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ART. XXXII.—*The Binary Systems of Alumina with Silica, Lime and Magnesia*; by E. S. SHEPHERD and G. A. RANKIN.
With Optical Study, by FRED. EUGENE WRIGHT.

ACCORDING to the calculation by Clarke,* the order of relative importance of the oxides which make up the rock-forming minerals stands,—silica, alumina, oxides of iron and lime, etc. It seems desirable to begin with the study of the systems of alumina, silica and lime, leaving the iron oxides until more experience with the difficulties of this work should enable us to meet the increased difficulties which are introduced by the different oxidation stages of iron. The first paper of the series† was published some time ago. We have now to present the result of experiments with three other groups of oxides.

The interest aroused by the study of the lime-silica series, not only among those engaged in pure science, but also among many in commercial work, would seem to warrant devoting some space not only to the methods but also to the limitations of this kind of investigation.

In developing a system of such immense usefulness, it is of the greatest importance that those who are interested in the application of physical chemistry to extreme cases of rock magmas shall have a firm grasp of the limitations, both of the theory and experimental possibilities. None of the laws of physical chemistry can be applied to such extreme conditions without some modification.

*Data of Geochemistry, F. W. Clarke, Bull. No. 330. U. S. Geol. Survey, 1908.

†The Lime-Silica Series of Minerals, Day, Shepherd and Wright, this Journal (4), xxii, 265, 1906.

As has often been said, the geologist is dependent on the petrographic study of rocks which have passed through many changes. A study of relatively simple two- and three-component systems shows the futility of attempting to *deduce* the past history of any polycomponent system from its *final* condition. Petrographers have already observed the order of crystallization for certain minerals, but the exact correlation of this order with the composition of the rock remains to be determined. The phase rule shows that the first mineral to separate from a freezing solution depends primarily on the initial composition and only indirectly on the melting point of the mineral. Furthermore, it is always possible for a mineral to be redissolved after it has begun to separate and subsequently to reappear at a lower temperature. If the eutectic relation was the only one encountered in the study of minerals, the classification of rocks, as well as the interpretation of the occurrence of the femic and salic rocks, would be relatively simple. But studies of simple systems leave no room for doubt that the phenomena in a great rock magma are exceedingly complex, and we have no choice but to begin with the laboratory study (quantitative measurement) of relatively simple mixtures of pure minerals. We are entering upon a new science in which it is absolutely essential that we proceed in an orderly way through simple relations and conditions to those which are more intricate. Experiments on the rocks, if undertaken first, would be as futile as to design a power plant without a first acquaintance with the physical properties of materials.

Take another obvious instance. It is of course desirable to know the molecular weight of the various minerals, whether or not they dissociate in solution, and the effect of these phenomena on their inter-reactions. At the present time such questions are practically unanswerable. The molecular weight of salts in aqueous solution is determined by the lowering of the freezing point, but even at this low temperature and with the most delicate apparatus, an error of five per cent is regarded as doing very well. Not only must the temperatures be measured to the nearest hundredth of a degree, but the formulæ have thus far been found to apply only to "infinitely" dilute solutions,—never over one per cent. Silicate melts are too viscous to be stirred, and freezing occurs in a region of variable temperature distribution and always over an interval of a whole degree or more. Furthermore, we have *as yet* no means of knowing that the *fundamental assumptions* underlying the Van't Hoff-Raoult relation hold true for silicates. We ought, therefore, to hesitate before forcing the

results thus far obtained into formulæ which were deduced for wholly different conditions and which apply none too accurately even then. Obviously, the calculation of molecular weights from concentrations of ten, twenty, and even fifty per cent, as has sometimes been done, can serve no useful purpose.

A glance at the technique of measurement of conductivity in aqueous solutions will reveal how unwise are generalizations based on experiments with the conductivity of silicates. Maintaining a constant temperature throughout even a relatively small volume is extremely difficult at a temperature of 1200° C. Electrodes and containing vessels can not be maintained constant in shape or dimensions, nor can perfect or constant contact relations between the electrodes and the melt be assumed. Until such essential conditions can be supplied, we cannot hope to derive much useful data from merely passing the electric current through a silicate. The effect of high and varying viscosity on conductivity is unknown.

Pyrometry has made great progress in the last decade, and for temperatures below 1600° C. the thermoelement is capable of reading accurately to one-tenth of one degree. But it does not follow that all thermal phenomena in silicates are definable with this precision. The phenomena of melting and inversion, for example, seldom occur with sharpness enough to allow of their being determined within less than $\pm 1^\circ$ for compounds, and $\pm 2^\circ$ for eutectics. We must guard against the too common error of assuming that we have determined the phenomena with the accuracy with which we can read the scale of the instrument.

Above 1600° C. the optical pyrometer must be used, and the accuracy is much less. With the thermoelement the evolution or absorption of heat which occurs in a charge registers itself, leaving nothing to the judgment of the observer. With the optical pyrometer, as ordinarily used, the melting temperature must be inferred from the apparent fusion of the charge, and the observer is dependent upon his arbitrary judgment as to what constitutes fusion. Usually he cannot determine the beginning of fusion nor can he tell the exact point where the change is complete. Here again, not enough is known of the viscosity of the various mixtures to allow for its effect upon the phenomenon which the observer sees. As Day and Allen have shown,* albite retains its rigidity long after fusion (deorientation of crystal structure) is complete. Quartz acts in a similar manner. The different concentrations in mixtures show all gradations between this extreme viscosity and the extreme

* Isomorphism and Thermal Properties of the Feldspars, Publications of the Carnegie Institution of Washington, No. 31.

fluidity, as in the case of Al_2SiO_5 . The best the observer can do at present in the region above 1600°C. is to determine the maxima and eutectics. Determination of the liquidus is beyond our present facilities.

There is also a tendency to expect reactions to proceed with the same dispatch which we are accustomed to meet with in the case of aqueous solutions. This has not only never occurred in our experience, but unstable forms often require much urging to bring them into the stable condition.

The very first difficulty which we encounter is in obtaining pure homogeneous preparations with which to begin. The natural minerals are rarely pure enough to give constant data. A natural mineral melts at a given temperature, depending (as indicated by the Van't Hoff-Raoult law) upon the amount of impurity which it chances to contain; but the next specimen, having different impurities and in different amount, will melt at a different temperature. That is, the data obtained apply only to the specimen examined and furnish no basis for determining general relations.

The Chemical Purity of the Ingredients.—One must begin with the purest possible components. The oxides of lime, alumina and silica on the market are not usually pure enough. The influence of small amounts of impurities, 1 to 3 per cent, cannot be neglected. A glance at the slope of the freezing point curves shows at once that the presence of one per cent of impurity may cause a variation of five or ten degrees in the melting temperature.

Calcium carbonate can be obtained very pure, but high purity cannot be taken for granted without testing it.

The C. P. alumina of commerce is likely to contain .5 to 2.0 per cent of alkalies, and one sample of especially pure (!) alumina contained over 3 per cent of SO_3 . Baker and Adamson succeeded in making for us a hydrated alumina which contained only .2 to .4 per cent alkali, and this alkali was then reduced to less than one-tenth of one per cent by further purification in platinum.

Pure silica is obtained from quartz, carefully selected with the microscope, and treated with aqua regia.

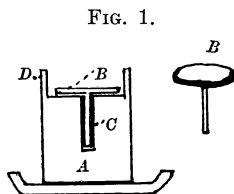
Magnesium carbonate usually contains from 1 to 3 per cent of CaCO_3 , and this impurity is usually not mentioned in the manufacturer's analysis. In this case also, Baker and Adamson produced a special preparation of high purity.

Homogeneity of the Mixtures.—After pure materials have been obtained, we have next to obtain chemically homogeneous products. It has been found necessary to melt the charge at least three times with fine grinding and mixing between the fusions, in order to obtain a product which is chemically

homogeneous. A conspicuous visible demonstration of the need for such careful preliminary mixing occurs with the composition Al_2O_3 8 per cent, CaO 69 per cent, SiO_2 23 per cent. As long as the mass is incompletely combined, quantities of calcium orthosilicate will disintegrate (dust), yielding a mixture of fine powdered orthosilicate and cinders of the more aluminous material. After three or four fusions and grindings, the charge remains solid, i. e., practical homogeneity has been secured. This shows that diffusion in silicate melts is extremely slow and emphasizes the necessity for the somewhat tedious care in preparation.

The effect of insufficient mixing on the observed melting points may be very great. Even in a sharply melting compound like anorthite, the cones prepared from the most carefully mixed oxides often melt 20° or more below those made from previously combined oxides. Here the heat of combination is evidently dominant. Obviously, quite the reverse might happen with other mixtures. One immediate consequence of this is that experiments in which the Seger cone method is employed for the measurement of temperature must always be made with carefully mixed and combined charges. It is also clear that comparison of the bending of a Seger cone with the bending of a cone of wholly different mixtures may mean very little, for the viscosities of the different mixtures bear no definite relation to each other, and viscosity is the chief factor in the bending of these cones.* Thus minerals like quartz or albite will retain their stiffness far above their melting points, i. e., after their crystalline structure is entirely gone.

Apparatus.—Those portions of the series which melt below 1600° were determined by the thermoelectric method described in the various publications from this laboratory. Above 1600° only the optical method described in the lime-silica paper is available, i. e., an optical pyrometer (Holborn and Kurlbaum type) sighted on a strip of platinum or iridium. We have found it useful to make a small tack of platinum, as figured (fig. 1, B). This tack has a polished upper surface upon which to sight. The prepared charge is moulded into a cylinder (A) of the shape shown; the shaft of the tack fits snugly into the hole (C) in the cylinder; the head of the tack (B) rests firmly on the flat surface of the charge, while the raised shoulder (D) diminishes the reflection from the walls of the furnace. If ideal conditions obtained, the tack would be invisible, i. e., we would have an absolute black body, but

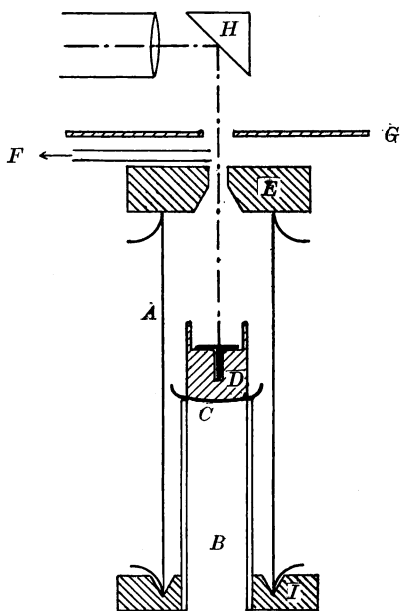


* See The Lime-Silica Series of Minerals, this Journal (4), xxii, 268.

at the melting point the retardation of the temperature of the charge, communicated along the shaft of the tack, should cause the head to flash, i. e., become visible. Although the condition of even approximate blackness is seldom attained in such furnaces, we were much assisted by this method of procedure.

At the present time observations of melting temperatures above 1600° are only determinable for the case of compounds at the maximum, and for eutectic compositions. The course of the liquidus cannot be established by any optical method yet devised. For that reason we have sketched all curves above 1600° in dotted lines to indicate that only the maxima and minima are determined. Of course the phases present along the liquidus can be determined microscopically, and this has been done in every case. The method of making these temperature observations is similar to that used on the orthosilicate of lime. A (fig. 2) is the tube of the iridium furnace; B, a

FIG. 2.



magnesia cylinder on which rests the iridium crucible C. D is the cylinder whose melting temperature is desired, with the iridium tack in position. E is a magnesia lid with a small hole through which to observe the charge; F an exhaust tube to carry away the iridium vapors and heated air which would affect the prism H of the pyrometer. G is an asbestos shield to further protect the pyrometer. The bottom of the furnace is closed by the circular cup, I, thus preventing air currents from passing up through the furnace. If the furnace acted as a perfect black body, neither the metal tack nor the charge would be visible. When such blackness does not occur, the scale of a

theoretically black body does not apply, and the pyrometer must be calibrated arbitrarily *in terms of the conditions in which it is used*. The difference between the theoretical and actual scales may reach 100° C. The necessity for frequent recalibration is also obvious.

