic soln. J. W. Mallet found that 100 parts of a sat. soln. of ammonium chloride dissolve 0·234 part of barium fluosilicate, and the solubility is diminished by diluting the soln. F. Stolba found that at 22°, 100 parts of a sat. soln. of ammonium chloride dissolved 0·327 part of the barium salt; and 100 parts of a 15 per cent. soln., 0·277 part. He also found that 100 parts of a boiling sat. soln. of sodium chloride dissolved 0·177 part of barium salt; a boiling 10 per cent. soln., 0·286 part, and a 10 per cent. soln. at 20°, 0·0458 part. When the boiling sat. soln. is cooled, some sodium fluosilicate crystallizes out. G. Tammann said that acetic and butyric acids have scarcely any action on barium fluosilicate at 100°; ammonium phosphate forms some ammonium fluosilicate and barium phosphate. T. Scheerer and E. Drechsel found that when a mixture of calcium fluosilicate, calcium chloride, and water is heated in a sealed tube at 250°, crystals of calcium fluoride are formed. J. J. Berzelius showed that when a mixture of barium salt and sulphuric acid is heated barium sulphate is formed; and F. Stolba, that when mixed with ammonium chloride and calcined, a mixture of barium chloride and fluoride remains; and that a soln. of potassium hydroxide decomposes the soln. easily, and the solid salt with difficulty; soln. of sulphates decompose barium fluosilicate completely; and alkali carbonates form barium carbonate.

According to J. J. Berzelius,[8] the evaporation of an aq. soln. of beryllium oxide in hydrofluosilicic acid furnishes a syrupy liquid which becomes opaque and white, and if an excess of acid is used, the product which remains after the volatilization of the acid is a hard, white, porcelainic mass readily soluble in water. The **beryllium fluosilicate** so obtained is decomposed by heat. J. C. G. de Marignac, and A. Atterberg also obtained the salt as an uncrystallizable syrup. C. Chabrié

obtained crystals of the salt by the prolonged boiling of a soln. of 0·5 grm. of freshly precipitated beryllium hydroxide in a large excess (200 grms.) of hydrofluosilicic acid, and cooling.

A number of fluoriferous magnesium silicates occur in nature—*e.g.* humite, prolectite, chondrodite, clinohumite, etc.; and A. Duboin,[9] by fusing a mixture of silica, magnesia, and potassium fluoride obtained two products which he regarded as *potassium magnesium fluosilicates*, $Mg_2SiO_2F_4.4K_2MgSi_3O_8$, and $K_4SiO_2F_4.Mg_3K_4Si_{10}O_{25}$, but there is little evidence of the chemical individuality of these substances. J. J. Berzelius obtained a transparent, yellowish, gum-like mass by evaporating a soln. of magnesia in hydrofluosilicic acid. The composition corresponded with **magnesium fluosilicate,** $MgSiF_6$. F. Stolba made crystals of **hexahydrated magnesium fluosilicate,** $MgSiF_6.6H_2O$, by adding hydrofluosilicic acid to a slurry made by rubbing magnesia with water; evaporating to a syrupy mass; dissolving in water; filtering; and evaporating spontaneously in a platinum dish. He also mixed a conc. soln. of magnesium acetate with hydrofluosilicic acid and alcohol, and quickly filtered the soln., since on standing silica is deposited. P. Engelskirchen said that to obtain good crystals it is necessary to finish the evaporation of the conc. soln. in a desiccator at ordinary temp. A. F. Meyerhofer made the fluosilicate from a mixture of silica, calcium fluoride, magnesium sulphate, and sulphuric acid. F. Stolba, and H. Töpsöe and C. Christiansen described the crystals as transparent colourless rhombohedra belonging to the trigonal system with the axial ratio $a:c=1:0{\cdot}5174$, and $\alpha=112°\ 9'$; and, added P. Engelskirchen, isomorphous with the corresponding fluostannate and fluotitanate. F. Stolba gave 1·788 for the sp. gr. at 17·5°, and H. Töpsöe, 1·761. The indices of refraction by H. Töpsöe and C. Christiansen are $\omega=1{\cdot}3427$ and $\epsilon=1{\cdot}3587$ for the *C*-line; $\omega=1{\cdot}3439$ and $\epsilon=1{\cdot}3602$ for the *D*-line; and $\omega=1{\cdot}3473$ and $\epsilon=1{\cdot}3634$ for the *F*-line. The double refraction is positive. F. Stolba found the crystals effloresce in dry air or over sulphuric acid; at 100°–120°, water and almost all the silicon tetrafluoride are expelled. He also noted that 100 parts of water at 17·5° dissolve 64·8 parts of salt to form a liquid of sp. gr. 1·235; when warmed, the soln. becomes opalescent owing to the separation of colloidal silica, but on cooling, the soln. becomes almost clear again. P. Engelskirchen found that hydrofluoric acid decomposes the salt into magnesium fluoride and hydrofluosilicic acid.

J. J. Berzelius[10] evaporated a soln. of zinc oxide in hydrofluosilicic acid, and obtained transparent, colourless, prismatic crystals of **hexahydrated zinc fluosilicate,** $ZnSiF_6.6H_2O$. J. J. Berzelius' analysis gave $7H_2O$. The trigonal crystals, according to J. C. G. de Marignac, have the axial ratio $a:c=1:0{\cdot}5173$, and $\alpha=112°\ 10°$; and, according to B. Gossner, they are isomorphous with the corresponding compounds of chromium, cobalt, and nickel, and with the nickel salt, zinc fluosilicate forms a continuous series of mixed crystals; W. Stortenbeker also found that the hexahydrated zinc fluosilicate and fluostannate form mixed crystals. The sp. gr. found by H. Töpsöe is 2·104, and by B. Gossner, 2·139. H. Töpsöe and C. Christiansen gave for the indices of refraction $\omega=1{\cdot}3808$ and $\epsilon=1{\cdot}3938$ for the *C*-line; $\omega=1{\cdot}3824$ and $\epsilon=1{\cdot}3956$ for the *D*-line; and $\omega=1{\cdot}3860$ and $\epsilon=1{\cdot}3992$ for the *F*-line. The double refraction is positive. J. J. Berzelius said that the salt is permanent in air and easily soluble in water. When heated in air, G. Gallo found that silicon fluoride escapes, and anhydrous zinc fluoride remains. The corresponding **hexahydrated cadmium fluosilicate,** $CdSiF_6.6H_2O$, was obtained by J. J. Berzelius in long, transparent, colourless prisms by a process similar to that employed for the zinc salt. P. Engelskirchen evaporated a soln. of cadmium carbonate in hydrofluosilicic acid, and obtained the salt by precipitation with alcohol, or by spontaneous evaporation. The hexagonal crystals are easily soluble in water, and in 50 per cent. alcohol; they effloresce in warm air, but in ordinary air they are fairly stable.

J. J. Berzelius[11] dissolved freshly precipitated and moist mercurous oxide in hydrofluosilicic acid, and on evaporating the pale yellow liquid obtained small

crystals of **dihydrated mercurous fluosilicate,** $Hg_2SiF_6.2H_2O$. R. Finkener, and C. Lemaire crystallized a soln. of mercurous carbonate in hydrofluosilicic acid, washed the crystals with a little water; pressed them between bibulous paper, and dried them over sulphuric acid. The clear crystals dissolve sparingly in water without decomposition. J. J. Berzelius said the crystals dissolve more readily in acidulated water, and that the salt is precipitated by hydrochloric acid. J. J. Berzelius obtained crystals of what was probably **hexahydrated mercuric fluosilicate,** $HgSiF_6.6H_2O$, from a conc. soln. of mercuric oxide in hydrofluosilicic acid, by evaporating until crystals begin to appear, and continuing the evaporation at 15°. The colourless rhombohedral crystals were found by R. Finkener to be very unstable. They deliquesce in air, and effloresce over sulphuric acid. They are almost completely soluble in water, and, as shown by J. J. Berzelius, and C. Lemaire, the crystals are resolved by water into an acid soln., and a yellow basic salt, which, according to R. Finkener, corresponds with **trihydrated mercuric oxyfluosilicate,** $HgO.HgSiF_6.3H_2O$. The basic salt, said J. J. Berzelius, is blackened by ammonia, and afterwards restored to a lighter colour by water; the salt is completely soluble in acidulated water, forming an acid soln. which by spontaneous evaporation forms a syrupy liquid, but does not crystallize until it has been evaporated by heat.

A number of fluoriferous aluminium silicates occur in nature—*e.g.* topaz, lepidolite, zunyite, etc. J. J. Berzelius[12] dissolved hydrated alumina in hydrofluosilicic acid, and obtained a gelatinous mass of presumably **aluminium fluosilicate,** $2AlF_3.3SiF_4$, or $Al_2(SiF_6)_3$. H. St. C. Deville dissolved calcined alumina and obtained a similar product. C. Chabrié found that by the prolonged boiling of 0·5 grm. of aluminium chloride or the recently precipitated hydrate, with 200 grms. of the acid, a distinctly crystalline fluosilicate separates on cooling, which does not alter on drying at 100°. Aluminium fluoride treated by this method yields a similar compound. H. St. C. Deville said that the addition of an excess of alumina to the soln. results in the precipitation of silica; and with sodium chloride, sodium fluosilicate and aluminium chloride are formed. A. Frank recommended this salt for use in the sterilization of potable waters.

The **rare earth fluosilicates** are obtained as gelatinous precipitates on adding an alkali fluosilicate to a neutral soln. of a rare earth salt; but in the presence of mineral acids, they are not precipitated in the cold, and on boiling, the metals cerium and scandium are precipitated as fluorides owing to the hydrolysis of the fluosilicates: $Sc_2(SiF_6)_3+6H_2O=2ScF_3+3SiO_2+12HF$. The yttrium elements are held in soln. by the mineral acid. Thus, J. J. Berzelius showed that **yttrium fluosilicate** is insoluble in water, but is dissolved by water containing hydrochloric acid, and on evaporating the liquid, the fluosilicate is again precipitated. F. Stolba prepared **cerium fluosilicate, lanthanum fluosilicate,** and **didymium fluosilicate** in this manner. He said that the precipitates are very sparingly soluble in water, acetic and fluosilicic acids, but are readily dissolved by mineral acids. The precipitates are also insoluble in alcohol. R. J. Meyer[13] based a method for separating scandia from the rare earths on the property possessed by **scandium fluosilicate** of decomposing and precipitating as scandium fluoride when the soln. is boiled.

By evaporating a soln. of thallous carbonate in hydrofluosilicic acid, F. Kuhlmann[14] obtained crystals of **dihydrated thallous fluosilicate,** $Tl_2SiF_6.2H_2O$; G. Werther likewise obtained regular octahedra, or six-sided, plates. J. Nicklès also obtained the salt by the action of hydrochloric acid, containing some silica, on thallium. The salt is soluble in water, the soln. has an acid reaction, and slowly deposits silica. The evaporation of the aq. soln. gives the original salt. When aq. ammonia is added to the aq. soln., there is formed a precipitate which soon becomes crystalline, and which cannot be freed from thallium by washing with aq. ammonia. G. Werther thinks that the precipitate is a basic fluosilicate or an ammino-compound.

P. Engelskirchen[15] found that freshly precipitated titanium hydroxide readily

dissolves in hydrofluosilicic acid, and on evaporating the soln., a syrupy liquid which does not crystallize is obtained. The product may be an impure **titanium fluosilicate**. J. J. Berzelius obtained white pearly crystals of **zirconium fluosilicate** from a soln. of the hydroxide in hydrofluosilicic acid. M. Weibull, and P. Engelskirchen made observations on the product, but without establishing definitely the nature of the compound. J. J. Berzelius said that it is very soluble in water, and that the soln. becomes turbid on boiling owing to the decomposition of part of the solute. P. T. Cleve reported a basic salt, **thorium dihydroxyfluosilicate,** approximating $Th(OH)_2SiF_6$, by the action of hydrofluosilicic acid on thorium hydroxide. A pulverulent mass of needle-like crystals is formed which gives off acid vapours when dried over sulphuric acid.

J. J. Berzelius reported the formation of long prisms of **stannic fluosilicate** by evaporating a soln. of stannous oxide in hydrofluosilicic acid, and he said that the stannous oxide is converted into stannic oxide and precipitated along with the silica. J. J. Berzelius first assumed that the stannous salt is formed, but later regarded it as a stannic salt. P. Engelskirchen also prepared an impure salt from a soln. of stannous hydroxide in hydrofluosilicic acid.

J. J. Berzelius said that a soln. of lead oxide in hydrofluosilicic acid dries up to a transparent gum of **lead fluosilicate** which is readily soluble in water. A. and L. Lefranc and A. Vivien obtained the fluosilicate by dissolving lead in the acid; W. Mills dissolved lead oxide or hydroxide in the acid, and mixed the filtered soln., which was slightly acid, with lead nitrate. The precipitated fluosilicate was washed and dried. T. Cobley mixed hydrofluosilicic acid with lead acetate or other lead salt and obtained lead fluosilicate; and the same salt was made by the action of hydrofluosilicic acid—gas or aq. soln.—on lead silicate; or by heating a mixture of lead silicate, calcium fluoride or cryolite, and sulphuric acid. J. C. G. de Marignac obtained the *dihydrate*, $PbSiF_6.2H_2O$, and by evaporating the soln. at ordinary temp. in air, he obtained the *tetrahydrate*, $PbSiF_6.4H_2O$. F. Fischer and K. Thiele added lead carbonate to hydrofluosilicic acid, filtered the soln. to remove lead fluoride and lead sulphate if present, evaporated the clear soln.; by neutralizing the acid soln. with lead carbonate, they obtained a basic salt; and by electrolyzing the neutral soln. in a cell with lead anodes, they also obtained lead fluosilicate. K. Elbs and R. Nübling obtained the dihydrate by electrolyzing a conc. soln. of sp. gr. 1·30, or very dil. hydrofluoric acid in a cell with lead electrodes and a diaphragm using a current of anode density 1–3 amps. per sq. dm. If the electrolyte be sat. with lead fluosilicate, and allowed to stand for some days, the tetrafluoride is formed. According to J. C. G. de Marignac, the dihydrate forms monoclinic prisms, of axial ratios $a:b:c=1{\cdot}4220:1:1{\cdot}4306$, and $\beta=103°\,44'$; and the tetrahydrate forms similar crystals but with the axial ratios $a:b:c=1{\cdot}5772:1:0{\cdot}9735$, and $\beta=91°\,30'$. The dihydrate loses hydrogen fluoride and water when heated; at 300°, lead fluoride remains; the tetrahydrate melts below 100°, loses water and silicon tetrafluoride; and according to K. Elbs and R. Nübling, it readily passes into the dihydrate. F. A. Patterson measured the electrical conductivity of the soln. F. Fischer and co-workers reported crystals of an acid salt.

J. J. Berzelius [16] slowly evaporated a soln. of antimonic oxide in hydrofluosilicic acid, and obtained prismatic crystals of **antimony fluosilicate** which crumble to powder when dried in air, and readily dissolve in water containing an excess of acid. According to J. J. Berzelius, when a soln. of vanadic oxide, $VO_2$, in hydrofluosilicic acid is rapidly evaporated, blue **vanadyl fluosilicate** is formed which at a moderate heat swells up into a pale-blue porous mass; but if the blue soln. evaporates spontaneously, it acquires a green colour, and forms a syrupy liquid containing crystals. According to A. Guyard, if the soln. be evaporated to dryness a grey deliquescent mass is obtained which is completely soluble in water. J. J. Berzelius found that vanadic acid, $V_2O_5$, dissolves in hydrofluosilicic acid, forming a red soln., which, on evaporation, yields an orange-yellow uncrystallizable mass of **vanadium fluosilicate.** It is partially soluble in water, forming a yellow soln.

The undissolved dark green portion forms a red soln. with sulphuric acid and gives off silicon tetrafluoride. The columbium silicate minerals, chalcolamprite and epistolite, are fluoriferous.

J. J. Berzelius [17] obtained a transparent green mass of **chromium fluosilicate** by evaporating a soln. of chromic oxide in hydrofluosilicic acid. The product is deliquescent, and when it contains an excess of acid, it swells up like an alum when heated, and the residue again deliquesces if exposed to air. S. M. Jörgensen made **chromic chloropentamminofluosilicate,** or *chromic purpureofluosilicate*, $[Cr(NH_3)_5Cl]SiF_6$, by adding hydrofluosilicic acid to a soln. of a soluble chloropentamminochromic salt. The dark rose-red rhombic crystals are isomorphous with the corresponding cobalt salt. He also made **chromic chloroaquotetramminofluosilicate,** or *chromic roseofluosilicate*, $[Cr(NH_3)_4(H_2O)Cl]SiF_6$, by treating the soluble chloride with a conc. soln. of zinc fluosilicate in hydrofluosilicic acid. The precipitate is washed with ice-cold hydrofluosilicic acid until free from zinc; it is then washed with alcohol until free from acid. The carmine-red rhomboidal plates are soluble in water; when the salt has been dried over sulphuric acid it does not lose weight by heating to 100°. According to J. J. Berzelius, a soln. of molybdic oxide, $Mo_2O_3$, in an excess of hydrofluosilicic acid does not dry up when exposed to air at ordinary temp., but when heated, the excess of acid is expelled, and a black neutral compound of **molybdenum fluosilicate** is formed which redissolves in the aq. acid. When the acid liquid is spontaneously evaporated, it acquires a bluish tinge and yields a black uncrystallizable mass from which water extracts the blue salt, and leaves a neutral black powder. The product is resolved by the prolonged action of water into a soluble acid salt and an insoluble basic salt. Aq. ammonia converts it into molybdenum silicate; and it dissolves in acidulated water without decomposition. When the yellow soln. obtained by dissolving molybdic acid in hydrofluosilicic acid is evaporated, a lemon-yellow opaque substance is formed which is decomposed by water forming a yellow soln. and a small quantity of an insoluble basic compound.

According to C. F. Rammelsberg,[18] when uranium chloride, $UCl_4$, is mixed with hydrofluosilicic acid, a bluish-green gelatinous precipitate is formed. If an excess of acid be present, the soln. retains the bluish-green colour. When the precipitated **uranium fluosilicate** is heated out of contact with air, it is decomposed, forming water, hydrofluoric acid, and silica. It is but slightly affected by a boiling soln. of potassium hydroxide; and after drying it is but sparingly soluble in acids. F. Stolba prepared **uranyl fluosilicate** soluble in water and in alcohol.

