

ART. XXXIV.—*The Stability Relations of the Silica Minerals*; by CLARENCE N. FENNER.

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INTRODUCTION.

MUCH work has been done at various times on the relations between the different forms of silica which are found as natural minerals, and the literature of the subject is extensive. A portion of what has been written has been based upon laboratory experiments, a portion upon observation of natural occurrences, and still a third portion upon theoretical considerations. Each method of attack, when properly applied, is a legitimate means of attempting to arrive at a solution of a problem, and in the paper which follows, each will be resorted to to a certain degree, but chief stress will be laid upon the results attained by experimental investigation.

In spite of the work done upon the problem, the results previously attained can hardly be considered to be satisfactory. The conclusions reached from the experimental side were not concordant; those derived from observation of natural occurrences indicated the relations in a general way, but were not sufficiently explicit and also contained contradictions which no theoretical consideration was able to clear up. For these reasons, the Geophysical Laboratory took up the problem several years ago, and the work done at that time resulted in considerable advance in our knowledge of the relations of the several forms. In the first publication in which the matter was discussed,* the inversion point between quartz and tridymite was placed at approximately 800° and the melting point of tridymite (or, more properly, the change from the crystalline to the amorphous condition) was considered to be about 1600°.

* The Lime-Silica Series of Minerals, A. L. Day, E. S. Shepherd and F. E. Wright, this Journal, (4), xxii, 265-302, 1906.

that time the relations were supposed to be much more simple than was found shortly afterward to be the case. This was due principally to the fact that the mineral cristobalite was almost unknown at the time, and only the relations between the two forms, quartz and tridymite, were considered. In reality, the products classed as tridymite consisted at times of tridymite and at other times of cristobalite. The optical properties of the two are so similar that the fact that two different products were obtained was not realized, although it was noted that the index of refraction in some preparations was slightly higher than normal. It may be noted also that the values of refringence and birefringence of cristobalite given in some of the standard mineralogies are in error. By consulting Mallard's* original paper, from which they are quoted, it is obvious that the value of the index has been misprinted and that of the birefringence probably misinterpreted.

In a second paper from the Geophysical Laboratory,† dealing with the matter, attention was called to the inaccuracy in some of the statements of the preceding paper, and it was stated: "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."

Through the courtesy of Professor Lacroix of Paris, to whom specimens of the artificial crystals obtained by the devitrification of silica glass and by heating quartz at high temperatures, had been sent, it had been shown that these were probably cristobalite and not tridymite as had formerly been supposed. The acceptance of this view, however, seemed to open up again the whole question, for if this mineral was cristobalite, what was the position of tridymite in the series? In fact, beyond the determination that tridymite and cristobalite were high temperature forms, nothing seemed certain regarding their relations. This uncertainty was increased by the fact that other investigators had reported the artificial production of tridymite and cristobalite under such conditions that it seemed even a question whether they were properly high temperature minerals. The manner of their occurrence in nature also suggested the possibility that their field of stability was in the region below 800°. On the other hand, Professor Koenigs-

* E. Mallard, *Bull. Soc. Min.*, xiii, 175, 1890.

† The Binary Systems of Alumina with Silica, Lime and Magnesia, E. S. Shepherd, G. A. Rankin and F. E. Wright, *this Journal*, (4), xxviii, 293-333, 1909.

berger,* in consideration of the evidence which he believed to exist for the precipitation of quartz from magmas at temperatures as high as 1000°, had expressed the opinion that the transformation quartz-tridymite might perhaps be monotropic.

The low temperature inversion of α into β quartz, of α - β tridymite, and of α - β cristobalite, was described in the later paper from this Laboratory, to which reference has been made. The velocity with which these reactions occur, compared with the reluctance with which quartz inverts into tridymite or cristobalite, had been noted as a very striking phenomenon, for which no explanation could be suggested. Further investigation of these reactions seemed desirable.

These problems were held in abeyance by the Laboratory for some time in the stress of other work. At the first opportunity, however, they were again taken up in the hope that with the advantage of the knowledge gained from previous investigations, the problem might be cleared up. The specific points which were obscure and for which a solution was desired, were the following:

1. Are the relations between the forms chalcedony, quartz, tridymite, and cristobalite monotropic or enantiotropic?

2. If enantiotropic, what are the fields of stability of each, and what are the inversion points?

3. What is the explanation of the observed fact that both in natural occurrences and in the results of experimental work, quartz, tridymite, and cristobalite appear to have been formed at times almost simultaneously, or at least under conditions under which not all could be stable?

4. What is the reason for the remarkable velocity of the α - β inversions of quartz, tridymite, and cristobalite as compared with the slowness of transformation of each of these minerals into one of the others?

5. To which form of silica does the previously determined melting point belong?

To these may be added a sixth question which arose in the course of the work and, from its theoretical importance, demanded solution.

6. Is the temperature of inversion of α into β cristobalite a fixed point and is its apparent variability due to some such recognized factor as impurity of material or lag, or is it actually a movable point and therefore an extraordinary type of phenomenon?

To some of these questions the present investigation has supplied categorical answers. To others the direction in which experimental work points for the explanation brings one upon debatable ground and caution must be used lest positive con-

* J. Koenigsberger, Neues Jahrb., Beilageband, xxxii, 113, 1911.

clusions be arrived at without supplementary evidence. The explanations suggested for these debatable problems must be looked upon merely as contributions toward a final solution of the theoretical questions involved.

After the investigation had been under way for some time a preliminary paper was published.* In this a brief outline was given of the chief results obtained up to that time. In the present paper it has seemed desirable to present the results as a consistent whole, so far as possible, and in order to do this all results of importance will be given and their relations discussed without much regard to the previous publication.

DETERMINATION OF THE INVERSION POINTS BETWEEN QUARTZ AND TRIDYMITITE AND BETWEEN TRIDYMITITE AND CRISTOBALITE.

As previous work had demonstrated that the above inversions take place very slowly, and that the minerals may be heated at high temperatures and for long periods with no indication of inversion or with only partial inversion as the result, it was realized at the outset that it was necessary to employ a flux or catalytic agent of some sort to hasten the process. This should be such a material as would melt at a comparatively low temperature and would not be volatilized to a serious degree at high temperatures. It should, moreover, not dissolve silica in large quantity or enter into solid solution with any of the silica minerals. A number of reagents were tried at various times, such as potassium and lithium chlorides, boric acid, and salt of phosphorus, but the one which best fulfilled the requirements was found to be crystallized sodium tungstate ($\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$). This possessed the added advantage that it could be removed by simple washing with water. The only difficulty found was that at high temperatures (1400° and over) it dissolves a considerable quantity of silica, and if much is used nothing but a glass results. This difficulty was easily overcome by using a small quantity.

For reactions at a high temperature, that is, in the neighborhood of the tridymite-cristobalite inversion-point, sodium-potassium silicate may likewise be employed. It offers no special advantages over sodic tungstate, except that it may be regarded as more similar in its nature to a magmatic melt.

In establishing the inversion points, the method of procedure was simple in principle but rather tedious in its application because of the slowness with which equilibrium is established. A charge was first prepared by melting sodic tungstate in a small platinum crucible over a Bunsen flame and adding the respective form of silica and mixing with a platinum stirrer. The crucible, to which a short wire had been fused on each

* The Various Forms of Silica and their Mutual Relations, C. N. Fenner, J. Wash. Acad. Sci., ii, 471-480, 1912.

end of a diameter so as to form a sort of bucket, was then suspended from corresponding wires hanging from the lower end of a Marquardt porcelain tube. A thermoelement, of the standard material used in the Geophysical Laboratory (pure platinum against 90 Pt.10 Rh), was run down through the Marquardt tube and into the charge. The thermojunction within the charge was bare, while the upper portions of the wires were insulated from each other by inclosing them within capillary porcelain tubes. The upper ends of the thermoelement wires were attached to corresponding terminals of the ice-bath, from which copper wires led to the potentiometer in the usual manner. Electromotive force was read from a mirror galvanometer in connection with the potentiometer, in the usual form adopted by the Geophysical Laboratory, whose details have been fully described in previous papers* and need not be gone into. Full precautions against leakage of electric current into the galvanometer circuit were employed. A check was maintained on the accuracy of the readings of the thermoelements by occasional calibration by comparison with the melting points of standard substances ($\text{MgCa}(\text{SiO}_3)_2 = 1391.2^\circ$, $\text{Li}_2\text{SiO}_3 = 1200^\circ$, gold = 1062.4° , $\text{Na}_2\text{SO}_4 = 884^\circ$, zinc = 419.4°).

By means of the device described, the bucket containing the charge could be inserted into a furnace heated by an electric current passing through a platinum resistance coil, and subjected to whatever heat treatment was desirable.

If one heats ground quartz in sodic tungstate at 1000° or more for several hours, it is found to have been more or less completely converted into tridymite. On the other hand, if tridymite so prepared is mixed with tungstate and heated at 800° for a long period, innumerable small quartz crystals can be perceived in the resultant product. Somewhere between these two temperatures, therefore, there must lie an inversion-point. At high temperatures the transformation of quartz into tridymite can easily be carried to completion. The reversion of tridymite into quartz can likewise be completely carried out but is more sluggish, and generally no attempt was made to convert the whole charge because of the length of time which would be required. The quantity of quartz increases with the period of heating, but having once established the reversibility of the process, nothing would be gained by continuing it for excessive periods. It simply remained to determine a temperature above which tridymite could be recognized as having been obtained from quartz and below which quartz as obtained from tridymite. It was found that within a few degrees of the

* A. L. Day, E. T. Allen, and J. P. Iddings, Publication No. 31, Carnegie Inst. of Washington; A. L. Day, E. S. Shepherd, and F. E. Wright, in this Journal, (4), xxii, 265-302, 1906; W. P. White, in Phys. Rev., xxv, 334-352, 1907; and in this Journal, (4), xxviii, 459-489, 1909.

inversion-point the velocity of transformation was extremely small and a long period of heating was required to insure the appearance of the stable phase, but outside of this range a noticeably less time was required. Fine grinding apparently did not increase the velocity of the reaction.

As the range within which the inversion lay was gradually narrowed down great care was exercised in the regulation of furnace temperature. The method of procedure was to hold the charge for a long period at some temperature previously decided upon, keeping close watch to see that some unexpected variation in the strength of the heating current did not cause a departure from this temperature. When necessary to continue heating from one day to the next (as was frequently the case) the current from the generator was replaced by that from storage batteries. These batteries possessed very constant voltage and were of such capacity that in a run of fifteen or sixteen hours the temperature of the furnace dropped only 8–10 degrees.

A description of several of the more significant experiments follows:

No. 82. A mixture of finely ground silica glass with sodic tungstate; length of heating, 11 hours 20 minutes, during which the temperature was kept very close to 865° , extreme variations 863° – 875° . The product was essentially tridymite, but distinct quartz grains were found, often with bipyramidal terminations. (As will appear a little later, the tridymite was an intermediate stage, and the point of significance is the fact that it was changing to quartz at this temperature.)

No. 102. A mixture of artificial tridymite and sodic tungstate; length of heating, $73\frac{1}{2}$ hours; utmost variation, 854° – 864° ; general temperature, 858° . The product was still mostly tridymite, but there were very numerous quartz crystals, mostly as nuclei of tridymite aggregates.

No. 103. Ground quartz with sodic tungstate; length of heating, 24 hours; general temperature, 875° ; range, 865° – 877° ; product, quartz with considerable tridymite in hexagonal plates.

Other experiments of the same nature might be described, confirming the above results and fixing the temperature of inversion at a point very close to 870° .

Because of the great difficulty of keeping the temperature of the furnace constant for such a length of time, some latitude must be permitted in expressing the temperature of inversion, but it is believed to lie within 10° of 870° .

It has not been considered necessary to tabulate the results of experiments conducted much above or below 870° , for at such temperatures quartz changed to tridymite in the one case and tridymite to quartz in the other in an unequivocal manner.

In determining the inversion-point between tridymite and cristobalite the same general method of procedure was followed, but the details were slightly different. As before, temperatures were first found above which tridymite changed to cristobalite and below which cristobalite changed to tridymite, and the range was gradually brought within narrow limits. For final determination, however, it was not considered advisable to depend upon the constancy of the storage batteries over night, because of the draught which would be imposed upon them by the heavy heating-current. Therefore the charge under treatment was withdrawn at night and quickly cooled, and replaced in the morning at the same temperature and heating continued. No difference in principle was involved in thus breaking up the time of heating into several periods.

The final experiments were as follows:

No. 114. Mixture of cristobalite and sodic tungstate; length of heating, $4\frac{3}{4}$ hours at $1460^{\circ} \pm 2^{\circ}$; the product is still mostly cristobalite, but there is a very appreciable quantity of tridymite.

No. 117. Mixture of tridymite and sodic tungstate; length of heating, 10 hours 25 minutes at $1475^{\circ} \pm 2^{\circ}$; product is mostly tridymite, but with considerable cristobalite.

No. 122. Tridymite and sodic tungstate; $21\frac{1}{4}$ hours at $1470^{\circ} \pm 2^{\circ}$; no cristobalite discoverable.

No. 120. Cristobalite and sodic tungstate; 16 hours at $1470^{\circ} \pm 2^{\circ}$; no tridymite discoverable.

From these experiments, in connection with many others at higher and lower temperatures, which gave consistent results, we appear to be perfectly justified in placing the tridymite-cristobalite inversion temperature at $1470^{\circ} \pm 10^{\circ}$.

The enantiotropic relations were confirmed by numerous experiments, modified in various ways. Starting with quartz either tridymite or cristobalite may be obtained, according to the temperature used. Likewise, tridymite may be converted into quartz or into cristobalite, and cristobalite into quartz or tridymite. Silica glass and amorphous precipitated silica have likewise been converted at will into any one of the three crystalline modifications. In all its relations to other forms precipitated silica behaves in the same way as silica glass, and may probably be considered as the same chemical substance, differing only in its state of physical division.

There can be no doubt that quartz, tridymite, and cristobalite are enantiotropic forms, each with a certain range of stability. Their general equilibrium relations are shown in fig. 1, in which the coördinates are temperature and vapor-pressure. The absolute values of vapor-pressure are, of course, unknown, but we may make use of the principle that the vapor-pressure rises with temperature, and that the vapor-pressure of a stable

form is less than that of an unstable form. An inversion-point lies at the intersection of two vapor-pressure curves. These same relations apply to the functions free energy and thermo-

FIG. 1.