This arbitrary calibration of the instrument was made with the help of certain fixed points. The melting temperatures of diopside and anorthite are now definitely known, and we are sure that the melting point of platinum is constant, though there is some doubt as to its exact temperature in degrees. We have assumed it to be 1750° . Diopside melts at 1395° , according to the values of Allen and White,* provisionally corrected by recent unpublished comparisons with the gas thermometer by Day and Sosman. On the same curve extrapolated, anorthite melts at 1542° . By calibrating the instrument in terms of these fixed points, the relative temperatures of our scale are definitely established. The absolute temperatures may shift with more accurate determinations of these fixed points.

The accuracy of the individual observations is determined by (1) the sharpness of the flash of the tack, and (2) by the delicacy with which the lamp filament can be matched up against the tack surface. In this work we found the points at which the filament was *distinctly* brighter or *distinctly* darker than the tack surface to lie 8 millivolts apart. The actual adjustment was ± 2 millivolts, so that the maximum error of observation was $\pm 20^{\circ}$ and the probable error $\pm 10^{\circ}$ or less. The actual variations in the melting point observed for platinum were ± 2 millivolts or 10° . At this temperature, therefore, the variation due to the material melted falls within the limits of error of the pyrometric system. The same is true of the anorthite and sillimanite. We feel justified in saying that the method is reliable, though rough and of limited usefulness compared with the thermoelement below 1600° . Several improvements have been suggested by this work and are now being tested.

Preliminary studies for locating the approximate position of maxima and minima were made in a 40^{mm} iridium tube furnace (Nernst type) by placing small amounts of the finely powdered and thoroughly combined charge on an iridium tray and exposing for a definite period at constant temperature. This temperature is then increased by degrees until the minima appear, after which the temperature is stepped up until the maximum is located. With sharply melting mixtures, and where there is a reasonably large difference of temperature between the maxima and minima, the *compositions* can be quite definitely determined. If, however, the eutectic is viscous, like that between Al_2SiO_5 and SiO_2 , the minima can be located only approximately by this method. Similarly, where the compositions of the maximum and minimum are

* This Journal (4), xxvii, 1, 1909.

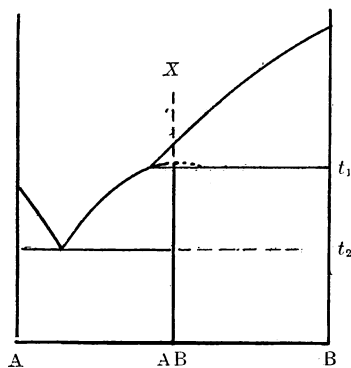
close together, like $\text{Al}_2\text{SiO}_5\text{--Al}_2\text{O}_3$, and the temperature difference is small, the exact location of the eutectic composition is very difficult to establish. Unfortunately, the microscope is also of little assistance in this case.

All such observations must be made in an oxidizing or neutral atmosphere; a reducing atmosphere not only reduces some of these oxides and silicates, but even where this is not the case, the flame playing about the furnace opening renders the optical pyrometer useless for exact measurements. A hydrogen atmosphere is perhaps the worst. At temperatures above 1000° , it reduces silica or silicates, setting free silicon which renders the platinum or iridium crucibles "hot short" and ultimately destroys them. This reaction is doubtless due to the silicon hydride, since it is by no means necessary that the silica and platinum be in contact in order that this destructive action occur. A platinum crucible in which a charge of silica was heated to 1100° in hydrogen, increased in weight by more than thirteen milligrams. On analysis, almost the theoretical quantity of SiO_2 was found. The crucible was highly crystallized and could be broken up to a coarse powder in the fingers. Wires less highly charged with silicon are very brittle when hot, even though not appreciably so when cold.

Carbon is known to react readily with lime above 1700° to give calcium carbide, so that a carbon atmosphere above 1200° introduces an undetermined error into the work.

One of the series studied (lime-alumina) presents the troublesome case of a compound unstable at the melting

FIG. 3.



point. If the composition of the compound be X (fig. 3), then the first crystals to separate on the freezing of this mixture are, of course, B. At the temperature t_2 these crystals should combine with component A to form the compound AB. But it often happens that the crystals become coated over with the compound AB and are thereby removed from the action of component A. The result is that the charge freezes at t_1 to a mixture of A, AB, and B, which of course is unstable in a two-component system. Theoretically, if the charge were held for a long time at a temperature between t_1 and t_2 , diffusion should cause all free B to disappear, so that the mass

when cooled down should consist entirely of the compound AB. By taking the fused charge of composition AB, grinding to a very fine powder and heating for a long time between temperatures t_1 and t_2 , we were successful in bringing about this reaction in the case of $3\text{CaO} \cdot \text{Al}_2\text{O}_3$.

Alumina-Silica.—In this series there is but one compound which is stable in contact with the melt. This is the mineral sillimanite, Al_2SiO_5 , composed of Al_2O_3 62.85 per cent, SiO_2 37.15 per cent. This occurs in nature widely distributed. The same compound has been found by Mellor in the crystallized glaze of porcelain. The pure artificial compound is colorless and occurs in well crystallized prisms of density of 3.031, slightly lower than the natural mineral, which averages 3.32. Hardness is 6 to 7. The compound is unaffected by water, hot or cold, and is but very slowly attacked by acids or alkalis. Sillimanite is practically unaffected by HCl , HNO_3 or H_2SO_4 , hot or cold, or by cold HF . It is decomposed slowly in mixed HCl and HF , and by fused Na_2CO_3 . The melting temperature of the pure compound is 1811°C .

TABLE I.

<i>a.</i> Melting point fused . sillimanite made from pure oxides.		<i>b.</i> Melting point of mixed and heated oxides of the same composition as <i>a.</i>	
Millivolts	T	Millivolts	T
·475	1812°	·472	1802°
·475	1812	·485	1850
·474	1810	·483	1850
·474	1810	·483	1850
Mean 1811°		·479	1833
		·480	1835

Table I, *b*, is given to show how great an error is introduced by observing incompletely combined oxides. These charges had been heated several times to about 1600° in the gas furnace, but still showed free silica and alumina. After fusion, they gave concordant results. The flash is also much sharper when the oxides are properly combined. It will be noticed that the observed melting temperature varies irregularly, and is not altogether dependent upon the rate of heating.

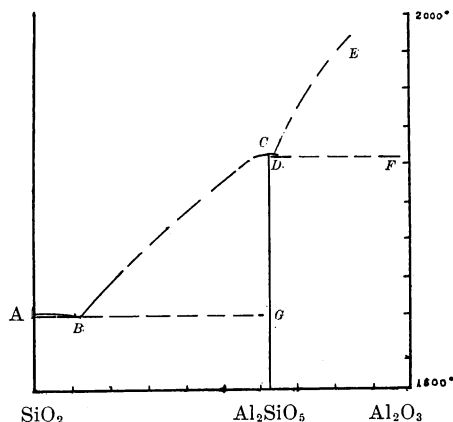
The eutectic Al_2SiO_5 - SiO_2 is very hard to place, owing to the extreme viscosity of the silica. Heated for one hour at 1550° in a platinum furnace, nearby mixtures show no evidence of fusion. The 15 per cent and 20 per cent Al_2O_3 charges show traces of fusion before pure SiO_2 . The eutectic must therefore fall at about 10 per cent and melt slightly below 1600°C . Throughout the range of concentrations from SiO_2 to $\text{Al}_2\text{O}_3 \cdot \text{SiO}_2$

cristobalite and sillimanite are the only phases. The eutectic for Al_2SiO_5 - Al_2O_3 is only very slightly below the melting temperature of the compound. There is, however, a rapid rise of the liquidus beyond 65 per cent Al_2O_3 , so that in default of a pyrometric method we must depend on the modified Joly method which indicates the location of the eutectic at about 64 per cent Al_2O_3 .

Corundum occurs in all compositions between Al_2SiO_5 and Al_2O_3 , and no phases other than sillimanite and corundum do appear. The optical properties of the sillimanite remain practically unchanged in the presence of SiO_2 or Al_2O_3 . We accordingly infer that little or no solid solution of the component minerals in sillimanite occurs here.

The corundum shows slightly altered properties, and probably takes up a limited quantity of sillimanite in solid solution. The melting point of corundum lies above the safe working range of the iridium furnace, and it is hardly worth while to attempt determinations in the carbon furnace. The nature of the equilibrium diagram is shown in fig. 4.

FIG. 4.



Unstable forms.—The two natural minerals of the same composition as sillimanite are cyanite or disthene, and andalusite. Neither of these minerals occurs in igneous rocks and Vernadsky has shown* that both change to something like sillimanite at temperatures above 1300° . He also states that the change is accompanied by an *evolution* of heat. We have verified the change of form, but have not been able to detect any heat change. Our experience led to the conclusion that

* Bull. Soc. Min., xii, 446; xiii, 257.

the inversion takes place so slowly as to completely veil the character of the corresponding heat change.

A very pure andalusite from Hill City, S. D.:

Heated	Temperature	Remarks
48 hours	1100°	Unchanged
62 "	1150°	"
168 "	1150°	"
28 days	900°	"
4 "	1500°	Much altered

If the transformation is reversible, the change is slow even at temperatures much above the supposed inversion point. All natural andalusite is contaminated with mica which masks the reaction. Using a flux in the hope of getting the transformation at lower temperatures, failed to yield satisfactory results.

Time	Flux	Temperature	Remarks
12 hours	NaCl	800°	Little altered
72 "	"	"	Andalusite still abundant
168 "	"	"	Andalusite still abundant. No sillimanite
48 "	CaV ₂ O ₆	1000°	Andalusite still present. No sillimanite
48 "	"	900°	Little changed. No sillimanite
216 "	"	900°	Little changed. No sillimanite

At higher temperatures the andalusite is decomposed without forming sillimanite. Andalusite heated seven days at 400° in a bomb containing 10 per cent NaCl solution showed no change. The result indicates that andalusite changes to sillimanite at high temperatures, but with considerable difficulty. The reverse change, sillimanite-andalusite, does not occur under any conditions which we have yet tried.

Cyanite.—Like andalusite, cyanite is much contaminated with mica, rendering satisfactory thermal study of the natural mineral difficult. It is not possible to separate it completely by purification with aqua regia and cold HF. Its specific gravity is 3·5 – 3·7. Hardness = 4–5 or 6–7, depending on the direction with respect to the prism axis. Vernadsky found the mineral changing to sillimanite above 1300°. We have found the change to be slow, though more rapid than the change from andalusite to sillimanite.

Time	Flux	Temperature	Remarks
½ hour	None	1500°	Decomposed, but no sillimanite identifiable
7 days	"	1150°	But little changed
2 "	"	1150°	But little changed
2 "	"	1000°	Unchanged
28 "	"	900°	Little changed

Borax decomposes the mineral.

Time	Flux	Temperature	Remarks
12 hours	NaCl	800°	Unchanged
72 "	"	800°	Little changed
48 "	CaV ₂ O ₆	1000°	Cyanite decomposed but no sillimanite formed

Cyanite is thus more readily decomposed than andalusite, but shows no sillimanite which can be determined with the microscope.

