A SUGGESTED NEW BASE POINT ON THE THERMOMET-RIC SCALE AND THE $\alpha \rightleftharpoons \beta$ INVERSION OF QUARTZ

By Frederick Bates and Francis P. Phelps

ABSTRACT

The $\alpha \rightleftharpoons \beta$ inversion of crystalline quartz has long been extensively studied, using nearly all major physical phenomena as a means of attack and culminating in the recent work of the elder Bragg and his associate Gibbs. Its bearing on the general theory of allotropy is important. In an attempt to measure the rotation of plane polarized light by crystalline quartz at high temperatures it was discovered that the rotation curve for heating was different from that obtained on cooling. A careful investigation of the so-called heating and cooling curves for crystalline quartz has been carried out. Temperature measurements were made by means of thermocouples inserted in small holes drilled in a crystalline plate. By holding the temperature of the furnace when passing through the inversion point as nearly constant as possible, considerable new experimental data bearing on the nature of the inversion were obtained. Superheating and supercooling accompany the transition. The temperature at which the inversion starts on both heating and cooling, as well as the true transition temperature, have been determined. From the characteristics of the curves it has been found possible to calculate the heat of transition at the inversion temperature.

Specimens of quartz from sources widely distributed geographically were studied and the temperature at which the inversion starts on heating found to be identical $(573.3_0^{\circ} \text{ C})$. This is found to be a fixed and definite temperature occurring with great sharpness and suitable for a new type of base point on the thermometric scale, as well as for the standardization and checking of thermocouples in the average physical laboratory.

Ever since the discovery of Le Chatelier¹ in 1889 that crystalline quartz undergoes a profound change when exposed to a temperature of approximately 575° C., numerous investigators have studied the accompanying phenomena. The character of the change assumes a unique importance for many theoretical purposes because it occurs in a transparent material of high purity. Important physical phenomena are produced. The latter proceed from a redistribution or regrouping of the atoms of the crystal without chemical reaction in the ordinary sense. Among the associated phenomena which manifest themselves and which have been carefully studied may be mentioned the energy changes, birefringence, rotation of plane polarized light, change in crystal angles, structural changes (Laue diagram), and expansion coefficients. More recently Bragg² and Gibbs,³ using

² Roy. soc. Proc., 109, p. 405; 1925.

S 557

¹ Compt. Rend., 108, p. 1046; 1889; 109, p. 339; 1890.

³ Roy. soc. Proc., 110, p. 443; 1926.

^{52046°-27}

X-ray crystal analysis, have made important studies of the structures

A-ray crystal analysis, have made important studies of the structures of both α and β quartz and their relation to piezo and pyroelectric effects and to twinning.

Quartz which is stable below the inversion temperature is generally designated α quartz, and that stable above, β quartz. Then the transformation $\alpha \rightarrow \beta$ occurs there is a change ⁴ from the trapezohedral class of the trigonal system to the trapezohedral hemihedral class of the hexagonal system. The axial ratios show a definite but small difference in the two crystals.

The determination of the exact temperature at which the inversion occurs is of importance. Wright and Larsen,⁵ utilizing optical phenomena, obtained $575^{\circ} \pm 2^{\circ}$. Subsequently Fenner,⁶ utilizing the differential thermocouple for obtaining the heating and cooling curves and using powdered quartz from a variety of sources fixed the inversion temperature at 575° on heating and 570° on cooling. The variations between the separate determinations amounted to several degrees. Studies of other physical phenomena associated with the change, although the methods used could not be described as accurate, seemed to indicate that the transformation occurred at approximately 575° . This temperature has come to be generally accepted as the true transition temperature in recent scientific literature, generally without recognition of any temperature difference between heating and cooling.