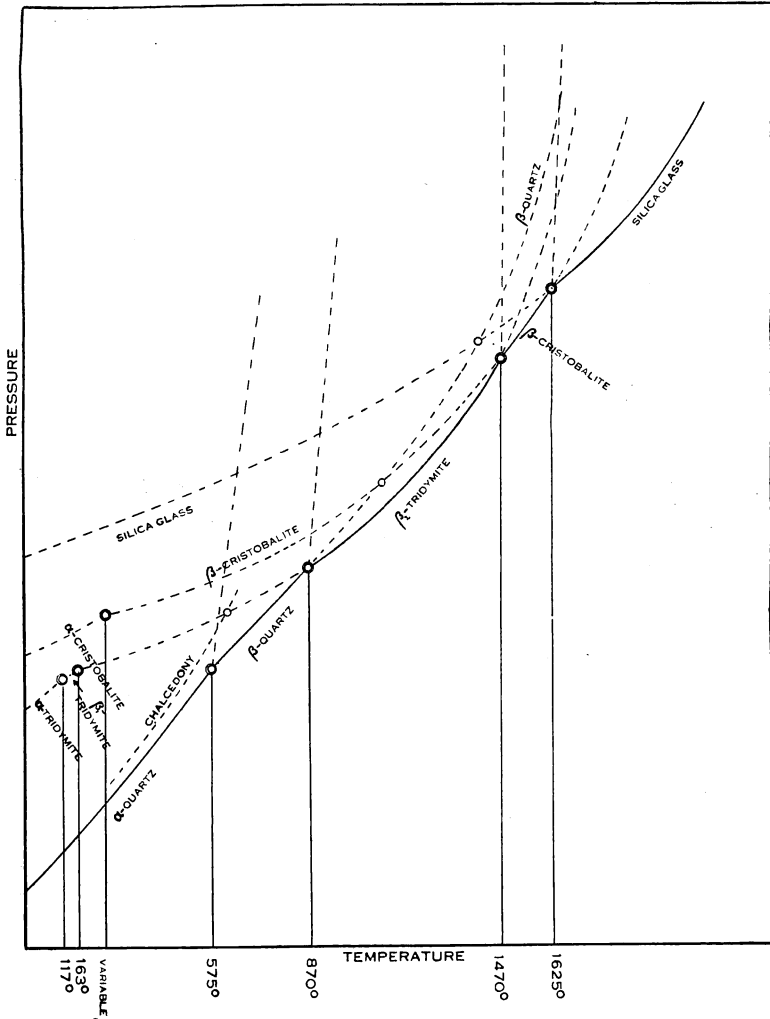


FIG. 1. Stability relations of the silica minerals.

dynamic potential, and, as absolute values are unknown, the vapor-pressure coordinate could as well be considered as a coordinate of free energy or thermodynamic potential.

THE APPEARANCE OF UNSTABLE PHASES.

In experiments on the relations of the various forms, certain phenomena were met which were rather puzzling at first, but after their explanation was perceived it was recognized that they threw considerable light upon discrepancies shown in the results obtained in previous work upon the silica minerals, and upon the conditions under which tridymite and cristobalite have been formed in nature. It was found, for example, that if silica glass or precipitated silica was heated with sodic tungstate for a number of hours at 800–850°, not quartz but tridymite was first obtained. It was only after much longer heating that quartz crystals began to appear, although this is the stable form at that temperature. It seems that in the passage from the amorphous condition to quartz, the whole is first converted into the intermediate form tridymite, and only secondarily into quartz.

Likewise, if either amorphous modification is heated without a flux at 1300° or 1400°, cristobalite alone is obtained, although the temperature is within the range of tridymite. The process halts at the cristobalite stage, and can only be carried to completion by the addition of a flux. Similarly, ground quartz heated without a flux at high temperatures but still below the 1470° inversion-point is changed to cristobalite and not tridymite, which might be expected.

A striking instance of the formation of unstable phases appeared in a series of experiments in which one or another form of silica was heated with a large excess of sodic tungstate over a Bunsen burner. In one instance in which amorphous precipitated silica was thus heated for 43 hours, quartz, tridymite, and cristobalite, all in good crystals, were found in the same melt. In other instances, quartz or tridymite or cristobalite was similarly employed and two or three of the phases were simultaneously obtained. The crystalline outlines were such as to indicate new formation of even that phase which was added at the beginning. Working in this manner one may start with tridymite and, keeping the temperature in all parts of the crucible within the tridymite range, convert part of the tridymite into cristobalite—a result which at first sight seems impossible.

The production of unstable phases in this manner has considerable theoretical importance. In its proper interpretation light may be thrown upon some apparent discrepancies in former work and make possible a reasonable explanation of natural occurrences of tridymite and cristobalite. It also seems to have some bearing upon recent theories of the structure of molecules and crystals. It will, therefore, be discussed at some length and an endeavor made to interpret its significance.

From the standpoint of the kinetic theory, the question of the formation and appearance of a mineral phase may be looked upon as a function of two variables; first, the *probability* of the requisite number of moving particles coming together in the pattern appropriate to the structure of the mineral in question, and second, the *strength of the bonds* by which the particles thus assembled are held together under the impact of other particles or under the stress of intramolecular forces. Both of these are again functions of the temperature and pressure, but vary with these according to very different laws.

Under this conception, when a number of substances enter into a reaction, or when a single substance is subjected to a change of conditions under which it is no longer stable, a certain assemblage of particles characterized by a simple* pattern may be formed at a given temperature and pressure in great numbers, while a second assemblage characterized by a more complex pattern is formed in the same interval in much less quantity; and the relative velocity of formation and destruction of the two may be such that the phase appropriate to the first pattern will appear as a new phase of the system, while the second is present in only infinitesimal quantity; but we may easily suppose that each group of the second phase, when once formed, is relatively indestructible under the given conditions, while the groups of the first kind are continually breaking down and reforming. The result will be that the phase which appeared with such rapidity at first will gradually yield place to the second phase, which will then be the *stable* phase. The second phase may, however, under some conditions, be formed with such slowness (on account of the small number of free particles which escape from the phase already formed or because of the complexity of its pattern) that it will not appear in recognizable quantity, and the unstable phase will persist indefinitely.

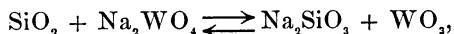
By changing the temperature and pressure, we change the two variables according to different laws, and the results obtained as regards the phases which first appear and as regards the phases which are stable, vary accordingly. At transition points the opposing tendencies are in equilibrium, or in other

* Simple and complex, as here used, refer to probability or improbability of the particles coming together in the manner to form the pattern in question.

R. J. Strutt (Proc. Roy. Soc. London, ser. A, lxxxvii, 302-9) has made some interesting calculations on this sort of molecular statistics. He concludes that probably a single collision with a silver surface is sufficient to destroy a molecule of O_3 , but that a molecule of active N must collide 500 times with an oxidized Cu surface before it is destroyed, and that two molecules of O_3 at 100° must collide 6×10^{11} times before the right sort of collision occurs for the formation from them of 3 molecules of O_2 . (Chem. Abstracts, vii, 6, 923, 1913.)

words, the formation and destruction of each of two phases proceed at the same rate. Below the inversion-point the formation of one of the phases exceeds its destruction; above it the other phase is thus characterized.

Let us apply this conception to the specific case of the simultaneous formation of crystals of quartz, tridymite, and cristobalite in a sodic tungstate melt. In this experiment there is some evidence that a reversible reaction of this kind proceeds:



going from left to right at higher temperatures and from right to left at lower. In this manner a multitude of SiO_2 molecules are constantly contributed to the liquid, in which they are in active movement. By chance collisions numbers of these meet in such manner as to form groups of definite patterns, which tend to cohere. According to their arrangement, they form the quartz, tridymite, or cristobalite molecules, each of which appears and disappears in countless numbers at each instant. Under the conditions of the experiment, a stream of ungrouped molecules is constantly added to the cooler portions of the melt by the breaking-up of Na_2SiO_3 (or by convection currents from below), yielding such an overwhelming excess over what would occur under more uniform conditions of temperature that all possible configurations of grouping (which seems to mean those appropriate to quartz, tridymite, and cristobalite) are formed, and the number of each kind formed is in great excess over those destroyed. Each sort of crystal is, therefore, deposited from the melt. If none of the crystals settled into the hotter regions below, we should ultimately find that after the exhaustion of the supply of ungrouped molecules, two of the kinds of crystals would pass into the third, as for this the excess of production over destruction would be greater than for either of the other two, and this would be the stable form at this temperature; but under the influence of convection currents, the process continues around and around in a circle indefinitely.

In the process thus presented, I have conceived that by regular arrangements of the simple SiO_2 molecule more complex groups corresponding to quartz, tridymite, and cristobalite *molecules* are first formed in the liquid, and that these again group themselves in appropriate patterns to form the respective *crystals*. The question may arise whether such primary groupings occur apart from the crystal groupings. There is abundant evidence, however, from various sources, that simple molecules do form groups of this nature in a liquid, so-called associated molecules. Moreover, evidence will be presented later that cristobalite crystals at least give phenomena which are best

explained by the assumption of two different kinds of molecules in the same crystals. It seems most probable, therefore, in consideration of all the phenomena, that different molecular groupings of SiO_2 take place in the melt under the circumstances described, and that when crystallization ensues, these complex molecules arrange themselves in the appropriate patterns corresponding to the respective crystals. The minerals are regarded, therefore, as being not only polymorphic but polymeric.

The reactions of silica which have been mentioned appear to follow very closely the requirements of the principle which Ostwald enunciated and which is known as Ostwald's rule, or the law of successive reactions. As formulated by him, it is as follows:* "In all reactions the most stable state is not straightway reached, but the next less stable or that state which is the least stable of the possible states." The reasoning by which he endeavors to show the necessity of reactions taking this course is based upon a consideration of the diminution of free energy of a system. It seems to imply that because the free energy in passing from a stage A to a lower stage C passes through the level B, the phase corresponding to this level must always appear, but there is no necessity that this should hold. The matter resolves itself into the question whether under *unstable* conditions the quantity of free energy in a system defines its state. Expressed in this form, we can answer definitely that it does not, any more than the somewhat parallel functions of vapor-pressure or thermodynamic potential.

Applying a kinetic conception, if we can imagine a sodic tungstate melt saturated with simple ungrouped silica molecules at 850° , and then allow such reactions as tend toward equilibrium to take place for a minute space of time, while it is probable that cristobalite groups, because of the relative simplicity of structure usually accompanying high temperature forms, will have been produced in greater numbers than tridymite groups, yet at the end of a longer interval it is doubtful if this would be the case. The strength of the union holding together the members of each cristobalite group would probably be so slight at this temperature that after the rapid attainment of a certain maximum number, equivalent numbers would be destroyed as rapidly as others formed, while the number of tridymite groups would continually increase until the solvent was saturated and crystals were deposited. In the latter sequence of events, the level of free energy represented by B would be that pertaining to a mixture composed mostly

* W. Ostwald, *Principles of Inorganic Chemistry*; translation by A. Findlay, 1904, p. 211.

of tridymite and unassociated silica instead of that pertaining to cristobalite.

Thus it seems that whether we regard Ostwald's principle from a thermodynamic standpoint, applying the principle of minimum free energy, or whether we use a kinetic conception of the process as a guide, its validity as a general law is questionable.

Although the reactions of silica show a number of phenomena to which Ostwald's principle is applicable, exceptions are also found. Thus if a mixture of amorphous silica and sodic tungstate is heated to 800–850°, in a few hours only tridymite can be found. By much longer heating quartz crystals appear. At no stage can cristobalite, the intermediate form between amorphous silica and tridymite, be detected. Likewise, silica glass or precipitated silica, heated without a flux at any temperature at which devitrification occurs, always gives cristobalite, but just above 1470° it should first give tridymite if Ostwald's rule applied. Quartz heated without a flux for a very long period at 1300° gives cristobalite, in obedience to Ostwald's principle. Heated with a flux for three hours at the same temperature, it gives tridymite with no indication of an intermediate cristobalite phase.

SUGGESTED EXPLANATION OF ANOMALOUS RESULTS PREVIOUSLY OBTAINED.

From the results obtained by former investigators of the silica diagram, it had been pretty well established that the quartz-tridymite inversion-point lay between 800° and 900°. The exact temperature was rendered uncertain from the fact that in a number of cases amorphous silica was employed as the initial material, which, as we have seen, in the presence of a flux yields tridymite at temperatures considerably below the true inversion-point. The significance of this has been discussed, and it has been shown that with longer heating the tridymite obtained would have gone over into the stable form quartz. Similarly misleading phenomena appeared in the endeavor to determine the position of cristobalite in the series. By heating either quartz or amorphous silica without a flux, cristobalite will be obtained at temperatures much below its field of stability.

These discordant phenomena may all be interpreted as instances in which Ostwald's principle applies, and their appearance need give rise to no uncertainty.

NATURAL OCCURRENCES OF TRIDYMITE AND CRISTOBALITE.

The mode of occurrence of natural tridymite and cristobalite implies that in many cases they have been formed as

unstable phases. Cristobalite especially could seldom if ever have been deposited as a stable mineral in the circumstances in which it is now found. Its usual occurrence is in cavities in eruptive rocks, which would certainly have been in a fluid condition at temperatures within the range of stability of this mineral. The appearance of the inclosing rocks in many cases, however, suggests that the formation of the cristobalite is to be ascribed to its deposition from mutually reacting vapors or to the decomposition of former silicate minerals or siliceous glass by pneumatolytic processes. In either of such modes of action, unassociated molecules of silica would be set free in quantity from their previous state of combination with other elements, and would probably tend to form groups among themselves corresponding to cristobalite. This is perfectly analogous in principle to the formation of cristobalite in tungstate melts over a Bunsen flame at a comparatively low temperature, which was obtained as a result of direct experiment and for which the explanation has been suggested. It is quite certain that for the deposition of the mineral in question under such conditions no excessively high temperature is demanded and its presence in no wise implies that the temperature requirements of stability obtained.

Many of the occurrences of tridymite are similar and likewise suggest the intervention of gases in its production, as has been pointed out in a number of instances by A. Lacroix.* An interesting association of tridymite and quartz in hollow spherulites of rhyolite is described by Iddings and Penfield,† and appears to be due to processes of this character. The presence of trapezohedral faces on the quartz crystals shows that it is of the α variety, and therefore formed below 575° .