We have shown that at about 1300° both andalusite and cyanite change, the one into sillimanite and the other, from Vernadsky's density determination, probably into sillimanite, though badly formed. It is now in order to determine whether sillimanite, which is stable at high temperatures, will change into cyanite or andalusite at low temperatures.

Sillimanite shows no heat effect between 1100° and 1500°.

Time	Flux	Temperature	Remarks
168 hours	None	600°	Unchanged
96 "	"	1100°	Unchanged

Heated four days at 1000° with a small amount of borax, the crystals show slight attack, but are not destroyed, and no andalusite or cyanite appeared. Heated 48 hours at 1100° with CaV₂O₆, the powdered crystals were slightly attacked and *new crystals of sillimanite formed*. Working in steel bombs with various aqueous solutions, negative results were obtained.

Time	Flux	Temperature	Remarks
7 days	5% NH ₄ F	400°	The original grains are pitted, but no new crystals formed
6 "	10% NaCl	450°	Unchanged
7 "	10% KBr	400°	Slightly attacked

Heated thirty days in a long steel tube which allowed a continuous current of hot water (250°) to pass over the mineral and then to a cooler part of the tube, no alteration was produced.

Thus at low temperatures no conditions were found under which sillimanite tended to change into andalusite or cyanite. Solutions of sillimanite in albite and borax gave always sillimanite. When fused sillimanite is rapidly cooled (quenched); it always crystallized as sillimanite.

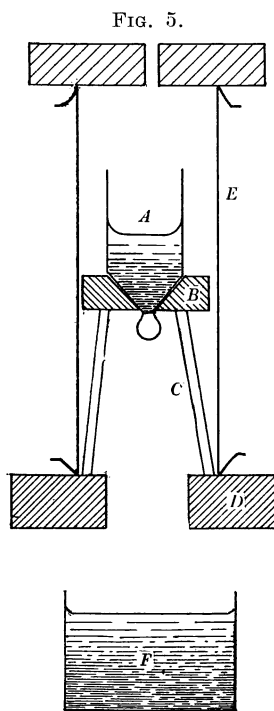
It would be a waste of time to tabulate all of the metathetical reactions by which we have sought to produce these two unstable forms. After overcoming the great difficulties of finding a suitable vessel which will withstand the pressure of aqueous solutions at high temperatures, and which will not be

attacked by the reagent, we have not yet been successful in our attempts to prepare andalusite and cyanite. Attempts to produce reactions between the hydrated oxide of silicon, i. e., the various hypothetical silicic acids, and alumina, hydrated or dry, gave no positive results. Certain reactions involving the attack upon anorthite and other minerals by $\text{Al}_2(\text{SO}_4)_3$ or AlCl_3 , have yielded but little promise of success. AlCl_3 acting on anorthite gave small spherulites of which the determinable properties agree with andalusite, but these crystals were too small for positive identification. We did not obtain positive results by the action of fluxes on the oxides.

Incidentally, we observed the formation of meionite by crystallizing glass of that composition in a bomb with 10 per cent NaCl solution, and grossularite by the reaction of AlCl_3 on calcium orthosilicate.

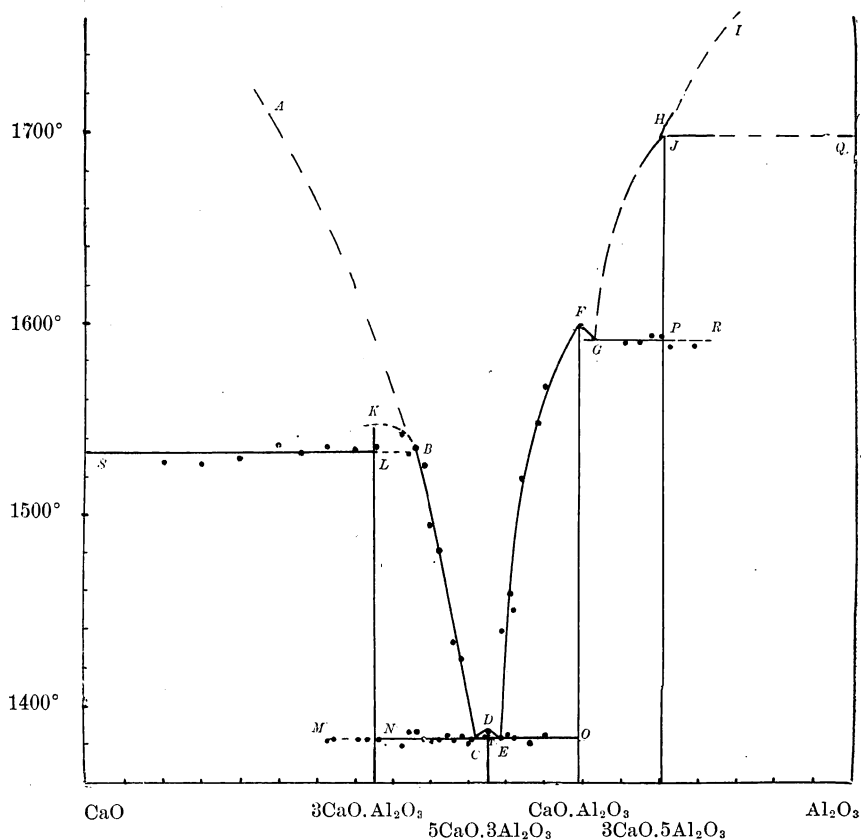
Sillimanite glass.—Sillimanite melts sharply to a very thin liquid which crystallizes with great rapidity. Dropping the crucible of molten sillimanite in water does not cool even a small charge rapidly enough to prevent crystallization. We used the system shown in fig. 5. A is an iridium crucible with a 3^{mm} hole in the bottom. It is supported in the furnace tube, E, on a magnesia ring, B, which is in turn supported by small magnesia rods, C, and the ring, D. The melted charge drops from the tip of the cone directly into the dish of water, F. In this way we obtained a number of globules of glass, with an index of refraction of about 1.625 and a density of 2.54, much lower than sillimanite. When crystallized, either by heat at 1200° or in bombs containing 10 per cent NaCl solution at 350°–400°, the glass yielded only sillimanite. It seems reasonably certain that sillimanite is the stable form and that andalusite and cyanite are formed by crystallization from solution at low temperatures.

Lime-Alumina.—It is much more satisfactory to deal with systems in which at least a part of the liquidus can be definitely located with the thermoelement. From about 15 per cent to 70 per cent of alumina, this series can be melted in platinum and all of the



eutectics with the exception of $3\text{CaO} \cdot 5\text{Al}_2\text{O}_3 - \text{Al}_2\text{O}_3$ can be precisely located by means of the thermoelement. The study of this system with the microscope shows seven phases in addition to the two components. The phases are $\text{CaO} \cdot \text{Al}_2\text{O}_3$, $5\text{CaO} \cdot 3\text{Al}_2\text{O}_3$, $3\text{CaO} \cdot \text{Al}_2\text{O}_3$ and an unstable form of both $3\text{CaO} \cdot 5\text{Al}_2\text{O}_3$ and $5\text{CaO} \cdot 3\text{Al}_2\text{O}_3$. The equilibrium diagram is shown in fig. 6.

FIG. 6.



The approximate melting temperature of lime is not known, except that it melts in the arc. The optical and other properties were given in the lime-silica paper to which reference has been made.

There is no eutectic between lime and the first compound, $3\text{CaO} \cdot \text{Al}_2\text{O}_3$, at 37.78 per cent of alumina. The compound being unstable at its melting point, the liquidus must show a

change of direction, but not a minimum. There is, however, an inversion temperature along the line L, where both CaO and $3\text{CaO} \cdot \text{Al}_2\text{O}_3$ separate at the temperature 1531° . For concentrations between L and B the lime which has crystallized combines to form $3\text{CaO} \cdot \text{Al}_2\text{O}_3$. Along the liquidus BC, $3\text{CaO} \cdot \text{Al}_2\text{O}_3$ is the stable phase. In practice, the time factor is a very important one in bringing about these reactions and some lime always becomes surrounded by crystals of the compound, so that the next phase, $5\text{CaO} \cdot 3\text{Al}_2\text{O}_3$, also occurs. This renders the eutectic observations along NC more irregular than they would otherwise be and, as the diagram shows, the eutectic, C, occurs as far over as M.

In order to prepare the pure compound $3\text{CaO} \cdot \text{Al}_2\text{O}_3$, it is necessary to bake the charge a long time at about 1400° . This allows diffusion to occur with the elimination of the excess of CaO and $3\text{CaO} \cdot 5\text{Al}_2\text{O}_3$. Experimentally, we found that the 37.78 per cent charge, held 21 days at 1400° , was free of the excess phases. Similarly, the compositions 35 per cent, 34 per cent and 32 per cent of Al_2O_3 , when merely fused and crystallized, without the long exposure, show $3\text{CaO} \cdot \text{Al}_2\text{O}_3$ with CaO and $5\text{CaO} \cdot 3\text{Al}_2\text{O}_3$, but were transformed into CaO and $3\text{CaO} \cdot \text{Al}_2\text{O}_3$ by heating at 1400° for the same length of time. In order to accelerate the reaction, we took the previously fused charges and ground them to a fine powder before starting the heat treatment. Such cases as this are not uncommon in silicate melts and the investigator must bear them constantly in mind or he will be led far astray.

The compound $3\text{CaO} \cdot \text{Al}_2\text{O}_3$ is isotropic, with density 3.038 for the annealed material. It is readily attacked by water, either hot or cold, and dissolves quickly in dilute hydrochloric acid.

The eutectic (C) between $3\text{CaO} \cdot \text{Al}_2\text{O}_3$ and $5\text{CaO} \cdot 3\text{Al}_2\text{O}_3$ at 52.22 per cent occurs at 51 per cent Al_2O_3 and melts at a temperature of 1382° .

The eutectic (E) between $5\text{CaO} \cdot 3\text{Al}_2\text{O}_3$ and $\text{CaO} \cdot \text{Al}_2\text{O}_3$ occurs at about 53 per cent Al_2O_3 and 1382°C .

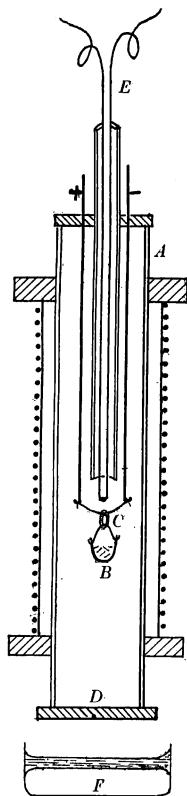
D is the maximum corresponding to the compound $5\text{CaO} \cdot 3\text{Al}_2\text{O}_3$ at 52.22 per cent Al_2O_3 , which melts at 1386°C . The maximum is so close to the eutectics, both in composition and temperature, that a precise determination is difficult. It is isotropic, has an index of refraction of about 1.61, and a density of 2.828.

This compound also occurs in an unstable form which is birefracting, but always changes into the isotropic form when given an opportunity to do so.

Between 40 per cent and 60 per cent Al_2O_3 a number of very small irregular heat effects were observed. It was

necessary to determine whether or not these changes were in any way related to the stable phases present in this region.

FIG. 7.



Quenching experiments made by removing the charge from the furnace and chilling in water were found to be too slow. Obviously, from a field like *E F O*, where we have the phase $\text{CaO} \cdot \text{Al}_2\text{O}_3$ in contact with the melt, great speed in cooling is necessary to prevent the whole mass from crystallizing in the presence of the excellent nuclei furnished by the solid phase. Therefore a special device was needed to secure more rapid cooling. The system adopted is shown in fig. 7. Passing through the furnace is a tube, *A*. Within this tube is placed the element, *E*. The charge is contained in a small platinum cup, *B*, suspended by a small porcelain ring from the fine platinum wire, *C*. This wire is attached to two heavy platinum leads marked + and —. The tube is closed at the bottom by the removable plug, *D*. *F* is a dish of mercury with a layer of water above it. In operation the charge is brought to the desired temperature and held for a suitable length of time. The plug *D* is removed and a strong current passed through the wire *C*. The current fuses the wire, dropping the charge into the vessel, *F*. The porcelain ring *C* prevents the wire of *B* from sticking to the suspending wire at *C*.