J. J. Berzelius [19] obtained long, regular, six-sided prisms of **hexahydrated manganese fluosilicate,** $MnSiF_6.6H_2O$, from a soln. of manganese oxide in hydrofluosilicic acid, and short prisms and rhombohedral crystals by the slow evaporation of the soln. F. Stolba evaporated at room temp. a soln. of manganese carbonate in hydrofluosilicic acid; and also mixed barium fluosilicate with a soln. of manganese sulphate. The rose-red, hexagonal, prismatic crystals belong to the trigonal system, and, according to J. C. G. de Marignac, have the axial ratio $a : c = 1 : 0{\cdot}5043$, and $\alpha = 112° 30'$. The crystals are isomorphous with the corresponding fluosilicates of the manganese family. F. Stolba gave 1·9038 for the sp. gr. at 17·5°, and H. Töpsöe, 1·858. H. Töpsöe and C. Christiansen found the indices of refraction to be $\omega = 1{\cdot}3552$ and $\epsilon = 1{\cdot}3721$ for *C*-light; $\omega = 1{\cdot}3570$ and $\epsilon = 1{\cdot}3742$ for *D*-light; and $\omega = 1{\cdot}3605$ and $\epsilon = 1{\cdot}3774$ for *F*-light. The double refraction is positive. The salt is stable in air, and when heated, J. J. Berzelius found that the water is first given off, then silicon tetrafluoride, and manganese fluoride remains. F. Stolba found that all the silicon tetrafluoride is not expelled after 40 hrs.' heating at 100°, and after slowly heating to 200°, a little silicon tetrafluoride still remains. The salt is readily soluble in water; F. Stolba found that 100 parts of water at 17·5° dissolve 140 parts of the salt, and the soln. has a sp. gr. 1·44825; the solubility is augmented by raising the temp. The solubility in alcohol is greater the less the conc. of the alcohol. F. Stolba found that a soln. of the salt is decomposed when

evaporated in the presence of conc. hydrochloric or nitric acid. Alkali fluosilicates are almost insoluble in a soln. of manganese fluoride, so that when alkali salts are added to a soln. of manganese fluosilicates these fluosilicates are almost quantitatively precipitated.

J. C. G. de Marignac could not make a fluosilicate with a higher proportion of manganese fluoride. T. L. Phipson found that when an aq. soln. of potassium fluoride, potassium permanganate, and nitric acid is allowed to stand for some days, crystals containing fluorine, manganese, potassium, and silica are produced—the latter is derived from the glass containing vessel.

According to J. J. Berzelius,[20] when a soln. of iron in hydrofluosilicic acid is evaporated in an iron dish, exposed to the air, pale, bluish-green, six-sided, prismatic crystals of what H. Dufet showed to be **hexahydrated ferrous fluosilicate,** $FeSiF_6.6H_2O$, are formed. F. Stolba prepared the salt by evaporating on a water bath the soln. acidified with a few drops of hydrofluosilicic acid; he also evaporated the soln. containing a little free hydrofluosilicic acid until a crust began to form. Conc. alcohol was added so long as a precipitate was produced. The salt was collected by filtration, and washed by suction with conc. alcohol, and dried on a porous tile. According to H. Dufet, the crystals belong to the trigonal system, and have the axial ratio $a:c=1:0{\cdot}5033$, and $\alpha=112°\ 32'$. F. Stolba gave 1·961 for the sp. gr. at 17·5°. The indices of refraction were found by H. Dufet to be $\epsilon=1{\cdot}3828$ and $\omega=1{\cdot}3619$ for Li-light; $\epsilon=1{\cdot}3848$ and $\omega=1{\cdot}3638$ for Na-light; and $\epsilon=1{\cdot}3867$ and $\omega=1{\cdot}3656$ for Tl-light at 20·5°. The crystals are oxidized in moist air, and F. Stolba found that 100 parts of water at 17·5° dissolve 128·2 parts of the salt. J. J. Berzelius also prepared what was once thought to be **ferric fluosilicate,** $Fe_2(SiF_6)_3$, by evaporating a soln. of hydrated ferric oxide in hydrofluosilicic acid. It appeared as a yellowish jelly which, after complete drying, appeared as a translucent gum-like mass, soluble in water. It is doubtful if normal ferric fluosilicate can exist under these conditions since when the attempt is made to prepare it by saturating the acid with ferric oxide, or by double decomposition, it breaks down at once: $2FeF_3.3SiF_4 \rightarrow 2SiF_4+2FeF_3.SiF_4$—the silicon fluoride is decomposed by water. When the soln. is slowly evaporated, a colourless syrup is obtained containing $FeF_3.SiF_4$ in aq. soln.; by further evaporation, this compound decomposes—silicon fluoride escapes and hydrated ferric fluoride remains.

J. J. Berzelius evaporated a soln. of cobalt carbonate in hydrofluosilicic acid and obtained pale red rhombohedra, and six-sided prisms of what J. Grailich and others showed to be **hexahydrated cobalt fluosilicate,** $CoSiF_6.6H_2O$; J. J. Berzelius considered the salt to be a heptahydrate. F. Stolba also made the salt by acting on barium fluosilicate with a boiling soln. of cobalt sulphate; and by the method employed for the ferrous salt. J. Grailich found the trigonal crystals have the axial ratio $a:c=1:0{\cdot}5219$, and $\alpha=112°\ 4'$. B. Gossner gave 2·807 for the sp. gr.; H. Töpsöe, 2·067; and F. Stolba, 2·113–2·121 at 19°. J. A. Groshans studied the mol. vol. and sp. gr. of the salt. H. Töpsöe and C. Christiansen gave $\omega=1{\cdot}3817$ and $\epsilon=1{\cdot}3872$ for the indices of refraction with the *C*-line; the double refraction is positive. B. Gossner studied the isomorphism of the corresponding cobalt, copper, nickel, and zinc salts. There is a limited miscibility between the cobalt and copper fluosilicates. P. Engelskirchen found that ammonium and cobalt fluosilicates do not form a double salt, but the ammonium salt separates first when a mixed soln. of the two salts is conc. by evaporation. F. Stolba found that 100 parts of water at 21·5° dissolve 118·1 parts of salt; and more at a higher temp.

A. Miolati and G. Rossi obtained **cobaltic hexamminofluosilicate,** or *cobaltic luteofluosilicate,* $[Co(NH_3)_6]F_3.2SiF_4$, as a yellow crystalline powder by the action of hydrofluosilicic acid on a soln. of the carbonate in hydrofluoric acid. S. M. Jörgensen obtained **cobaltic nitropentamminofluosilicate,** or *cobaltic xanthofluosilicate,* $[Co(NH_3)_5NO_2]SiF_6$, by the action of hydrofluosilicic acid on the chloride of the base. W. Gibbs, and S. M. Jörgensen prepared **cobaltic chloropentamminofluosilicate,** or *cobaltic chloropurpureofluosilicate,* $[Co(NH_3)_5Cl]SiF_6$, by a cold soln. of chloropentamminocobaltic salt to an excess of

hydrofluosilicic acid. W. Gibbs regarded the salt as a trihydrate. S. M. Jörgensen made **cobaltic chloraquotetramminofluosilicate,** $[Co(NH_3)_4(H_2O)Cl]SiF_6$, in violet crystals by the action of hydrofluosilicic acid on a soln. of the chloride of the base. The crystals were washed with alcohol. S. M. Jörgensen made dark violet, rhombic, tabular crystals of **cobaltic bromopentamminofluosilicate,** or *cobaltic bromopurpureofluosilicate,* $[Co(NH_3)_5Br]SiF_6$, by heating the nitrate or chloride of the base with hydrofluosilicic acid, and washing the product with water and alcohol. The crystals are isomorphous with the analogous chloro-compound. S. M. Jörgensen made **cobaltic tetramminodiaquodiammino-fluosilicate,** $[(NH_3)_2(H_2O)_2Co(OH).O.Co(NH_3)_4]_2(SiF_6)_3.2H_2O$, in hexagonal prisms, by treating a soln. of the chloride of the base with hydrofluosilicic acid.

J. J. Berzelius evaporated a soln. of nickel carbonate in hydrofluosilicic acid and obtained green rhombohedral and six-sided prismatic crystals of what were shown by J. Grailich and others to be **hexahydrated nickel fluosilicate,** $NiSiF_6.6H_2O$. J. J. Berzelius supposed the salt to be a heptahydrate. F. Stolba employed the method used for the ferrous salt. J. C. G. de Marignac showed that the trigonal crystals have the axial ratio $a:c=1:0{\cdot}5136$ and $\alpha=112°\,16'$. H. Töpsöe gave 2·109 for the sp. gr. V. von Lang measured the heat conductivity; and H. Töpsöe and C. Christiansen found the indices of refraction to be $\omega=1{\cdot}3876$ and $\epsilon=1{\cdot}4036$ for the *C*-line; and $\omega=1{\cdot}3910$ and $\epsilon=1{\cdot}4066$ for the *D*-line; and $\omega=1{\cdot}3950$ and $\epsilon=1{\cdot}4105$ for the *F*-line. J. J. Berzelius said that the salt is very soluble in water.

J. J. Berzelius [21] found that the yellow soln. of hydrated platinic oxide in hydrofluosilicic acid dries to a yellow gum-like mass of **platinic fluosilicate,** which is decomposed by water, forming a brown insoluble basic salt. L. Wöhler showed that the salt is readily hydrolyzed and a great excess of hydrofluosilicic acid is needed to prevent hydrolysis. The subject was also investigated by O. Ruff. By adding hydrofluosilicic acid to an aq. soln. of a tetramminopalladous salt, H. Müller obtained **palladous tetramminofluosilicate,** $[Pd(NH_3)_4]SiF_6$. The colourless crystals are sparingly soluble in cold water; easily soluble in hot water; insoluble in alcohol; decomposed at 160°; and, when treated with hydrochloric acid, give a precipitate of the chloride. S. M. Jörgensen prepared **rhodic chloropentammino-fluosilicate,** $[Rh(NH_3)_5Cl]SiF_6$, in yellow rhombohedra by adding hydrofluosilicic acid to a cold soln. of the chloride of the complex base.

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## § 57. Silicon Chlorides

In 1823, J. J. Berzelius [1] discovered **tetrachlorosilane,** or **silicon tetrachloride,** $SiCl_4$, when he showed that this compound is formed by the direct union of the elements silicon and chlorine. In addition, the derivative *trichlorosilane,* or *silicochloroform,* $SiHCl_3$; *dichlorosilane,* $SiH_2Cl_2$; and *monochlorosilane,* $SiH_3Cl$, have been made. In addition, the members of the homologous series, *hexachlorosilicocthane,* or *hexachlorodisilane,* $Si_2Cl_6$; *octochlorosilicopropane,* or *octochlorotrisilane,* $Si_3Cl_8$; *decachlorosilicobutane,* or *decachlorotetrasilane,* $Si_4Cl_{10}$; *dodecachlorosilicopentane,* or *dodecachloropentasilane,* $Si_5Cl_{12}$; and *tetradecachlorosilicohexane,* or *tetradecachlorohexasilane,* $Si_6Cl_{14}$, have been prepared. Some chlorobromo- and chloriodo-silanes are known—*vide infra.*

When silicon is heated in chlorine gas, it ignites and burns, forming the vap. of silicon tetrachloride which condenses to a liquid on cooling. If any air or oxygen is present some silica or, according to L. Troost and P. Hautefeuille, an oxychloride is formed. According to W. Hempel and H. von Haasy, the reaction between silicon and chlorine begins at 280°, and it proceeds with incandescence at 480°. If the silicon contains sodium fluoride, A. F. Holleman and H. J. Slijper showed that silicon tetrachloride is not obtained by heating it in chlorine, on account of the reaction: $SiCl_4+4NaF=SiF_4+4NaCl$. H. C. Oersted made the tetrachloride by passing chlorine gas over an intimate mixture of silica and charcoal at a red heat. H. Buff and F. Wöhler, J. J. Ebelmen, and H. Schnitzler made the gas by this process, which may be conducted in the following manner:

An intimate mixture of precipitated silica and finely ground willow charcoal is made into a stiff paste with oil; rolled into balls; ignited in a closed crucible; and loosely packed in a wide porcelain tube. A stream of chlorine is passed through the tube heated to bright redness. The condensed liquid is at first colourless, but it soon acquires a yellow colour owing to the absorption of chlorine. To remove the colouring, J. J. Ebelmen, and J. B. A. Dumas allowed the yellow liquid to stand in contact with mercury or

with copper turnings. The liquid can then be rectified by fractional distillation. According to J. J. Ebelmen, the yield with natural silica—amorphous or crystalline—is not so good as with precipitated silica.

According to the Konsortium für elektrochemische Industrie, the temp. of the reaction can be lowered some 300° to about 900°, by adding chlorides of the alkalies or alkaline earths, manganese or aluminium, or of mixtures of chlorides. R. Weber found that if the temp. is raised high enough silica reacts with chlorine in the absence of carbon. H. St. C. Deville showed that hydrogen chloride also furnishes silicon tetrachloride when passed over a mixture of carbon and silica, but the temp. must be higher than is required with chlorine. A. Faure made silicon tetrachloride by passing a mixture of hydrogen chloride and a hydrocarbon gas over red-hot silica. C. W. Watts and C. A. Bell were not very successful in the attempt to make silicon tetrachloride by the action of carbon tetrachloride, chloroform, or a mixture of carbon monoxide, and chlorine on red-hot silica. According to L. Troost and P. Hautefeuille, if chlorine be passed over a mixture of silicon with one-tenth of its weight of boron, the latter generates so much heat in reacting with the chlorine that the temp. of reaction of silicon with the chlorine is attained; boron trichloride also reacts with silica at a bright red-heat forming silicon tetrachloride: $4BCl_3+3SiO_2=3SiCl_4+2B_2O_3$; if unglazed porcelain be used instead of silica, some aluminium chloride is formed; and with glazed porcelain, some potassium aluminium chloride is formed. R. Weber, and A. Daubrée found that when amorphous silica, powdered quartz, or a powdered silicate, is strongly heated in the vapour of phosphorus pentachloride, some phosphorous oxychloride and silicon tetrachloride are formed. P. Didier found some silicon tetrachloride is produced when cerium trichloride and silica are heated in the presence of a feeble oxidizing agent. C. Matignon and F. Bourion showed that when a mixture of chlorine and the vapour of sulphur chloride is passed over silica at about 450°, silicon tetrachloride is formed. E. Baudrimont said that a mixture of potassium chlorate and silica at a temp. exceeding 360°, furnishes oxygen, chlorine, and a little silicon tetrachloride, but G. Rauter observed that no silicon tetrachloride is formed when silica is heated with the chloride of potassium, sodium, silver, chromium, sulphur, manganese, or iron. E. Jüngst and R. Mewes obtained metal silicides and silicon tetrachloride by heating a mixture of a metal chloride and silicon. R. Weber found that when a mixture of trichlorosilane and chlorine is heated, tetrachlorosilane is formed; H. Buff and F. Wöhler, and C. Friedel and A. Ladenburg noted that when silicochloroform is heated it forms the tetrachloride. W. Hempel and H. von Haasy obtained the tetrachloride in the reaction between chlorine and the sulphosilicates; H. N. Stokes, in the reaction between the aromatic silicon esters and phosphorus oxychloride; and A. Colson, in the reaction between mercuric chloride and silicon sulphide.

H. N. Warren, and F. de Carli made silicon tetrachloride by passing chlorine over heated ferrosilicon; and L. Gattermann used magnesium silicide obtained by heating a mixture of silica and magnesium. The best yield was obtained by working at 300°–310°. The product of the reaction contained about 80 per cent. of silicon tetrachloride; 20 per cent. of hexachlorosilicoethane; and 0·5–1·0 per cent. of octochlorosilicopropane. The distillate was separated into its components by fractional distillation. G. Rauter used copper silicide in place of ferrosilicon; O. Hutchins, silicon carbide; and E. Vigouroux, aluminium silicide. G. P. Baxter and co-workers describe the purification of silicon tetrachloride for their work on the at. wt. of silicon. G. Martin's directions for making silicon tetrachloride from ferrosilicon are as follows:

The chlorine cylinder *A*, Fig. 199, delivers gas into the washbottles *B*, connected with an iron tube fitted with iron caps *cc*, and heated to 180°–200° in the tube-furnace *C*. The iron tube is packed with coarsely crushed ferrosilicon. The liquid products of the reaction collect in the flask which has an exit-tube connected with the inverted condenser *E*, and an exit leading into the fume chamber. A force-pump, *K*, drives air, as required, through

the mercury bottle *J*, up the drying tower *I*, and so forces the liquid as required from *D* into the fractionating flask *F*, fitted with Young's still-head. The distillation flask *F* is connected with the condenser *G* and receiver *H*, which has an exit-tube leading into the fume chamber. The manometer and safety-tube *M* contain mercury and sulphuric acid in order to prevent an explosion if the tubes get blocked and the press. rises too high. The flask *F* is heated on a water-bath; and the bottles *H* of crude silicon chloride are stoppered and removed as they are filled. When the flask *F* is nearly full of high-boiling residues, the water-bath is replaced by an oil-bath, and silicon hexachloride distils over

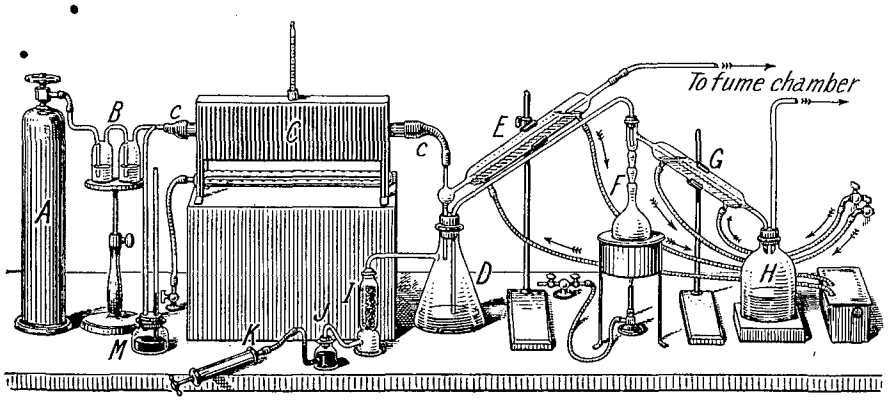



FIG. 199.—The Preparation of Silicon Chlorides.

between 147° and 149°. In this way, 143 kgrms. of chlorine gas passed over 50 kgrms. of 50 per cent. ferrosilicon furnished 54 kgrms. of silicon tetrachloride, 3 kgrms. of silicon hexachloride, and 500 grms. of a residue which yielded nearly 200 grms. of silicon octochloride. If the furnace be heated to 300°–310°, the iron tube is quickly corroded by the chlorine, but at 180°–200°, this action is too slow to be troublesome. If the temp. is 170°, the action of chlorine on the ferrosilicon is too slow for effective work. If the temp. be 300°–310°, the yield of the disilicon hexachloride is about 4 per cent.; if 250°–260°, the yield is 4·6 per cent.; and if 180°–200°, the yield rises to 8·6 per cent. The crude products must be further rectified by fractional distillation. Great care must be taken that the apparatus is thoroughly dried before the silicon chloride is introduced. The attachment *IJK* enables the chlorides to be transferred from one vessel to another without contact with undried atm. air.

The formation of more complex chlorides during the reaction between chlorine and the metal silicide is attributed by L. Gattermann and K. Weinlig to a secondary reaction between the tetrachloride and silicon: $3SiCl_4+Si=2Si_2Cl_6$; but at the temp. of the reaction, silicon tetrachloride does not react with silicon to produce an appreciable amount of the hexachloride. Consequently, G. Martin suggested that the mols. of the element silicon are chains of atoms, and the first action of chlorine on silicon is not to break the chains of atoms into single atoms, but rather to form complex chlorination products, which, reacting with more and more chlorine, break down into simpler and simpler chlorides: *e.g.* $Si_2Cl_6+Cl_2=2SiCl_4$. Instead of regarding silicon tetrachloride as the first product of the reaction, it is considered to be the end-product of a process which progresses in a series of stages. The complex chlorides obtained in the receiver are supposed to have escaped destruction owing to their having been removed from the seat of the reaction and quickly cooled.