In addition to such occurrences, which point to pneumatolytic action, tridymite is sometimes found as an essential constituent of acid effusives, associated in such manner with other minerals as to imply its separation from the melt as a primary constituent. In such instances the implication is simply that at some period in the previous history of the magma the temperature was such that the excess of silica not required to form other minerals had formed the molecular groupings corresponding to tridymite, and when rapid cooling ensued these groups crystallized out in the tridymite form. The temperature at the time of crystallization may have been either above or below the 870° inversion-point. If below, the viscosity of the melt acted as an effective obstacle to prevent that rearrangement of the molecules which would be demanded to form quartz. With less rapid cooling and especially with

* A. Lacroix, *Bull. Soc. Min.*, xxviii, 56, 1905.

† Iddings and Penfield, *this Journal*, (3), xlii, 39, 1891.

decrease of viscosity by the retention of volatile substances (mineralizers)—conditions implying a crystallization of the magma under pressure—tridymite if once formed would become unstable at 870° and would pass over into quartz. This matter will be taken up a little later.

Through the kindness of Dr. E. S. Larsen, of the U. S. Geological Survey, my attention has been called to an interesting occurrence of cristobalite in a basalt found by Dr. Whitman Cross in the Hawaiian Islands. In the calculation of the norm from the chemical analysis of the rock, no olivine appeared, while examination of thin sections showed abundant olivine. The explanation was found in the discovery of small crystals of cristobalite in cavities. In another set of rocks from Colorado which Dr. Larsen brought to my attention, the flow-structure of acid effusives is well developed and certain of the bands show innumerable tridymite crystals whose arrangement with respect to the other constituents of the rocks indicates their simultaneous crystallization from the melt. It seems probable that these minerals are not so rare as has been generally supposed and that with careful search they might often be found.

Emphasis should be laid upon the fact that the presence of cristobalite or tridymite in a rock does not necessarily imply that at the time of formation of these minerals the temperature was above the respective inversion-points (1470° and 870°). Any set of conditions which will bring together quantities of ungrouped SiO₂ molecules in such a manner as to favor their rapid assemblage in definite groupings without giving time for perfect equilibrium to be established (as in the reactions of vapors); or which will suddenly bring a system in which equilibrium prevails into new conditions, at the same time introducing obstacles to the establishment of a new equilibrium (as in the sudden chilling of a melt), will favor the deposition of unstable forms. It is evident that there will be two factors to be considered; first, the question of whether change of conditions has been too rapid for equilibrium to follow, and second, the question as to what was the previous condition from which the state in question has been reached.

Certain phenomena which Lacroix and others* have described, where quartzose inclusions in volcanic rocks have been partly or wholly transformed to tridymite or to cristobalite, seem to show that here the 870° inversion-point has been exceeded. Some uncertainty on this point arises from the observation which Lacroix makes† that, in the

* A. Lacroix, *Les Enclaves des Roches Volcaniques*, 1893; *Bull. Soc. Min.*, xiv, 185, 1891; K. v. Chruschhoff, *Tschermak Min. Pet. Mitth.*, vii, 295, 1886.

† *Les Enclaves des Roches Volcaniques*, p. 570.

cases which he has observed, such newly formed tridymite seems always to be due in some way to the intervention of mineralizers, and, as previously shown, the reactions of vapors are likely to produce tridymite at a temperature below its range of stability. Nevertheless the most probable explanation for the phenomena which Lacroix describes seems to be that the temperature was sufficiently high to break up the quartz molecule and give opportunity for the formation of new groupings corresponding to tridymite and cristobalite.

A reproduction of the essential conditions attending the engulfment of quartzose material by a liquid magma was attempted in one experiment. Potassium carbonate, sodium bicarbonate, and ground basalt were mixed in approximately equal proportions, and eight or nine times as much ground quartz was added. The whole was heated in a Fletcher furnace to a high temperature (1500–1600°) and melted to a clear, slightly greenish glass, in which small spherulites had formed on cooling. This glass was then placed in the electric furnace and devitrified by holding at 1000° to 1400° for five hours. It was then found to be filled with a mass of tridymite crystals. A portion of this was mixed with a large excess of quartz and the whole well ground. Heated again for 22 hours at 1200–1400°, the final result was a mixture of tridymite and cristobalite, although the temperature appropriate to the cristobalite region had never been reached. The results are similar in kind to those observed in the basaltic rocks of Mayen,* where quartz inclusions have been partly converted into cristobalite and tridymite, and is to be ascribed to the breaking-up of the quartz molecules by the high temperature attained, giving opportunity for new arrangements to form, without facilitating rearrangement to such a degree that all the groups reached stability.

The question arises, whether in the cooling of a magma quartz may appear outside of its range of stability, as several authors have supposed. The possibility of this is not wholly excluded, but nothing has been found in the experimental work which suggests anything of the kind, and on theoretical grounds it appears inherently improbable. The equilibrium from which the magma has cooled is one corresponding to the presence of tridymite molecules in the solution. It is difficult to conceive the formation and precipitation of quartz from such a solution *above* the inversion-point, while the precipitation of tridymite *below* this point is perfectly intelligible when the cooling is rapid. The effect of pressure in shifting the inversion-point itself is not here considered, but will be taken up later.

* A. Lacroix, Bull. Soc. Min., xiv, 185, 1891. P. Gaubert, idem, xxvii, 42, 1904.

A question of considerable importance is, whether the general absence of tridymite in rocks which have cooled slowly (such as large bodies of deep-seated intrusives) must be understood as proving that the temperature of crystallization was below the tridymite-quartz inversion-point. Considered solely from the experimental evidence on the quartz-tridymite relations, it may probably be said that the temperature during the *final* stages of crystallization of the quartz was below this point, but nothing is implied regarding the *first* stages; for if tridymite were precipitated at an earlier stage, but remained in contact with a fluid portion of the magma after the temperature dropped below the inversion-point, it would probably pass over into quartz within a short time (probably within a few days). Examples are not lacking in which traces of such inversion appear to survive. The peculiar form of quartz in some eruptives has been thus explained. Professor Lacroix* has found a number of instances of such relations, and Dr. Per Geijer† has recently described others.

In the examples just referred to, the peculiar form of the quartz bears testimony to the history through which it has passed, but under different conditions, especially those obtaining during the crystallization of a coarsely granular rock, the newly formed quartz would undoubtedly tend to assume its proper crystallographic structure, and no evidence of the intermediate steps of the process could be found in the final product.

It is hardly necessary to consider in detail the various natural occurrences of tridymite and cristobalite which have been described in the literature. So far as I have been able to ascertain, the descriptions given bear out the principles of origin which have been outlined.

EFFECT OF PRESSURE UPON THE QUARTZ-TRIDYMITE INVERSION.

In the preliminary paper on the silica minerals which the writer published, some inquiry was made into the effect which pressure would have in displacing the inversion point. By employing the Clausius-Clapeyron equation $\left(\frac{dT}{dp} = \frac{T}{L}(v_2 - v_1)\right)$ and assuming probable values of L , the heat of inversion, and $v_2 - v_1$, the volume change, a displacement (rise) of 0.10537° per atmosphere was deduced. It is doubtful, however, if a calculation of this kind serves any useful purpose because of the lack of certainty of the values assumed and the consequent

* A. Lacroix: Sur la tridymite du Vésuve et sur la genèse de ce minéral par fusion, Bull. Soc. Min., xxxi, 323, 1908.

† Per Geijer: Geol. Fören. Förhandl., xxxiv, 1, pp. 51-80, 1913. References are given in this paper to instances cited by other writers.

unreliability of the results and the danger that they will be misinterpreted. The data for such a calculation would be of great value, but until they are available, we can hardly make a more positive statement than to say that pressure will raise the inversion-point by some unknown amount.

INFORMATION TO BE OBTAINED FROM THE STUDY OF TRIDYMITE-BEARING ROCKS.

A careful study of the relations and characteristics of the minerals in tridymite-bearing rocks should give us important information on certain problems connected with the processes of volcanic activity. The position of the quartz-tridymite inversion-point is within a critical region as regards the temperatures of vulcanism, and the history of the tridymite, as revealed by petrologic study, may, with the accumulation of evidence, be able to settle a number of debated points. The kind of evidence to which I refer may be illustrated by an example. In the set of rocks from Colorado which Dr. Larsen kindly placed at my disposal, I have found certain very suggestive features, which appear to show that quartz phenocrysts which were formed in the magma at depth, became converted into tridymite during the process of extrusion. The nature of the evidence is as follows: When in laboratory experiments ground quartz is converted into tridymite in a sodic tungstate flux, it is frequently found that many of the quartz grains retain their individuality during the process, but are replaced by an aggregate of tridymite crystals. If the replacement has not been quite complete, very irregular nuclei of quartz remain, corroded by the encroaching tridymite. Similar phenomena have been remarked in the transformation of quartz bricks into tridymite in metallurgical establishments or glass furnaces.* In the Colorado rocks certain tridymite aggregates suggest the same sort of process carried to completion. They are distinctive units, quite sharply set off from the surrounding matrix, which frequently bends around them in flow lines. They are not spherulites, as the component crystals are disposed at random instead of in a radial form, and are much larger than ordinarily found in spherulites. Perhaps most important of all is the observed fact that in several instances the outlines of the nodules are those of slightly rounded hexagons. All in all, the appearance suggests a derivation from quartz phenocrysts. The rocks in which the phenomena occur may be called tridymite-latites; that is, rocks corresponding in mineralogical make-up to quartz-latites but in which the rôle of quartz as an essential constituent is taken by tridymite.

* E. Mallard, *Bull. Soc. Min.*, xiii, 172, 1890; P. J. Holmquist, *Geol. Fören. Förhand.*, xxxiii, 4, 245-260, 1911; K. Endell, *Stahl u. Eisen*, Nr. 10, 1912.

This single observation requires support from other directions. If it should be confirmed its interpretation leads to interesting deductions. The explanation which first suggests itself is that under great pressure quartz phenocrysts had formed in the magma at a temperature considerably above the 870° inversion-point, and that with relief of pressure accompanying the movement toward the surface, the position of the inversion-point was lowered to such a degree that tridymite became the stable phase and transformation followed as a natural consequence; but we are not justified in accepting this explanation at once. We cannot focus our attention upon this one phenomenon and neglect the results which would arise among the accompanying constituents, that is, upon the magma as a whole, from relief of pressure. In a mixture of such great complexity as a partly solidified magma, consisting of solids, liquids, and dissolved gases, a change of pressure will be accompanied by transformations and reactions among all the components tending toward a new condition of equilibrium. The direction of all such reactions will be governed by a single principle, that the net result shall be an increase of volume of the mass as a whole when the pressure is decreased. Necessarily such reactions will be attended by an evolution or absorption of heat, but this factor does not influence the direction of reaction except secondarily, and, moreover, there is no general parallelism between the amount of the volume change and the quantity of heat evolved or absorbed. It is certain that from such internal reactions (neglecting losses of heat by conduction or radiation to the surroundings) the temperature of the magma will either rise or fall, but observations of volcanic phenomena have not yet supplied data from which it is possible to affirm which is the general result. There is, therefore, at least the possibility that in the rise of a magma from the depths the temperature may actually become greater, perhaps even to a notable degree. If this should be the case, the transformation from quartz to tridymite might well be explained from this alone, and the fact that the direction of volume-change in this one constituent is that demanded of the magma as a whole would be a mere coincidence.

PHYSICAL PROPERTIES OF ARTIFICIAL QUARTZ, TRIDYMITE, AND CRISTOBALITE.

In determining the transition points between quartz and tridymite and between tridymite and cristobalite, it was necessary, as previously explained, to use a solvent or catalytic agent in order to cause the transformation to proceed at an appreciable rate, and sodic tungstate was selected for the purpose. The use of this material is permissible if it gives rise to no

product which enters into solution with one or another form of silica. If such solution occurred, the inversion-points would be displaced and the determinations made would have no special significance. It is necessary, therefore, to show that the artificial products do not represent solid solutions. For this purpose chemical analysis has little value. A number of analyses were made by volatilizing the silica with hydrofluoric acid and weighing the residue. This residue was always rather small (0.19–0.60 per cent.), but its effect depended wholly upon the question as to whether it was mixed with the crystalline silica as a mechanical impurity or whether it had entered into solution with it. To settle this, the determination of physical properties fortunately provides effective criteria. Certain of these properties are of such a nature that they would be even more affected by a slight amount of foreign material in solid solution than would the transition points mentioned. Therefore, by a comparison of the properties of the artificial minerals with those of their analogues in nature, the probability of identity can be established. Outside of this, the physical constants are inherently of value and their determinations should be recorded.

Properties of Quartz.—The quartz obtained in sodic tungstate melts seldom exceeds 0.1^{mm} in length. The crystals appear to be simple combinations of prism and pyramids. Frequently the forms are rounded or distorted, an effect which, with some crystals, can be seen to be due to oscillatory development of faces. Ordinarily, each crystal is a separate individual, with double terminations, and a general habit similar to quartz phenocrysts in porphyries. Determination of refractive indices was made in sodium light by matching the index of the crystals with that of various oils by the Becke line method, the index of the oil mixture which matched being immediately determined on a total refractometer. The agreement with natural quartz was very close. For artificial $\omega = 1.544$ $\epsilon = 1.551$ (temperature 23°), for natural $\omega = 1.544$ $\epsilon = 1.553$.

Strong confirmation of its identity with natural quartz was furnished by comparison with the α - β inversion point of the natural mineral (to be described later). The quantity of heat involved in this transformation is so insignificant (3–4 calories* per gramme, according to unpublished determinations by W. P. White of this Laboratory) that a small amount of material in solution would tend to produce a decided shift. The average of three determinations gave the point as 577.2° on heating and 568.5° on cooling. Within the limits of error of the method, these points coincide with those of natural quartz.

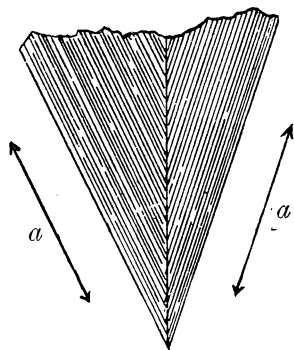
* The exact amount of heat change to be considered is variable because of an increase of specific heat just prior to the inversion, which must be taken into account when the displacement is considerable.