By this method we were able to quench samples of the partly melted charge, obtaining well-formed crystals of the primary phase imbedded in glass. In other words, we were able to bring the charge to room temperature rapidly enough to prevent its changing over. The results of this study are given below: *Time* is the time during which the charge was held at the temperature, *T*, before quenching; *IB*, traces of unstable form of $5\text{CaO} \cdot 3\text{Al}_2\text{O}_3$; || present; *tr*, trace.

	Time	T	Glass	CaO	$5\text{CaO} \cdot 3\text{Al}_2\text{O}_3$	IB	$3\text{CaO} \cdot \text{Al}_2\text{O}_3$
41% Al_2O_3	30 min.	1544°					
	"	1513°					--
	"	1487°				--	--
	60 "	1457°	--				
	30 "	1454°	--				
	60 "	1427°	--			--	h
	90 "	1394°	--			--	

	Time	T	Glass	3CaO . Al ₂ O ₃	IB	3CaO . Al ₂ O ₃
44% Al ₂ O ₃	30 min.	1544°			--	--
	"	1513°			--	--
	"	1484°			--	--
	"	1454°			--	--
	"	1425°			--	--
	60 "	1425°			--	--
	"	1394°	--		--	--
	"	1394°	--		--	
	Time	T	Glass	IB	3CaO . Al ₂ O ₃	5CaO . 3Al ₂ O ₃
42% Al ₂ O ₃	30 min.	1535°			--	--
	"	1535°		--	--	--
	"	1530°			--	--
	"	1527°			--	--
	"	1531°			--	--
	"	1520°				--
	"	1520°				--
	"	1520°				--
	"	1520°				--
	"	1506°				--
	"	1506°				--
	"	1508°				--
	"	1491°		--		--
	"	1484°		--		--
	"	1476°			--	--
	"	1458-52		--	--	--
	"	1439°			--	
	60 "	1443°		--		--
	"	1423°		--		--
	105 "	1419°		--		--
47% Al ₂ O ₃	60 "	1394°		--		--
	240 "	1513°	--	--		
	"	1503°		--		--
	"	1549°			--	--
	60 "	1513°		--	--	--
	30 "	1513°		--	--	--
	"	1484°		--	--	--
	"	1458°		--		tr
	"	1427°		--		--
	"	1394°	--	--		
50% Al ₂ O ₃	"	1549°		--	--	tr
	"	1513°		--	--	tr
	"	1484°		--	--	--
	50 "	1456°		--	--	--
	30 "	1427°		--	--	tr
	60 "	1394°	--	--		
	Time	T	Glass	IB	3CaO . Al ₂ O ₃	5CaO . 3Al ₂ O ₃
51% Al ₂ O ₃	60 min.	1404°	--	--		
	30 "	1409°		--		
	60 "	1420°		--	--	
	105 "	1430°		--	--	tr
	60 "	1439°		--	--	tr
	30 "	1454°		--	--	tr
	"	1484°		--	--	tr
	"	1513°		--	--	tr
	60 "	1513°		--	--	--
	"	1544°		--	--	--

	Time	T	Glass	IB	$3\text{CaO}.$		
					Al_2O_3	$5\text{CaO} \cdot 3\text{Al}_2\text{O}_3$	$\text{CaO} \cdot \text{Al}_2\text{O}_3$
52.22% Al_2O_3	30 min.	1565°		--	--	--	--
	"	1513°		--	--	--	--
	"	1484°		--	--	--	--
	"	1454°		--	--	--	--
	"	1424°		--	--		tr
	"	1394°		--	--		
53% Al_2O_3	"	1544°		--	--	--	--
	"	1513°		--	--	--	--
	"	1484°		--	--	--	--
	"	1454°		--	--	tr	--
	"	1427°		--	--		
	60 "	1431°		--	--		
	30 "	1385°	--	--	--		
55% Al_2O_3	"	1394°	--	--	--		
	"	1424°		--	--	--	
	"	1458°		--	--	--	
	"	1486°		--	--	--	--
	"	1513°		--	--	--	--
	"	1544°		--	--	--	--
	Time	T	Glass	IB	$5\text{CaO} \cdot 3\text{Al}_2\text{O}_3$		$\text{CaO} \cdot \text{Al}_2\text{O}_3$
57% Al_2O_3	30 min.	1394°	--	--			
	"	1428°		--			
	"	1454°		--			
	"	1484°		--			
	"	1513°		--			
	"	1544°		--	tr		tr
60% Al_2O_3	45 "	1544°			--		
	30 "	1513°			--		
	120 "	1513°			--		
	"	1513°		--	--		
	"	1454°		--	--		
	30 "	1424°		--			
	180 "	1424°	--	--			
	120 "	1394°	--	--			

Examination of this series of quenchings shows that the birefracting phase, which was found to be homogeneous at 52.22 per cent Al_2O_3 , is not present as a stable phase. It appears in small amounts (indicated by IB) in certain quenchings and not in others. It usually occurs in mixtures where a large charge is taken from the furnace and air-cooled. It appears in the same charge along with the stable phase, but disappears when the mass is baked at 1300°, passing into the stable form. The heat effects due to this unstable form occur irregularly both as to temperature and time of development. They are destroyed by holding the charge just below NO for a time before making the heating curve.

The spinel analogue $\text{CaO} \cdot \text{Al}_2\text{O}_3$ melts at 1587°. It has a density of 2.981. It is a birefracting crystalline substance,

attacked slowly by cold water and readily by hot. The densities of all of these aluminates were determined in dry turpentine at 25° and reduced to water at 25°=1. Hydrochloric acid dissolves all of these compounds.

The eutectic $\text{CaO} \cdot \text{Al}_2\text{O}_3 - 3\text{CaO} \cdot 5\text{Al}_2\text{O}_3$ is located at about 67·5 per cent Al_2O_3 . The liquidus falls but slightly from 65 per cent to 67·5 per cent, the temperature of the eutectic being 1580°.

At 75·22 per cent the preparation is homogeneous. The melting point, determined optically, is:

		Millivolts	T
Al_2O_3	75·22	{ .452	1710°
		.455	
CaO	24·78	{ .452	
		.452	

There is a second crystal form of the $3\text{CaO} \cdot 5\text{Al}_2\text{O}_3$ compound which shows different optical properties and a specific gravity of 3·05, determined by flotation. It seems probable that the relation of the two is monotropic, though the speed with which this higher form changes into the lower, together with the high temperature, makes quenching experiments unsatisfactory. Crystals of the low form usually show indications of having inverted during cooling, while preparations quenched from above line GP do not. GP is an inversion point, and as it extends to R, indicates that the 75·22 compound is unstable at its melting point. In the iridium furnace, the 75·2 per cent Al_2O_3 preparation seems to melt before the 76·5 per cent. This means either that the $3\text{CaO} \cdot 5\text{Al}_2\text{O}_3$ is unstable at its melting point or that the eutectic is so close to the maximum that the necessarily crude method will not determine it. The evidence indicates the former relation and we have adopted it. The 76·5 per cent Al_2O_3 shows free alumina, as do all preparations between this and 100 per cent Al_2O_3 .

TABLE II.—Invariant System $\text{CaO} + 3\text{CaO} \cdot \text{Al}_2\text{O}_3$. (Line S L B, Fig. 6)

Percentage of Al_2O_3	10	15	20	25	28	31·29	35	37·78	41	42	43
Eutectic melts....	1526°	1524°	1530°	1536°	1531°	1535°	1534°	1535°	1543°	1529°	1535°
	28	26	30	35	30	35	--	35	42	31	34
	28	26	29	36	31	35	33	34	35	31	35
	28	26	29	36	32	35	33	36	35	33	34
	28	26	29	36	32	35	34	33	35	33	34
	27	26	29	36	32	35	33	34	34	--	34
	--	--	--	--	33	38	33	33	--	--	35
	--	--	--	--	34	37	35	--	--	--	--
Mean.....	1528	1526	1529	1536	1532	1536	1534	1534	1537	1531	1534

TABLE III.—Eutectic $3\text{CaO} \cdot \text{Al}_2\text{O}_3 + 5\text{CaO} \cdot 3\text{Al}_2\text{O}_3$. (Line T N M)

Percentage Al_2O_3	51	50	49	48	47	46	45	44	43	42	41	37·78	35	31·29
Eutectic melts---	1383°	1383°	1386°	1386°	1383°	1387°	1385°	1384°	1387°	1384°	1377°	1377°	1374°	1380°
	83	84	80	83	85	85	81	83	86	86	84	77	75	84
	84	71	81	82	82	79	80	82	81	81	76	77	77	80
	83	83	81	74	84	80	81	78	--	--	--	75	--	--
	84	78	90	86	--	76	79	83	--	--	--	--	--	--
	84	81	84	81	--	78	83	79	--	--	--	--	--	--
	--	77	80	84	--	79	--	85	--	--	--	--	--	--
	--	78	--	--	--	76	--	83	--	--	--	--	--	--
	--	77	--	--	--	87	--	--	--	--	--	--	--	--
	--	78	--	--	--	89	--	--	--	--	--	--	--	--
	--	--	--	--	--	85	--	--	--	--	--	--	--	--
	--	--	--	--	--	88	--	--	--	--	--	--	--	--
Mean.....	1384	1379	1383	1382	1383	1382	1381	1382	1385	1384	1379	1377*	1375*	1381*

* Eutectic points occurring beyond 37·78 composition, due to failure to reach equilibrium.

TABLE IV.—Eutectic $\text{CaO} \cdot \text{Al}_2\text{O}_3 + 5\text{CaO} \cdot 3\text{Al}_2\text{O}_3$. (Line T O)

Percentage of Al_2O_3	60	59	57	56	55	54
Eutectic melts -----	1384°	1388°	1381°	1388°	1390°	1384°
	----	86	75	82	83	81
	----	83	78	81	80	82
	----	78	78	81	80	82
	----	83	84	81	78	86
	----	77	89	79	83	88
	----	--	79	88	89	80
	----	--	82	--	--	--
	----	--	78	--	--	--
	----	--	79	--	--	--
Mean.....	1384	1382	1380	1383	1383	1383

TABLE V.—Melting Points.