**The physical properties of silicon tetrachloride.**—Silicon tetrachloride at ordinary temp. is a transparent, colourless, fuming liquid. J. J. Berzelius [2] said that when exposed to the air the liquid evaporates as a white cloud leaving a residue of silica; the vapour has a suffocating odour and reddens litmus. L. Köster gave for the **specific gravity** of the liquid 1·54; J. I. Pierre, 1·52371 at 0°; D. I. Mendeléeff, 1·50068 at 10·98°, 1·4928 at 15°, and 1·1929 at 99·9°; C. Friedel and J. M. Crafts, 1·522; A. Stiefelhagen, 1·524 at 16°; O. Ruff and C. Albert, 1·4933 at 15°; G. Abati, 1·47556 at 22°; O. Haagen, 1·4878 at 20°; and T. E. Thorpe, 1·52408 at 4°. J. B. A. Dumas gave for the **vapour density,** 5·939; and H. V. Regnault,

5·86 when the calculated value for $SiCl_4$ is 5·868. The vap. shows no signs of dissociation at the softening temp. of porcelain. W. Ramsay and J. Shields found for the **surface tension** 16·31 dynes per cm. at 18·9° and 13·66 dynes per cm. at 45·5°; and for the **specific cohesion** at these temp., 2·24 and 1·95 sq. mm. respectively. P. Walden gave for the surface tension, $\sigma$, at $\theta°$, $\sigma=18{\cdot}20(1-0{\cdot}00548\theta)$, and for the sp. cohesion $a^2=2{\cdot}731(1-0{\cdot}00461\theta)$; D. I. Mendeléeff gave 15·13 for the surface tension of the liquid at the b.p. The **association factor**, according to G. G. Longinescu, is unity; and observations on this subject were made by W. Ramsay and J. Shields, I. Traube, P. Vaubel, and L. Henry. I. Traube estimated $a$ at 273° K. in J. H. van der Waals' equation to be $121\times10^6$; and $b$ at 273° K. to be 88·5; $v-b=23{\cdot}1$; and $a/v^2=890$ atm.

The coefficient of **thermal expansion** of the liquid at 20° was found by J. I. Pierre to be 0·001430; and 0·001446 by T. E. Thorpe. The former found unit vol. at 0° becomes $1+0{\cdot}0012941190\,69\theta+0{\cdot}0_5218414363\,1\theta^2+0{\cdot}0_7408642\,20\theta^3$ at $\theta°$; and the latter, $1+0{\cdot}0013309\,46\theta+0{\cdot}0_5280978\theta^2+0{\cdot}0_8215657\theta^3$. J. J. Saslawsky studied the relation between the coeff. of expansion and the structure. The expansion and **compressibility** of the vap. was studied by L. Troost and P. Hautefeuille. For the **boiling point** of the liquid, G. S. Sérullas gave 50°; O. Haagen, 58° at 756 mm.; I. J. Pierre, J. B. A. Dumas, and C. Matignon and F. Bourion, 59° at 766 mm.; H. V. Regnault, 56·81° at 760 mm.; T. E. Thorpe, 58°–58·5° at 765·33 mm., and 57·57° at 769 mm.; W. Becker and J. Meyer, 56·9° at 760 mm.; and A. Stock and co-workers, 56·8° at 760 mm. According to S. Young, the observed b.p., $\theta$, at a barometric press., $p$, is corrected by adding on the term $0{\cdot}000126(760-p)(273+\theta)$. G. Rauter gave −102° for the **melting point** of solid silicon tetrachloride; W. Becker and J. Meyer, −89°; W. M. Latimer, −70°; and A. Stock and co-workers, −68·7°. The discrepancy in the data is in part due to the earlier preparations having been contaminated with higher boiling and lower melting chlorides. W. M. Latimer gave for the mol. sp. ht., $C_p$, per mol ÷5, at different temp.:

| °K. | 77·4° | 81·3° | 86·6° | 131·3° | 181·0° | 185·8° | 208·8° | 294·3° |
|---|---|---|---|---|---|---|---|---|
| $C_p$ | 3·60 | 3·70 | 3·83 | 4·80 | 5·95 | 6·08 | 6·74* | 6·94* |

The numbers marked with an asterisk refer to the liquid, the others to the solid. The **entropy** at 25° is 56·43. H. V. Regnault represented the **vapour pressure**, $p$ mm., at $\theta°$ by $\log p=4{\cdot}5959425-3{\cdot}3287708\alpha^{\theta+26}$, where $\log\alpha=9{\cdot}9965260-10$. R. Wintgen gave $\log p=7{\cdot}6443-1572{\cdot}0T^{-1}$. W. Becker and J. Meyer gave:

| | 0° | 5° | 10° | 15° | 20° | 25° | 56·9° |
|---|---|---|---|---|---|---|---|
| $p$ | 11·6 | 13·3 | 15·0 | 17·5 | 21·6 | 26·1 | 76 cm. |

and H. V. Regnault gave:

| | −25° | −10° | 0° | 10° | 30° | 50° | 60° | 65° |
|---|---|---|---|---|---|---|---|---|
| $p$ | 1·966 | 4·646 | 7·802 | 12·590 | 29·449 | 60·746 | 83·723 | 97·274 cm. |

D. I. Mendeléeff gave 230° for the **critical temperature**; W. Ramsay and J. Shields calculated 213·8°; and C. M. Guldberg, 221°. D. A. Goldhammer applied the theory of corresponding states to silicon tetrachloride; and calculated for the **critical density** 0·5275. W. M. Latimer gave 10·85 cals. per gram for the heat of fusion at −70·3°. J. Ogier found the **heat of vaporization** to be 6·3 Cals. per mol., and A. Stock and co-workers, 7·19 Cals. per mol. R. Wintgen gave 7185 cals., and for the mol. heat of vaporization, at 0° K., 7946·2 cals., or 6925 cals. at T° K.; 21·0 for Trouton's constant. H. V. Regnault gave 0·1904 for the **specific heat** of the liquid between 10° and 15°; J. Ogier obtained a similar result; and L. Kahlenberg and R. Koenig gave 0·1904 between 20° and 40°. H. V. Regnault found for the sp. ht. of the gas between 90° and 234°, $C_p=0{\cdot}1322$. J. W. Capstick obtained 1·129 for the ratio of the two sp. hts. of the vap. M. Berthelot, and L. Troost and P. Hautefeuille gave for the **heat of formation**, $Si_{cryst.}+4Cl=SiCl_{4gas}+121{\cdot}8$ Cals.; and with $SiCl_{4liquid}$, 128·1 Cals. M. Berthelot measured the heat of decomposition

by water: $SiCl_4+Aq.=SiO_2.aq.+4HCl.aq.+69$ Cals. J. Thomsen gave 69·3 Cals. L. Gattermann and K. Weinlig gave 1·404 for the **index of refraction** for red light. O. Haagen gave for the red ray, $H_\alpha$, 1·4119; for the green ray, $H_\beta$, 1·4200; and for the violet ray, $H_\gamma$, 1·4244. G. Abati gave 1·41019 for the $H_\alpha$-ray; 1·41829 for the $H_\beta$-ray; 1·41257 for the $D$-ray; and 1·42306 for the $H_\gamma$-ray, and he calculated 47·528 for the mol. **refraction** for $H_\alpha$ from the $n$-formula, and 28·55 from the $n^2$-formula; for the sp. refraction, the numbers are respectively 0·277989 and 0·167978. The sp. **dispersion** for $H_\gamma$ and $H_\alpha$ is 0·008722. J. H. Gladstone made some observations on this subject; and A. Stiefelhagen gave for the index of refraction of rays of wave-length $\lambda=226$, 394, and $589\mu\mu$, the index of refraction $\mu=1·50823$, 1·43334, and 1·4182 respectively, and $\mu^2=1·31377+0·66590\lambda^2(\lambda^2-125·56^2)^{-1}$. H. H. Marvin studied the optical dispersion. The **spectrum** was examined by L. Troost and P. Hautefeuille, W. Jevons, and G. Salet. According to C. Lüdeking, silicon tetrachloride is not decomposed by the electric discharge, and P. Hautefeuille found that the effect of heat, and of the voltaic arc, resembles that with silicon tetrafluoride (*q.v.*). P. Walden found the **electrical conductivity** of liquid silicon tetrachloride to be negligible. H. Schlundt gave 2·40 for the **dielectric constant** at 16° with wave-lengths $\lambda=80$ cm. P. Pascal measured the **magnetic susceptibility** of silicon tetrachloride.

**The chemical properties of silicon tetrachloride.**—The composition of silicon tetrachloride was established by the analyses of J. Pelouze,[3] J. B. A. Dumas, and J. Schiel. K. Fajans studied the electronic structure of the silicon halides. According to C. Friedel and A. Ladenburg, when a mixture of silicon tetrachloride vap. and **hydrogen** is heated to redness a little silicochloroform, $SiHCl_3$, is produced. A. C. Vournasos found that the nascent hydrogen produced when silicon chloride vap. is passed over heated sodium formate, furnishes a little silane; C. Friedel and A. Ladenburg, when a mixture of silicon tetrachloride vap. and dry **oxygen** or **air** is heated, an oxychloride is formed: $4SiCl_4+O_2=2Si_2OCl_6+2Cl_2$; and, according to M. Berthelot, some silica is also formed. L. Troost and P. Hautefeuille obtained the same oxychloride by passing the gas through a heated porcelain tube with or without a packing of fragments of felspar or alkali silicate: $2SiCl_4+K_2SiO_3=2KCl+SiO_2+Si_2OCl_6$. The presence of hydrogen chloride does not accelerate the reaction. L. Troost and P. Hautefeuille found that on sparking a mixture of oxygen and silicon tetrachloride vap., the same oxychloride is formed, and if the free chlorine simultaneously produced is absorbed by mercury as fast as it is formed the oxychloride can be collected. According to J. J. Berzelius, silicon tetrachloride first floats on the surface of **water,** and it then dissolves with decomposition, forming hydrated silica and hydrochloric acid. W. Becker and J. Meyer said the reaction is very slow with ice-cooled water. According to A. Stock and F. Zeidler, silicon tetrachloride and water form $Si(OH)_2O$. N. V. Sidgwick explained the reaction with water on the basis of the co-ordination theory. C. Langlois found that the hydrated silica produced by exposing silicon tetrachloride to moist air resembles hydrophane. At a red heat, A. Daubrée found that water-vapour and silicon tetrachloride furnish crystals of silicon dioxide. The fumes which are developed when the tetrachloride is scattered in the atm. by means of an explosive bomb were utilized to a small extent as clouds in the 1914–1918 war; sometimes in conjunction with ammonia. The subject was discussed by G. A. Richter.

H. Moissan found that **fluorine** does not act on silicon tetrachloride at −23°, but at 40°, the formation of silicon tetrafluoride is accompanied by a feeble flame. N. W. Taylor and J. H. Hildebrand measured the solubility of **chlorine** in silicon tetrachloride and found at 0°, 0·131 grm. gas per gram of solvent is taken up. W. Biltz and E. Meinecke found the f.p. curves of mixtures of silicon tetrachloride and chlorine have a eutectic at −117° and 80 at. per cent. chlorine as indicated in Fig. 200. P. Hautefeuille found that when a mixture of silicon tetrachloride vap., hydrogen, and a little **iodine** is passed through a tube at a dull red heat, a heavy liquid is formed which, when fired from iodine by digestion with mercury, and fractionally

distilled, furnishes a series of chloroiodides. J. A. Besson found **hydrogen iodide** and silicon tetrachloride vap. at a dull red-heat furnish a mixture of chloroiodides; but O. Ruff and C. Albert observed no reaction at 120° in a sealed tube. J. A. Besson also reported the formation of chlorobromides when a mixture of **hydrogen bromide** and silicon tetrachloride is passed through a tube at a dull redness. O. Ruff and C. Albert found that in the presence of copper, silicon tetrachloride does not react with gaseous or liquid bromine. Silicon tetrachloride is not decomposed in the cold by hydrogen bromide or iodide. G. Gustavson found that with **carbon tetrabromide** in a sealed tube at 150°–200°, some silicon tetrabromide is formed.

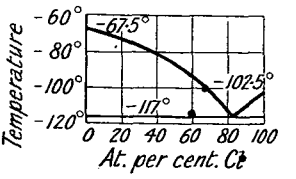



FIG. 200. — Freezing-point Curves of Cl–$SiCl_4$ Mixtures.

G. Rauter observed no reaction between silicon tetrachloride and **sulphur** at 200°–300°. J. I. Pierre, and C. Friedel and A. Ladenberg found that **hydrogen sulphide** does not act on silicon tetrachloride at ordinary temp., but at a red heat, silicon tetrahydrosulphide is formed; and M. Blix and W. Wirbelauer likewise obtained the chlorosulphide, $SiSCl_2$. O. Ruff and C. Albert found that in the presence of zinc, silicon tetrachloride does not react with **hydrogen chloride;** nor when treated with hydrogen chloride in a sealed tube at 100°. G. S. Sérullas found that conc. **sulphuric acid** decomposes silicon tetrachloride, forming silica and hydrochloric acid; G. Gustavson found that the tetrachloride is decomposed by **sulphur trioxide**, forming pyrosulphuryl chloride—*vide infra*, silicon oxychlorides; F. Clausnizer also found that the tetrachloride is decomposed by **chlorosulphonic acid** in sunlight or at 170°. J. F. X. Harold, and G. Rauter observed no reaction between **sulphur chloride** and silicon tetrachloride.

F. Lengfeld said that gaseous **ammonia** reacts with silicon tetrachloride alone or dissolved in benzene, forming silicon tetramide; and M. Blix and W. Wirbelauer showed that by saturating silicon tetrachloride with dry ammonia, a white mass of **silicon hexamminotetrachloride,** $SiCl_4.6NH_3$, is formed; the compound is decomposed by water. The ammine was made by J. Persoz in 1830, M. Blix and W. Wirbelauer showed that the hexammine is possibly a mixture of ammonium chloride and silicon imide, $SiCl_4.6NH_3=Si(NH)_2+4NH_4Cl$, because liquid ammonia washes out the ammonium chloride—*vide* boron hexamminotrichloride, and zirconium octamminotetraiodide. F. Lengfeld also obtained a product approximating *silicon octamminotetrachloride*, $SiCl_4.8NH_3$, by passing ammonia gas into a soln. of silicon tetrachloride in benzene in an atm. of dry nitrogen. The product is probably a mixture of silicon tetramide and ammonium chloride. E. Lay found that with **hydrazine,** a white, fuming compound, probably **silicon tetrahydrazine tetrachloride,** $SiCl_4.4N_2H_4$, is formed by the action of a benzene soln. of silicon tetrachloride on an emulsion of hydrazine in benzene. He also showed that the tetrachloride reacts with **sodamide,** $NaNH_2$, at 150°, forming silicon, and a sublimate of ammonium chloride, and silicon tetramminotetrachloride. J. F. X. Harold said that the tetrachloride does not react with **nitrogen peroxide,** or a mixture of nitrogen peroxide and chlorine. R. Weber found that neither **nitric acid** nor **aqua regia** unites with silicon tetrachloride; with nitrous acid, it forms nitrosyl chloride. C. Friedel and A. Ladenburg, and G. Rauter found that at a red heat, **phosphorus pentoxide** forms oxychlorides of phosphorus and, probably, silicon. J. F. X. Harold observed no reaction between silicon tetrachloride and **phosphorus chlorides.** A. Besson observed that silicon tetrachloride does not absorb phosphine at ordinary temp., but at −20° it dissolves 20 times its vol. of phosphine, and 40 times its vol. at −50°. By strong compression at −23° there is formed what is thought to be **silicon diphosphinetetrachloride,** $SiCl_4.2PH_3$. The product is liquid at −60°. Another product was obtained which is crystalline at 10° and 20 atm. press., or at −35° and atm. press. H. Moissan found that **arsenic trifluoride** reacts in the cold, forming silicon tetrafluoride and arsenic trichloride. G. Rauter examined the

action of silicon tetrachloride on the **arsenic oxides,** and the **antimony oxides ;** no reaction occurred with **arsenic sulphide** and the **antimony sulphides.**

L. Troost and P. Hautefeuille obtained evidence of the possible formation of a subchloride when silicon tetrachloride vap. is passed over heated **silicon,** and L. *Gattermann and K. Weinlig represent the reaction* $3SiCl_4+Si=2Si_2Cl_6$ ; but G. Martin could not confirm this. O. Ruff found that silicon tetrachloride is not affected by **carbon** at high temp. ; while J. N. Pring and W. Fielding observed the formation of silicon carbide only in the presence of hydrogen at 1700°—*vide* silicon. G. Rauter observed no reaction between silicon tetrachloride and **carbon disulphide.** J. F. X. Harold found that the tetrachloride does not react with **cyanogen chloride.** Silicon tetrachloride reacts with **fatty acids** forming their chlorides, and with **alcohol** *forming ethyl silicate.*

The tetrachlorides of carbon and silicon possess acidic characters in common with the other group elements, and combine with the bases to form stable well-defined compounds. Ammonia, the substituted ammonias, and other bodies of a distinctly basic character, so far as has been observed, react similarly with all. Titanium, one of the sub-group elements with the least pronounced metallic character, and tin in the other sub-group, having a distinct metallic character and a high at. wt., appear to be the most reactive members of group IV. when in the form of their tetrachlorides. Titanium tetrachloride, the metal with the lowest atomic weight of the first sub-group, is the most reactive since it forms compounds with bodies of a distinctly acidic nature—hydrogen cyanide, cyanogen chloride, nitrogen oxide ; zirconium tetrachloride, on the other hand, and the next tetrachloride, germanium, show no such tendency, for their combinations seem limited to compounds of a basic character. In the first sub-group, therefore, the reactivity decreases with increasing at. wt. The following selection from J. F. X. Harold's list of the double compounds of the tetrachlorides of elements of group VI with various acidic and basic compounds, shown in Table XXXV, illustrates these statements. In the table *c* denotes that a compound is formed, *n* indicates that no compound is formed, and – means that no data are available.