Properties of Tridymite.—The most frequent form of tridymite as obtained by the inversion of quartz in a tungstate melt is as aggregates of crystals of random orientation replacing each quartz grain. In addition, large numbers of perfectly formed hexagonal plates are almost always present in the same preparation. Ordinarily the crystals are quite minute, but it is not difficult to produce them at will of such size that individual crystals are plainly visible to the naked eye. The essentials seem to be a long period of heating and a moderately high temperature. After one experiment, conducted at 1300° for 23 hours, the crust of the mass in the crucible appeared somewhat fissured and the openings were lined with relatively large, separate crystals of a tabular form. Under a binocular of moderate power their hexagonal form could be distinguished. Interpenetration twinning was developed to a high degree, and although the crystals were too frail for goniometric work, the resemblance to the twins and trillings figured in Dana and Hintze was striking. In another experiment the heating was continued for 140 hours at a temperature varying from 900° to 1200° and still better crystals were obtained.

The crystals in random aggregates frequently show elongated or lath-like shapes, due to their being cross-sections of the thin scales. In such cases the extinction is parallel to the elongation, and the elongation has the vibration direction a . In other cases the wedge-like twinning frequently noted in descriptions appears. This has the appearance shown in fig. 2.

The hexagonal scales, when of the thinness ordinarily obtained, appear perfectly isotropic when lying on the base. The larger ones secured by special effort are found to be divided into slightly birefringent fields, as shown in fig. 3. The acute bisectrix in each distinct area is normal to the plate and the optical character is positive. The planes of the optic axes are related to the exterior crystal boundaries in such a way as to be always normal to an edge. The shape of the fields, though quite irregular, is also plainly related to the crystal outline. The hyperbolic brushes are broad and rather faint, and the value of the axial angle is therefore difficult of accurate determination. Three measurements gave the following results for $2V$:— 32.6° , 38.0° , 35.8° , average 35.5° , or $2E = 58.6^{\circ}$. Determination of refractive indices in sodium light by the immersion method gave for vibrations parallel to plates (a and β)

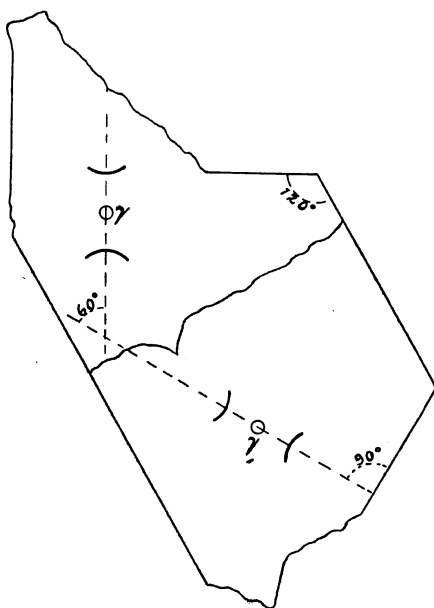
FIG. 2.



1.469 (difference too small to be determined), perpendicular to plates (γ) 1.473 (temp. 24°). All these characteristics agree closely with those of the natural mineral, as given by Mallard,* whose determinations and descriptions are usually cited. Mallard found difficulties in exact determinations of optical constants, but gives $\frac{\beta + \gamma}{2} = 1.477$, $\gamma - \alpha = 0.00185$, $2E = 66^\circ$ about, and $2V = 43^\circ$ about.

A determination of specific gravity was made by the method of Day and Allen.† The value found was 2.270 for tridymite

FIG. 3.

FIG. 3. Tridymite crystal in basal position ; length about 1.0^{mm}.

at 27° referred to water at 27°. Mallard gives 2.28 for the natural mineral.

The optical characteristics of the low temperature ($\alpha -$) form of tridymite indicate orthorhombic symmetry. Each hexagonal plate appears to be made up of several orthorhombic individuals whose vertical axes are parallel with the vertical axis of the hexagonal crystals, but which are twinned after a 60° orthorhombic prism coinciding with the 60° hexagonal

* E. Mallard, *Bull. Soc. Min.*, xiii, 161, 1890.

† Publication No. 31, Carnegie Inst. of Washington, p. 55, 1905.

prism. In the transformation from the high temperature to the low temperature form there appears to be but little shifting of the elements of the space-lattice.

The low temperature inversion of tridymite has long been known. Further investigation has made it appear that there are in reality two inversions lying less than 50° apart, of which the lower is the one ordinarily observed. The method of determining the temperature of these inversions and their meaning will be discussed later. Only a small energy change is involved in either, and therefore a small amount of material in solid solution would probably cause a noticeable shift in their positions. This fact gives to the lower inversion a value as a criterion for judging the identity of the natural and artificial minerals. Mallard* placed the inversion-point of natural tridymite at $130^\circ \pm 5^\circ$. This seems to be the only determination recorded. My own observation on natural tridymite from Cerro San Cristobal in a thermal microscope indicated a somewhat lower value, about 112° . With artificial tridymite the average of a number of closely concordant results obtained by methods in which I place greater confidence, gave 117.4° .

On the whole, the physical properties of artificial tridymite show close agreement with those of the natural mineral, and there is little reason to doubt that they are the same substance.

Properties of Cristobalite.—It is a little more difficult to prove that the cristobalite obtained from tungstate melts carries no foreign material in solid solution. A peculiar situation arises from the fact that the inversion of α into β cristobalite does not take place at a definite temperature like the corresponding inversions of quartz and tridymite, but the temperature for any given preparation depends upon the conditions under which it was formed, and that entirely apart from any question of impurity. This variability eliminates it as a criterion. Moreover, the properties of natural cristobalite are rather imperfectly known. Efforts were made by this Laboratory to obtain specimens of the mineral from dealers for purposes of comparison, but the material submitted was practically useless. Nevertheless it is possible to establish a strong presumption of the identity of the natural and artificial minerals.

The values of the index of refraction and birefringence usually cited in standard works are those of Mallard.† Mallard gives the value of the index as 1.432, which is evidently a misprint for 1.482, for he immediately states "c'est-à-dire sensiblement égal, ou peut-être un peu supérieur à celui de la tridymite." P. Gaubert‡ has called attention to the error, and has made a redetermination, which, however, he did not con-

* E. Mallard, Bull. Soc. Min., xiii, 171, 1890.

† Ibid., 175, 1890.

‡ P. Gaubert, *ibid.*, xxvii, 42, 1904.

sider entirely satisfactory. The mean index, he says, is near 1.49. For artificial crystals prepared in a tungstate melt I have determined the indices in the manner described for quartz, and obtained $\gamma = 1.487$ $\alpha = 1.484$ (sodium light, temperature 24°). Mallard determined the value of the birefringence as 0.00053. There seems to be here also an error of some kind. At any rate, the artificial crystals show a birefringence nearly equal to that of tridymite, probably a little less. M. Bauer, describing the crystals of vom Rath's* original discovery, speaks of the "ziemlich kräftige Doppelbrechung."

Determination of the specific gravity by the method of Day and Allen gave 2.333 for cristobalite at 27° referred to water at 27°. Mallard found 2.34 for natural crystals.

As ordinarily obtained, the artificial cristobalite shows considerable general resemblance to the elongated form of tridymite. The difference in indices of refraction, however, while slight, is sufficient ordinarily for discrimination. Moreover, the extinction of cristobalite in such aggregates is not parallel to any recognizable crystallographic feature, and again, cristobalite grains frequently show a distinct polysynthetic twinning like that of albite, or a plaid effect like microcline. It is a fact not without significance in considering the possibility of material being taken up in solution by cristobalite formed in tungstate melts, that cristobalite, unlike quartz and tridymite, can be formed without a flux and the material so prepared does not differ observably from that formed with a flux. Even those preparations obtained by aid of a flux show very little impurity, 0.19–0.35 per cent according to several analyses.

The best crystals of cristobalite have been obtained by heating amorphous silica with sodic tungstate over a Bunsen burner. They then show an attempt to develop a definite crystal form, but generally arrive at no better results than the forms illustrated in fig. 4. Many of the dihedral and polyhedral angles are nearly perfect, but the remainder of the crystal is a mere skeleton framework. At times the principal growth has been in the direction of one axis only, more often along two or three at right angles to each other. Crystals frequently show many more branches than those illustrated, but the general form of growth has been the same.

In every case where terminal caps have been developed they appear to be octahedra. It is not possible to get very exact measurements of such small crystals under the microscope, but, as nearly as determinable, the edges make angles of 90° with each other and the plane faces make angles of practically 70°. From the relations of the caps to the axes of elongation,

*G. vom Rath and Max Bauer, *Neues Jahrb.*, i, 200, 1887.

it seems that the direction of elongation is always that of cubic axes. In many cases the direction of growth has been influenced by twinning. This is evident at once in such a form as shown at *c* and is the natural explanation wherever the angles between axes differ from 90° . The best measurements that could be made with the microscope show that angles which do not differ sensibly from 45° and 60° occur. The mode of

FIG. 4.

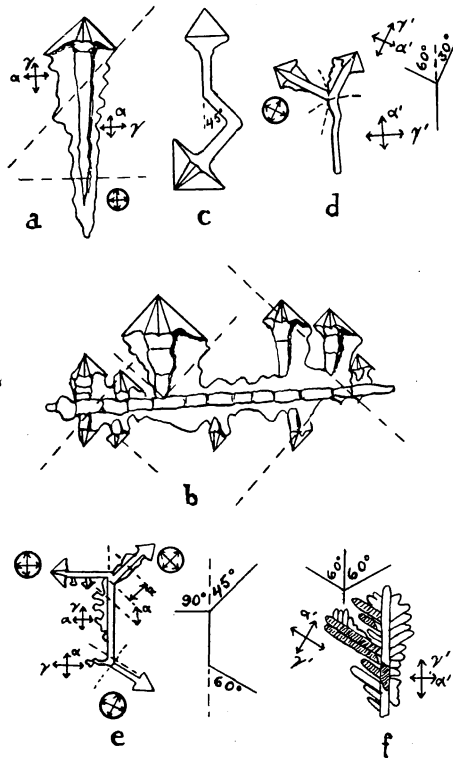


FIG. 4. Cristobalite crystals; size 0.1-0.2mm.

twinning which would give such results as regards the directions of the axes and which is in accord with the observed positions of the faces is twinning after the octahedron (111) or spinel twinning. If, after twinning has occurred at some point during the growth along an axis, the same axis continues to grow, an angle of 60° is formed. If, however, a second axis, which would normally assume a 90° position, starts growth in the twinned position, an angle of 45° results.

The general crystallographic symmetry of cristobalite indicates that under the conditions of formation it is actually an isometric mineral, but in cooling to ordinary temperatures it passes through an inversion, by which it becomes birefringent. In the sketches of cristobalite crystals shown in fig. 4, dotted lines indicate the birefringent fields and arrows show vibration directions. Crossed arrows in a circle show that no birefringence is perceptible. In the last case, the crystals should be perpendicular to an optic axis, or nearly so, but because of the weak birefringence of the mineral and the small thickness of the crystal, no indication whatever of an interference figure could be perceived in convergent light. The sections which showed maximum birefringence, however, gave a figure apparently perpendicular to an optic normal (β). From this it was possible to determine that the acute bisectrix is a and hence the mineral is negative. This agrees with Mallard's determination on natural crystals. The manner in which the birefringent fields are arranged also agrees with Mallard's observations. The plane of secondary twinning is generally quite sharp and makes an angle of 45° or 90° with the cubic axis which it crosses. In some instances, however, the border of adjacent fields is quite irregular, as in f . The position of the secondary twinning plane and the relations which the vibration directions bear to each other is concordant with the idea of tetragonal or orthorhombic* symmetry of the low-temperature form, with twinning after a 45° pyramid parallel to an octahedral edge of the original crystal. During inversion, therefore, the crystallographic space-lattice seems to suffer but little distortion. The tendency to assume skeleton forms agrees with the description of natural crystals, as does the occurrence of twinning after the spinel law.†

PREPARATION OF QUARTZ IN AQUEOUS SOLUTION.

Quartz may be prepared without difficulty by heating either silica glass or amorphous precipitated silica with water and sodic carbonate in a silver-lined steel bomb at 400° to 500° for two or three days. The relative proportions of materials need not be very exact; approximately the following were used in several experiments: water 8^{cc} , silica 2–3 g., crystallized sodic carbonate 0.7 g., capacity of bomb 16^{cc} .

Experiments of this kind have been performed a number of times and have no special interest. Of more importance was an investigation as to the possibility of obtaining tridymite or

* E. Mallard, Bull. Soc. Min., xiii, 175, 1890. A. Lacroix, *ibid.*, xiv, 186, 1891.

† G. vom Rath, Neues Jahrb., i, 198, 1887. P. Gaubert, Bull. Soc. Min., xxvii, 242, 1904.

crystalite under such conditions. A number of experimenters have reported the formation of these two minerals in aqueous solution and this fact had, in the beginning, given rise to uncertainty in regard to the stability relations of the three.

In all my experiments with amorphous silica in alkaline solutions, quartz was obtained. When artificial tridymite or cristobalite was substituted for amorphous silica, quartz was likewise obtained as the end-product. This removed any uncertainty that had been felt as to the relative stability of the three minerals under such conditions and confirmed the results obtained in tungstate melts.

To obtain as much information as possible on the question, it was thought desirable to repeat several of the experiments cited in the literature, in which tridymite or cristobalite was reported.

E. Baur,* in one of his experiments (No. 8) took 5 g. SiO_2 , 4.3 g. Al_2O_3 , Na (composition between soda leucite and nephelite) and obtained quartz, tridymite, and albite. The tridymite was described by Weinschenk as follows: "tablets, made up of countless differently oriented individuals, plainly less refringent than Canada balsam, weakly birefringent, small axial angle, optically positive." To repeat this, I placed in a bomb of 16^{cc} capacity a thorough mixture of 2.5 g. amorphous precipitated silica and 2.15 g. NaAlO_2 (the latter made by heating a mixture of Na_2CO_3 and Al_2O_3 in molecular proportions to 1400°); 6^{cc} of water was added. The bomb was heated to approximately 520° for five hours, then heating current was turned off and the bomb cooled with furnace over night. The resulting product consisted apparently of two different minerals. The first was in sharp, hexagonal prisms cut off squarely by basal pinacoid, elongation negative, both indices >1.530 and <1.535 . The crystals are attacked by dilute HCl, leaving at times crystalline fragments in an amorphous material (probably gelatinous SiO_2). This conforms to nephelite except for slightly lower index. The second material was in roundish granules having at times a suggestion of crystal outline, was isotropic and had index just below 1.490; apparently analcite.

This experiment was performed three times, with some variation as to length of heating and rate of cooling. The products were always the same.