Percentage of Al_2O_3	60	57	50	46	45	44	43	42	41	37·78	31·29
Melts.....	1473°	1467°	1458°	1435°	1446°	1430°	1454°	1455°	1426°	1427°	1458°
	75	77	45	39	38	29	36	51	28	23	49
	63	62	53	39	24	28	34	51	21	59	--
	--	58	45	38	30	47	38	49	--	--	--
	--	--	--	39	24	47	36	--	--	--	--
	--	--	--	31	29	40	--	--	--	--	--
	--	--	--	23	27	--	--	--	--	--	--
	--	--	--	20	--	--	--	--	--	--	--
	--	--	--	20	--	--	--	--	--	--	--
	--	--	--	18	--	--	--	--	--	--	--
	--	--	--	16	--	--	--	--	--	--	--
Mean.....	1470	1466	1450	1429	1431	1437	1440	1452	1425	1436	1454

TABLE VI.—Curve of melting points. (Curve A, B, C, D, E, F, G, H)

Percentage of Al ₂ O ₃	75.22 *	67.5	64.58	60	59	57	56	55	54	53
Component in excess melts	1710° ----- ----- ----- ----- ----- ----- -----	1581° ----- ----- ----- ----- ----- ----- -----	1587° ----- ----- ----- ----- ----- ----- -----	1568° 66 66 64 68 65 68	1537° 48 50 48 48 49 49	1495° 1500 1499 98 -- -- --	1444° 54 50 50 48 47 47	1458° 63 -- -- -- -- -- --	1443° 35 37 33 34 38 40	1389° 85 87 86 82 -- -- --
Mean	1710	1581	1587	1566	1547	1498	1449	1461	1437	1386

Percentage of Al ₂ O ₃	52.22	51	49	48	47	46	45	44		
Component in excess melts	1387° 90 85 84 83 84 -- -- -- --	1388° 83 84 83 84 84 -- -- -- --	1429° 23 25 24 25 20 -- -- -- --	1435° 36 32 33 33 28 28 33 32	1440° 40 37 36 -- -- -- -- --	1480° 79 82 81 83 -- -- -- --	1495° 93 98 97 90 93 -- -- -- --	1525° 24 25 -- -- -- -- -- -- --		
Mean	1386	1384	1424	1432	1438	1481	1494	1525		

* Determination in iridium furnace with optical pyrometer.

TABLE VII.—Eutectic CaO.Al₂O₃ + 3CaO.5Al₂O₃. (Line G R)

Percentage Al ₂ O ₃	67.5	70	73.22	74.2	75.22	76.5
Eutectic melts	1581°	1582°	1582°	1578°	1577° 1579	1572° 1574 1574
Mean	1581°	1582°	1582°	1578°	1578°	1573°

The Al₂O₃ melts too high for safe determination in the iridium furnace. Apparently, some 3CaO.5Al₂O₃ crystallizes with the alumina since its optical properties are slightly changed, but we have been able to detect CaO.Al₂O₃ in the 95 per cent mixture, so that the range of this solid solution is less than five per cent.

Lime-Magnesia and Magnesia-Alumina.—While the melting temperatures of both of these series lie beyond our present

methods, we have made some preliminary fusions in order to ascertain whether or not compounds formed between them. It was necessary to use a furnace made of the purest artificial graphite, the cone being supported on a graphite block which did not form a part of the furnace resistance.

It was found that in all fused mixtures of CaO and MgO the two oxides crystallized out side by side, showing no evidences of combination, from which we conclude that there is no compound between the two. These temperatures are beyond the working range of the iridium furnace. Even with the purest graphite, small amounts of silica will get into the cones, giving a small amount of birefracting material which is identical in all determinable properties with Mg_2SiO_4 . This would seem to account for the birefracting material sometimes found when these oxides are fused in the arc. The amount of this birefracting substance was independent of the nominal composition.

The location of the eutectic was rendered uncertain because of the attack on the lime by the graphite.

Magnesia-Alumina.—This series, melted in graphite, gave one well-formed compound, $\text{MgO} \cdot \text{Al}_2\text{O}_3$, similar to the lime-alumina series. There was no other compound formed. Between 0 per cent and 71.6 per cent Al_2O_3 , the solid phases are MgO and $\text{MgO} \cdot \text{Al}_2\text{O}_3$. Between 71.6 per cent Al_2O_3 and 100 per cent Al_2O_3 , $\text{MgO} \cdot \text{Al}_2\text{O}_3$ and Al_2O_3 are the solid phases. The melting temperature of the $\text{MgO} - \text{MgO} \cdot \text{Al}_2\text{O}_3$ eutectic is at about 1950° .

These last two series are given only for the purpose of guidance in calculating the possible effect of small amounts of magnesia, which in commercial work are always present in the lime-alumina-silica mixtures. In time, some one may devise a furnace and containing vessel which will allow their more precise examination.

The results of the present thermal study may be summarized as follows:

1. There is but one compound (Al_2SiO_5) of alumina and silica stable in contact with the melt. This is the mineral sillimanite. The two minerals andalusite and cyanite pass slowly into sillimanite on being heated above 1300°C .
2. There are four definite compounds of lime with alumina, namely, $3\text{CaO} \cdot \text{Al}_2\text{O}_3$; $5\text{CaO} \cdot 3\text{Al}_2\text{O}_3$, melting point 1387°C .; $\text{CaO} \cdot \text{Al}_2\text{O}_3$, melting point 1587°C .; $3\text{CaO} \cdot 5\text{Al}_2\text{O}_3$.
3. $3\text{CaO} \cdot \text{Al}_2\text{O}_3$ and $3\text{CaO} \cdot 5\text{Al}_2\text{O}_3$ have no true melting point, but the former will be completely melted at about 1550° and the latter at about 1725°C .
4. Two of these compounds, $5\text{CaO} \cdot 3\text{Al}_2\text{O}_3$ and $3\text{CaO} \cdot 5\text{Al}_2\text{O}_3$, have an unstable form each, while $3\text{CaO} \cdot \text{Al}_2\text{O}_3$, and probably $3\text{CaO} \cdot 5\text{Al}_2\text{O}_3$, are unstable at the melting point, i. e., do not produce a maximum on the liquidus.

5. Of these aluminates it seems probable that only $3\text{CaO} \cdot \text{Al}_2\text{O}_3$ will occur in portland cement.

6. There is one compound, $\text{MgO} \cdot \text{Al}_2\text{O}_3$, between magnesia and alumina.

7. There is reason to believe that the system $\text{MgO}-\text{CaO}$ is a eutectic series with no compound and little if any solid solution. The temperature range is too high for satisfactory investigation.

Having established the nature of the binary systems, experimental study of the ternary system $\text{CaO}-\text{Al}_2\text{O}_3-\text{SiO}_2$ is now under way.

Optical Study ; by FRED. EUGENE WRIGHT.

In the foregoing pages the general problem of the lime-alumina series has been considered in detail, the different compounds in the series have been described and their stability relations at different temperatures discussed ; in brief, all data, chemical, thermal and optical, which bear on the problem, have been used, and the conclusions reached are based on the entire evidence at hand. In this treatment of the problem, its physico-chemical aspects have been especially emphasized because the established generalizations of physical chemistry best explain and define the limits in the relations of the combining minerals, and such data are of fundamental significance in the general study of rock and ore genesis. A restatement of the entire lime-alumina problem from the optical standpoint with the thermal and chemical data as confirmatory evidence, although possible, is, therefore, deemed unnecessary, and in the following pages only the detailed optical description of the different components of this series will be given, followed by a brief account of the character, significance and interrelation of the different kinds of experimental evidence which require to be brought to bear upon such problems of petrogenesis for their effective solution.

Calcium Oxide.—Crystals of this substance were not prepared especially for this investigation, since its optic properties have been described in detail in a former paper.* Free lime crystallizes readily in the isometric system, is isotropic and occurs in the different preparations of this series in the form of rounded grains. A remeasurement of the refractive index by the immersion method in a liquid consisting of methylene iodide, arsenic bromide and arsenic sulphide, was made, and the index found to be $1.832 \pm .005$. The high probable error is partly due to the lack of distinctness of the phenomena observed and to the slight attack of the lime by the solution itself.

* This Journal (4), xxii, 294, 1906.

The most interesting fact with respect to the lime which has come to light in the course of this investigation is the evident growth of the grains at temperatures above 1300° . Fine impalpable powder resulting from the calcination of calcite was heated for a week in the electric resistance furnace at 1300° – 1400° and found at the end of that time to consist of rounded grains of lime measuring as high as $.01$ – $.02^{\text{mm}}$ in diameter in place of the submicroscopic material which went into the furnace. This temperature is 1000° or more below the melting temperature of crystallized calcium oxide, and yet at ordinary atmospheric pressure and in the dry state crystals of calcium oxide grow rapidly at 1400° and resemble in all respects those formed out of melts of different compositions. This principle of causing crystal growth many degrees below the melting point and in the dry state is being applied constantly in this laboratory to render fine microscopic preparations suitable for optical examination. Experience thus far gained has shown that not all compounds grow with equal rapidity under these conditions, and in fact free alumina seems to be little affected by this treatment. The growth of calcium oxide crystals under these conditions is, however, definitely established, and is an important fact to be taken into consideration in connection with crystal formation and growth.

The $3\text{CaO} \cdot \text{Al}_2\text{O}_3$ compound: CaO 62.22, Al_2O_3 37.78.—Preparations of this composition have never been obtained perfectly homogeneous and free from grains of free lime and also of the lower refracting $3\text{CaO} \cdot 5\text{Al}_2\text{O}_3$ compound. The amounts of the latter, however, are not large and their presence has been shown to be due to dissociation. Optically this compound is simple in its properties. It crystallizes in the isometric system and exhibits no pronounced cleavage. Indications of cleavage after (111) or (110) were observed here and there, but only imperfectly developed. The fracture is conchoidal; the hardness is about 6. Although no separate crystals for goniometric measurement could be obtained, the frequent hexagonal and rectangular outlines of the grains in the thin section indicate the rhombic dodecahedron (110) or octahedron as the predominating form. The grains are colorless, of glassy luster, and isotropic, with refractive index $n_{\text{Na}} = 1.710 \pm .001$ measured on the Abbe total refractometer. Occasionally faint gray interference colors were observed on certain grains and were evidently due to strain. No definite arrangement of inclusions or zonal growth was noticeable, even on the largest grains, measuring 0.1^{mm} in diameter.

The $5\text{CaO} \cdot 3\text{Al}_2\text{O}_3$ compound: CaO 47.78, Al_2O_3 52.22.—Separate crystals of this compound were not obtained and no

distinct cleavage was observed, either in the crystalline powder or in the thin sections of the different crystallized melts. In the thin section, however, minute inclusions, apparently air cavities, are often arranged in systems of parallel lines intersecting at different angles and occasionally there appears a tendency to fracture along these lines, although it is not sufficiently pronounced to be called even poor cleavage. The sections are completely isotropic in all positions and the crystal system is therefore isometric. The melts are frequently colored especially in shades of yellow or brown, the color being probably due to contamination with platinum from the crucibles in which the melts were made. The luster is vitreous and the fracture conchoidal and often interrupted. The hardness is about 5. The refractive index, measured on the total refractometer, was found to be $n_{Na} = 1.608 \pm 0.002$. The refractive indices of crystals from preparations slightly different in composition from the $5CaO.3Al_2O_3$ compound were measured with the following results:

CaO 43, Al_2O_3 57	$n_{Na} = 1.61 \pm 0.003$
CaO 49, Al_2O_3 51	$n_{Na} = 1.611 \pm 0.003$
CaO 51, Al_2O_3 49	$n_{Na} = 1.611 \pm 0.003$

None of these measurements were good, and in view of the lack of homogeneity of preparations adjacent to the $5CaO.3Al_2O_3$ compound in chemical composition, it is evident that solid solution in this compound is not pronounced, but is, in fact, extremely limited if present at all.

The refractive index of the glass of the composition of this compound is about 1.662; it is interesting to note that in this compound crystallization means molecular rarefaction and not molecular condensation, which is usually the case.

The unstable $5CaO.3Al_2O_3$ compound: CaO 47.78, Al_2O_3 52.22.—The crystallographic development is much less favorable for optical examination than that of other members of the lime-alumina series. The very fact of its unstable character precludes crystal growth for a long period of time under any but very special conditions, and as a result the material available for investigation is finely crystalline and usually intricately intergrown, either as radial spherulites or in aggregates of overlapping and often roughly parallel fibers. The optic properties which can be obtained with such material are few and less accurate than those from well-developed crystals. The crystal habit is fibrous to prismatic; cleavage if present is parallel with fiber direction but not perfect. The luster is vitreous and the color usually green and due possibly to slight admixture of platinum from the crucible. The hardness is about 5. The refractive indices were measured by the immersion method and found to be $\alpha = 1.687 \pm 0.002$, $\gamma = 1.692 \pm 0.002$. The birefringence

is not strong and only rarely were interference colors as high as yellow red of the first order observed, and even then the color appeared slightly abnormal, due evidently to the effect of overlapping fibers. The optic axial angle is large and the optical character apparently negative, but not easy to determine satisfactorily because of the aggregate effect of superposed fibers. The plane of the optic axes is parallel with the elongation of the fibers. The fibers show parallel extinction with the ellipsoidal axis c parallel with the direction of elongation. Some of the more deeply colored grains are pleochroic with a =blue green, c =olive green. Absorption $a > c$.