TABLE XXXV.—DOUBLE COMPOUNDS OF THE TETRACHLORIDES OF ELEMENTS OF GROUP VI.

| — | Aniline, etc. | Fatty amines. | Acid amides. | Hydrogen cyanide. | Acetonitrite (and Benzonitrite). | Cyanogen chloride. | $S_2Cl_2$. | $NO_2$. | $PCl_5$. | $PCl_3$. | $NH_3$. |
|---|---|---|---|---|---|---|---|---|---|---|---|
| $CCl_4$ . | *c* | – | *n* | – | – | – | – | *c* | – | – | *c* |
| $SiCl_4$ . | *c* | *c* | *n* | *n* | *n* | *n* | *n* | *n* | *n* | *n* | *c* |
| $TiCl_4$ . | *c* | *c* | *c* | *c* | *c* | *c* | *c* | – | *c* | – | *c* |
| $ZrCl_4$ . | *c* | *c* | *n* | *n* | *n* | *n* | *n* | *n* | *n* | *n* | *c* |
| $GeCl_4$ . | – | – | – | – | – | – | – | – | – | – | – |
| $SnCl_4$ . | *c* | *c* | – | *c* | *c* | *n* | *c* | – | *c* | – | *c* |
| $PbCl_4$ . | *c* | *c* | *n* | *n* | *n* | *n* | *n* | *n* | *n* | *n* | *c* |
| $ThCl_4$ . | *c* | *c* | *n* | *n* | *n* | *n* | *n* | *n* | *n* | *n* | *c* |

Silicon tetrachloride is a convenient starting-point for the preparation of the so-called organic derivatives of silicon, because the chlorine atoms can be exchanged for organic radicles through the agency of zinc alkyls, or of sodium and alkyl bromides or iodides—*Fittig's reaction ;* or by the *Grignard's reaction* in which magnesium reacts with one alkyl or aryl bromide in ethereal soln. producing magnesium alkyl or aryl bromide, MgBrX, which can then exchange its organic radicle for a chlorine atom of silicon tetrachloride : $MgBrX+SiCl_4=MgBrCl+SiCl_3X$. Reactions between silicon tetrachloride and organic compounds have been studied

by F. S. Kipping and co-workers, A. Harden, J. E. Reynolds, A. Rosenheim and co-workers, F. Lengfeld, C. Friedel and co-workers, G. Rauter, O. Ruff and C. Albert, W. Dilthey, C. Willgerodt, H. N. Stokes, F. Taurke, F. Eduardoff, etc.

G. S. Sérullas found that silicon tetrachloride can be distilled from **sodium** or **potassium** and the tetrachloride boils below the m.p. of these metals. A. C. Vournasos observed no action at the temp. of boiling toluene. J. J. Berzelius found that when potassium is heated in the vap. of silicon tetrachloride, the metal burns forming potassium chloride and silicon; if molten potassium be dropped into liquid silicon tetrachloride an explosion results. H. C. Oersted found that potassium amalgam does not react with the tetrachloride at ordinary temp. C. Friedel and A. Ladenburg, and N. N. Beketoff showed that sodium, **zinc,** and **silver** at a red heat withdraw the chlorine from the tetrachloride without forming higher chlorides. O. Ruff and C. Albert found that **sodium hydride,** and **calcium hydride** do not react at 100°, and in the presence of aluminium chloride. G. Rauter found that zinc, **aluminium, beryllium,** and **magnesium** react at 200°–300° forming the metal chloride and silicon. K. Seubert and A. Schmidt observed that with magnesium at a dull red-heat, magnesium silicide and silicon are formed without incandescence; G. Rauter observed no reaction with **iron** at 200°–300°. N. Parravano and C. Mazzetti found that silicon tetrachloride reacts with iron at 900° forming an iron silicide. E. Vigouroux showed that with reduced iron at a dull red-heat, iron silicide and ferrous chloride are formed; **cobalt** similarly reacts at 1200°–1300°; **nickel** also forms silicides.

According to G. Rauter, most of the **metal oxides** react with silicon tetrachloride, forming the metal chloride or oxychloride and silica. In some cases, the reaction occurs at ordinary temp.; in others, the oxide must be heated. At higher temp., crystalline silica and different silicates may be formed as in the syntheses by A. Daubrée, and L. Troost and P. Hautefeuille. G. Rauter examined the reaction with silver oxide and the two copper oxides; G. Rauter, and A. Daubrée, the reaction with *calcium, strontium, and barium oxides;* and also with *beryllium and magnesium oxides;* G. Rauter, the reaction with *zinc, cadmium, and mercuric oxides,* and with *boric oxide;* G. Rauter, A. Daubrée, and L. Troost and P. Hautefeuille, the reaction with *aluminium oxide;* G. Rauter, the reaction with *thallium oxide,* the *bismuth oxides,* and *tin and lead oxides.* With heated lead oxide, C. Friedel and A. Ladenburg said the reaction occurs with incandescence, forming lead chloride and silicate; L. Troost and P. Hautefeuille, the reaction with *zirconium oxide;* G. Rauter, the reaction with *titanium oxide; chromium oxides; molybdenum oxides; tungsten oxide, uranium oxide;* the *manganese oxides;* the *iron oxides; cobalt oxide;* and *nickel oxide.* The **metal salts** with inorganic acids generally behave like mixtures of the acid anhydrides and the basic oxides; *borax* has scarcely any action on silicon tetrachloride; but G. Rauter observed the reaction with the *alkali carbonates; potassium nitrite and nitrate; potassium chromate and dichromate; cupric sulphate;* and with *potassium permanganate, chlorate, bromide, and iodide;* no action was observed with *calcium fluoride, sodium sulphite, potassium polysulphide,* or *mercuric sulphide.* In general, the heavy **metal sulphides** have scarcely any action. A. F. Holleman and H. J. Slijper found that sodium fluoride reacts, forming **sodium chloride** and silicon tetrafluoride; and P. Miquel found that at ordinary temp. **lead thiocyanate** forms silicon tetrathiocyanate and lead chloride. C. Friedel and A. Ladenberg represented the reaction with red-hot **sodium oxide,** $SiCl_4+4Na_2O=Na_4SiO_4+4NaCl$; the alkali oxide is supposed to be contained in the sodium silicate.

From the analogy between methane and silane, it would be anticipated that the hydrogen atoms of silane could be replaced by chlorine atoms one by one. All three substitution products have been obtained so that the series of **silicon chlorohydrides,** $SiH_nCl_{4-n}$,

| | $SiCl_4$ | $SiHCl_3$ | $SiH_2Cl_2$ | $SiH_3Cl$ | $SiH_4$ |
|---|---|---|---|---|---|
| B.p. . . . | 58° | 34° | 12° | −10° | −11° |

is complete. The first substitution product was discovered by H. Buff and F. Wöhler [4] in 1857, and it was at first supposed to be a compound of silicon chloride and hydrogen chloride; but in 1867, C. Friedel and A. Ladenburg showed that the compound has a formal analogy with chloroform, $CHCl_3$, and it was therefore called **silicochloroform,** $SiHCl_3$. It is also called **trichlorosilane.** O. Ruff and C. Albert were not able to obtain this compound by the action of reducing agents on silicon tetrachloride; but A. J. Besson and L. Fournier did obtain a small quantity of silicochloroform by passing the vap. of silicon tetrachloride over red-hot calcium hydride. H. Buff and F. Wöhler made trichlorosilane by heating silicon in a current of dry hydrogen chloride. This process was employed by C. Friedel and A. Ladenberg, and E. Vigouroux. The product was separated by fractional distillation from the other silicon chlorides formed at the same time. The trichlorosilane distils between 35° and 37°, and the silicon tetrachloride towards 60°. L. Cambi found trichlorosilane to be the chief product of the action of dry hydrogen chloride on silicon sulphide, SiS. L. Gattermann obtained it among the products of the action of dry hydrogen chloride on the crude silicon or magnesium silicide obtained by reducing quartz sand with magnesium. F. Lengfeld said the yield is improved by using an excess of sand with the magnesium. H. N. Warren passed hydrogen chloride over ferrosilicon containing 15 per cent. of silicon; and H. Moissan and A. Holt, by passing hydrogen chloride over heated vanadium silicide, $V_2Si$. In all these cases, the trichlorosilane is to be separated by fractional distillation from the condensed liquid. C. Combes passed dry hydrogen chloride over copper silicide heated in a vap.-bath of sulphur, mercury, or diphenylamine. The yield of trichlorosilane is about 80 per cent. of the theoretical, and the remaining 20 per cent. is mainly the tetrachloride which can be separated by fractional distillation. O. Ruff and C. Albert considered this to be the best method of preparation. A. Stock and F. Zeidler worked at 300°, and found the purification by distillation in vacuo to be very tedious because the hydrogen chloride and silicon tetrachloride are retained very tenaciously; indeed, the former appears to be continuously produced probably owing to the slight but unavoidable water-content of the glass.

Trichlorosilane at ordinary temp. is a colourless, mobile liquid with a smell like that of silicon tetrachloride. The analyses of H. Buff and F. Wöhler, C. Friedel and A. Ladenburg, and O. Ruff and C. Albert established the composition; and C. Friedel and A. Ladenburg's **vapour density,** 4·64, agrees with the value 4·69 calculated for the formula $SiHCl_3$. H. Buff and F. Wöhler gave 1·65 for the **specific gravity** of the liquid; while O. Ruff and C. Albert gave 1·3438 at 15°; and A. Stock and F. Zeidler gave 1·35 at 0°. H. Buff and F. Wöhler gave 42° for the **boiling point;** C. Friedel and A. Ladenburg, 35°–39°; L. Gattermann, 35°–37°; A. J. Besson, 34°; O. Ruff and C. Albert, 35°–34°; C. Pape, 33°; A. Stock and F. Zeidler, 31·8°. The last-named gave for the **vapour pressure,** $p$ mm., at different temp.:

| −85·0° | −70·1° | −50·0° | −30·5° | −10·5° | 0° | 10·5° | 25·0° | 32·0° |
|---|---|---|---|---|---|---|---|---|
| 0·7 | 2·8 | 13·0 | 45·5 | 132 | 218 | 338 | 598 | 765 |

They also gave for the **melting point** −126·4° to −126·6°, and O. Ruff and C. Albert gave −134°. It will be observed that chloroform boils at 61·5°, and that in general, apart from polymerization, the silicon compounds are generally more volatile than the corresponding carbon compounds. H. Buff and F. Wöhler found trichlorosilane to be a non-conductor of electricity.

According to H. Buff and F. Wöhler, when the vap. of trichlorosilane is passed through a red-hot tube, hydrogen chloride, silicon tetrachloride, and a brown mirror of amorphous silicon are produced; O. Ruff and C. Albert deny the production of hydrogen chloride, and they represent the decomposition as a balanced reaction: $4SiHCl_3 \rightleftharpoons Si + 2H_2 + 3SiCl_4$; and if hydrogen be mixed with the vap., the temp. of decomposition is higher—about 900°. A. Stock and F. Zeidler said that trichlorosilane is remarkably stable towards heat, but at 900° it suffers almost quanti-

tative decomposition into silicon, hydrogen, hydrogen chloride, silicon tetrachloride, and a trace of liquid less volatile than the latter. A. J. Besson and L. Fournier found that when a mixture of dry **hydrogen** and the vap. of trichlorosilane is exposed to the dark electric discharge, a yellow oily liquid containing a mixture of more or less condensed silicon chlorides of the series $Si_nCl_{2n+2}$ is formed. H. Buff and F. Wöhler reported that the vap. of trichlorosilane is as inflammable as that of ether, and it burns in **air** with a green-mantled flame like that of chloroform, producing white clouds of silica, and hydrogen chloride; a mixture of trichlorosilane and air can be exploded, forming silica, silicon chloride, and hydrogen chloride. C. Friedel and A. Ladenburg said that a warm body like a hot glass rod will ignite the mixture. H. Buff and F. Wöhler noted that a detonation occurred during the distillation when air was present in the retort. A. J. Besson and L. Fournier found that if trichlorosilane at −80° be sat. with dry **oxygen** and the soln. left for some days in a sealed tube exposed to sunlight, a mixture containing silicon oxychloride, $Si_2OCl_6$, is produced; and a similar reaction occurs with a mixture of **ozone** and oxygen at 0°. Unlike chloroform or carbon tetrachloride, but like silicon tetrachloride, trichlorosilane fumes in moist air, and is decomposed by **water** with the evolution of heat, forming silicic and hydrochloric acids; and A. Friedel and A. Ladenburg observed that if the reaction with water occurs at 0°, the hydrogen is retained and a white insoluble powder of the so-called silicoformic anhydride, H.SiO.O.OSiH, is produced: $2HSiCl_3+3H_2O=6HCl+(HSiO)_2O$. A. Stock and F. Zeidler say that the polymerized dioxodisiloxane (silicoformic anhydride) has been isolated in the homogeneous condition, and is then remarkably stable towards water. In the gaseous condition, the chloro-compound reacts only slowly with a deficiency of water vap., without giving any indication of the formation of products intermediate between it and dioxodisiloxane. Attempts to isolate the latter in a less highly polymerized form by decomposing trichloromonosilane in the presence of benzene were unsuccessful. It gives indications of its ability to form salts in the absence of water. At ordinary temp., **chlorine** converts trichlorosilane into hydrogen chloride and silicon tetrachloride; **bromine,** at 100°, converts it into hydrogen bromide and silicon chlorobromide. A. J. Besson and L. Fournier showed that trichlorosilane reacts slowly with **hydrogen chloride,** forming unsaturated silicon chlorides.

O. Ruff and C. Albert observed no change when trichlorosilane and **sulphur** are heated in a sealed tube to 150°. H. Buff and F. Wöhler found that trichlorosilane is not changed by **hydrogen sulphide.** O. Ruff and C. Albert showed that when trichlorosilane is treated with **sulphur dioxide,** some sulphur, silica, silicon tetrachloride, and hydrogen chloride are formed; and with **sulphur trioxide,** sulphuryl chloride, silica, silicon oxychloride, chlorosulphonic acid, and hydrogen chloride are formed; while A. J. Besson and L. Fournier found that at 100° sulphur trioxide forms sulphur dioxide, pyrosulphuryl chloride, chlorosulphonic acid, and viscous silicon oxychlorides. Aq. **ammonia,** like water, was found by C. Friedel and A. Ladenburg to form silicoformic anhydride, followed by a further decomposition: $SiHCl_3+3NH_4OH=H_2+SiO_2+3NH_4Cl+H_2O$. O. Ruff and C. Albert showed that trichlorosilane unites with gaseous ammonia, but the product has not a definite composition. A. Stock and F. Zeidler found that in the gaseous phase under diminished press. and at atm. temp., the reaction is symbolized: $2SiHCl_3+9NH_3=6NH_4Cl+(NH:SiH)_2NH$; the same products are obtained if the components are successively condensed in the same vessel and the mixture gradually warmed. When the product is gradually heated, the imide decomposes: $(NHSiH)_2NH=NH_3+2SiNH$. A. J. Besson and L. Fournier showed that an explosion occurs when trichlorosilane is mixed with **nitrogen peroxide** at −20°; and if the materials are diluted with carbon tetrachloride, the reaction is symbolized: $SiHCl_3+2NO_2=SiO_2+2NOCl+HCl$. Red **phosphorus** produces some phosphine and a high boiling silicon compound. A. Besson found that with **phosphine** and trichlorosilane at 15° under a press. of 40 atm., or at −35° under a press. of 20 atm., an unstable

crystalline compound is formed. O. Ruff and C. Albert showed that alkaline or neutral soln. of **arsenious oxide,** or **antimonious oxide,** are reduced to the metal by the action of the liberated hydrogen. A soln. of **arsenic trifluoride** furnishes trifluosilane and arsenic; with **arsenic trichloride** in a sealed tube at 150°, no alteration was observed. Arsenic trichloride is miscible in all proportions with trichlorosilane.

C. Friedel and A. Ladenburg found that with absolute **alcohol,** trichlorosilane forms not ethyl orthosilicate but *ethyl orthosilicoformate*, $SiH(OC_2H_5)_3$. According to C. Combes, when trichlorosilane is treated with an excess of **aniline,** $C_6H_5NH_2$, in benzene soln., white acicular crystals of *trianilinosilane*, $H-Si\equiv(NHC_6H_5)_3$, are formed. This compound begins to decompose at 114°, and regenerates trichlorosilane when exposed to dry hydrogen chloride. O. Ruff and C. Albert found trichlorosilane to be miscible in all proportions with **carbon disulphide, carbon tetrachloride, chloroform,** and **benzene; paraffin** is dissolved by the hot liquid, and given up again on cooling. Other reactions with organic compounds have been reported by C. Pape, C. Combes, L. Gattermann, A. Polis, etc.

O. Ruff and C. Albert showed that trichlorosilane suffers no perceptible change when heated in a sealed tube to 150° with **sodium,** sodium-amalgam, **mercury, silver, copper,** or **tin;** on the other hand, A. Stock said that it reacts with sodium-amalgam: $SiHCl_3+3Na=3NaCl+(SiH)_n$, since volatile compounds are not produced in appreciable amounts. When heated 12 hrs. with **chromic anhydride** in a sealed tube at 160°, silica, chromic oxide, and chromyl chloride are formed. A. J. Besson and L. Fournier said that the reaction takes place at ordinary temp. when an unstable brown compound, $Cr_3OCl_7$, is formed. The reaction with a dil. soln. of **sodium hydroxide** is represented: $3NaOH+SiHCl_3+H_2O=Si(OH)_4+3NaCl+H_2$. Trichlorosilane does not react when heated with **silver fluoride** or **lead fluoride;** but with **stannic fluoride** or **titanic fluoride,** trifluosilane is formed. Trichlorosilane is miscible in all proportions with **silicon, tin,** and **titanium tetrachlorides.** A. Stock and F. Zeidler found aluminium chloride has no action at 175°.

F. Lengfeld[5] thought that **silicomethylene chloride,** or **dichlorosilicomethane,** or **dichlorosilane,** $SiH_2Cl_2$, was formed as a by-product in the preparation of trichlorosilane. A. J. Besson and L. Fournier obtained this compound and also **silicomethyl chloride,** or **chlorosilicomethane,** or **monochlorosilane,** $SiH_3Cl$, by passing dry hydrogen chloride over heated amorphous silicon, and absorbing the products in silicon tetrachloride cooled by means of solid carbon dioxide. By fractional distillation of the soln., the compounds, $SiH_3Cl$, which boils at about −10°, and $SiH_2Cl_2$, which boils at about 12°, were obtained. Both these chlorides are colourless, mobile liquids, which have a large coeff. of expansion, and are decomposed by water and alkalies with evolution of hydrogen. A sulphur compound boiling at about −25° was also obtained in small quantity; the formation of this is attributed to the presence of sulphur as an impurity in the amorphous silicon. In an attempt to make these compounds by passing silicon tetrachloride vap. over calcium heated to a temp. below redness, the products obtained were hydrogen, hydrogen chloride, silico-chloroform, calcium chloride, and either calcium silicide or an amorphous silicon, depending on the temp. At a relatively low temp. and with excess calcium hydride, calcium silicide is formed, whereas at a higher temp. and with excess of silicon tetrachloride, amorphous silicon is obtained. According to A. Stock and F. Zeidler, with water, and ammonia, monochlorosilane yields respectively the substances $(SiH_3)_2O$ and $(SiH_3)_3N$, which are unimolecular and volatile. According to A. Stock and C. Somiesky, monochlorosilane and silver cyanide at 150° yield hydrogen cyanide and cyanogen as gaseous products. At 300°, monochlorosilane is decomposed by silver sulphide into non-volatile silicon compounds, hydrogen, and hydrogen sulphide. Monochlorosilane and hydrogen sulphide at 150° in the presence of aluminium chloride give hydrogen, dichloromonosilane, and a volatile compound containing sulphur—possibly $SiH_3.SH$ or $(SiH_3)_2S$. The main products of the action of sodium amalgam on dichloromono-

silane are monosilane and the unsat., yellow, polymerized hydride, $(SiH)_x$. The course of the reaction is represented by the equations $SiH_2Cl_2+4Na=SiH_2Na_2+2NaCl$; $SiH_2Na_2+$mercury$\rightarrow SiH_2+$sodium amalgam; $3SiH_2\rightarrow SiH_4+2(SiH)_x$. A. Stock and F. Zeidler found that when the dichloro-compound is treated with water, and ammonia, it gives respectively the products $SiH_2O$ and $SiH_2:NH$, which can be preserved for a short time in the volatile form with low mol. wt., but rapidly become associated to non-volatile polymerides. Trichlorosilane yields respectively $(SiOH)_2O$, and $(NH:SiH)_2NH$; and tetrachlorosilane, respectively $Si(OH)_2O$, and $Si(NH_2)_2NH$. R. Wintgen represented the vap. press., $p$, of monochlorosilane and dichlorosilane respectively by $\log p=7{\cdot}6251-1148{\cdot}1T^{-1}$, and $\log p=7{\cdot}8001-1378{\cdot}8T^{-1}$; the latent heat of vaporization by 5248 and 6302 cals.; the mol. heat of vaporization at 0° K. by 6329·9 cals. and 5929·5 cals.; and at $T$° K., by 4802 cals. and 6016 cals.; and Trouton's constant by 19·8 and 21·4.