Although these results do not agree with those obtained by Baur, I do not consider that one disproves the other. There can hardly be any question that quartz is the stable mineral under these conditions, but it might well happen that from some combination of circumstances the intermediate form

* E. Baur, Zs. phys. Chem., xlii, 567-576, 1902.

tridymite was first produced and from lack of time did not pass over completely into quartz.

K. v. Chrustschoff,* by heating soluble amorphous silicic acid in an aqueous solution of hydrofluoboric acid for five hours, obtained the following results: at 180–228°, regular crystals, perfectly isotropic, index = 1.58 (possibly a misprint for 1.48), contain 99.78 per cent SiO₂; 240–300°: quartz; 310–360°: tridymite with some quartz.

The regular crystals were considered to be cristobalite, although the index as quoted is markedly different. No data on the tridymite are given in the German abstract.

The writer placed in a bomb of 18^{cc} capacity 4 g. amorphous precipitated silica, 3^{cc} hydrofluoboric acid, made by saturating a 40 per cent solution of HF with B₂O₃; and 3^{cc} water. These were heated 22 hours at 350–380°. The product was mostly unchanged amorphous silica, with which there were a few small but perfectly formed crystals of quartz.

Cristobalite and especially tridymite have been reported as formed similarly in a wet way in numerous instances and natural occurrences due to a similar mode of formation have likewise been reported. There is no reason known why they should not have been deposited as *unstable* forms under such conditions, but these two minerals possess such neutral properties that great care must be exercised in identification and other possibilities must be eliminated before reaching a positive conclusion in such instances.

GENERAL OBSERVATIONS ON THE QUARTZ-TRIDYMITE-CRISTOBALITE INVERSIONS.

The experimental work which has thus far been described has been concerned principally with establishing the stability relations of the three minerals. During the course of the investigation, however, a considerable amount of data was accumulated regarding the conditions under which one form may be converted into another regardless of whether the product was the final or stable form, and regarding the reactions which may be expected under various conditions of treatment. Some of these results are important in establishing points in the unstable fields of the complete silica diagram. The whole may be summarized as follows:—

Neither quartz nor tridymite has been formed under any conditions in the absence of a solvent.

At temperatures below 870° quartz was always produced when any form of silica was heated for a sufficient length of time in a sodic tungstate melt or in aqueous solution. In a sodic tungstate melt the most favorable temperature seemed to

* K. v. Chrustschoff, Neues Jahrb., i, Referate 240, 1897.

be about 825°. Here the conversion of the whole charge takes about three days. A lower working limit to the use of sodic tungstate is imposed by its solidification at 698°. Although quartz is the stable form below 870°, either amorphous silica or cristobalite first yields tridymite and only after much longer heating does quartz appear.

Between 870° and 1470° tridymite is always formed in a tungstate melt. From 1300° upward the reaction is fairly rapid. At high temperatures (1400° and upward) an alkaline silicate glass may be used as a flux. The best crystals of tridymite have been obtained in a tungstate melt at 1300° or thereabouts. Within the tridymite range amorphous silica in fused sodic tungstate or alkaline silicate yields at first a mixture of cristobalite and tridymite, which later becomes entirely tridymite.

From 1470° upward to the melting-point any form of silica heated in a tungstate melt is changed into cristobalite. At 1500° and upward the reaction is fairly rapid.

At high temperatures quartz, heated without a flux, changes to cristobalite even below the tridymite-cristobalite inversion-point. The upper limit of this reaction is set by the melting-point of cristobalite. The lower limit is uncertain. A practical experimental limit is set by the length of time required. Fine grinding much increases the rate of reaction, but finely ground quartz heated 108 hours at 1250° ± showed only a small percentage of inversion. After 90 hours at 1360° ± the product consisted of about $\frac{2}{3}$ cristobalite and $\frac{1}{3}$ unchanged quartz. At 1570° the reaction is nearly complete in an hour.

At 1570° tridymite heated without a flux is converted to cristobalite.

At any temperature below the melting-point of cristobalite down to a limit only conditioned by the length of time required, amorphous silica (either glass or precipitated silica), heated without a flux, changes to cristobalite. At 1030° ± precipitated silica appeared completely changed after 69 hours' heating. (The change may have been complete in rather less time.)

LOW TEMPERATURE INVERSIONS.

The inversions so far discussed have been characterized by a complete change of crystal form. Under the most favorable conditions they take place slowly and with difficulty, and any of the species can be exposed to temperatures far exceeding the limits of stability without any abrupt change occurring. There is another class of inversions however, whose character is markedly different. There is no noticeable change in the outer form of the mineral in question, but some small rearrange-

ment of the internal structure befalls, attended by slight changes in the optical properties, and the transformation occurs promptly and at a definite temperature when the mineral is heated. On cooling, reversion follows with similar promptness, usually not at exactly the same temperature, but at only a few degrees lower. The fact that each of the minerals in question exhibited a phenomenon of this kind has been known for some time, but further investigation has brought out some new facts, which suggest an explanation of the radical differences between the two types of phenomena and have a bearing upon theories of the internal structure of the crystals.

The new phenomena are exhibited most prominently by cristobalite; hence the investigation of this mineral will first be taken up, and later the same sort of inquiry extended to quartz and tridymite.

The α - β Cristobalite Inversions.—Mallard* determined that upon heating cristobalite crystals the birefringence disappeared abruptly at a certain temperature, to reappear upon cooling. Above the transition point the crystals possessed the isotropic character consistent with their crystallographic form. The temperature was placed by him at 175°. Later, F. E. Wright† made a redetermination by heating in the thermal microscope plates of cristobalite cut from spherulites crystallizing in silica glass, and found that Mallard's determination was too low. He placed the temperature at approximately 225°. Recently, Endell and Rieke‡ have found by dilatometric methods a noticeable volume-change taking place at about 230°.

In my own work the problem appeared at first to be merely the determination of the inversion-point by methods as exact as possible. By the application of a very simple device (to be described immediately) it was found possible to determine the inversion-point in a manner which left nothing to be desired, but it was soon observed that the results obtained differed from each other most remarkably. Whereas the inversion-point of any given preparation determined under varying conditions gave results which agreed most satisfactorily, another preparation might differ by twenty or thirty degrees from the first. There was thus revealed a line of investigation which demanded attention, namely, the determination of the limits within which the temperature of inversion could be made to vary, and the factors influencing the variation; finally, the development of an explanation which would be in harmony with the observed facts, and the elimination of all other possibilities which could be conceived by showing that they were inconsistent in one way or another when put to the test.

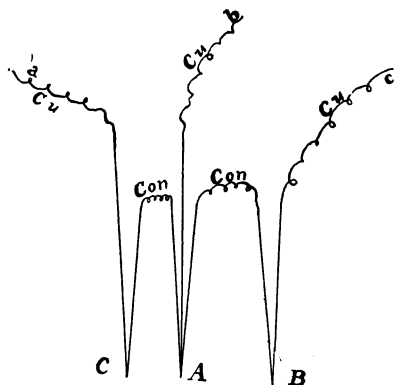
* E. Mallard, *Bull. Soc. Min.*, xiii, 176, 1890.

† F. E. Wright, *J. Ind. Eng. Chem.*, iii, 4, 223, 1911.

‡ K. Endell and R. Rieke, *Zs. anorg. Chem.*, lxxix, 239, 1912.

The inversion from α - to β -cristobalite which occurs upon heating is perfectly sharp but is accompanied by a very small energy-change. Therefore the heating-curve method ordinarily applicable for the determination of a sharply defined transition-point is not adapted for this particular case. By means of a simple modification,* however, very precise measurements may be made. The essential feature of the appliance consisted of the use of two thermocouples, one of which was imbedded in the substance in question and gave directly its temperature in terms of electromotive force, and the second was imbedded in a neutral body which was exposed to the same temperature-treatment as the first, but underwent no transformation involving an

FIG. 5.



absorption of heat within the temperature range under observation. The two thermocouples were connected in such a manner that the electromotive force due to the temperature of one charge was opposed by that of the second, so that readings expressed differences in temperature between the two. The general arrangement is shown in fig. 5. The materials of the thermoelement wires were pure copper and the alloy constantan, whose electromotive force at different temperatures up to 360° has been determined by Adams and Johnston.† These metals give a much larger electromotive force than Pt against Pt-Rh, but can only be used for rather low temperatures.

In the arrangement shown in fig. 5 the element A is placed within the charge under investigation, and the ele-

* Due to W. Roberts-Austen. See G. K. Burgess, Bull. Bureau Standards, v, p. 210, 1908-9.

† L. H. Adams and J. Johnston, this Journal, (4), xxxiii, 534, 1912. The constantan wire used in making my own thermoelements was from the same bobbin as that used by Adams and Johnston for the calibration curve above published.

ment B in the ice-bath. Terminals *b* and *c* are connected to the galvanometer and give the temperature of A. C is placed within the neutral charge alongside of A, and the connections *a* and *b* give the difference in temperature between A and C. By means of a switch one may read first the current in *a-b* and then the current in *b-c* on the same galvanometer. As ordinarily carried out the temperature of A was read and noted every second minute during heating or cooling, and the difference A-C every half or quarter minute except at the two-minute points.

Under ideal conditions the neutral body should be of such a nature and so placed in the furnace that its temperature should be exactly equal to that of the other, and hence the temperature-reading between them should be zero up to the point at which the substance under observation begins to undergo transformation, which would cause its temperature to rise less rapidly than that of the neutral body. In practice this could not, of course, be realized absolutely, but it was not difficult to approach the ideal condition with satisfactory closeness.

Ordinarily the powdered cristobalite was placed in a thin-walled test-tube of about 10^{mm} diameter, and the junction A was imbedded within the powder. In a similar tube was placed a like amount of powdered quartz or feldspar inclosing B. The two tubes, placed close together but separated by an air-space, were symmetrically disposed in the furnace and the heating current turned on. As the temperature rose the differential reading showed some variation, which, however, was small and followed a smooth curve up to a certain point, after which the progress of transformation could be plainly perceived by an increasing magnitude of deflection. This rapidly reached a maximum and then fell back with equal rapidity. The graph of a typical heating and cooling curve has been plotted in fig. 6. The temperature at which the peak of the differential curve was attained was considered the temperature of inversion and its value was calculated by interpolation between the nearest temperature readings on either side. A linear interpolation under such conditions is not strictly correct, but the magnitude of the error, due to this source and to one or two others, which might be mentioned, is believed to be so small as to be negligible. In practice a repetition of determinations was frequently made under variation of conditions and gave closely concordant results. An agreement within 2° was common, and a variation of 4° was quite unusual. As the errors are not of such a nature as to be systematic, the limits found undoubtedly show the degree of approximation to the correct value. In the figures which are given later the calculated temperatures are expressed to the nearest tenth of a degree, but only the integers should be considered of real significance.

The results first obtained were much higher than those found by Mallard and Wright, and I was inclined to attribute the differences to foreign material taken up in solid solution, as the cristobalite which was being employed had been obtained from a tungstate melt. It was found, however, that the amount of variation was independent of the quantity of

FIG. 6.

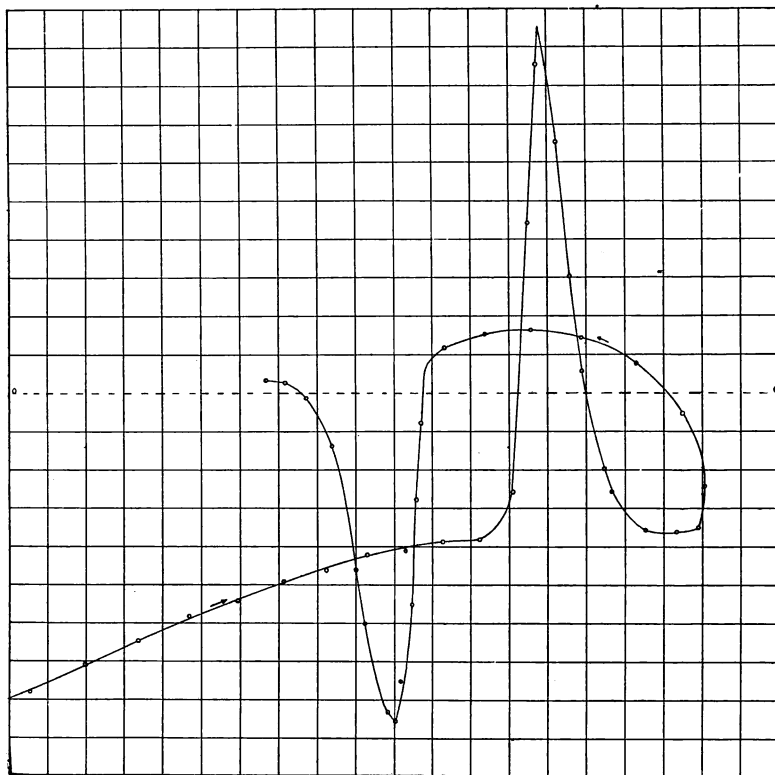


FIG. 6. Heating and cooling curve of the α - β cristobalite inversion. Temperature-differences plotted against temperatures.

Horizontal scale ; 1 square = 500 microvolts (approximately 10°).

Vertical scale ; 1 square = 20 microvolts (approximately 0.4°).

impurity shown by analysis, and the possibility was entirely eliminated by using cristobalite obtained by the inversion of almost chemically pure quartz at a high temperature without a flux. The quartz used for this purpose was specially purified material supplied by Baker and Adamson, which was shown

by a number of analyses to contain only 0.04–0.07 per cent impurity. The results from these preparations were no more concordant than before, and by further investigation it was brought out that we had to do with a phenomenon of a rather different nature from any which had been encountered in previous work in this Laboratory. After considerable preliminary experimentation the results began to point in a definite direction. A tentative hypothesis was formulated as a working basis and investigation was directed along the course indicated by this conception and tended to confirm it. As a final result it can be said that while absolute proof is lacking, the results obtained are perfectly in harmony with the conception and all other hypotheses which have presented themselves as possible explanations have been pretty well disproved.

Briefly stated the conception is this: that cristobalite consists not of one but of at least two different molecular species in the same crystal. The relative proportions of these depend upon the conditions present at the time of crystallization, such as the nature of the solution, if formed in a melt, or the temperature at the time of inversion, if formed in a dry way. The relative proportions of the polymeric molecules as fixed by the conditions of formation are not affected by cooling quickly to room temperatures, but by a second exposure to a high degree of heat a variation in the proportions is brought about by a transformation of some of the molecules of one kind into the other, and upon cooling again the properties are found to have become different in accordance.