These properties indicate that this compound is probably orthorhombic in crystal system. Compared with the other members of the series, its chief characteristics are the refractive indices about 1.69, weak birefringence and tendency to fibrous development.

Evidence of solid solution of other compounds in this form was looked for but was not decisive. In a preparation containing 50 per cent Al_2O_3 the unstable form was observed and there appeared to have slightly higher refractive indices, but the differences were only in the third decimal place and practically within the errors of observation.

The $CaO.Al_2O_3$ compound: CaO 35.44, Al_2O_3 64.56.—No single crystals of this compound were obtained and the determination of the crystal system rests entirely on the optical data. In one preparation of this composition from the iridium furnace elongated needles and prisms were observed, but on examination were found to be not single crystals but intricately twinned individuals with only indications of poorly developed crystal faces.

Twinning is a characteristic feature of this compound and is especially noticeable on sections nearly normal to the acute bisectrix. Such sections are intricately divided into a hexagonal meshwork of interlocking sextants which extinguish in different positions. On such sextants the plane of the optic axes was found to be usually normal to an edge. On plates cut at an angle with the acute bisectrix, polysynthetic twinning lamellæ were often observed and in aspect were not unlike plagioclase lamellæ. The general development of the material from the crystallized melts is prismatic with a tendency toward fibrous character. Cleavage is occasionally indicated and is then parallel with the direction of elongation and apparently prismatic or pinacoidal in character. The fibers extinguish often parallel with their elongation, the ellipsoidal axes a being then parallel with the long direction; but in many sections the extinction is not parallel with the prismatic axis and makes large angles with the same.

The crystalline aggregates are colorless and vitreous in luster. The hardness is about 6.5. The refractive indices α and γ were determined on the Abbe total refractometer, while β was measured by the immersion method. $\gamma=1.661\pm.002$; $\beta=1.654\pm.003$; $\alpha=1.641\pm.002$. The birefringence is fairly strong and interference colors of the first to third orders are common. The optic axial angle was measured by use of the double screw micrometer ocular on sections showing an optic axis in the field of vision. Owing to the frequent twinning some difficulty was experienced in finding suitable sections and the values obtained also varied slightly in consequence. Five fairly satisfactory measurements were made and the average value $2V=36^\circ\pm4^\circ$ obtained. Dispersion of the optic axes is very slight and ordinarily not noticeable. On one section the relations seemed to be $2V_\rho > 2V_\sigma$. Occasionally a section with apparently smaller $2V$ than usual was observed, almost uniaxial, but this was possibly due to the effect of overlapping twinning.

These data indicate that the crystal system of the compound $\text{CaO}.\text{Al}_2\text{O}_3$ is either monoclinic or triclinic and probably the former. Unfortunately, no well-developed crystals were obtainable and a more definite statement in regard to the symmetry relations is not possible.

The $3\text{CaO}.5\text{Al}_2\text{O}_3$ compound: $\text{CaO } 24.78$, $\text{Al}_2\text{O}_3 75.22$.—No separate crystals of this compound were obtained and the evidence as to its crystal system, whether tetragonal or hexagonal, is not satisfactory. The grains are rounded and range from .02 to .05^{mm} in diameter. Basal sections are usually without definite outline, though occasionally there is a tendency toward quadratic outline, and it is possible that the crystal system is tetragonal. No distinct indications of cleavage were observed. Rarely rhomb-shaped to square grains were noted which extinguish parallel with the diagonals and may indicate poor pyramidal cleavage, or if hexagonal, rhombohedral cleavage, but such grains were rare, and if cleavage be present it is imperfect. The luster is vitreous and the hardness about 6.5. The refractive indices were determined by the immersion method: $\omega=1.617\pm.002$; $\epsilon=1.651\pm.002$. On a section parallel with principal axis the birefringence was measured roughly under the microscope and the value $\gamma-\alpha=.032$ obtained. The birefringence is, therefore, fairly strong and the interference colors, even in minute grains, are of the first and second orders. In convergent polarized light a normal uniaxial, optically positive interference figure was observed on basal sections. The interference cross is well marked and on thicker sections the inner edge of the first colored interference ring is visible on the margin of the microscope field. In

some of the sections a slight opening of the interference cross was observed as though the substance were biaxial with small $2E$, but so many of the sections were perfectly uniaxial that there is little doubt of the uniaxial character of the substance. This compound is readily distinguished from the $\text{CaO} \cdot \text{Al}_2\text{O}_3$ compound by its interference figure, optical character and constant refractive index, $\omega = 1.617$. On practically every basal section thin threadlike inclusions of a higher refracting, weakly birefracting to isotropic substance, were observed and although small in actual quantity they are nevertheless present and may be free Al_2O_3 or the unstable $3\text{CaO} \cdot 5\text{Al}_2\text{O}_3$ compound. They are too fine for satisfactory identification by optical methods.

In several of the preparations the crystallographic habit of the compound was entirely different from the small granular type. The individuals were elongated, lath-shaped and intricately intergrown and resembled in aspect $\gamma\text{Ca}_2\text{SiO}_4$ after inversion from the β -form.* The optic properties, refractive indices, birefringence, uniaxial optical character, proved to be identical with the normal $3\text{CaO} \cdot 5\text{Al}_2\text{O}_3$ compound and the peculiar appearance is due in fact to inversion from a high unstable form, just as in the case of calcium orthosilicate.

The unstable $3\text{CaO} \cdot 5\text{Al}_2\text{O}_3$ compound: $\text{CaO } 24.78, \text{Al}_2\text{O}_3 75.22$.—This compound was obtained only after considerable experimentation with preparations in the iridium furnace. Its presence was surmised first from the difference in crystallographic habit of different preparations of the optically positive form of this composition. In no case was it obtained in pure state but invariably showed more or less alteration to the optically positive form, and could not therefore be used for density determinations.

No crystals of this phase were obtained and the determination of its crystal system rests entirely on the optical evidence. The crystalline melts are colorless and often porcelain-like in appearance. Here and there minute cleavage faces of lath-shaped individuals glisten in strong light. On the whole, the melts were well crystallized, some of the grains under the microscope measuring as much as $.5^{\text{mm}}$ in length. The crystals are usually prismatic in habit and show under the microscope fairly well-marked prismatic cleavage. Their luster is vitreous and hardness about 5.5 to 6. The refractive indices were measured by the immersion method $\gamma = 1.674 \pm .002$, $\beta = 1.671 \pm .002$; $\alpha = 1.662 \pm .002$. A direct determination of the birefringence was made and $\gamma - \alpha$ found to be approximately .013. The interference colors in ordinary powder sections rarely exceed the second order blue and are usually gray to

* This Journal (4), xxii, 296, 1906.

yellow of the first order. The optic axial angle was measured by the double screw micrometer ocular $2V = 35^\circ \pm 5^\circ$. This value is the average of seven different measurements and part of the large probable error is due to the strong axial dispersion, which is pronounced with $2V_\rho > 2V_v$. The attempt was made to determine the angular amount of this dispersion, but the axial figures observed were not sharp enough for precise work and only the general statement can be made that $2V_\rho$ is several degrees larger at least than $2E_v$. The optical character is negative. The grains extinguish parallel with the prismatic cleavage. The ellipsoidal axis a , and with it the plane of the optic axis, is parallel with the direction of prismatic elongation of the crystals.

The alteration to the optically positive form is clearly marked in the powder. It proceeds from the surface of the grains and works toward the center along the cleavage cracks and occasional transverse cracks, so that as it proceeds the original substance is replaced by a fine meshwork of the optically positive form. The alteration is accompanied by a slight expansion in volume, about 2 per cent judging from the refractive indices, and this in turn tends to facilitate further change by producing further cleavage cracks and causing the crystal to break down entirely. The resulting product of change resembles γ -orthosilicate in appearance and this fact suggested the existence of this probably unstable phase of the $3\text{CaO} \cdot 5\text{Al}_2\text{O}_3$ compound.

The above optical data indicate that this compound is in all probability orthorhombic in symmetry. Its chief characteristics are refractive indices about 1.67, medium birefringence, small negative optic axial angle with strong axial dispersion, the plane of the optic axes and the ellipsoidal axis a lying parallel with the prismatic cleavage direction of elongation.

Aluminum oxide: Artificial corundum.—This substance melts at an exceedingly high temperature, and in the present series of experiments no special attempt was made to procure measurable crystals. The optic properties were determined on a fine-grained preparation prepared by heating fine impalpable precipitated alumina in the iridium furnace to about 2100° . The crystal grains thus formed are less than $.05^{\text{mm}}$ in diameter and of rounded outline. No definite crystal outlines nor cleavage cracks were observed. Air cavities and minute bubbles are characteristic and abundant. The hardness is 9. The refractive indices were determined by the immersion method, $\omega = 1.768 \pm .003$, $\epsilon = 1.760 \pm .003$. The birefringence was found to be roughly .009 on a small section parallel with the principal axis.

In convergent light a faint optically negative, uniaxial interference figure was observed. In short, the optical characteristics of artificial corundum were, so far as determined, practically identical with those of the natural mineral.

Silicium oxide.—In the paper on the lime-silica series,* the thermal and optical behavior of silica at high temperatures was described. Recent work on the silica problem, at low temperatures, has shown it to be much more complicated than was at first supposed. In fact several phases have now been found to occur in that region which were not disclosed by the first investigation. The problem as a whole is not simple and has not yet been satisfactorily solved, so that in the following paragraphs only a report of progress can be made. Apparently six distinct phases occur: α -quartz, β -quartz, α -tridymite, β -tridymite, α -cristobalite, and β -cristobalite. These will be considered in the order named.

α -quartz, or simply quartz, is the ordinary quartz of mineralogists, and requires no further mention. On heating to 575° it passes into β -quartz, which is also hexagonal but trapezohedral-hemihedral in its symmetry relations and in other respects slightly different from α -quartz. The change at 575° is reversible and is exceedingly sensitive to minute temperature variations, a rise or fall of $1/10^{\circ}$ at the inversion temperature being sufficient to cause the inversion. These relations have been described in detail and the literature references given in a recent paper in this Journal. †

Tridymite (α -tridymite) occurs in nature in flakes of hexagonal outline. It has been made artificially by several different methods but in practically every case in the presence of a flux. ‡ At ordinary temperatures tridymite is intricately twinned, biaxial and apparently orthorhombic in symmetry (pseudo-hexagonal). On heating, the crystals become uniaxial at about 130° , § and the complicated twinning disappears; the expansion coefficient also changes abruptly at this temperature. || On cooling the reverse process takes place slowly and the change is therefore enantiotropic. This inversion of α - to β -tridymite occurs without evidence of great strain or fracturing of the crystals and it is probable that the specific volumes of the two phases are nearly equal. The fact that natural tridymite crystals are hexagonal with respect to outline and orthorhombic in optic properties, while at 130° they invert to a truly hexagonal substance, indicates that in all probability such hexagonal plates

* Day, Shepherd and Wright, loc. cit.

† Quartz as a Geologic Thermometer, this Journal (4), xxvii, 421-447, 1909.