The **homologous series** of the chlorine derivatives of the silanes, $Si_nCl_{2n+2}$, has been followed as far as $n=6$:

| | $SiCl_4$ | $Si_2Cl_6$ | $Si_3Cl_8$ | $Si_4Cl_{10}$ | $Si_5Cl_{12}$ | $Si_6Cl_{14}$ |
|---|---|---|---|---|---|---|
| B.p. . . | 56·9° | 147° | 216° | 150° | 190° (15 mm.) | Sublimes 200° |

L. Troost and P. Hautefeuille [6] prepared **hexachlorosilicoethane,** or **hexachlorodisilane,** or *perchlorosilicoethane*, $Si_2Cl_6$, by passing the vap. of silicon tetrachloride over white-hot silicon, contained in a porcelain tube, and by cooling the products rapidly. The hexachlorodisilane is separated by fractional distillation from the unchanged tetrachloride and other silicon chlorides. L. Gattermann and K. Weinleg obtained hexachlorosilane by fractionating the products obtained by the action of chlorine on the crude silicon obtained by reducing quartz sand with magnesium. 50 grms. of crude silicon tetrachloride so obtained furnished 10 grms. of hexachlorodisilane. C. Friedel obtained this compound by the action of chlorine on the corresponding iodide, $Si_2I_6$; and C. Friedel and A. Ladenburg, by gently heating a mixture of this iodide with mercuric chloride. A. J. Besson and L. Fournier obtained hexachlorodisilane by the fractional distillation of the complex liquid obtained by the action of the electrical discharge on a mixture of dry hydrogen and silicon tetrachloride.

L. Troost and P. Hautefeuille showed that the hexachlorodisilane is not formed by the action of the vap. of silicon tetrachloride on silicon below 250°, and the vap. of hexachlorodisilane is not decomposed at this temp. This is regarded by P. Duhem as *une region des faux équilibres*. At 350°, the vap. is decomposed very slowly and the action is limited: $2Si_2Cl_6\rightleftharpoons 3SiCl_4+Si$. The deposit of silicon is scarcely appreciable after 24 hrs. The reverse action is quite inappreciable. As the temp. is raised, the decomposition of the hexachlorodisilane becomes more and more marked—at 440°, the decomposition is marked, and at 800°, complete. On the other hand, the decomposition is partial at 1000°, and at this temp. the tetrachloride unites with silicon to form hexachlorodisilane. The observations of L. Troost and P. Hautefeuille are illustrated graphically by Fig. 201, due to P. Duhem—*vide* volatility of silicon. In the preparation of hexachlorodisilane the need for rapid cooling past the region of complete decomposition will be apparent. The diagram also explains how during the passage of silicon tetrafluoride or tetrachloride over heated silicon, an annular deposit of crystalline silicon is formed about that part of the porcelain tube which is just below red heat in the case of the tetrafluoride, and when the temp. is 500°–800° in the case of the tetrachloride.

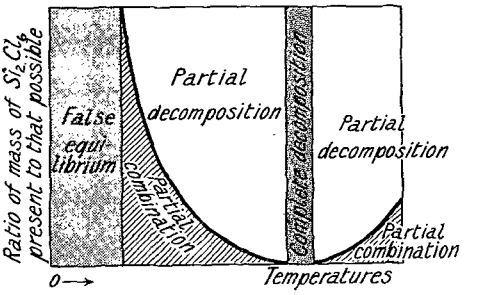



FIG. 201.—Equilibrium Conditions of Hexachlorodisilane (Diagrammatic).

Hexachlorodisilane is a colourless fuming liquid at ordinary temp. L. Troost and P. Hautefeuille gave 1·58 for the sp. gr. at 0°; G. Martin, 1·5624 at 15°/4°; and for the vap. density, 9·7 at 239°, when the theoretical value for $Si_2Cl_6$ is 9·29. The b.p. is 146°–148°. G. Martin gave for the b.p. at different press., $p$ mm.:

| $p$ | 12 | 20 | 50 | 105 | 130 | 150 | 200 | 760 |
|---|---|---|---|---|---|---|---|---|
| B.p. | 40° | 50° | 65° | 84° | 92° | 95° | 102° | 144°–145·5° |

L. Troost and P. Hautefeuille found that hexachlorodisilane freezes at −14° to large tabular crystals resembling those of boric acid. L. Gattermann and K. Weinleg gave −1° for the m.p. of the crystals; and 1·45 for the index of refraction in red light. G. Martin gave 7·4748 at 18° for the $D$-line. P. Pascal studied the magnetic susceptibility of this compound. L. Troost and P. Hautefeuille found that the heated vap. of hexachlorodisilane inflames in air; and that the liquid in contact with water decomposes, forming silico-oxalic acid and hydrochloric acid: $Si_2Cl_6+4H_2O=HOOSi.SiOOH+6HCl$; and with soln. of ammonia or potassium hydroxide, silicic acid is formed since silico-oxalic acid is decomposed by alkalies: $Si_2Cl_6+6H_2O=2H_2SiO_3+6HCl+H_2$. G. Martin showed that hexachlorodisilane reacts with chlorine $Si_2Cl_6+Cl_2=2SiCl_4$. With gaseous ammonia it forms **hexachlorododecamminodisilane,** $Si_2Cl_6.12NH_3$, which begins to lose ammonia at 100°, and is slowly decomposed by water. According to A. J. Besson, phosphine is reduced by hexachlorodisilane at −10°, forming a solid phosphorus hydride. L. Gattermann and K. Weinleg found that with sodium and chlorobenzene, tetraphenylsilicon, not hexaphenylsilicon, is formed. When silicon tetrachloride is poured into absolute alcohol, there appears to be a momentary evolution of heat followed by a powerful cooling action. The cooling appears to be a secondary effect due to the rapid evolution of a large amount of hydrogen chloride, so that the heat of the chemical action is masked by the cooling due to the passage of dissolved hydrogen chloride into the gaseous state. In the case of the hexachlorodisilane, the cooling is so great that hoar-frost collects on the side of the reaction vessel. With silicon tetrachloride, **ethyl orthosilicate,** $Si(OC_2H_5)_4$, b.p. 160°, is formed. G. Martin has isolated six substitution derivatives from the products of the reaction between hexachlorodisilane and alcohol. Some properties of these compounds are indicated in Table XXXVI.

TABLE XXXVI.—ETHOXY-DERIVATIVES OF HEXACHLORODISILANE.

| Compound. | Formula. | B.p. (<34 mm.). | Sp. gr. 15°–20°. | Refractive index $D$-line 14·5°. |
|---|---|---|---|---|
| Hexachlorodisilane | $Si_2Cl_6$ | 60·5° | 1·562 | 1·4748 (18°) |
| Pentachlorethoxydisilane | $Si_2Cl_5(OC_2H_5)$ | 84° | 1·388 | 1·4568 |
| Tetrachlorodiethoxydisilane | $Si_2Cl_4(OC_2H_5)_2$ | 104° | 1·270 | 1·4432 |
| Trichlorotriethoxydisilane | $Si_2Cl_3(OC_2H_5)_3$ | 122° | 1·163 | 1·4433 |
| Dichlorotetrethoxydisilane | $Si_2Cl_2(OC_2H_5)_4$ | — | — | — |
| Chloropentethoxydisilane | $Si_2Cl(OC_2H_5)_5$ | 138° | 1·092 | 1·4205 |
| Hexethoxydisilane | $Si_2(OC_2H_5)_6$ | 141° | 0·972 | 1·4134 |

There is a progressive increase in the b.p., a progressive decrease in the sp. gr., and in the refractive indices as the chlorine atoms are replaced one by one by the ethoxy-group, $OC_2H_5'$. The member $Si_2Cl_2(OC_2H_5)_4$ was not obtained pure enough for the determination of the constants. Theoretically, there should be a pair of isomeric forms for the third, fourth, and fifth members of the above table, but only one form of each has, as yet, been obtained.

By the rectification between 210° and 215°, of the products of the action of chlorine on the crude silicon obtained by the action of magnesium on quartz sand, L. Gattermann and K. Weinleg[7] obtained **octochlorotrisilane,** or **octochloropropane,** $Si_3Cl_8$. The unrectified product, consisting mainly of silicon tetrachloride and hexachloro-

disilane, contains 0·5–1·0 per cent. of octochlorotrisilane. According to L. Gattermann and E. Ellery, and C. Combes, its formation depends on the presence of magnesium silicide in the crude silicon. A. J. Besson and L. Fournier obtained octochlorodisilane by the fractional distillation of the complex liquid obtained by the action of the electrical discharge on a mixture of hydrogen and trichlorosilane. Octochlorosilane is a colourless liquid and, according to L. Gattermann and K. Weinleg, has a vap. density 13·0 when the theoretical value for $Si_3Cl_8$ is 12·8. G. Martin found for the sp. gr. 1·61 at 15°/4°. According to A. J. Besson and L. Fournier, the b.p. is 215°–218°; and G. Martin found for the b.p. at a press., $p$ mm.:

| $p$ | 17 | 30 | 60 | 80 | 90 | 110 | 760 |
|---|---|---|---|---|---|---|---|
| B.p. | 100° | 113° | 129° | 139° | 143° | 149° | 210°–213° |

A. J. Besson and L. Fournier obtained, after solidification, the m.p. —67°. L. Gattermann and K. Weinleg found the index of refraction for red light to be 1·52; and G. Martin, 1·5135 at 14·5° for Na-light. This substance is quickly decomposed by water, and, if the temp. be about 0°, mesosilico-oxalic acid is formed: $Si_3Cl_8+6H_2O=8HCl+HOOSi.Si(OH)_2.SiOOH$.

A. J. Besson and L. Fournier found that the silicon chlorides obtained by the action of an electric discharge on silicochloroform are of the sat. series, so that the action which occurs in an atm. of hydrogen or of hydrogen chloride is accompanied by a liberation of hydrogen and hydrogen chloride. The fraction of the product intermediate between $Si_2Cl_6$ and $Si_3Cl_8$ shows, however, an undoubted deficit of chlorine, and may contain small quantities of unsaturated chlorides. The mixture of silicon tetrachloride and dichlorosilane obtained by acting on amorphous silicon with hydrogen chloride, when submitted to the electric discharge, seems to give the same mixture of sat. compounds instead of unsat. substances. Seemingly, the excess of hydrogen chloride acts on the unsat. silicon chlorides with the liberation of hydrogen. By the action of the electric discharge on hydrogen and silicon tetrachloride, a mixture of sat. silicon chlorides is produced, which are, however, present in proportions differing from those in the mixture just described. The fractional distillation of the mixture of silicon chlorides obtained by the action of the electrical discharge on a mixture of hydrogen and silicon tetrachloride, after separating the tetrachlorosilane, hexachlorosilane, and octochlorotrisilane, furnished **decachlorosilicobutane** or **decachlorotetrasilane,** $Si_4Cl_{10}$, as an oily liquid, boiling at 149°–151° and 15 mm. The liquid fumes in the air, is readily decomposed by water, forming a white product resembling silica, and often gives off sparks and ignites when gently rubbed. They also obtained **dodecachlorosilicopentane,** or **dodecachloropentasilane,** $Si_5Cl_{12}$, as a very viscous liquid boiling at about 190° and 15 mm.; and **tetradecachlorosilicohexane,** or **tetradecachlorohexasilane,** $Si_6Cl_{14}$, as a white solid, melting at 170° with decomposition, and subliming in vacuo at about 200°. The sublimate consists of crystals with a waxy consistency, and which are readily decomposed by water giving a white combustible substance. After the above-named compounds have been removed by prolonged heating at 200°–210° in a vacuum, there remains a solid, reddish-yellow, glassy mass, which is almost entirely soluble in light petroleum or carbon tetrachloride, and is apparently a mixture of a number of chlorides.

**The silicon oxychlorides.**—The reaction between sulphur trioxide and carbon tetrachloride furnishes phosgene, $COCl_2$, and pyrosulphuryl chloride, $S_2O_5Cl_2$, if no moisture be present: $2SO_3+CCl_4=COCl_2+S_2O_5Cl_2$; and in the presence of moisture some chlorosulphonic acid is formed. According to G. Gustavson,[8] silicon tetrachloride furnishes pyrosulphuryl chloride when it reacts with sulphur trioxide. C. R. Sanger and E. R. Riegel, however, have shown that there is no sign of the formation of *silicophosgene,* or *silicyl chloride,* $SiOCl_2$, analogous to phosgene, or carbonyl chloride, $COCl_2$. Sulphur trioxide is dissolved by silicon tetrachloride, and at ordinary temp. reacts very slowly, but at 50° the reaction

is quicker (5–6 hrs.), and when the product is distilled at atm. press. a fuming liquid is obtained between 135° and 150°, which reacts vigorously with water. The indefiniteness of the b.p. suggests that the distillate is a mixture; but the constituents have not been separated. Analyses and the b.p. of artificial mixtures indicate that the product contains pyrosulphuryl chloride, $S_2O_5Cl_2$, and silicon oxychloride, $Si_2OCl_6$, in equimolar proportions. This is confirmed by redistillation from a great excess of phosphorus pentoxide or of sodium chloride, whereby the silicon is largely decomposed and an impure pyrosulphuryl chloride is formed. The main reaction between sulphur trioxide and silicon tetrachloride is therefore symbolized: $2SO_3+2SiCl_4=S_2O_5Cl_2+Si_2OCl_6$, and not $2SO_3+SiCl_4=S_2O_5Cl_2+SiOCl_2$. The fraction which distils below 135° is a mixture of silicon tetrachloride and sulphur trioxide. If a mixture of the reacting constituents be allowed to stand for three summer months, a considerable amount of silica separates, and the distillate contains an excess of pyrosulphuryl chloride, accordingly, after the reaction $2SO_3+2SiCl_4=Si_2OCl_6+S_2O_5Cl_2$; when the sulphur trioxide is in excess, it is assumed that a consecutive reaction occurs: $Si_2OCl_6+6SO_3=2SiO_2+3S_2O_5Cl_2$.

The first silicon oxychloride was made by C. Friedel and A. Ladenburg [9] by passing the vap. of silicon tetrachloride through a porcelain tube packed with fragments of felspar, and heated to whiteness. The condensed liquid was fractionally distilled to free it from unchanged silicon chloride. The required fraction was collected between 136° and 139°. The composition corresponded with **silicon oxychloride,** or **hexachlorodisiloxane,** $Si_2OCl_6$, or $(SiCl_3)_2O$. C. R. Sanger and E. R. Riegel found this oxychloride among the products of the action of liquid sulphur trioxide on silicon tetrachloride—*vide supra.* L. Troost and P. Hautefeuille made it by passing a mixture of chlorine with one-half or one-fifth its vol. of oxygen, over crystalline silicon, when a mixture of silicon oxychlorides and chlorides is obtained. The heat evolved is sufficient to continue the reaction when once it has commenced. Too high a temp. is to be avoided, since the vap. of the dichloride and oxychlorides form a thick cloud which is only condensed with difficulty. The action of the mixture on silicon is not so violent as that of chlorine alone; but it is not known whether silicon tetrachloride is first formed and chlorine afterwards displaced in it, or the oxygen and chloride both unite directly with the silicon. A. J. Besson and L. Fournier prepared hexachlorodisiloxane and some of the other oxychlorides by the action of oxygen or chromic acid on trichlorosilane. A. Stock and co-workers obtained it by the action of chlorine on disiloxane, $(SiH_3)_2O$, which is vigorous even at —125°. The primary product may be isolated, but most of it decomposes into silica and silicon tetrachloride: $4(SiCl_3)_2O=2SiO_2+6SiCl_4$. H. N. Stokes tried unsuccessfully to make this compound by the action of phosphoryl chloride on the chlorohydrins of ethyl ortho- and di-silicates. Hexachlorodisiloxane is a colourless, limpid, fuming liquid; and the vap. density, 10·05, obtained by C. Friedel and A. Ladenburg, is very close to the value 9·86 calculated for $Si_2OCl_6$. The constitution is therefore likely to be $Cl_3Si.O.SiCl_3$. The liquid boils at 137° to 138°, and A. Stock and co-workers obtained 137° at 760 mm. for the b.p., and —33° for the m.p. R. Wintgen gave for the vap. press., $p$, of hexachlorodisiloxane, $\log p=8{\cdot}2936-2197{\cdot}4T^{-1}$; 10044 cals. for the latent heat of vaporization; 11,174·7 cals. for the mol. heat of vaporization at 0° K., and 8868 cals. at $T$° K.; and 2·16 for Trouton's constant. C. Friedel and A. Ladenburg found that the compound can be heated much above its b.p. without decomposition, but it is decomposed on exposure to air, and vigorously when in contact with water, forming silicic and hydrochloric acids; it is miscible in all proportions with carbon disulphide, carbon tetrachloride, chloroform, silicon tetrachloride, and ether; but with absolute alcohol it forms hexethoxydisiloxane: $(SiCl_3)_2O+6C_2H_5OH=6HCl+Si_2O(OC_2H_5)_6$; and with zinc ethyl at 180°, its reaction is supposed to be in accord with the equations, $(SiCl_3)_2O+4Zn(C_2H_5)_2=2Si(C_2H_5)_4+ZnO+3ZnCl_2$, and $(SiCl_3)_2O+3Zn(C_2H_5)_2=3ZnCl_2+Si_2O(C_2H_5)_6$. According to C. R. Sanger and E. R. Riegel, hexachlorodisiloxane and pyrosulphuryl chloride appear to

form a compound on warming, which solidifies at —78°; a simple mixture of the two substances solidifies about —38°.