It will be recognized that this is essentially the theory which A. Smits and his co-workers have urged strongly in the last three years in a series of papers appearing especially in the *Zeitschrift für physikalische Chemie*, and the *Proceedings of the Koninklijke Akademie van Wetenschappen at Amsterdam*,* and confirmation of this conception has been furnished by certain phenomena exhibited by mercuric iodide, sulphur, phosphorus, etc. Upon it a theory of allotropy has been founded. Smits' theory is a conception of great moment and it is important that all possible evidence should be brought to bear upon it. In this connection the properties of cristobalite appear to have some value.

The point of departure of Smits' theory is that investigation has shown that liquids, either pure melts or solutions, contain as a rule a given substance in two or more sorts of molecular aggregation, each of which is capable of transformation into the others by a change in the mode of linkage of the simple molecules, but the proportions of the various modifications are

* A. Smits, *Zs. phys. Chem.*, lxxvi, 421, 1911; lxxxii, 657, 1913; *Kon. Akad. v. Wet.*, Mar. 26, 1910; Sept. 30, 1911; Sept. 28, 1912. A. Smits and H. L. DeLeeuw, *Kon. Akad. v. Weten.*, Sept. 24, 1910; Nov. 30, 1912.

fixed for any given condition of equilibrium. From this it is but a short step to suppose that when a solid crystallizes from such a liquid not only one but two or several molecular species go to form it. The proportions of the several molecular species in the solid and liquid will differ from each other but a certain equilibrium will exist between the two phases. In the crystallization of such a system the substance in question *may* behave as a unary substance. This is accounted for by the fact that the condition of inner equilibrium in the melt, when disturbed by the appearance of a new phase, is immediately restored by the necessary transformation of molecular species, and in this manner equilibrium is constantly maintained. When, however, the molecular transformations are not accomplished with sufficient facility to maintain equilibrium under rapidly changing conditions, the binary or ternary nature of the substance will show forth. The crystallization of such a pseudo-unary substance will be analogous to that of mixed crystals and should show a similar temperature-range of crystallization. Inversions in the solid state should be characterized by similar phenomena. When inversion occurs the components of the pseudo-unary mix-crystals unmix, as Smits expresses it, and the temperature of inversion will depend upon the relative proportions of the two or more species of molecules as determined at the time of formation.

A further thesis as stated by Smits is "that this theory requires that every substance which shows a transition point must consist of two different kinds of molecules, which are in equilibrium at every temperature."* The necessity of this as a consequence of the main theory is not wholly evident and certain phenomena which will be described later tend to throw doubt upon its validity as a universal proposition. We may suppose that a liquid consisting of the molecular species λ and μ in the proportions demanded by equilibrium starts to crystallize, but that the requirements of the distribution of forces within the crystal-structure can be met only by the species λ . Then the crystallizing solid will withdraw λ only from the liquid, leaving a surplus of μ . This, however, will be met by a transformation of some of the μ molecules into λ until equilibrium is restored, and this process will continue until the whole has crystallized in λ molecules. Moreover such a crystal may possess an inversion-point. The process here will not be an *unmixing* of molecular species as Smits conceives, but it will be more probably a rearrangement of the one kind of molecule within the crystal structure due to the fact that the equilibrium of forces has become unstable when a certain

* A. Smits, Koninklijke Akademie van Wetenschappen te Amsterdam, Proceedings of Mar. 26, 1910 (English text).

has been formed at a very high temperature it will give a peak on the heating curve (such as shown in fig. 6) at about 270° , and on the cooling curve at about 240° ; if formed at successively lower temperatures these two points will drop step by step until at the lowest limit at which cristobalite has been produced the corresponding points are 220° and 198° , a drop of about 50° and 40° respectively.

If cristobalite is of the pseudo-unary but actually binary nature which has been suggested, the temperature-composition diagram should be of the general form shown in fig. 7.

In this the two kinds of molecules are represented by λ and μ . The proportions of these in equilibrium at different temperatures from A to B are given by the line AB, and the β - α inversions of the pseudo-unary mix-crystals are given by the curves CBD and CED. In the inversion of a β -crystal of the composition B a small amount of α -crystal of the composition E is first formed and by the continuation of inversion the composition of the β -crystal moves along BG and of the α -crystal along EF. At F the whole has been inverted. This diagram, however, represents merely a theoretical conception involving the requirement that equilibrium keeps pace with changes of temperature. With such a substance as cristobalite this requirement cannot, of course, be strictly fulfilled and the process will vary in accordance. The composition of the material formed at any temperature such as A or H will be reached only after very long heating, if at all. It is found, in fact, that the actual composition (that is, relative proportions of λ and μ molecules) of the material formed at any given temperature depends upon the nature of the material with which we start. If quartz is employed at the temperature H a composition I is attained, if amorphous silica, a composition K. This is not surprising, if we consider that in the one case we are approaching the composition H from a lower form, and in the second case from a higher. The inference is that the quartz molecule, in breaking up, forms at first relatively more of the lower (λ) molecule than does amorphous silica at the same temperature. The velocity of reaction in converting one kind of molecule into another is so slow (as are all changes throughout the silica diagram which involve the formation of new molecules) that the composition which, at the temperature H, should be represented by the point H on the AB line, is actually represented by the point I in one case and the point K in the other. Moreover, after the material has once been formed and its composition fixed it retains it during cooling. Indeed it is from this fact that differences of composition can be recognized, for material of the composition K', when cooled, will still retain this composition (instead of changing along K'B) and will give the β - α inversion corresponding to

the point K' . For this reason, also, only a small portion of the compositions represented by AB can be realized, that is, the compositions corresponding to very high temperatures. It has been found, however, that if material corresponding in composition to I' , whose β - α inversion temperature is determined, is placed again in the furnace at the temperature K' , a well-marked tendency to change to the composition K' is shown by a shift in the inversion-point toward the right. Likewise material of the composition K' can have its composition shifted toward the left by a second heating at a lower temperature.

In another respect the course of the β - α inversion differs from the theoretical course first outlined. Upon cooling material of the composition represented by K the transformation from the β to the α form might be supposed to start at K'' and be spread throughout the range of temperature from K'' to K''' . There is, however, some undercooling, as is often found in transformations in solids, and the temperature K''' or possibly even a little lower temperature is reached before transformation starts and then the whole transformation goes off at once. Upon the heating-curve also there is a similar delay and the temperature rises to K'' or above before transformation occurs.

These variations from the simple diagram are easily explained and do not obscure the broad, general fact of great variations in the temperatures of inversion produced by previous heat-treatment.

In Table I, I have collected the experimental data which have a bearing upon the matter.

These tabulated figures bring out in a striking manner the general decrease of the α - β inversion temperature with decrease of the temperature to which the material has been previously exposed. The irregularity introduced by the tendency of material made from amorphous silica to give higher figures than quartz is also quite evident. Cristobalite formed in a tungstate melt, it may be noticed, shows similarity to that from amorphous silica rather than to that from quartz.

A certain source of irregularity requires a few words of explanation; that is, that two preparations which give closely coincident inversion-points on heating may differ a number of degrees in the cooling temperature. I think this may be due, in part at least, to some slight variation in composition (proportion of λ and μ molecules) among different crystals in the same preparation. Frequently a sample of cristobalite formed by the inversion of quartz shows still an occasional grain of unchanged quartz, and it seems likely that there should be various degrees of transition between such an unchanged remnant and crystals whose composition is far advanced toward the equilibrium demanded by the temperature to which they have been

TABLE I.

Temperature of α - β Inversions of Cristobalite, showing effects of previous heat-treatment.

Method of formation of the cristobalite	Inversion temperature on heating	Reversion temperature on cooling
No. 108. Made by heating finely ground purified quartz with Na_2WO_4 at 1580°	(a) 272.1° (b) 273.6°	272.8° ----- 238.5°
No. 111. Same as above, at 1570°	(a) 274.5° (b) 272.5° (c) 276.9°	274.6° 238.1°
No. 158a. Produced by heating fine-grained cristobalite with Na_2WO_4 over blast-lamp. Is mixture of tridymite and cristobalite crystals	(a) 272.1° (b) 272.0°	272.0° 231.9° 233.5° 233.7°
No. 179. From ground quartz heated in Fletcher furnace about 40 min. at $1640^\circ \pm$	268.2°	240.5°
No. 116a. Made by devitrifying SiO_2 glass without flux at 1600°	271.1°	234.3°
No. 116b. From large quartz crystals without flux at 1600°	(a) 264.8° (b) 263.5°	264.1° 233.2° 233.7° 233.4°
No. 124. From finely ground quartz without flux at 1580°	(a) 261.7° (b) 260.8° (c) 261.6°	261.4° 231.4° 232.8° 232.1°
No. 168. Made by heating tridymite without flux at $1580^\circ \pm$	268.3°	238.2°
No. 160a. From finely ground quartz without flux at 1580°	(a) 259.9° (b) 262.6°	261.3° 231.5° 229.3° 230.4°
No. 134. From purified quartz without flux at melting-point of platinum	259.9°	232.3°
No. 125. From amorphous precipitated silica without flux at 1450°	258.5°	229.1°
No. 183. From devitrification of silica glass at $1360^\circ \pm$ for 93 hours	(a) 258.5° (b) 255.1° (c) 257.0°	256.9° 218.5° 217.2° 217.8°
No. 126. From ground quartz without flux at 1510°	248.0°	224.5°
No. 121. From ground quartz without flux at 1470°	240.1°	218.8°
No. 133. From finely ground quartz heated 66 hours at 1300° - 1400°	232.5°	209.2°
No. 142. From amorphous precipitated silica heated 70 hours at $1100^\circ \pm$	230.8°	207.2°
No. 175. From amorphous precipitated silica heated 69 hours at $1030^\circ \pm$	225.1°	205.1°
No. 184. From ground quartz heated without flux $90\frac{1}{2}$ hours at $1360^\circ \pm$	(a) 229.5° (b) 229.1°	229.3° 213.8° 212.9° 213.3°
No. 166a. From silica glass heated 68 hours at approximately 1025° - 1075°	219.7°	198.1°

exposed. In inversion the effects due to the different components of such a mixture would be superposed upon each other and could not be distinguished.

Mention has been made of the fact that the temperatures of inversion-points can be changed by heating the sample a second time at a temperature different from that at which it was first prepared. This is shown by the following figures:—No. 142 was prepared from amorphous precipitated silica heated 70 hours at $1100^{\circ}\pm$. Inversion-points 230.8° and 207.2° . After reheating at a high temperature (probably 1500° – 1600°) in a Fletcher gas furnace the inversion-points were 267.5° and 235.5° . No. 175 was from amorphous silica at $1030^{\circ}\pm$ for 69 hours. Inversion-points 225.1° and 205.1° . After reheating to 1570° the inversion-points were 258.3° and 217.6 . No. 166a was made by devitrifying silica glass at approximately 1025° to 1075° . Inversion-points 219.7° and 198.1° ; after heating to 1580° , 258.2° and 225.8° .

When the temperature of the first heating was high the effect of a second heating at a lower temperature was not so striking, though still noticeable. No. 172 was prepared at 1580° and gave inversion-points 268.8° and 226.9° . After reheating 46 hours at $1200^{\circ}\pm$ the points were 263.8° and 227.6° .

From the data which have been assembled there is hardly room for doubt that the position of the inversion-points is dependent upon the previous heat treatment, and the behavior of the material seems to be perfectly consistent with the theory that the crystals are composed of two different molecular species. It remains to be shown that other explanations which have been conceived as possible are not competent to explain the facts when put to the test. There are a number of these possibilities with a greater or less degree of apparent probability.

1°. The variation may be due to foreign material in solid solution. This has already been discussed and its impossibility pointed out.

2°. The effect may be due to differences in lag in the α - β inversion. This was considered as a possible explanation before the amount of variation was known. When it was discovered that the inversion on cooling with some preparations was above that on heating with others, this possibility was eliminated. Before this, however, evidence of another sort had been obtained. It was found that large variations in the rate of heating or cooling made no observable change in the inversion-points. Furthermore, a certain preparation which gave a break at 272.1° on heating and 238.5° on cooling was heated to 320° , then cooled slowly, holding for $1\frac{1}{4}$ hrs. at 247.5° – 244.4° (9° to 5.9° above the lower inversion-point). The temperature was then allowed to drop and the break found at 238.0° , practically the same as before. Heating from room-temperature

and holding for an hour at 7° below the upper inversion-point likewise failed to produce inversion. With the same preparation a device was arranged by which a platinum wire passing through the charge could be brought to a red heat by an auxiliary current at any instant. This would, of course, convert the material immediately in contact with it from the α to the β form and might induce transformation in the remainder of the charge at a lower temperature than before. The auxiliary current was applied at different points during heating, but transformation of the charge as a whole did not occur until 269.1° was reached, which, within the limits of error, may be considered the same point as before.

Probably there is some lag-effect, but so small in amount as to be almost negligible.

3°. The effect may be due to differences in fineness of material. With very fine material, size of grain is a theoretical factor, as the amount of free energy involved in passing from the α to the β form is dependent upon it. Because of the small total energy-change involved in the inversion, any means by which the amount of free energy of one form over that of the other was changed might be conceived to have a large effect in shifting the inversion-point. Experiments were made to determine the amount of the effect which fine grinding would produce, and the results seemed to show that the inversion-point might be shifted a few degrees by this means, but that nothing approaching the differences of 40° or 50° which had been attained could be produced by this process. A certain preparation (No. 160a) gave inversion-points at 261.3° and 230.4° . A portion of this, which was so fine as to settle from suspension in water only after long standing, gave 262.0° and 227.3° . Another portion was ground for about 35 hours in a mechanically driven mortar, being kept moist with kerosene. At the end the grains were so small that they were almost beyond the resolving powers of a No. 9 objective. The kerosene was driven off by gentle heat and the resultant powder gave inversion-points at 259.6° and 218.5° .

Another preparation was divided into two portions by a 200-mesh sieve. The coarser portions gave inversions at 266.4° and 236.0° . The portion which passed through was further ground in a mortar and gave inversions at 271.2° and 231.3° .

Several experiments gave similar results. There is evidently some effect, but its nature may be an increase of the lag in inversion rather than a real shift of the inversion-point, and in any case the effect is of rather a minor order.