‡ Literature references cited in Hintze, Mineralogie I, 1459-1462.

§ Mallard, Bull. Soc. Min., xiii, 169, 1890.

|| Le Chatelier, Compt. Rendus, cxi, 123, 1890.

were actually formed above 130° .—At ordinary temperatures tridymite, having inverted in the solid state, is intricately twinned and intergrown, and its optical examination is not as a rule satisfactory, especially on artificial crystals. The birefringence is weak and the average refractive index about 1.477.*

Crystal aggregates formed out of pure melts of SiO_2 or from SiO_2 glass or by inversion of quartz heated to a high temperature, show the above properties except that the refractive index is slightly higher, about $1.484 \pm .003$ instead of 1.477. In the description of the tridymite from the lime-silica series, the writer noted this higher refractive index but was unable to account for it. Through the courtesy of Professor Lacroix of Paris, however, to whom specimens of the artificial crystals had been sent, this difference can now be explained. Professor Lacroix, after examination of the material, pronounced it to be in all probability cristobalite, and not tridymite, and subsequent examinations here have confirmed Professor Lacroix's determinations. Cristobalite has been found in nature only rarely, and then usually together with tridymite. Its crystals are octahedral in habit, but, like tridymite, are intricately twinned and very weakly birefracting, so that the optical examination is not satisfactory. Its refractive index is slightly higher than that of tridymite, about 1.49.† The optical behavior of cristobalite was first studied by Mallard,‡ who found that at about 175° the crystals became abruptly isotropic, and remain so at higher temperatures. On cooling the reverse process takes place, β -cristobalite changing back to the α form abruptly, the minute birefracting patches flashing up throughout the entire slide as the inversion temperature is reached. The volume change on this inversion is apparently very slight. The fact that this change is reversible and that natural crystals of cristobalite are octahedral in habit indicates that they were in all probability formed above 175° , the inversion temperature.

In the irregular crystalline aggregates obtained in laboratory preparations, tridymite and cristobalite can best be distinguished by heating in the thermal microscope. At about 130° tridymite becomes uniaxial and remains so at higher temperatures, while in cristobalite no change occurs until about 175° , when the interference colors disappear completely, the material becoming isotropic and remaining so at higher temperatures. The refractive index of tridymite (1.477) is slightly lower than that of cristobalite (about 1.484), but the difference is not great, and ordinarily would not, perhaps, be relied on to distinguish the two in very fine powder.

* Mallard, Bull. Soc. Min., xiii, 169, 1890.

† Gaubert, Bull. Soc. Min., xxvii, 244, 1904.

‡ Bull. Soc. Min., xiii, 175, 1890.

On heating crystal aggregates obtained from the SiO_2 melts, also from SiO_2 glass and from inverted quartz powder, it was observed that at about 175° , or slightly higher, they become isotropic and remained so at still higher temperatures. This behavior proved them to be cristobalite and not tridymite, as had been heretofore supposed.

Several preliminary tests of the heat change involved in this immersion have been made and found to be clearly marked. The investigation of the stability relations between the crystal quartz, tridymite and cristobalite has not yet been completed, and need not therefore be discussed at this point.

Al_2SiO_5 : *Sillimanite*; Al_2O_3 62.85 per cent, SiO_2 37.15 per cent.—This compound crystallizes from the melt with great rapidity on cooling, and as a result the preparations available for the optical work are in general too fine-grained for accurate determination. The crystallites are fibrous and lath-shaped in habit, and, like the natural mineral sillimanite, are often in close parallel groups. The optical effect is, therefore, usually that of an aggregate rather than of a single individual. End views of the fiber bundles show that each lath is prismatic in shape with a prism angle of approximately 90° . In the center of nearly every section a minute inclusion is present, often in the shape of a cross, the arms of which are parallel with the sides. In this respect the sections resemble in a way the chialtolite variety of andalusite. The end sections are weakly birefracting and extinguish parallel with the diagonals. The refractive indices, which were measured by the immersion method, are noticeably lower than those of pure natural sillimanite, a fact for which no explanation has yet been found. $\alpha=1.638\pm.003$; $\beta=1.642\pm.003$; $\gamma=1.653\pm.003$. Direct measurements of the birefringence were made and averaged roughly $\gamma-\alpha$ about .014, but they were not satisfactory owing to the fibrous character of the material and consequent lack of transparency for good thickness measurements. For the same reason the optic axial angle could not be measured satisfactorily. Judging by its general appearance, $2E$ lies between about 40° and 75° , but unfortunately it was not possible to obtain a more definite value with the material at hand. The optical character is positive, and the acute bisectrix c lies in the direction of elongation of the fibers. On one preparation of the composition Al_2O_3 60, SiO_2 40, the crystallization was somewhat coarser, and there the optical axial angle was measured with the double screw micrometer ocular and the value $2V=45^\circ\pm 4^\circ$ obtained. Dispersion of the optic axes was not observed, and if present is slight. In this preparation well-marked pinacoidal cleavage was also observed parallel with the plane of the optic axes. The same cleavage is characteristic of natural sillimanite.

In every preparation of sillimanite examined, there was present between the sillimanite fibers an isotropic substance of much lower refractive index, about 1.530. This same substance appears in other preparations of the alumina-silica series, and is probably glass, since its refractive index n , about 1.525–1.530, agrees with that of sillimanite glass obtained by extremely rapid quenching of the melt from the iridium furnace. Sillimanite crystallizes with great rapidity, but its melting point is high and probably in the iridium furnace preparations, where comparatively rapid cooling goes on throughout the region of rapid crystallization for this silicate, not enough time was given for the entire melt to crystallize out, and small threads of glass are included between the crystallized fibers and laths. If the refractive indices be used as a criterion, crystallization in sillimanite means high molecular condensation, and, as a result, numerous air spaces and cavities appear in the crystallized mass.

The presence of glass and minute elongated air cavities tended to render the optical tests for homogeneity in preparations adjacent to the pure compound uncertain. No free corundum was observed in the preparation SiO_2 35, Al_2O_3 65, but it was readily detected in the preparation SiO_2 30, Al_2O_3 70. So far as the optical evidence goes, solid solution of Al_2O_3 in Al_2SiO_5 may extend to the composition SiO_2 35, Al_2O_3 65, but not to SiO_2 30, Al_2O_3 70. The refractive indices of the sillimanite fibers in the preparation SiO_2 35, Al_2O_3 65, were practically identical with those of the pure compound, but measurements of a high degree of accuracy were not possible, because of the character of the material.

Magnesium Oxide: Artificial periclase.—Preparations of this oxide were made both by crystallizing the pure melt in the electric arc and also from fluxes of magnesium chloride and silica. The crystals from the latter were well developed and octahedral in habit with occasional small cube faces. From the melt they occur as rounded grains often irregular in shape and without polyhedral outline in aggregated clusters and masses. Cubic cleavage is well marked even on the grains and was produced directly on the octahedral crystals. Octahedral cleavage if present is not distinct. The crystals and grains are colorless and perfectly isotropic with refractive index $1.734 \pm .002$, determined by immersion method. The hardness is about 6, apparently slightly above 6, since the grains appeared to scratch adularia very slightly. Solid solution in periclase is not great if it occurs at all. In a preparation MgO 90, CaO 10, free lime was present in the usual rounded grains, while the refractive index of the periclase was practically unchanged.

MgO.Al₂O₃: Artificial spinel, MgO 38.32, Al₂O₃ 71.68.—Crystals of this compound were obtained by direct crystallization from the pure melt in the electric arc furnace. The resulting crystals were minute but sharply developed octahedrons, clear and transparent, colorless and splendid in luster. In the aggregate they occur frequently with approximately parallel orientation in rows and clusters, not unlike skeleton salt crystals in appearance.—Evidence of twinning after the usual spinel law was sought for but without decisive results, chiefly because of the fineness of the material. Cleavage if present is imperfect and not well marked in the powdered material. The hardness is about 8. The refractive index, $n = 1.723 \pm .002$ (determined by immersion method), is slightly higher than that of spinel ordinarily, although spinels of even higher refractive index have been observed. Under the microscope the grains and crystals are isotropic and without abnormal interference phenomena.

Evidence of slight solid solution, both with alumina and magnesia, was indicated by the slightly lower refractive index of the spinel crystals from preparations adjacent to the true compound in composition (Al₂O₃ 75, MgO 25 and Al₂O₃ 60, MgO 40). Satisfactory tests for homogeneity of adjacent preparations were, however, not possible because of the presence of small quantities of a birefracting substance of refractive index about 1.66 and medium birefringence, but too fine for definite identification. This substance occurred in different members of the alumina-magnesia series and together with both periclase and spinel, and is therefore possibly due to impurity from the carbon in which the preparations were melted.

Solid solution over a long range in the above series does not exist. This is evident not only from the thermal work but also from the optical tests for homogeneity and the determination of the optical constants especially of refractive indices of the components of preparations intermediate in composition between the compounds. The refractive indices of the compound 5CaO.3Al₂O₃ appear slightly higher in preparations on either side of the true compound, and this might be taken to indicate very limited solid solution, but the observed differences are practically within the limit of possible observational error, and too much stress cannot be placed on the evidence. The same holds true for the optically positive compound 3CaO.5Al₂O₃, and also the optically negative form of the same composition, for which the refractive index γ appeared very slightly lower in the preparation CaO 25.78, Al₂O₃ 74.22, than in the true compound, but the difference was within the possible error limit and the evidence is not definite. The

optically positive uniaxial $3\text{CaO} \cdot 5\text{Al}_2\text{O}_3$ compound appears noticeably biaxial in certain sections, and this may have been due to solid solution, but if so the extent of solid solution is not great. The unstable $5\text{CaO} \cdot 3\text{Al}_2\text{O}_3$ compound and also the $\text{CaO} \cdot \text{Al}_2\text{O}_3$ compound showed slight variations in the optic axial angle which might be ascribed to the effects of solid solution, but in such instances the quality of the material was not favorable for decisive optical tests. Evidence of slight solid solution of MgO and also Al_2O_3 in spinel was indicated by refractive index determinations on preparations adjacent to spinel in composition.— CaO may also take up small amounts of MgO in solid solution, so far as could be ascertained by the microscopic examination.

The geologic significance of these binary series.—In the preceding pages the optic properties of the several different compounds of the different series have been cited in detail and this evidence, in turn, has been used in general presentation of this problem in the first part of this paper. The bearing of such data, however, on geologic work has not been mentioned, and it may be of interest to outline in a few paragraphs the particular kinds and scope of evidence which the different methods, chemical, physical and optical, furnish in a problem like the present one, which in turn is only a detail of still larger problems whose ultimate solution will be of fundamental importance in the consideration of questions of rock and ore genesis and allied phases of geologic inquiry.

In the general attack upon complex problems of this nature, experience has shown that exact and definite data along three distinct lines of evidence, chemical, thermal, and optical, are necessary and usually adequate for their satisfactory solution. No one of these three lines is of itself sufficient for the complete solution of the problem, nor yet are they entirely independent of each other. Although supplementary to a certain extent, they overlap in their spheres of application, so that the results obtained by one method can be and usually are confirmed by those of a second, thus strengthening the foundation of fact on which subsequent reasoning is based.—By careful chemical work the purity of the preparations is insured; by thermal measurements the relative energy content of the different preparations at different temperatures is investigated; while by optical methods the number of compounds in a given preparation is determined (mineral composition), their optical constants ascertained and their special relation to each other recognized (texture).—To present more clearly the scope of these three fundamental lines of evidence which are essential for the solution of problems of this type, it will be well to

consider each separately first, and then to indicate briefly wherein they overlap and are mutually confirmatory.