A number of the less volatile oxychlorides was found to accompany hexachlorodisilane; and L. Troost and P. Hautefeuille found that the best method of preparing them was by the direct action of oxygen on hexachlorosiloxane. A mixture of oxygen and vap. of hexachlorodisiloxane was passed several times backwards and forwards through a glass tube filled with fragments of porcelain, and heated by a gas-furnace. At the end of the operation, a liquid was obtained, containing, besides the excess of hexachlorodisiloxane employed, a whole series of oxychlorides of silicon. They were separated, their percentage compositions, and their condensation in the state of vapour at 440° were determined. Some properties of these compounds are as follows:

| | B.p. | Vap. density at 440°. Found. | Theory. |
|---|---|---|---|
| $SiO_2OCl_6$ . . . | 136°–139° | (10·05) | 9·86 |
| $SiO_4O_3Cl_{10}$ . . . | 152°–154° | — | — |
| $Si_4O_4Cl_8$ . . . | 198°–202° | 15·5 | 15·9 |
| $Si_3O_{10}Cl_{12}$ . . . | c. 300° | 31·2 | 28·0 |
| $(Si_2O_3Cl_2)n$ . . . | <400° | — | — |
| $(Si_4O_7Cl_2)n$ . . | (solid) 440° | — | — |

There is no actual evidence of the constitution of these compounds. The second, **decachlorotetrasiloxane,** $(SiCl_3)_2O_3(SiCl_2)_2$, and the third, **octochlorotetrasiloxane,** $(SiCl_2)_4O_4$, in the list may be related to the phenyl derivative prepared by F. S. Kipping, and represented:

| | | |
|---|---|---|
| $Cl_2Si.O.SiCl_3$<br>O<br>$Cl_2Si.O.SiCl_3$ | $Cl_2Si.O.SiCl_2$<br>O O<br>$Cl_2Si.O.SiCl_2$ | $(C_6H_5)_2Si.O.Si(C_6H_5)_2$<br>O O<br>$(C_6H_5)_2Si.O.Si(C_6H_5)_2$ |
| Decachlorotetra-siloxane, $Si_4O_3Cl_{10}$. | Octochlorotetra-siloxane, $Si_4O_4Cl_8$. | Octophenyltetra-siloxane, $Si_4O_4(C_6H_5)_8$. |

The fourth member, **dodecachloro-octosiloxane,** $(SiCl_2)_4(SiCl)_4O_{10}$, may consist of two rings of the preceding member of the series united by oxygen atoms:

$$\begin{array}{c} Cl_2Si.O.Si.ClO.SiCl.O.SiCl_2 \\ O \quad O \quad O \quad O \\ Cl_2Si.O.SiCl.O.SiCl.O.SiCl_2 \end{array}$$

Dodecachloro-octosiloxane, $Si_8O_{10}Cl_{12}$.

The mol. wt. of the other two members of the series are unknown. The complexity of the oxychlorides recalls that of the complex silicic acids and of the silicates.

## References.

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## § 58. The Silicon Bromides

G. S. Sérullas [1] made **silicon tetrabromide,** or **tetrarbomosilane,** $SiBr_4$, by passing the vap. of bromine over a red-hot intimate mixture of silica and carbon. J. E. Reynolds made the carbon-silica mixture from pellets of silica and syrup of sugar, dried, and ignited. J. E. Reynolds purified the crude product by passing dry hydrogen through the liquid to remove most of the free bromine ; and the product was then shaken up with metallic mercury. The liquid was then subjected to fractional distillation, and the fraction boiling at 153° collected. G. P. Baxter and co-workers described the purification of silicon tetrabromide for their work on the at. wt. of silicon.

E. Lay said that only a poor yield was obtained by passing bromine over a mixture of freshly precipitated silica and carbon. L. Gattermann made silicon tetrabromide by passing bromine vap. over the crude silicon made by reducing quartz sand with magnesium. The liquid, which was collected in a receiver cooled with ice and salt, was purified by fractional distillation ; shaking with mercury ; and redistilling. M. Blix made the compound by the action of bromine vap. on purified silicon at a red heat, and he purified the product by digesting it with mercury on an oil-bath. E. Lay recommended making silicon tetrabromide by the action of a mixture of bromine vap. and hydrogen on ferro-silicon at 60°, and purifying the product by J. E. Reynolds's process. It is also made by passing a rapid current of hydrogen bromide over silicon at a red heat, and purifying the product by fractional distillation. L. Gattermann found that a better yield of the tetrabromide is obtained by passing hydrogen bromide over the crude silicon freed from magnesia by washing with dil. acid. The product is separated from the accompanying tribromosilane by fractional distillation. G. Gustavson obtained

silicon tetrabromide as a product of the action of silicon tetrachloride on carbon tetrabromide. A. J. Besson and L. Fournier found silicon tetrabromide among the products of the action of an electrical discharge on tribromosilane.

Silicon tetrabromide is a heavy colourless liquid which evolves dense white fumes when exposed to air. The ethereal odour in G. S. Sérullas' preparation was attributed to the presence of carbon tetrabromide. J. I. Pierre gave 2·9128 for the sp. gr. at 0°; J. E. Reynolds, 2·82; G. Abati, 2·77223 at 23·5°. G. S. Sérullas gave 148°–150° for the b.p.; J. E. Reynolds, 153°; L. Gattermann, 153°–154°; G. Abati, 153·4° at 774·4 mm.; and M. Blix, 150·8° at 751·4 mm. G. S. Sérullas said that the liquid freezes at −12° to −15°; and M. Blix gave 5° for the m.p. of the solid. C. M. Guldberg gave 383° for the critical temp. J. I. Pierre found the vol., $v$, which unit vol. of liquid acquires at $\theta°$ is $v=1+0_3952572440\theta+0·0_67567426^2+0·0_92920746^3$; or the coeff. of expansion at 20° is $0·0_3983$. J. J. Saslawsky studied the relation between the coeff. of expansion and the structure. M. Berthelot gave for the heat of formation with crystalline silicon and liquid bromine $Si+4Br=SiBr_{4liquid}+71$ Cals.; and with $SiBr_{4gas}$, 858 Cals. G. Abati gave for the indices of refraction, 1·55820 for the $H_\alpha$-line; 1·57410 for the $H_\beta$-line; 1·56267 for the $D$-line; and 1·58370 for the $H_\gamma$-line; for the mol. refraction for the $H_\alpha$-line with the $n$-formula, 70·07; and with the $n^2$-formula, 40·48; and for the sp. dispersion, $(\mu_\gamma-\mu_\alpha)/D=0·00920$.

The general properties of the tetrabromide resemble those of the tetrachloride; but, unlike silicon tetrachloride, A. J. Besson and L. Fournier found that when the tetrabromide is mixed with hydrogen, and subjected to the electrical discharge, there is very little change. C. Friedel and A. Ladenburg found that oxygen decomposes the vap. of silicon tetrabromide. According to G. S. Sérullas, water rapidly decomposes silicon tetrabromide with a considerable rise of temp.; the hydrolysis is accompanied by the formation of silicic and hydrobromic acids. M. Berthelot gave $SiBr_{4liq.}+2H_2O+Aq.=SiO_{2aq.}+4HBr+85·8$ Cals. A. J. Besson showed that when distilled with iodine, with or without hydrogen, over heated silicon, bromoiodides are formed; and with dry hydrogen iodide, at a red heat, silicon bromoiodide is produced. M. Blix found that hydrogen sulphide is without action on the liquid tetrabromide; G. S. Sérullas, that under sulphuric acid, the tetrabromide is resolved into silica and bromine in the course of a few days; and A. J. Besson, that silicon tetrabromide absorbs ammonia, forming white amorphous *silicon heptamminotetrabromide*, $SiBr_4.7NH_3$, which is decomposed by water. E. Lay could not make the heptammino-compound, but by mixing ammonia with the vap. of silicon tetrabromide, diluted with hydrogen to keep down the temp., he obtained **silicon hexamminotetrabromide,** $SiBr_4.6NH_3$; and the same compound was obtained by the action of ammonia on a soln. of silicon tetrabromide in benzene.

The white pulverulent hexammine has a sp. gr. 2·307 at 17°. It is slowly decomposed by exposure to moist air; and when heated, both bromine and ammonia are given off. All the bromine can be expelled by heating the hexammine to 900° in a stream of ammonia, or carbon dioxide. Lead peroxide is reduced to lead; and, when heated with potassium chlorate, there is a vigorous reaction and much bromine is evolved. Two mols. of ammonia are lost in contact with water—slowly in the cold, rapidly when heated; with boiling alkali-lye, ammonia is evolved; conc. nitric acid reacts vigorously, giving off bromine and nitrogen oxides; and when heated with conc. sulphuric acid, bromine is given off: $SiBr_4(NH_3)_6+5H_2SO_4=Si(OH)_4+3(NH_4)_2SO_4+2Br_2+2SO_2$.

A. J. Besson found that silicon tetrabromide is without action on phosphine under ordinary press., even at the f.p.; but after repeated compression, and maintaining the press. for several hours, a colourless liquid is formed which becomes white and opaque, and changes into an amorphous white solid. As shown by J. E. Reynolds, silicon tetrabromide forms additive compounds with various organic bases, aniline, and thio- and alkylated ureas. G. S. Sérullas noted that when gently heated with potassium, the hexammine explodes violently and breaks the glass containing vessel. C. Friedel and A. Ladenburg found that with lead oxide at 250°, lead bromide and silicate are formed. A. J. Besson obtained yellow

tabular crystals of what was considered to be a *silicon oxybromide* when air reacts gradually with a mixture of silicon tetrabromide and tribromosilane. The oxybromide is volatile in a current of nitrogen, and is decomposed by water into hydrobromic and silicic acids.

As in the case of silicon tetrachloride, a complete series of hydrogen substitution products, **silicon bromohydrides,** $SiH_nBr_{4-n}$, has been obtained with silicon tetrabromide.

| | $SiBr_4$ | $SiHBr_3$ | $SiH_2Br_2$ | $SiH_3Br$ | $SiH_4$ |
|---|---|---|---|---|---|
| B.p. . . . | 150·8° | 111° | 66° | 1·9° | −11° |

H. Buff and F. Wöhler[2] made **silicobromoform,** or **tribromosilane,** $SiHBr_3$, from the products obtained by passing hydrogen bromide over heated silicon as in the case of silico-chloroform. A. J. Besson and L. Fournier used a similar process. They found that 98 per cent. of the liquid consisted of silicon tetrabromide and the remaining 2 per cent. consisted of the tri- and di-bromosilanes. The compound was purified by shaking it with mercury, and by fractional distillation. L. Gattermann used the crude silicon obtained by reducing quartz sand with magnesium, after washing out the magnesia with dil. acid; and C. Combes used copper silicide containing 20 per cent. of silicon. The preparation of this bromide by O. Ruff's method used for tri-iodosilane was unsatisfactory because tribromosilane and benzene boil so close together that they cannot be separated by fractional distillation. The colourless, fuming, liquid tribromosilane, according to A. J. Besson, ignites spontaneously in air. H. Buff and F. Wöhler found the sp. gr. of the liquid to be 2·5; and L. Gattermann, 2·7 at 17°. The latter said that the preparation of H. Buff and F. Wöhler was probably impure. A. J. Besson said that in a neutral atm., tribromosilane boils without decomposition at 109°–110°. A. J. Besson and L. Fournier gave 110°–122°, and L. Gattermann, 115°–117°. A. J. Besson said that the liquid does not freeze at −60°. Tribromosilane is decomposed by water, and if the mixture be kept cool, silicoformic anhydride is produced. It reacts with iodine forming silicon tribromoiodide. It reacts energetically with ammonia with the development of heat and light, but the white product contains silicon, hydrogen, and ammonia. Phosphine does not combine with tribromosilane at −40° under ordinary press., but at 15° and 25 atm. press., it produces a white solid *phosphinetribromosilane.*

A. J. Besson and L. Fournier obtained **dibromosilane,** or **silicomethylene bromide,** or **dibromosilicomethane,** $SiH_2Br_2$, as indicated above, from the products of the action of hydrogen bromide on red-hot silicon. Under ordinary conditions the reaction between bromine and silane is very violent, but A. Stock and C. Somiesky found that if an excess of gas is led into a large vessel on the walls of which solid bromine is deposited, and the temp. maintained at about −80° to −70°, the mono- and di-bromides can be obtained comparatively free from silicon tetrabromide and tribromosilane. The products can be separated and purified by fractional distillation. A. J. Besson and L. Fournier found dibromosilane to be a mobile, highly refracting, colourless, fuming liquid which inflames spontaneously when exposed to air. A. Stock and C. Somiesky found that it can be kept a long time in thoroughly dried vessels; and that the sp. gr. of the liquid is 2·17 at 0°. A. J. Besson and L. Fournier gave *c.* 75° for the b.p., and A. Stock and C. Somiesky, 66° at 760 mm., or 18° at 123 mm. The m.p. is −70·1°. R. Wintgen gave for the vap. press., $p$, of dibromosilane, $\log p = 7{\cdot}6542 - 1620{\cdot}2T^{-1}$; for the latent heat of vaporization, 7405 cals. The liquid is very sensitive to moisture, and is decomposed by water into hydrobromic acid, and a solid, $(SiH_2O)_n$. Alkali-lye decomposes it in accord with $SiH_2Br_2 + 4NaOH = 2H_2 + 2NaBr + Na_2SiO_3 + H_2O$.

A. J. Besson and L. Fournier obtained evidence of **silicomethyl bromide, monobromosilane,** or **bromosilicomethane,** $SiH_3Br$, in the low-boiling products of the action of hydrogen bromide on red-hot silicon; and, as indicated above, A. Stock and C. Somiesky isolated it from the products of the action of silane on solid bromine at −80° to −70°. At ordinary temp., monobromosilane is a colourless gas

with a pungent odour reminiscent of silane. The liquid has a sp. gr. 1·533 at 0°; it boils at 1·9° and 760 mm.; its m.p. is −94°. R. Wintgen gave for the vap. press., $p$, of monobromosilane, $\log p = 7{\cdot}5243 - 1276{\cdot}5T^{-1}$; for the latent heat of vaporization, 5834 cals.; for the mol. heat of vaporization at 0° K., 5386·0 cals., and at $T$° K., 5852 cals.; and for Trouton's constant, 21·3. It may be preserved over mercury for some time, but it detonates on exposure to the air, giving silicic acid and brown silicon. It reacts with cold water according to the equation: $2SiH_3Br + H_2O = 2HBr + (SiH_3)_2O$; whilst it may be analyzed by measuring the vol. of hydrogen produced under treatment with 30 per cent. sodium hydroxide, according to the equation: $SiH_3Br + 3NaOH = 3H_2 + NaBr + Na_2SiO_3$.

A complete series of **silicon chlorobromides** has been obtained ranging between the extremes silicon tetrachloride and tetrabromide:

| | $SiBr_4$ | $SiClBr_3$ | $SiCl_2Br_2$ | $SiCl_3Br$ | $SiCl_4$ |
|---|---|---|---|---|---|
| B.p. . . . | 150·8° | 127° | 104° | 80° | 58° |

G. S. Sérullas[3] obtained **chlorotribromosilane,** $SiClBr_3$, as a by-product in the manufacture of the tetrabromide, and J. E. Reynolds found it to be present in the fraction boiling between 140° and 144°. A. J. Besson separated it from the by-product in the preparation of the dichlorodibromide by fractional freezing, not fractional distillation. A. J. Besson and L. Fournier found it among the products obtained by passing the electrical discharge through a mixture of silicon tetrachloride, bromine, and hydrogen. All three chlorobromides are formed. The dichlorodibromide appears to be the chief constituent of the mixture, and when this is submitted in the presence of hydrogen to the further action of the discharge, it undergoes decomposition in accordance with the equation: $2SiCl_2Br_2 = SiCl_3Br + SiClBr_3$. If a mixture of the three chlorobromides is treated in the same way, derivatives of the type $Si_2X_6$ appear to be formed, but their separation has not been satisfactorily accomplished. The chlorotribromide appears as a colourless liquid which fumes in air. J. E. Reynolds gave 2·432 for the sp. gr. and 10·43 for the vap. density when the value calculated for $SiClBr_3$ is 10·47. A. J. Besson found that it solidified when cooled below −50°; and the m.p. of the solid is −39°; J. E. Reynolds gave 140°–141° for the b.p., and A. J. Besson, 126°–128°. When treated with water it rapidly decomposes, forming silicic, hydrochloric, and hydrobromic acids. A. J. Besson obtained a white solid **silicon hemihenadecamminochlorotribromide,** $2SiClBr_3.11NH_3$, which is decomposed by water. The composition may be really that of a hexammine.

C. Friedel and A. Ladenburg heated trichlorosilane and bromine in a sealed tube over 100°, and obtained a mixture of trichlorobromosilane and **dibromodichlorosilane,** $SiBr_2Cl_2$, which were separated by fractional distillation at about 100°; the trichlorobromosilane collects between 78° and 82°. The products are purified by shaking with mercury followed by redistillation. A. J. Besson likewise obtained it from the products which are formed when a mixture of bromotrichlorosilane and hydrogen bromide is passed through a red-hot porcelain tube; and, as indicated above, A. J. Besson and L. Fournier found it among the products obtained by passing the electric discharge through a mixture of silicon tetrachloride, bromine, and hydrogen. A. J. Besson found that the colourless fuming liquid does not freeze when cooled to −60°, and also that it boils at 103°–105°; C. Friedel and A. Ladenburg gave 100°. It forms **silicon pentamminodibromodichloride,** $SiBr_2Cl_2.5NH_3$, when treated with dry ammonia. The white amorphous pentammine is decomposed by water. It may be a hexammine.

C. Friedel and A. Ladenburg prepared **trichlorobromosilane,** $SiBrCl_3$, as indicated above, and also by dropping the calculated quantity of bromine into silicon trichlorohydrosulphide; there is a copious evolution of hydrogen bromide; and sulphur bromide is formed: $SiCl_3(HS) + 3Br = SBr + HBr + SiCl_3Br$. The product is purified by fractional distillation, and shaking with mercury. A. J. Besson obtained trichlorobromosilane by the rectification of the products obtained when

a mixture of hydrogen bromide and silicon tetrachloride vapour is passed through a red-hot porcelain tube; and, as indicated above, A. J. Besson and L. Fournier found it among the products obtained by passing an electric discharge through a mixture of silicon tetrachloride, bromine, and hydrogen. The colourless fuming liquid was found by A. J. Besson not to freeze at −60°. C. Friedel and A. Ladenburg gave 80° for the b.p., and they found that it is decomposed by water into silicic, hydrochloric, and hydrobromic acids. A. J. Besson obtained a white solid, **silicon hemihenadecamminotrichlorobromide,** $2SiBrCl_3.11NH_3$, which is decomposed by water. It may really be a hexammine. He also found that with phosphine, at 0° and 25 atm., or −22° and 17 atm., a white addition product is obtained which is decomposed when the temp. is raised. The **homologous series** of the bromine derivatives of the silane series, $Si_nBr_{2n+2}$, has been followed as far as $n=4$:

| | $SiBr_4$ | $Si_2Br_6$ | $Si_3Br_8$ | $Si_4Br_{10}$ |
|---|---|---|---|---|
| M.p. . . . . | 5° | 95° | 133° | 185° |

C. Friedel[4] discovered **hexabromosilicoethane,** or **perbromosilicoethane,** or **hexabromodisilane,** $Si_2Br_6$, in 1869. C. Friedel and A. Ladenburg made it by the action of bromine on an eq. amount of hexaiododisilane dissolved in carbon disulphide; the liberated iodine was removed by decantation; the soln. was shaken with mercury; and the solvent evaporated from the soln., taking care to exclude moisture from the atm. The solid can be purified by re-soln. in carbon disulphide, and agitation with mercury. A. J. Besson and L. Fournier found it among the products of the action of an electrical discharge on the vap. of tribromosilane. H. Moissan and A. Holt obtained it by the action of bromine on vanadium silicide. At ordinary temp., hexachlorodisilane forms white, crystalline plates which are optically biaxial. C. Friedel and A. Ladenburg said that it boils at about 240°; and A. J. Besson and L. Fournier gave 265° for the b.p., and 95° for the m.p. When treated with potash-lye, it develops the theoretical quantity of hydrogen. Its general reactions resemble those of hexachlorosilane.