4°. The effect may be due to variations among different preparations in the size of the twinned areas in the α form. If one preparation in passing from the isotropic to the birefringent state gave rise to large twinned areas, and another to

small, forces of surface energy would come into play and might produce analogous effects to those considered under 3°. But it was found, as shown above, that surface energy is not an important factor in displacing the inversion-point. However, it was thought desirable to see if any perceptible change could be effected by great variations in the rate of cooling through the inversion-point. The preparation selected gave inversions at 266.2° and 236.2°. A portion was heated 16 minutes at 416°–377° and then plunged directly into water. It gave 265.6° and 235.4°. The same charge was heated to 308° and then held overnight at about 270°. It was then cooled and inversion-points determined. Results were 262.4° and 237.4°. The charge was then heated to 286° and cooled very slowly, requiring three hours to pass from 280° to 229°. The inversion-points were then 266.2° and 236.7°. Apparently, therefore, no treatment of this kind had any effect in changing the temperature of inversion.

5°. As an efficient cause an hypothesis might be considered which seems rather far-fetched but which should be taken into account; that is, that the high-temperature form which appears to be isometric is in reality the same as the low-temperature form, the apparent high degree of symmetry being due to sub-microscopic twinning. Under this conception the so-called inversion-point would be merely a point at which the sub-microscopic areas suddenly grew to perceptible size. This possibility, however, seems inherently improbable from our general knowledge of crystal structure and is further controverted by the crystal characteristics of the α and β forms as described on p. 355. It was shown there that not only is the exterior form of the high-temperature cristobalite consistent with isometric symmetry, but that the manner in which the axes became twinned during growth showed twinning after the spinel law, and gave angles of 45° and 60° between adjacent portions of the axes. In the low-temperature form, on the other hand, the twinning was around a 45° pyramid and caused the axes to assume positions at 90° with each other.

As a result of the investigations on the α and β inversions of cristobalite, we appear to be brought to the conclusion that the variations are due to the presence of two or more molecular species in the mineral, whose proportions are conditioned by the previous heat treatment. Certain minor variations arise from other causes, but their magnitude is so small that the main effect is not seriously obscured thereby.

THE LOW-TEMPERATURE TRIDYMITTE INVERSIONS.

The method used for the determination of the temperature of the tridymite inversions was the same as has been described

for cristobalite; that is, a differential method by which the differences in temperature between the tridymite charge and a neutral substance were read. Previous work with natural tridymite had shown that there was a change in optical properties at a temperature which had been placed at about 130° ; and the intention was to determine this point rather more accurately. It was found, however, that when the curve of temperature-differences against temperatures was plotted, two well-defined breaks were revealed, as shown in fig. 8. It was then considered desirable to investigate this phenomenon more closely and to determine the properties of tridymite formed under varying conditions and ascertain whether the two points were always shown and whether their temperatures were constant. The results are given in Table II.

FIG. 8.

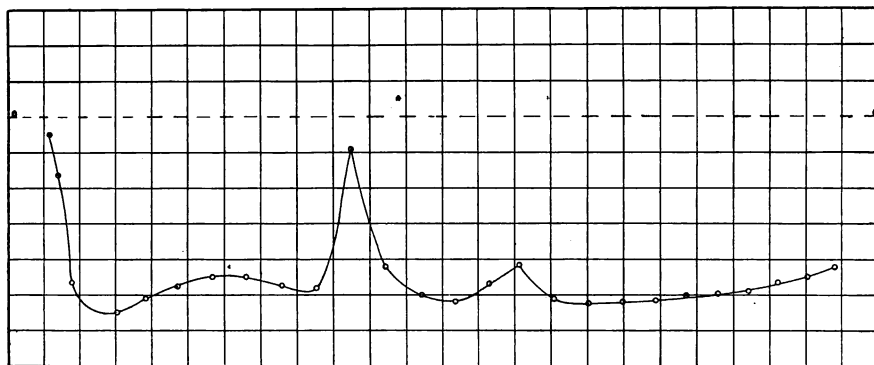


FIG. 8. Heating curve of the α - β_1 - β_2 tridymite inversions. Temperature-differences plotted against temperatures. Horizontal scale: 1 square = 500 microvolts (approximately 10°); vertical scale: 1 square = 10 microvolts (approximately 0.2°).

From this table it will be seen that variations in conditions of formation appear to have no effect upon the inversion. The two breaks always appear and the temperatures are practically constant.

A number of attempts were made to determine by the same method the corresponding breaks on the cooling curves, but nothing which seemed significant could be detected. In order to ascertain the reason for this, optical methods were resorted to. Several tridymite crystals were taken from a specimen of rock from Cerro San Cristobal, which the U. S. National Museum kindly furnished us. These were placed on a glass slide, immersed in a heavy oil, and a cover slip placed above. The slide was laid above a hole in a heavy copper bar on the

TABLE II.
Inversion Points of Tridymite formed under varying conditions.

Method of formation	Temperature of inversion	
	No. 1	No. 2
No. 112. Quartz and Na ₂ WO ₄ heated } to 1000° ± for 118 hours..... }	(a) 116·2° (b) 119·2°	164·0° 160·9°
No. 106. Quartz and Na ₂ WO ₄ heated } to 1000° ± for 71 hours..... }	(a) 117·6° (b) 118·7°	161·7° 161·2°
No. 144. Quartz and Na ₂ WO ₄ heated } to 1300° ± for 3 hours..... }	(a) 117·6° (b) 117·0°	165·6° 164·7°
No. 155. Mixture of quartz, tridymite } and cristobalite made from amor- } phous, precipitated SiO ₂ with } Na ₂ WO ₄ over Bunsen burner..... }	117·1°	162·9°
No. 159b. Precipitated SiO ₂ and } Na ₂ WO ₄ heated over blast. Some } cristobalite formed at same time.... }	115·2°	162·2°
No. 173. Precipitated SiO ₂ and } Na ₂ WO ₄ heated 41 hours at 870° ±-- }	118·4°	162·5°
Average.....	117·4°	162·8°

stage of a microscope, and the ends of the bar were heated by burners. Heating was equalized by covering the bar with sheets of asbestos. The approximate temperature was given by a thermoelement resting against the bottom of the slide. By this means heating and cooling could be conducted rapidly or slowly. In addition to observations on cooling phenomena a close watch was kept during heating to see if any observable change occurred at the second inversion-point. Several experiments were made, running the temperature up to 200° or more and then allowing it to drop. The results were practically identical in each instance. At a temperature of about 120°, on heating, the faint birefringence of a basal section suddenly disappeared. From this temperature on up to 200° (or as far as heating was carried) nothing further could be detected either on isotropic basal sections or on slightly birefringent tilted sections. Upon cooling, the first change noticeable took place considerably below 120° and was not so abrupt as upon heating. At about 90° basal sections began to show a little birefringence, and at 70° to 65° the reversion was apparently complete.

From these results it is inferred that the optical changes attendant upon the second inversion are of a very low order, and that reversion upon cooling occurs considerably below the point obtained on heating and is spread over a range of temperature. For that reason no break can be detected upon the cooling curve by the methods first employed.

In the absence of direct evidence an opinion upon the significance of the second inversion-point (at 163° ca.) is some-

what speculative, but a suggestion may be made as to the probable nature of the phenomenon. This inversion may very well be analogous to that of quartz in passing from the α to the β form. The latter has been supposed to be a change from tetartohedral to hemihedral symmetry within the hexagonal system. With tridymite the change may be one from hemihedral hexagonal to holohedral hexagonal.

The low temperature form of tridymite has been called α -tridymite, and I have adhered to this usage, although it is contrary to the usual custom, which applies the term α to the highest form. The term β -tridymite, it seems now, covers two forms, which it is necessary to distinguish. The system of nomenclature which is in use is not well adapted to meet such a contingency, and I can only suggest that the form stable between 117° and 163° be called β_1 -tridymite and the form stable above 163° be called β_2 -tridymite.

It was seen in the case of cristobalite that the experimental phenomena observed in the inversion from the α to the β form seemed to necessitate a conception of two different sorts of silica molecules within the crystal. As a consequence, the temperature of inversion could be made to vary over a wide range by changing the conditions of formation. With tridymite nothing of this nature can be detected. The temperatures of the two inversions appear to be fixed, whatever the temperature of formation and whether quartz or amorphous silica be employed at the start. Even under conditions of formation of such a nature that quartz, tridymite, and cristobalite are simultaneously precipitated from a melt (as in Exper. 155, Table II), implying the presence of several kinds of molecules in solution at the same time, the tridymite obtained gives temperatures of inversion coinciding with those given by other samples. It seems probable, therefore, that the nature and distribution of forces within a tridymite crystal are such as to admit only one kind of molecule, and in this respect tridymite differs from cristobalite. The supposition might be made that two kinds of molecules are present in tridymite but that equilibrium is maintained by a sufficiently rapid transformation of one kind of molecule into another to keep pace with changes of temperature. A strong argument against this hypothesis is the general reluctance manifested in the transformations of silica molecules.

The low-temperature forms of tridymite and cristobalite are somewhat unique. Although the reaction α -cristobalite \rightleftharpoons β -cristobalite, for instance, is perfectly reversible α -cristobalite has no stable existence and its relation toward quartz is that of monotropy. The same is true of α - and β -tridymite. In this respect the reactions of sulphur are quite analogous.*

* R. Brauns, Neues Jahrb., Beilageband, xxxix, 1900.

The α - β Quartz Inversion.

This inversion has been the subject of considerable investigation since the phenomenon was first observed by Le Chatelier in 1890. The attendant changes in expansion coefficients, circular polarization, and birefringence have all been studied, and O. Mügge* has been able to show by means of etch-figures combined with crystallographic reasoning that the inversion signifies a change from tetartohedral hexagonal to hemihedral hexagonal symmetry, the axial ratios of the two forms being

FIG. 9.

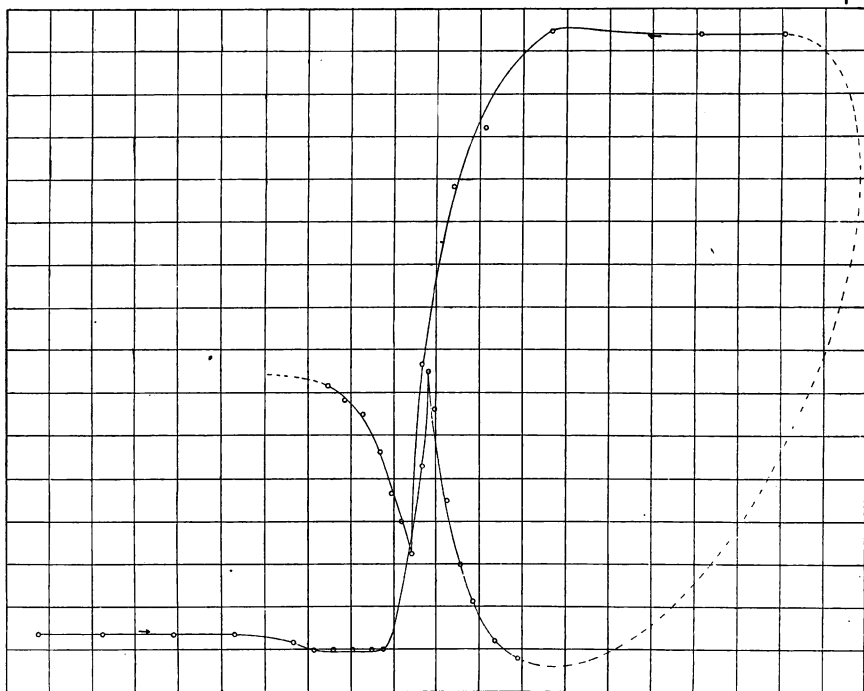


FIG. 9. Heating and cooling curve of the α - β quartz inversion. Temperature-differences plotted against temperatures. Horizontal scale: 1 square = 200 microvolts (approximately 20°); vertical scale: 1 square = 6 microvolts (approximately 0.6°).

nearly identical. Quite recently Wright and Larsen† have extended Mügge's work and have shown that the possibility of distinguishing between α and β forms gives to quartz considerable value as a geologic thermometer. The temperature of inversion as determined in a thermal microscope is given as $575^\circ \pm 2^\circ$.

* O. Mügge, Neues Jahrb., Festband, 1907, 181-196.

† F. E. Wright and E. S. Larsen, this Journal, (4), xxvii, 162, 421-447, 1909.

The subject of this inversion has been so thoroughly studied that there seemed to be little to be added. The chief point to which the writer directed his attention was the possibility of finding a variation in the temperature of inversion similar to that which is so well marked in cristobalite.

The method of determining inversion temperatures was the same as that used for cristobalite and tridymite, but the higher temperature prohibited the use of copper-constantan thermoelements and the standard Pt-Pt Rh elements were substituted. The sensitiveness of these is only about one-fifth that of copper-constantan and the accuracy of determination was slightly diminished, nevertheless very satisfactory results were obtained. The form of curve is shown in fig. 9.

In general, natural quartz of different modes of occurrence was employed, but artificial material obtained by the conversion of cristobalite in a tungstate melt at 800°-835° was also used, and in addition determinations were made on the pure quartz of the Laboratory stock previously heated to very high temperatures. All the results with one exception were almost identical. With this one exception, they are tabulated below.

TABLE III.
Inversion Temperatures of Quartz.

Material used	Inversion on heating	Reversion on cooling
1. Ground quartz, Laboratory stock, } untreated.....	(a) 576.4° (b) 575.5°	570.7° 572.3°
2. Same, heated over Bunsen.....	576.6°	571.5°
3. Same, heated 11 minutes at 1515°.. }	(a) 572.7° (b) 573.7°	567.8° 570.4°
4. Same, heated 10 minutes at 1527°- } 1543° and cooled slowly.....	573.4°	569.1°
5. Same, heated 20 hours at 1200° ± ..	574.7°	567.9°
6. Quartz phenocrysts from granite } near Meissen.....	575.6°	571.1°
7. Amethystine quartz from Paterson, } N. J.....	575.2°	569.7°
8. Milky quartz from Dutchess Co., N.Y.	575.1°	569.3°
9. Crystals of water-clear quartz from } Moritz Co., N. Y., showing right } trapezohedron.....	574.5°	568.9°
10. White quartz from pegmatite vein, } District of Columbia.....	574.6°	567.2°
11. Rose quartz from near Paris, } Maine.....	(a) 574.4° (b) 573.9°	571.2°
12. White quartz from a pegmatite } vein, Maine.....	574.5°	569.5°
13. Abnormal-looking green quartz } from Copper Mt., Alaska.....	574.1°	569.7°
14. Artificial quartz made from cristo- } balite in a tungstate melt.....	(a) 577.1° (b) 577.1° (c) 577.5°	570.2°
Average.....	574.9°	568.9° 568.2° 568.5°
		569.5°

The average of all determinations gives practically the figure 575° for the inversion-point on heating, and 570° for the point on cooling. The very slight variation from these figures given by any sample, whatever its mode of origin or previous treatment, indicates the presence of but one sort of molecule in quartz-crystals, but an element of doubt enters into the question because of the anomalous behavior of one sample not listed above. This material was from a quarry in basalt at Paterson, N. J., and was associated with zeolites. The quartz was doubtless deposited from aqueous solution at a comparatively low temperature. The material collected consisted of separate crystals, $\frac{1}{2}$ cm. in length, perfectly clear and colorless at top, a little milky at base. A little scaly hematite in small aggregates was present. The amount of material unfortunately was not large. Although the crystals all presented the same appearance, it appears probable that some were of normal quartz, as the results from different samples were not strictly identical, though consistently different from the usual values. The amethystine quartz listed as No. 7 in Table III was from the same quarry and collected at the same time.