Chemical data.—Modern research has shown that as a rule rock minerals are not single, simple compounds but complex mix-crystals containing various other mineral compounds in solid solution. The investigation of such minerals and their relations in rocks can only be satisfactorily carried on, therefore, after the characteristics of the simple compounds have been ascertained, as well as the extent and the effect of the by-mixture. In the general investigation of problems of such wide scope it is necessary to begin with the simplest conditions, and after these have been thoroughly mastered, to work up to the more complex. From a physico-chemical standpoint, rocks are as a rule complex systems, too complex in fact to be treated satisfactorily until the simple integral systems of which they are made up have been studied in detail. The present lime-alumina series is only one of a number of two-component systems which mark the limits of larger three-component systems, and these in turn lead to still larger systems. Such systems eventually become exceedingly complex, and the only hope the observer has of mastering them is to begin with the simplest cases first and then with the experience thus gained to proceed step by step to the more complex. The simplest systems are the two-component systems, as the lime-alumina series, and the chief function of the chemical work is to make up preparations of definite composition and to guarantee their purity throughout the investigation. Natural rock minerals are almost never rigidly pure, in the sense of definite and invariable chemical composition, and yet their investigation from the standpoint of laboratory synthesis requires that at first only chemically pure preparations of definite composition be taken, and the properties of these determined accurately; later the actual minerals can be reproduced artificially and the effect of solid solution of different substances in different proportions can be studied and definite information obtained. Impurities in solid solution tend only to veil the true relations of the compound itself, and for the observer to allow such a variable factor as impurity into the investigation at the very outset would operate not only to increase the difficulties but also to decrease the clean-cut aspect of the problem and the laws underlying it.

Other data which are of a physico-chemical nature, such as questions of relative solubility, concentration and the like, may properly be considered in a later paragraph.

Thermal data.—The object of experimentation along these lines is not only to reproduce rock-making minerals artificially, but especially to study the conditions of their formation and the

temperature and pressure ranges over which they are stable. From such data general laws of equilibrium can be deduced and tested and then applied directly to the rocks themselves, which in effect are the end-products of physico-chemical systems. In the case of igneous and metamorphic rocks we have to deal with chemical systems that have been subjected to certain physical conditions which, in turn, have left their imprint or seal on the end-product or rock now accessible to the geologist. It is the task of the geologist to decipher this seal as he finds it expressed in terms of mineral composition and texture, and from it to infer the conditions of original formation. The actual processes of formation have not been and in general cannot be witnessed by him, and he must base his conclusions on the existing evidence, weighed in the light of his own experience. Such evidence is in part geologic, but in no small degree experimental, and the more evidence of an experimental nature there is at hand, the more confident is he of his conclusions. Exact thermal data especially are lacking, but are of fundamental significance, since they indicate limits at which the energy content of the system changes abruptly; any change of this kind, such as the melting and inversion temperatures of compounds, or eutectic temperatures of mixtures, is most important, since it is the outward expression of a shift of the equilibrium of the system, as a result of which profound changes may occur. What before was stable may become unstable, and vice versa; a rearrangement of forces accompanies the change in energy content and new stability relations are at once established.

Under normal conditions, therefore, thermal measurements are adapted to indicate the relative energy content of any preparation at different temperatures. But by so doing they indicate the presence of different compounds in a series and establish temperature ranges over which these compounds and mixtures of the same are stable.

Optical data.—The microscopic examination of the preparations, at ordinary room temperatures and after the changes have taken place, does not of itself directly prove an energy change in the system. In the thermal microscope such changes can be followed in their effect on the optical properties (melting down of crystal plates, abrupt changes in birefringence, optic axial angle, and the like), but such evidence is used ordinarily only to confirm the purely thermal data. The purpose of the microscopic investigation is primarily to determine the compounds present in any preparation (composition, with special reference to homogeneity and crystallization), to study the relation of the different components to each other (texture) and to establish by measurement the degree of departure of

natural minerals with their varying admixtures, from the chemically pure ultimate types. By the microscopic examination of preparations of different composition in a given series, the number of compounds in the series can be ascertained, the different phases in which any given compound appears, and also the extent to which any particular compound takes up an adjacent compound in solid solution. The exact determination of the optic constants of the different members of the series furnishes, moreover, data which permit any one of them to be recognized, even in the presence of others. From a textural standpoint, the formation of eutectics should give rise to special textures, and in some instances it has been observed to do so, but as a rule crystallization in silicates at high temperatures does not proceed with sufficient regularity to produce clearly defined textures, and in most instances differences between the crystals first to form (phenocrysts) and the portions last to crystallize out (groundmass, entectic), are not well marked and the attention of the observer is directed chiefly to the crystal development of the individual crystals themselves. This condition, together with the fact that the preparations are usually examined in the powder form, tends greatly to reduce the value and usefulness of textural evidence in the microscopic investigation of such preparations.

The optic properties which are made use of in the microscopic examination of artificial products are the usual ones employed in mineral determinations in rock sections, and would require no comment at this point were it not for the fact that artificial preparations are usually much finer-grained than rock sections, and that in addition it is necessary to know the degree of accuracy of all measurements on such products. This has led the writer to make practical tests of available microscopic methods to establish their accuracy and adaptability to the new conditions found in artificial melts. In the course of the general investigation, several new methods were devised with special reference to the new requirements and have proved satisfactory. At the present time, the following methods and optic properties have been found most serviceable in the study of artificial preparations.

(1) *Refractive indices*.—In powder preparations the refractive indices are most readily determined by the immersion method (Schroeder van der Kolk)* in refractive liquids of known refractive index. On favorable clear grains the refractive indices can be determined by this method on grains measuring even less than $\cdot 01^{\text{mm}}$ in diameter and with a prob-

* J. L. C. Schroeder van der Kolk, *Zeitschr. f. wiss. Mikrosk.*, viii, 458, 1898; also F. E. Wright, *T. M. P. M.*, xx, 239, 1900; this *Journal* (4), xxii, 385, 1904; xxvii, 35, 1909.

able error of about $\pm .002$. The Becke line method can also often be used to advantage with refractive liquids. The refractive index of the liquids or mixtures of liquids used is determined on the total refractometer.

(2) *Birefringence*.—In this measurement the thickness of the plate is measured with the fine adjustment screw of the microscope by focusing a high power objective first on the upper surface of the plate or grain and then on the lower surface as it appears through the plate or grain itself. The apparent thickness thus obtained is then reduced to the true thickness by multiplying by the refractive index of the substance measured. The interference color is determined either with the Babinet compensator, the calibrated quartz wedge or the Michel-Lévy interference-color chart. This is only an approximate method, and the results may be in error 10 per cent or more, but usually the percentage error is less and the numerical error is confined to the third decimal place.

(3) *Optic axial angles* are measured most readily in the powder section by means of the double screw micrometer ocular.* On favorable sections ($.025^{\text{mm}}$ and over in diameter), the probable error of such measurements is about $\pm 1^\circ$ in case both optic axes appear in the field of vision, and $\pm 3^\circ$ in case only one optic axis is seen. For such measurements the grains should be immersed in a liquid of the refractive index β to eliminate errors caused by refraction on the uneven surfaces of the grains. In weakly birefracting substances and interrupted sections the axial bars are less sharply defined and the axial angle values obtained thereon are correspondingly less accurate.

(4) *Extinction angle*.—By use of the bi-quartz wedge plate† the position of total extinction can be determined on a single trial within $\pm 10'$ on favorable sections. The extinction angle itself is the angle between a given crystallographic direction and a particular optical direction on a particular crystal face, and the accuracy with which it can be determined depends in part on the quality of the crystallographic development of the crystallite itself. Under favorable conditions of crystallographic development, extinction angles can be determined within $10'$ and less, dependent on the number of readings taken, on crystals measuring only $.02$ – $.03^{\text{mm}}$ in length.

(5) Color, pleochroism and absorption can usually be determined on grains measuring $.02^{\text{mm}}$ and over, and in certain instances on still smaller particles.

(6) Other properties, such as *dispersion* of the optic axes and bisectrices, and the general correlation of optic and crystallographic properties, can occasionally be accomplished on

* This Journal (4), xxiv, 317–369, 1907.

† Ibid. (4), xxvi, 349–390, 1908.

isolated grains $\cdot 02\text{--}\cdot 03^{\text{mm}}$ in diameter, although for ease of manipulation and general accuracy larger grains and sections are preferable. It may be stated as a general rule that most of the optic properties can be determined with sufficient accuracy on grains measuring $\cdot 02\text{--}\cdot 05^{\text{mm}}$ in diameter, and certain optical properties on still smaller particles.

The great advantage of examining a preparation in powder form rather than in the thin section is two-fold: (1) by the use of refractive liquids, the refractive indices can be determined at once and traces of inhomogeneity in a compound appear most clearly if it be immersed in a liquid of the same refractive index; (2) the individual grains in the powder are isolated and can be rolled about in the liquid and examined along different directions if necessary. These two conditions are difficult to obtain in the thin section. The chief disadvantage of the examination of preparations in the powder form is the loss of texture. In the thin section, the texture or relation of the different crystallites to each other is much more clearly marked than in the haphazard particles of a powder preparation.

As a general rule, the morphologic development of crystallites from artificial melts is poor and crystals suitable for goniometric measurement are very rarely obtained. The crystal system of any compound has to be inferred, therefore, from the optic and crystallographic properties obtained by the microscopic investigation alone.

Briefly summarized, the optical investigation is adapted primarily to ascertain the mineral composition of the preparations of any given series, while the thermal work serves chiefly to establish the stability ranges of these compounds, both alone and in the aggregate, at different temperatures throughout the series. Other evidence—specific gravity determinations, crystallographic features, chemical behavior, etc.—tends further to supplement and to substantiate the thermal and optical data.

Evidence of this nature is in part chemical and part physical, and properly falls in the domain of physical chemistry, for its interpretation—wherefore the extreme importance of this science in the study of rock and ore formation.

Geologic data.—In the study of rocks their microscopic examination and bulk chemical analysis have heretofore received the most attention, and in fact petrography, which has primarily to do with rock description and classification, is a result of this study. The general science of rocks, however, demands not only rock description and classification, but also inquires into their formation and genesis, and this fact postulates thermal evidence. In the petrologic treatment of rocks, exact thermal evidence is just as essential as precise optical

and chemical data, and this can only be supplied by experiment, since the amount of exact field evidence along these lines which has been obtained up to the present time is exceedingly slight.

A rock has been defined as a geologically independent part of the earth's lithosphere. It owes its position to the action of certain geologic forces and stands in causal relation to these. These forces are in part physical and crystallographic and in part chemical, and the rock as it appears to the geologist is the resultant end-product of a certain chemical system acted upon by the geologic forces; such forces, however, have not always remained the same throughout the history of any given rock, but have changed from time to time, either slowly or abruptly, and each change has brought with it new conditions of equilibrium in the crystallized mass, and possible consequent readjustment of mineral composition and texture. Such readjustment in texture and composition, however, is rarely complete, and the imprints or scars of each period of geologic activity are often clearly marked in the rock and to the trained eye serve to indicate its past history. The geologist has to rely chiefly on field evidence in his interpretation of the history of the earth, but such evidence is in large measure qualitative and does not of itself yield exact data along certain lines, particularly with reference to rock genesis and the actual character of subsequent transformations. This evidence is best obtained by direct experiment, by studying the crystallization of definite chemical systems under definite and determinable conditions of pressure and temperature. The difficulties of complicated texture and composition will undoubtedly be much diminished when the simpler chemical systems have been experimented upon and their behavior under different conditions studied. The technical difficulties in such problems are formidable, but once overcome in the simpler systems, they are mastered for all.

Geophysical Laboratory,
Carnegie Institution of Washington,
Washington, D. C., June, 1909.