According to R. Mahn, the interaction of bromine and silane furnishes a little silicon tetrabromide, and **pentabromodisilane,** $Si_2HBr_5$, which was separated from the excess of bromine by distillation in a stream of carbon dioxide. The solid melts at 89°, and on cooling furnishes a mass of needle-like crystals which can be distilled at 230° in a stream of hydrogen or carbon dioxide. It sublimes slowly at 100°. It inflames when heated in air. The crystals fume in air, and when treated with water give hydrobromic acid and a white amorphous solid which gives off hydrogen when treated with aq. ammonia, and forms silicic acid. The alleged pentabromodisilane may be impure hexabromodisilane. The impure *silicon bromohydride,* $Si_3H_4Br_4$, of H. Buff and F. Wöhler is probably impure silicon tetrabromide and tribromosilane.

A. J. Besson and L. Fournier, after separating silicon tetrabromide, and hexabromodisilane from the products of the action of an electric discharge on tribromosilane, obtained colourless crystals of **octobromosilicopropane,** or **octobromotrisilane,** $Si_3Br_8$, m.p. 95°, b.p. 265°; crystals of **decabromosilicobutane,** or **decabromotetrasilane,** $Si_4Br_{10}$, melting with decomposition at 185°; and a yellow residue.


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## § 59. Silicon Iodides

J. J. Berzelius said that silicon ignited in iodine vap. does not absorb any iodine. In their study of the action of dry hydrogen iodide on silicon at a temp. above a red heat, H. Buff and F. Wöhler [1] obtained a product containing hydrogen, and they assigned to it the formula $Si_2HI_7$, which C. Friedel showed to be a mixture of silicon tetraiodide and tri-iodosilane, and he prepared **silicon tetraiodide, tetraiodosilicomethane,** or **tetraiodosilane,** $SiI_4$, in a fairly pure condition by passing the vap. of iodine entrained in carbon dioxide over red-hot silicon, and purifying the sublimate by dissolving it in carbon disulphide, shaking it with mercury, and distilling the liquid in a stream of carbon dioxide. L. Gattermann used the crude silicon obtained by reducing quartz sand with magnesium. A. J. Besson obtained silicon tetraiodide mixed with other products by passing silicon chloroiodide, or a mixture of silicon tetrachloride and iodine over heated silicon; and M. Guichard prepared it by passing iodine vap. over silicon heated under reduced press. to 500°. O. Ruff found the solid residue obtained when tri-iodosilane is heated to 300° consists chiefly of silicon tetraiodide, which can be isolated by sublimation.

According to C. Friedel, the vap. of silicon tetraiodide condenses to the solid state when cooled to atm. temp., and the compound can be readily crystallized from its soln. in carbon disulphide. Silicon tetraiodide then furnishes octahedral crystals belonging to the cubic system, and they are isomorphous with those of carbon tetraiodide. The crystals are colourless or tinged slightly yellow. The vap. density, 19·12, corresponds with 18·56 calculated for $SiI_4$. Silicon tetraiodide melts at 120·5°, and boils at about 290°. According to M. Berthelot, the heat of formation is $Si_{cryst.}+4I_{solid}=SiI_{4solid}+6{\cdot}7$ Cals., and with the $4I_{gas}$, 33·9 Cals. When the compound is exposed to air, it acquires a colour owing to the separation of iodine; and water decomposes it into silicic and hydriodic acids. M. Berthelot gave $SiI_4+2H_2O+Aq.=SiO_{2aq.}+4HI_{soln.}+85{\cdot}7$ Cals. When heated in air, the vap. burns with a red flame which gives off iodine vap. With bromine, silicon tetraiodide furnishes silicon bromoiodide; and when heated with finely divided silver, it forms hexaiododisilane. 100 parts of carbon disulphide at 27° dissolve 220 parts of silicon tetraiodide. The tetraiodide reacts with alcohol with avidity, forming not ethyl silicate, but silicic and hydriodic acids and ethyl iodide: $SiI_4+2C_2H_6O=SiO_2+2C_2H_5I+2HI$; and with ether it does form ethyl silicate: $SiI_4+4(C_2H_5)_2O=4C_2H_5I+Si(OC_2H_5)_4$.

H. Buff and F. Wöhler obtained impure **silicoiodoform,** or **tri-iodosilane,** $SiHI_3$, by passing hydrogen iodide over silicon at a red heat. C. Friedel showed that the product contained about 8 per cent. of tri-iodosilane; and that the yield is much greater if the hydrogen iodide be mixed with hydrogen in its passage over the heated silicon. The mixture of crystals of tetraiodosilane and liquid tri-iodosilane which is formed, is separated and the liquid purified by fractional

distillation. O. Ruff found that tri-iodosilane can be obtained by the action of hydrogen iodide on silicon imide, SiNH, suspended in cold carbon disulphide $SiNH+4HI=SiHI_3+NH_4I$; or more readily by treating in benzene soln., triphenylaminosilane, $SiH(NHC_6H_5)_3$, with hydrogen iodide: $SiH(NHC_6H_5)_3+6HI=SiHI_3+3C_6H_5NH_2.HI$. R. Mahn obtained a mixture of silicon tetraiodide and tri-iodosilane by the action of iodine on silane. C. Combes could not make it by the action of hydrogen iodide on copper silicide. Tri-iodosilane is a colourless liquid which C. Friedel found to have a sp. gr. about 3·362 at 0° and 3·314 at 20°; O. Ruff gave 3·286 for the sp. gr. at 23°, and 8° for the f.p. Tri-iodosilane decomposes slowly when heated above 150°, liberating hydrogen, and what is probably a volatile silicon iodohydride. The b.p. is about 220° at 760 mm. press., and the temp. of the vap. 205°; but on continued boiling the temp. slowly rises to 300°, and the residue remaining in the retort is mainly silicon tetraiodide. The tri-iodosilane can be distilled under reduced press. at 106° and 14 mm.; 111° and 22 mm.; 132° and 67 mm.; and at 155° and 122 mm. On exposure to air, the liquid reacts slowly with oxygen with the separation of iodine, and the formation of what is probably a *silicon oxyiodide;* it is combustible in air, forming water, silica, and iodine. The vap., admixed with air, is explosive. The liquid is decomposed by water, forming hydriodic acid and silicoformic anhydride. The liquid is miscible in all proportions with benzene and carbon disulphide.

A. J. Besson [2] found that dry hydrogen iodide has no action on silicon tetrachloride at the ordinary temp., but at a high temp., products of partial substitution are obtained; the determining cause of the reaction being the difference between the heats of formation of hydrogen chloride and hydrogen iodide, and the partial dissociation of the latter at the temp. of the experiment. Hydrogen iodide, mixed with vap. of silicon tetrachloride, is passed somewhat rapidly through a glass tube heated to redness; the product is agitated with mercury to remove free iodine, and when fractionated furnishes a complete series of **silicon chloroiodides,** $SiCl_nI_{4-n}$:

| | $SiCl_4$ | $SiCl_3I$ | $SiCl_2I_2$ | $SiClI_3$ | $SiI_4$ |
|---|---|---|---|---|---|
| B.p. | 58° | 113°–114° | 172° | 234°–237° | 290° |

A. J. Besson also found that the three chloroiodides are produced when the vap. of iodine monochloride is passed over crystallized silicon heated nearly to redness. The product is purified from free iodine by distillation from copper turnings, and fractionally distilled. A. J. Besson and L. Fournier prepared the chloroiodides by the analogous method employed for the chlorobromides (*q.v.*). In addition to the general methods of preparation, **silicon trichloroiodide,** or **trichloroiodosilane,** $SiCl_3I$, can be made by heating silicon tetrachloride with iodine in a sealed tube at 200°–250°. Silicon trichloroiodide is a colourless liquid which boils at 113°–114°, and does not solidify, even at —60°. It is not affected by light alone, but when exposed to air it becomes brown from separation of iodine, and this change is accelerated by light. It fumes in the air, is decomposed by water, and combines with ammonia to form a white, amorphous **silicon hemihenadecamminotrichloroiodide,** $2SiCl_3I.11NH_3$, which is also decomposed by water; it does not form a compound with hydrogen phosphide, even under press. and at a low temp.

In addition to the general methods of preparation, where the yield is small, **silicon dichlorodiiodide,** or **dichlorodiiodosilane,** $SiCl_2I_2$, can be made by saturating trichloroiodosilane with hydrogen iodide at —22°; and heating the soln. for 24 hrs. in a sealed tube at 250°. Dichlorodiiodosilane boils at 172°, does not solidify even at —60°, and rapidly becomes brown, owing to separation of iodine. It fumes in the air, burns with liberation of iodine, and is decomposed by water; when dissolved in carbon tetrachloride, it combines with ammonia to form a white, amorphous **silicon pentamminodichlorodiiodide,** $SiCl_2I_2.5NH_3$, which is decomposed by water.

There is only a small yield of **silicon chlorotriiodide,** or **chlorotriiodosilane,** $SiClI_3$, by the general methods of preparation. Chlorotriiodosilane is a colourless

liquid which, on exposure to air, rapidly becomes red, and gives off a combustible vap. It boils at 234°–237°, and when strongly cooled remains in a surfused condition, but when strongly agitated furnishes a white solid which melts at 2°. Chlorotriiodosilane combines with ammonia gas forming a white solid.

A. J. Besson[3] obtained a mixture of the three **silicon bromoiodides,** $SiBr_nI_{4-n}$, by several different methods.

| | $SiBr_4$ | $SiBr_3I$ | $SiBr_2I_2$ | $SiBrI_3$ | $SiI_4$ |
|---|---|---|---|---|---|
| B.p. . . | 150·8° | 192° | 230°–231° | 255° | 290° |

(i) Tribromosilane and iodine were heated in a sealed tube at 200°–250°; the main product was the iodotribromide mixed with a small quantity of the other two bromoiodides. (ii) Dry hydrogen iodide and silicon tetrabromide vapour at a little below red-heat furnish the tribromoiodide as the main product and a small quantity of the other bromoiodides. The yield is small. (iii) Iodine monobromide was passed over crystalline silicon nearly at a red heat and a mixture of the three bromoiodides, and some silicon tetrabromide and tetraiodide results. The products may be decolorized by fractionation over copper turnings. The separation of the last two mixed halides by fractional distillation is very difficult.

The first mixed halide, **silicon tribromoiodide,** or **tribromoiodosilane,** $SiBr_3I$, is comparatively easy. It forms a colourless liquid distilling at 192°, and it may be cooled to —20° without solidifying, but the solid melts at 14°. **Silicon dibromodiiodide,** or **dibromodiiodosilane,** $SiBr_2I_2$, is a white solid which melts at about 38° and distils at 230°–231°. **Silicon bromotriiodide,** or **bromotriiodosilane,** $SiBrI_3$, is a white solid melting at 53° and distilling at 255°. It is difficult to separate it from silicon tetraiodide. The silicon bromoiodides colour rapidly in the air; they absorb dry ammonia gas with the production of white, solid compounds decomposed by water. Silicon tetrabromide in which much iodine has been dissolved may be used in place of the iodine bromide; with the tetrachloride, no reaction occurs.

The second member of the **homologous series,** $Si_nI_{2n+2}$, **hexaiodosilicoethane,** or **hexaiododisilane,** $Si_2I_6$, was made by C. Friedel and A. Ladenburg.[4] The compound was made by heating silicon tetraiodide with finely divided silver (reduced by zinc from moist silver chloride), in sealed tubes at 290°–300° for several hours. The contents of the tube were freed from unaltered tetraiodide by repeated washing with small portions of dry carbon disulphide; a larger quantity of hot carbon disulphide was then added, and the mixture filtered as rapidly as possible out of contact with the moisture of the air. On cooling, the soln. deposited small, colourless, hexagonal prisms of the hexaiodosilane. The compound is of interest since in its formation there is a linking of the silicon atoms in pairs:

$$\left.\begin{matrix} SI_3I \\ SI_3I \end{matrix}\right\} + 2Ag = 2AgI + \begin{matrix} SiI_3 \\ SiI_3 \end{matrix}$$

Hexaiododisilane furnishes colourless, hexagonal, doubly refracting, prismatic or tabular crystals which can be fused in vacuo, with partial decomposition at 250°. It cannot be distilled at atm. press. or in vacuo, but on heating, a portion sublimes, and the remainder decomposes into silicon tetraiodide, and orange-coloured tetraiodosilene, $Si_2I_4$. When hexaiododisilane is treated with water at 0°, it forms hydrated silico-oxalic acid. It is converted by bromine into hexabromodisilane; and by mercuric chloride into hexachlorodisilane. It dissolves in potash-lye with the evolution of hydrogen: $Si_2I_6+6KOH=2SiO_2+2H_2O+6KI+H_2$. At 19°, 100 parts of carbon disulphide dissolve 19 parts, and at 27°, 26 parts of hexaiodide.

As indicated above, when hexaiodisilane is heated, the orange-red residue with the ultimate composition $SiI_2$ is considered to be **tetraiodosilene,** or **tetraiodosilicoethylene,** or **tetraiodosilicoethene,** $Si_2I_4$. Water decomposes it, forming a greyish-white mass, probably silico-formic acid, $SiH_2O_2$, since, when dried in vacuo and treated with potash-lye, the hydrogen evolved corresponds with

$SiO_2H_2+2KOH=K_2SiO_3+H_2O+H_2$, and when heated in air it oxidizes to silica with detonation. Tetraiodosilene is decomposed by potash-lye: $Si_2I_4+8KOH=4KI+2K_2SiO_3+2H_2O+2H_2$; and it does not dissolve in carbon disulphide, chloroform, benzene, or silicon tetrachloride.

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## § 60. Silicon Sulphides

According to J. J. Berzelius,[1] **silicon disulphide,** $SiS_2$, is formed when silicon is ignited in the vap. of sulphur, or when the sulphur vap. is passed over silicon at a white heat; the combination is attended by incandescence. Part of the silicon may be protected from the sulphur by the sulphide which is formed. I. G. Rankin and S. M. Revington's analyses agreed with J. J. Berzelius' view of the nature of the white silicon sulphide. W. Hempel and H. von Haasy considered that the best way to make this sulphide is to heat to redness an intimate mixture of amorphous silicon and three times its weight of sulphur in a crucible. The product contains 92–95 per cent. of silicon disulphide which can be isolated by sublimation at 60 mm. press. E. Vigouroux, and A. F. Hollemann and H. J. Slijper prepared the disulphide by a similar process. G. L. J. de Chalmot obtained some disulphide by heating over 300° a mixture of one of the copper sulphides and sulphur; and H. Moissan, by the action of lithium silicide on molten sulphur. P. Sabatier, and N. D. Costenau made it by passing a current of hydrogen sulphide over crystalline silicon at a red heat. E. Vigouroux also used this process; but W. Hempel and H. von Haasy obtained poor yields. A. Gautier and L. Hallopeau obtained it by heating metal silicides at 1300°–1400° in a stream of carbon disulphide; and E. Frémy made pellets from an intimate mixture of oil, lampblack, and silica, and heated them to redness in a crucible. The pellets were then heated to the highest available temp. in a porcelain tube through which was passed a slow current of carbon disulphide. The silicon disulphide collected in long needles in the cooler part of the tube—if moisture is present the product is contaminated with silica. E. Frémy found that if carbon be not present along with the quartz—glass, porcelain, or felspar—there is only a very small yield of silicon disulphide. In any case, W. Hempel and H. von Haasy found that the yield is poor. E. Frémy was unable to obtain any appreciable quantity of the disulphide by passing sulphur vap. over an intimate mixture of silica and carbon at a red heat. A. Gautier obtained some silicon disulphide by heating china clay to redness in a stream of carbon disulphide; and by heating silica in a mixture of hydrogen sulphide and carbon disulphide. J. I. Pierre obtained the disulphide by the action of silicon tetrachloride on hydrogen sulphide. After distilling the first product of the reaction, there remains a mixture of silicon disulphide and sulphur; and the latter can be removed by distilling off the sulphur in a stream of nitrogen. W. Hempel and H. von Haasy obtained only a poor yield by this process; M. Blix and W. Wirbelauer also obtained the disulphide as a by-product in the dry distillation of silicon dichlorosulphide: $2SiSCl_2=SiCl_4+SiS_2$. R. Amberg, M. Haff, W. Fielding, and

B. Neumann discussed the formation of silicon disulphide in the action of ferro-silicon on iron sulphide, and the part it plays in the desulphurization of iron.

When free from uncombined silicon, the disulphide prepared by J. J. Berzelius was white and earthy; that prepared by sublimation forms white or grey acicular crystals. The heat of formation obtained by P. Sabatier with octahedral sulphur was $Si_{cryst.}+2S=SiS_{2solid}+10{\cdot}4$ Cals. J. J. Berzelius found that water instantly decomposes silicon disulphide into hydrosulphuric and silicic acids; in the moist air, it gives off hydrogen sulphide and is gradually transformed into silicic acid. It can be preserved in sealed glass tubes. P. Sabatier found that decomposition of one eq. of silicon disulphide by water gives 38·5 cals. at 9·5°. E. Frémy said that *une vive effervescence* is produced when silicon disulphide is projected on water; and he emphasized the stability of the resulting colloidal soln. of silica. He added that the formation of hydrogen sulphide and soluble silica by the action of water on silicon disulphide is of great geological interest since it explains the production of silica incrustations and the presence of silica in mineral waters, and also the formation of natural sulphurous waters. Silicon disulphide burns to sulphur dioxide and silica when it is heated in air. E. Frémy found that it reacts vigorously with nitric acid, forming sulphuric and silicic acids; and it reacts at ordinary temp. with alcohol and with ether. A. Colson found it to be insoluble in benzene. M. Blix and W. Wirbelauer showed that it reacts with liquid ammonia, forming silicon di-imide, $Si(NH)_2$. A. Colson showed that mercuric salts in benzene soln. do not act on silicon disulphide; powdered mercuric chloride forms silicon tetrachloride; and mercuric cyanide gives silicon cyanide. A. C. Vournasos observed that nascent hydrogen obtained by heating the sulphide with sodium formate yields a little silane.