The first sample of the abnormal material gave for inversion points 567.3° and 556.4° . A second gave (a) 564.4° and 559.8° (b) 564.7° and 559.7° . After heating 3 to 4 hours over blast it gave 564.5° and 560.0° .

A third sample was then taken and subjected to various treatments in the endeavor to obtain evidence as to the cause of the abnormal results. The material was ground very fine in a mortar and heated with concentrated HCl for several days on a steam bath. It was then washed and dried and inversion determined. Next it was heated at 1400° for 17 minutes and inversion again determined. The results were as follows:

Untreated material.				
(a)	569.1°	568.8°	558.2°	556.9°
(b)	568.5°	565.6°	555.6°	556.9°
Treated with HCl.				
(a)	566.3°	565.2°	560.5°	560.2°
(b)	564.9°	559.9°	559.9°	560.2°
Treated with HCl and heated to 1400° .				
(a)	566.5°	567.1°	561.8°	559.4°
(b)	567.8°	557.8°	557.8°	559.4°

The variations are not large and apparently the treatment to which the material has been subjected has not effected any significant change in the inversion-point. In the absence of evidence no definite conclusion can be drawn as to the cause of the abnormality. It seems most probably due to foreign

material in solid solution. The presence of a second molecular species of silica in the crystals is a possibility, but the normal behavior of other quartz from the same locality is opposed to this explanation.

Quartz in Pegmatites.—The criteria for distinguishing quartz formed above 575° from that formed below this temperature, which Wright and Larsen have developed, have enabled these writers and E. S. Bastin* to show that the quartz of pegmatite veins has frequently been formed in the neighborhood of the 575° inversion-point. This may be, in part, merely a coincidence, but it may be suggested that the contraction of the quartz in siliceous masses when cooling through the inversion temperature may be a contributing factor. Recent unpublished work by R. B. Sosman in this Laboratory has shown that in cooling from 600° to 550° the volume of quartz decreases about 2 per cent. This rather sudden contraction being superposed upon the normal contraction which a mass of quartziferous igneous rock undergoes in cooling will favor the development of fissures and their subsequent filling at about the inversion temperature.

Two types of Silica Inversions.—We have seen that the inversions of silica belong to two radically different types. One is distinguished by a small energy-change, small change of optical and crystallographic properties, and readiness of reaction; the other by a much greater change of optical and crystallographic properties, by sluggishness of reaction, and by energy-changes probably of considerable amount. The evidence which has been presented suggests an explanation of the differences. It points to the conclusion that in inversions of the first type the process is simply a small rearrangement of the molecules within the crystal-structure; in those of the second type the change is much more radical and involves the destruction of one sort of molecular species and the formation of another.

RELATIONS OF CHALCEDONY TO OTHER FORMS OF SILICA.

Evidence on the relations of chalcedony to quartz has been mostly of an optical character. The difficulties in the determination of the optical properties of fibrous chalcedony have been so great that no really conclusive proof of identity or lack of identity with quartz has been forthcoming. Arguments on both sides have been presented and at the present time the question seems to be largely a matter of personal opinion among those mineralogists who adhere to one side or the other. Some thermal work has been done by Le Chatelier and the results are frequently quoted, but careful study shows that they are

* Wright and Larsen, op. cit., pp. 446-447. E. S. Bastin, *Jour. Geol.*, xviii, 4, 310, 1910.

very difficult of interpretation and can hardly be considered as evidence. Frequently the specimens of chalcedony were given a preliminary heating and only those which did not become badly cracked were used in the experimental work. The degree of heating is important but is seldom mentioned. In one case,* however, rods of chalcedony whose expansion was to be determined were placed in a porcelain-furnace at 1500°. This naturally converted the chalcedony into cristobalite, and the sudden increase in expansion between 170° and 245° which he found is what would be expected. Le Chatelier speaks of the uncertainty† caused by the multitude of fissures which traverse the specimens after heating and affect the results. I have replotted the values given for a number of experiments and am not able to perceive any definite evidence of sudden expansion corresponding to that of quartz at 575°.

As quartz gives a plainly-marked break on the heating and cooling curves when passing through the inversion-point, chalcedony should give similar breaks if it is identical with quartz. To determine this a number of samples of chalcedony were tested in the manner described under quartz. The specimens were from various localities. One was from the state of Chihuahua, Mexico, another from Tampa Bay, Florida, and a third from Kerguelen Island. The appearance of all was that of typical chalcedony. They were nearly transparent, waxy, and of a botryoidal form, and under the microscope showed a finely fibrous development. The details of experimentation were made precisely the same as for quartz. Heating and cooling curves were run and the region on both sides of 575° was carefully explored, but no indication of a break in the curves was perceptible.

In another form of investigation powdered chalcedony from the localities mentioned was mixed with sodic tungstate and heated at a temperature of 750° to 850°. It will be remembered that amorphous silica, when so treated, gave tridymite at first and quartz later, and the reason for this has been discussed. For the same reason chalcedony, if unstable at these temperatures, might be expected to act similarly, but if it is the same mineral as quartz no change could be expected to occur except that quartz crystals might conceivably grow to a larger size in the melt. In all cases the result was that new quartz crystals were formed and usually tridymite also, often in great abundance. If only a small amount of tridymite were formed under such conditions its origin might be attributed to intermixed amorphous (opaline) silica in the original chalcedony, but the quantity is so large that this hardly seems possible.

* Le Chatelier, *Compt. rend.*, cxi, 123, 1890.

† Le Chatelier, *ibid.*, cviii, 1046, 1889.

The behavior of chalcedony in the thermal microscope has also been studied. A thin section was ground, approximately parallel with the fibers, and carefully polished on both sides so that there was almost no surface diffusion. This was placed in the thermal microscope and the temperature raised rather slowly. The birefringence was observed carefully, especially through the tridymite, cristobalite, and quartz inversion temperatures. No sudden change in birefringence was perceptible up to 725°. There the section began to break up and at 820° was badly cracked, though certain areas were still quite clear. It was then cooled to 400° and no change of significance was observed.

All the work done upon chalcedony failed to show any relationship with quartz, and its conversion into tridymite at 800° to 850° points strongly to its being a different mineral.

Natural occurrences of chalcedony indicate its formation at rather low temperatures, but the evidence is not yet sufficient to decide whether it is stable under the conditions of formation or whether it is an unstable form whose precipitation is due to some peculiarity of conditions.

FUSION OF CRISTOBALITE AND QUARTZ.

In the former work of Day and Shepherd* the melting-point of silica was placed at approximately 1600°. The determination was made by exposing powdered quartz in an iridium furnace to various temperatures determined by an optical pyrometer, and observing the lowest point at which evidences of melting could be established. Under the conditions of experiment there may be a question as to whether the melting point of quartz or of cristobalite was realized. Lately Endell and Rieke† have made a new determination by heating cristobalite in an iridium resistance-furnace, temperatures being measured by means of a carefully calibrated Ir—Ir Ru thermoelement. They place the melting temperature at $1685^{\circ} \pm 10^{\circ}$. Although their work shows evidence of great care the results are not free from suspicion because of the high volatility of iridium at these temperatures and the possibility of contamination of the thermoelements, for which proper allowance cannot be made.

In making a new determination I employed a carbon-resistance furnace through which a current of carbon-monoxide gas was continually passing. Through the middle of the furnace an inner tube of magnesia was placed and a rapid current of dry air passed through it. By this means the atmosphere in contact with the carbon walls was kept of a reducing character, while the inner tube in which the thermoelement and charge

* A. L. Day and E. S. Shepherd, this Journal (4), xxii, 265, 1906.

† K. Endell and R. Rieke, Zs. anorg. Chem., lxxix, 239-259, 1912.

were placed was filled with an oxidizing atmosphere. Thus the contaminating effect of a reducing atmosphere upon the thermoelement was obviated. The charge consisted of a small pinch of cristobalite powder (made from specially purified quartz) wrapped in platinum foil and attached by wires to a standard Pt-Pt Rh thermoelement in direct contact with the junction. Any desired temperature could be attained in a few minutes and kept nearly constant for as long a time as wished. After exposure to the desired temperature the thermoelement and attached charge were withdrawn and the powder was examined under the microscope for indications of the formation of glass.

The reluctance in fusion was so great that length of heating was found to be an important factor. At first a period of fifteen minutes was supposed to be ample and a temperature between 1680° and 1690° was determined upon as that of fusion. Then the effect of longer heating was tried and the previous determination was shown to be too high. In all the later experiments heating was prolonged for half an hour and the lowest temperature at which a minute quantity of glass could be detected was considered to be the temperature of fusion. At a temperature of 1640° (uncorrected) the amount of glass was small, but could be plainly seen; at 1630° most of the grains were unaltered, but a few showed a little glass in minute ridges; at 1620° glass was believed to be visible, but there was a little uncertainty.

A check on the accuracy of the thermoelement was maintained by two calibrations, one made during the course of the experiments and one immediately after their close. The temperature of the furnace was run up to the point at which the platinum wire of the element fused, and the observed reading compared with the correct reading for the melting point of platinum. In one case the reading was 10° low and in the other 13° low. It is evident, however, that the correction to be applied is not of this magnitude, for the same contamination which caused the reading to be too low caused the wire to melt below the true melting temperature of platinum. It seems probable, on the whole, that the readings were not more than 5°-6° low, and I have, therefore, placed the fusing point of cristobalite at 1625° as derived from these experiments.

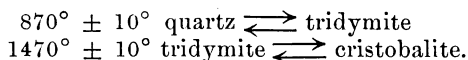
From theoretical considerations the temperature of fusion of quartz should be less than that of cristobalite. There was a question, however, whether the velocity of transformation to cristobalite might not equal that of fusion and prevent the experimental realization of the melting-point of quartz. To try this a quantity of ground quartz (Laboratory stock—0.04-0.07 per cent impurity) was placed in a platinum bucket suspended from a Marquardt tube. A thermoelement was imbedded in

the charge. The furnace having been brought to a constant high temperature the bucket of quartz was introduced and maintained at the same temperature for 30 minutes to 1 hour. After exposure to 1530° for 30 minutes the mass was tightly sintered. Microscopic examination showed the quartz grains to be bordered by a band of appreciable width, whose index was generally less than 1.475 and in some instances less than 1.465; it was isotropic to faintly birefringent; and consisted apparently of a mixture of glass ($n=1.460$) and cristobalite ($n=1.485$). After exposure to 1470° for one hour in another experiment the mass was likewise tightly caked. When immersed in a liquid of index 1.485 many of the quartz grains were seen to be surrounded by a narrow border of distinctly lower index. This same material also cut across many grains, leaving detached portions of crystals, and caused an irregular pitting and corrosion of others. It was found to be generally faintly birefringent and was probably a mixture of glass and cristobalite. That it was not entirely cristobalite was shown by the fact that it could be discerned in liquids of successively lower index—1.480, 1.475, and 1.470. In liquid 1.465 it appeared in most cases to have a higher index than the liquid, but several good cases were found in which the index was lower and the material was isotropic. It appears, therefore, that the fusing-point of quartz is lower than 1470°, but that at this temperature it passes into cristobalite almost as rapidly as it melts.

The fusing-point of tridymite should lie between those of quartz and cristobalite. The artificial material obtained from tungstate melts always retains a small amount of the flux, which would affect the melting-point, and no attempt was made to determine it.

SUMMARY.

The relations between the mineral species quartz, tridymite, and cristobalite have been found to be enantiotropic. The inversion-temperatures under atmospheric pressure are

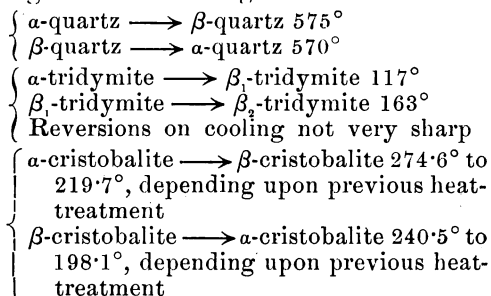


The velocity of transformation of one form of silica into another has been found to be very slow and in many cases the process follows Ostwald's rule; that is, an unstable form does not pass directly into the most stable form, but the action progresses through successive steps, and intermediate phases appear, which eventually reach the stage of greatest stability. The appearance of unstable phases in this manner has suggested an explanation of natural occurrences of tridymite and cristobalite under such conditions as preclude the idea of their

deposition within their range of stability, and an inquiry has been directed toward the circumstances attending their formation.

The preparations of artificial tridymite and cristobalite which have been made have yielded the minerals in very pure form and a re-determination has been made of a number of their optical and other physical constants. The relations of chalcedony have been investigated and evidence has been obtained tending to show that it is a distinct mineral species.

New determinations of the α - β inversions of the several species have given the following results :



A study of the remarkable variations in the temperature of inversion of α - into β -cristobalite has led to the conclusion that this mineral is made up of two different molecular species of silica within the same crystal. Various other properties of the silica minerals seem to have considerable bearing upon theories of the structure of molecules and crystals. The nature of the radical differences existing between the two different types of inversion has been discussed in some detail.

The melting-point of cristobalite has been found to be close to 1625° . Quartz melts at least 155° lower.

The general stability relations are shown diagrammatically in figure 1.

Geophysical Laboratory,
Carnegie Institution of Washington,
Washington, July, 1913.