Silicon disulphide, said J. J. Berzelius, unites with potassium sulphide, forming a sulphide—presumably *potassium sulphosilicate;* and, according to W. Hempel and H. von Haasy, when silicon sulphide unites with metal sulphides, **sulphosilicates**, or *thiosilicates*, are formed. The same salts were found by A. Gautier to be formed by the action of sulphur, hydrogen sulphide, or carbon disulphide on some silicates at a red heat. These products are usually insoluble in water, and decomposed by steam at 250°, forming hydrogen sulphide, the metal hydroxide, and silicic acid.

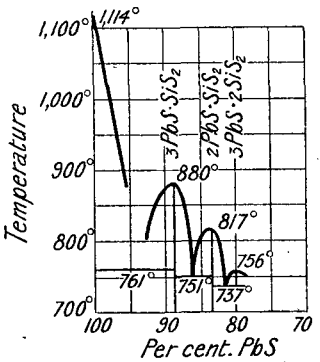



FIG. 202.—Freezing Points of the $PbS$–$SiS_2$ System.

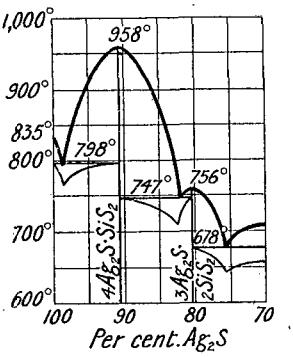



FIG. 203.—Freezing Points of the $Ag_2S$–$SiS_2$ System.

When heated, they may decompose into their components. W. Hempel and H. von Haasy formed **sodium sulphosilicate,** $Na_2SiS_3$, by melting together sodium sulphide and silicon disulphide. The dark brown mass is decomposed by water, forming hydrogen sulphide; and all the residue is dissolved; the aq. soln. gives off no hydrogen sulphide when treated with acids. L. Cambi prepared a number of sulphosilicates by heating mixtures of finely divided silicon and metals in an atm. of hydrogen sulphide to 800° or 1000°. The thermal analysis of the $PbS$–$SiS_2$ system, Fig. 202, showed the presence of the compounds, namely,

$3PbS.2SiS_2$; $2PbS.SiS_2$; and $3PbS.SiS_2$. $Pb_3Si_2S_7$ is brick-red; the last-mentioned compound appears as brilliant crystals and fuses, accompanied by decomposition, at 737°; **lead orthosulphosilicate,** $Pb_2SiS_4$, is reddish-brown, forms large crystals which fuse, accompanied by decomposition, at 767°; and **tri-lead pentasulphosilicate,** $Pb_3SiS_5$, is reddish-brown, does not occur in equilibrium with the soln., but as a result of a reaction between the solid constituents at 748°. In the $Ag_2S$–$SiS_2$ system, Fig. 203, the compound $4Ag_2S.SiS_2$ only has hitherto been determined, **octo-silver hexasulphosilicate,** $Ag_8SiS_6$, forming greyish-black crystals which melt without decomposition at 960° C. **Silver orthosulphodisilicate,** $Ag_6Si_2S_7$, melting at 756°, was prepared; and products richer in silicon disulphide, up to **silver metasulphosilicate,** $Ag_2S.SiS_2$, were also obtained. The colour of these ranged from orange-red to yellow, and they often exhibit evidence of under-cooled or metastable forms. J. P. Lebedeff's study of the system CaS–$CaSiO_3$ has been previously discussed; and for the association of calcium aluminium silicates with sulphides, *vide* ultramarine, and *lapis-lazuli*. L. Cambi made **calcium sulphosilicate;** and W. Hempel and H. von Haasy, **magnesium sulphosilicate,** $MgSiS_3$, by melting together the components, magnesium sulphide and silicon disulphide. It is decomposed into its components by heat. L. Cambi also made magnesium, **zinc, and mercury sulphosilicates.** W. Hempel and H. von Haasy prepared an impure **aluminium sulphosilicate,** $Al_2(SiS)_3$, by the action of sulphur vapour on an aluminium silicide, and by melting aluminium sulphide and silicon disulphide. The compound is unstable; attempts to make **ferrous sulphosilicate** on similar lines furnished a mixture $FeSiS_3+7FeS$.

The corresponding *orthosulphosilicic acid*, $H_4SiS_4$, and *metasulphosilicic acid*, $H_2SiS_3$, have not been made. F. Wöhler obtained a kind of *polysulphosilicic acid*, $H_8Si_4O_5$, which was called *sulphosilicon*, by the action of sulphurous acid and a little hydrochloric acid on calcium silicide. The reddish-brown plates after extracting the sulphur with carbon disulphide, and drying, furnished a light brown powder. The mass smells of hydrogen sulphide, and burns explosively when heated in air; with water, hydrogen sulphide is evolved; and with aq. ammonia, it gives off hydrogen, forming silica and sulphur.

In the preparation of silicon sulphide by heating amorphous silicon in a current of hydrogen sulphide, P. Sabatier [2] observed in the cold parts of a tube a large quantity of a yellowish-brown substance, consisting of a mixture of the ordinary sulphide, $SiS_2$, and silicon. The production and the transference of the silicon was explained by supposing the formation of a volatile subsulphide at a *low* temp., which at a *higher* temp. is decomposed into the subsulphide and silicon, the change being analogous to that of hexachlorodisilane. A. Colson passed the vap. of dry carbon disulphide over silicon in a porcelain tube at a white heat for about an hour and obtained a yellow volatile compound with a composition corresponding with **silicon monosulphide,** SiS, and a yellowish substance, probably silicon oxysulphide, SiOS. I. G. Rankin and S. M. Revington also made the monosulphide. F. Wüst and A. Schüller obtained a substance with a similar composition by the action of ferrosilicon on iron sulphide in an atm. of nitrogen; L. Cambi prepared the monosulphide as a sublimate when a mixture of sulphur and ferrosilicon is heated in the electric arc furnace; and W. Hempel and H. von Haasy obtained it as a by-product in the preparation of silicon disulphide. The yellow monosulphide obtained by F. Wüst and A. Schüller was in needle-like crystals. According to L. Cambi, when silicon (in the form of ferrosilicon) and sulphur are heated together in an electric-arc furnace, a vigorous reaction takes place, and a grey mass results, from which, by sublimation in the electric furnace, silicon monosulphide may be obtained. The compound sublimes at 940°–980° at 20–30 mm., and it occurs in two forms, namely, a black solid which may assume a vitreous character, and a yellow powder. On resublimation of either form, both are produced, the yellow one being deposited in the colder parts of the tube employed. The sp. gr. is 1·853 at 15°/4°. The yellow sulphide is less stable than

the black, and it rapidly absorbs moisture from the air and gives off hydrogen sulphide.

The yellow sulphide is decomposed by water with the evolution of hydrogen sulphide and the formation of a white insoluble substance, $H_2Si_2O_3$, which yields hydrogen when treated with alkalies, and reacts with alkali-lye with the evolution of hydrogen: $SiS+2KOH=SiO_2+K_2S+H_2$. The black sulphide is also decomposed by water with the formation of soluble silica and an oxygenated silicon hydride. Dry hydrogen chloride was found by L. Cambi to act on silicon monosulphide at 240°–260°, forming hydrogen sulphide, etc.; by condensing the products of the reaction in a freezing mixture, a liquid consisting of trichlorosilane is produced.

According to A. Colson, if the contents of the tube used in preparing the silicon monosulphide are further heated with boiling potash-lye to remove the excess of silicon and its sulphur compounds, and then digested for some time with warm hydrofluoric acid, a greenish powder of the composition of $Si_4C_4S$, *silicon sulphocarbide*, is obtained: when heated in a current of oxygen the weight is not altered, but the compound is converted into an oxygenated product, $Si_4C_4O_2$. A. Colson thus infers that the analogy of sulphur and oxygen does not hold good at high temp., for $CO_2$ yields $Si_4C_4O_2$, and $CS_2$ yields $Si_4C_4S$.

As indicated above, A. Colson, in preparing silicon monosulphide, obtained **silicon oxysulphide,** or **silicyl sulphide,** SiOS. A. Gautier obtained it by passing a mixture of hydrogen sulphide and carbon disulphide at a red heat over silica and aluminium silicate; some silicon disulphide was formed at the same time. A. Colson found the yellow substance is decomposed by water with the evolution of hydrogen sulphide; and it dissolves in cold dil. alkali-lye, without giving off hydrogen. The compound was also prepared by I. G. Rankin and S. M. Revington, who also reported *silicon dioxysulphide*, $SiO_2S$, but no confirmation or details are available.

J. I. Pierre [3] discovered what he called *chlorosulphure de silicium* and gave an analysis corresponding with **silicon sulphodichloride,** or **silicon dichlorosulphide,** $SiSCl_2$, but C. Friedel and A. Ladenburg showed that the alleged thiodichloride is really silicon trichlorohydrosulphide (*q.v.*). Silicon dichlorosulphide was first obtained by A. J. Besson, who found that the reaction which results in the production of silicon tetrachloride and sulphur from sulphur dichloride and silicon at a temp. below redness extends at a higher temp. to the formation of silicon thiochloride. A current of chlorine sat. with sulphur dichloride vap. is led over a quantity of crystalline silicon heated to bright redness in a porcelain tube, the silicon sulphide which rapidly chokes the tube being removed from time to time by allowing the chlorine to pass alone. The liquid product is fractionated from excess of sulphur chloride, and is purified from oxychloride by recrystallization from carbon tetrachloride, and subsequent sublimation in a current of dry air at 100°. M. Blix and W. Wirbelauer made it by passing silicon trichlorohydrosulphide through a glass tube at a dull red-heat—in an apparatus so arranged that the gases continually circulate in a closed system—and crystallized the product from its soln. in chloroform. E. Lay obtained the dichlorosulphide as a by-product in the action of chlorine on a mixture of ferrosilicon and sulphur. Silicon dichlorosulphide is a white solid which furnishes acicular crystals. A. J. Besson said its b.p. is 185° and its m.p. 74°; M. Blix and W. Wirbelauer gave 75° for the m.p., and added that it distils at 92° under 22·5 mm. press.; and that it is very easily decomposed by moisture or by distillation at ordinary temp. into silicon disulphide and tetrachloride. A. J. Besson found that it is unstable in moist air, and reacts violently with water, forming hydrogen sulphide and chloride, and silica. M. Blix and W. Wirbelauer said that it reacts readily with liquid anhydrous ammonia, forming silicon di-imide, $Si(NH)_2$.

As indicated above, J. I. Pierre made **silicon trichlorohydrosulphide,** $Si(HS)Cl_3$, by passing a mixture of the vap. of silicon tetrachloride and dry hydrogen sulphide through a red-hot porcelain tube: $SiCl_4+H_2S=SiCl_3(HS)+HCl$. He added:

The best mode of preparation is to pass a current of hydrogen sulphide gas through silicon tetrachloride contained in a stoppered retort, the conducting tube being made to dip just under the surface of the liquid. The retort is then connected by means of a good cork with one end of a porcelain tube, the other end of which is attached to a U-shaped tube kept constantly cool. The porcelain tube is then made red hot, and as the mixture passes through, a fuming liquid rapidly condenses in the U-tube. The liquid thus obtained has a pungent, offensive odour resembling both silicon tetrachloride and hydrogen sulphide; it becomes clear on standing, and is then distilled, the liquid which comes over at a temp. between 90° and 100° being kept apart. The process is stopped as soon as the pasty mass in the retort begins to evolve white fumes.

C. Friedel and A. Ladenburg employed a similar mode of preparation. Silicon trichlorohydrosulphide is a colourless fuming liquid which, according to J. I. Pierre, has a sp. gr. 1·45, and a b.p. of 100°. J. I. Pierre's, and C. Friedel and A. Ladenburg's analyses and vap. density, 5·24–5·74 between 155° and 161°, agree with the formula $Si(HS)Cl_3$ for which the calculated vap. density is 5·83. J. I. Pierre found that in contact with water the trichlorohydrosulphide is decomposed, forming hydrogen sulphide, hydrochloric and silicic acids, and a little free sulphur; and if a mixture of hydrogen sulphide and the vap. of the trichlorohydrosulphide is passed through a strongly heated porcelain tube, a small quantity of a liquid is formed—possibly the dichlorosulphide—which decomposes into silicon disulphide, etc., when distilled. C. Friedel and A. Ladenburg showed that with bromine, the trichlorohydrosulphide is converted into chlorobromide; sodium does not remove the hydrogen; alcohol in excess forms hydrogen sulphide, hydrogen chloride, and ethyl silicate; and if 3 mols. of alcohol are present to one mol. of trichlorohydrosulphide a liquid—silicon triethoxyhydrosulphide, $Si(OC_2H_5)_3HS$—boiling at 164°–167°, is formed.

According to M. Blix, **silicon sulphodibromide,** or **silicon dibromosulphide,** $SiSBr_2$, is formed by the interaction of silicon tetrabromide and hydrogen sulphide at 150° in the presence of aluminium bromide as catalyst. The bromosulphide is separated from the unchanged tetrabromide by fractional distillation under reduced press. Silicon dibromosulphide forms colourless plates which can be recrystallized from carbon disulphide. It melts at 93°, forming a liquid which boils at 150° under 18·3 mm. press. The crystals fume in moist air, and react *explosionsartig* with water with the separation of silicic acid and the evolution of hydrogen bromide and sulphide. A soln. of the dibromosulphide in dry benzene reacts with dry ammonia, forming *silicothiourea*: $SiSBr_2+4NH_3=SiS(NH_2)_2+2NH_4Br$.


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## § 61. Silicon Phosphates

F. Mylius and A. Meusser found that phosphoric acid at 400° has a strong corrosive action on quartz glass; while K. Hüttner showed that at ordinary temp. orthophosphoric acid has scarcely any action on glass, but at 100°–150° the attack is marked—silicyl phosphate, and metaphosphates are produced. Phosphorus pentoxide can be sublimed in glass vessels without affecting them appreciably. W. Skey, E. Laufer, and J. Hirschwald observed the behaviour of silica in fused sodium phosphate, and a well-known test for silica is based on the sparing solubility of silica in that menstruum. According to A. Müller,[1] phosphoric acid has a slight action on quartz at a low temp., and a vigorous action at a higher temp. when the quartz is transformed into hydrated silica. P. Hautefeuille and P. Margottet fused a dried mixture of gelatinous silica and metaphosphoric acid, extracted the mass with hot water, and so obtained transparent, colourless, isotropic, octahedral crystals. The composition corresponds with $SiO_2.P_2O_5$, which K. Hüttner considers to be that of **silicyl metaphosphate,** $SiO(PO_3)_2$. The substance so obtained has a sp. gr. 3·1 at 14°; it scratches glass, and when heated melts to a glass which does not devitrify on cooling.

In their memoir: *Sur le polymorphisme du phosphate de silice*, P. Hautefeuille and P. Margottet showed that when a mixture of hydrated silica and orthophosphoric acid is gradually heated to 260°, about 5 per cent. of silica is dissolved, and a still larger proportion can be obtained in soln. by gradually heating a mixture of phosphoric acid and silicon tetrachloride. The soln. deposits crystals of silicyl phosphate in forms varying with the temp. at which the deposition takes place. They found that (i) when the soln. of silica in orthophosphoric acid is allowed to cool below 260°, it deposits crystals having the appearance of flattened discs. Similar crystals are obtained when the soln. is mixed with conc. sulphuric acid and heated for some time at a temp. somewhat above the b.p. of the latter. These crystals are hexagonal prisms, frequently macled in the same manner as lamellar hæmatite. They act strongly on polarized light, and are somewhat rapidly attacked by water, but do not alter in contact with alcohol. (ii) If the temp. of the soln. of silica is gradually raised from 260° to about 360°, it deposits an abundance of very thin hexagonal lamellæ, which act feebly on polarized light and resemble tridymite in appearance. They are, however, distinguished from the latter by the fact that they yield silver phosphate when fused with silver nitrate. These lamellæ are not altered by alcohol, but are slowly attacked by water with formation of orthophosphoric acid and soluble silica. (iii) If the soln. be heated rapidly, it remains limpid up to about 700°, but between 700° and 800° it deposits regular octahedra which are almost always modified by cubical faces. This form of silicon phosphate is that described above. (iv) When phosphoric acid containing only a small proportion of silica is rapidly heated to about 900°–1000°, the crystals obtained are monoclinic prisms which act strongly on polarized light. At a high temp., these prisms are more stable than the other forms. If orthophosphoric acid sat. with silica be slowly heated to 1000°, a mixture of all four forms is obtained; but if the temp. is maintained the lamellæ and octahedra are quickly attacked, whilst the prisms continue to increase.

The crystals all have the same composition. The hexagonal crystals are formed below 300°, the lamellæ resembling tridymite at about 360°, the regular octahedra between 700° and 800°, and the monoclinic prisms between 800° and 1000°. This polymorphism is not due to different groupings of the same crystalline elements, for the hexagonal crystals are attacked by water, which has no action

on the octahedra or prisms. According to H. N. Stopes, silicyl metaphosphate is probably formed when silicopyrophosphoryl chloride is heated above 200° until vap. of phosphoryl chloride is no longer evolved. P. Hautefeuille further found that if a conc. soln. of orthophosphoric acid containing about one-quarter of the quantity of silica required to saturate it, is heated at 125° for 7 or 8 days, it deposits concretions which gradually increase in size. They are separated from the mother liquor by pouring the hot liquid on to a previously heated porous plate, and are dried by exposure to dry air for about a week. The spherical globules thus obtained have the composition **tetrahydrated silicyl metaphosphate,** $SiO_2.P_2O_5.4H_2O$. When suspended in sulphuric acid, they act strongly on polarized light. Under the microscope, the concretions are seen to be formed of concentric cones of prismatic crystals with their principal axes radiating from the centre. The silicyl metaphosphate decomposes rapidly in moist air, and dissolves completely in water at 0°, but it is decomposed by water at the ordinary temp., with separation of gelatinous silica.

H. N. Stokes prepared a chloride corresponding with a second unknown *silicopyrophosphoric acid*, $SiO(O.PO_2.OH)_2$, by heating a mixture of ethyl trichlorosilicate, $C_2H_5O.SiCl_3$, or ethyl orthosilicate, $Si(OC_2H_5)_4$, and phosphoryl chloride in a sealed tube at 180° : $4(SiCl_3.OC_2H_5)+2POCl_3=3SiCl_4+4C_2H_5Cl+SiP_2O_6Cl_2$. The product is **silicopyrophosphoryl chloride,** $SiP_2O_6Cl_2$, or $SiO=(O.POCl)_2=O$. If the ethyl trichlorosilicate be in excess, an analogous reaction occurs, but the composition of the silicopyrophosphoryl chloride is different. Silicopyrophosphoryl chloride is a white, hygroscopic, amorphous powder which is freely soluble in alcohol and water. It loses hydrochloric acid when in contact with moist air. The aq. soln. is turbid owing to the separation of gelatinous silica, but a clear aq. soln. can be obtained by adding enough water to the alcoholic soln. Neither the acid nor its salts could be isolated. It decomposes slowly when warmed to 200°, and rapidly at a higher temp., forming phosphoryl chloride. When mixed with phosphorus pentachloride, and heated to 100°, silicon tetrachloride and phosphoryl chloride are formed. A cold aq. soln. from which the chlorine has been removed by silver nitrate in excess yields in order, when ammonia is added, silver pyrophosphate, silver orthophosphate, and silica.

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