In a recent precision measurement of the rotation of plane polarized light in quartz at high temperatures the authors discovered that the shape of the rotation-temperature curve on heating was different from that obtained on cooling. These curves rendered uncertain what the criteria for the inversion temperature should be, and indicated, if the energy changes are coincident and associated with the changes in optical activity, that previous investigators in studying the various physical changes accompanying the inversion had taken the temperature corresponding to the most abrupt change in the direction of their curves as defining the inversion temperature. This procedure may be attributed to the absence of sufficiently sensitive experimental equipment or methods and to the employment of too rapid heating and cooling.

In view of these facts a new study of the so-called heating and cooling curves was undertaken to obtain them with a precision corresponding to the optical rotation curves.

The furnace used was 19 cm long and 3 cm inside diameter. The core consisted of a porcelain tube wrapped with nichrome wire, one layer in the center and two layers near the ends. Surrounding this

[•] O. Mugge, Neues Jahrb., Festband, pp. 181-196; 1907.

⁵ Am. J. Sci., 27, p. 430; 1909.

⁶ Am. J. Sci., 36, p. 331; 1913.

Bates Phelps]

core was a brass tube 10 cm in diameter, fitted with asbestos ends and filled with calorox. On 300 watts the furnace attained a temperature of about 1,200° C.

The quartz samples were from crystals collected from sources widely distributed geographically. All were cut in the form of cylinders, with the geometrical axis parallel to the optic axis of the crystal. The dimensions are given in Table 1. All the plates were drilled to permit the insertion of a thermocouple made of 0.2 mm wire. Plate No. 21 had both faces polished. The others were rough ground.

Designation	Diameter	Thickness		
1 21 A B C D E	mm 14. 7 16. 3 14. 5 14. 5 14. 5 14. 8 22. 0	mm 6.2 1.6 7.1 6.4 7.6 4.6 53.0		

TABLE 1.—Dimensions of quartz plates

The plates were loosely mounted in the furnace by means of the holder shown in the diagrammatic sketch (fig. 1). For the large plate, E, the asbestos holder was replaced with brass to insure a more uniform temperature throughout the plate.

The six thermocouples were made from 0.2 mm Pt-90Pt10Rh wire, three of which were made of wire from Heraeus and three of wire from the American Platinum Works. Great care was exercised by the heat division of the Bureau of Standards in the standardization of these couples. The first five were calibrated against the freezing points of Zn (419.4₃), Al (658.7), and Cu (1,083), and a parabolic curve of the form $E=a+bt+ct^2$ passed through the three points. The temperature corresponding to any given emf. of the couple was calculated from this curve, which was also checked at 573° by a platinum resistance thermometer with the following results:

Thermo- couple	Platinum- resistance thermometer			
572. 96	573. 00			
578. 75	578. 70			
577. 86	577. 84			

Couple No. 6 was calibrated by comparison with No. 4 after fusing the two together. In calibrating, the potentiometer used was the one with which the subsequent experimental work was carried out. The couples were thus calibrated directly in terms of the scale of the

Scientific Papers of the Bureau of Standards

instrument with which they were used instead of in international volts, and the necessity of applying a potentiometer correction to the observations was eliminated. The potentiometer had previously been calibrated and found to have negligible corrections. The couples were insulated and protected by pairs of thin, fused quartz tubes, the larger tube fitting over the entire couple and the bare junction being allowed to project about 5 mm. The method of inserting the couples into the furnace is shown in Figure 1.

A sensitive d'Arsonval galvanometer was used for measuring the emf's. The standard cell was checked at frequent intervals. The sensitivity of the apparatus was such that at 573° C., a deflection of 1 cm on the scale of the galvanometer corresponded to 0.2° C. Stray thermal emf's were reduced to a minimum by using all copper to copper connections except in the potentiometer itself.

The apparatus was so arranged that both the battery current and the emf to be measured could be quickly reversed, thus balancing



out any extraneous emf's. The system was frequently checked by replacing the thermocouple ends in the cold-junction box by a short piece of platinum wire, thus short-circuiting the leads at the cold junction. The residual extraneous emf seldom exceeded 0.5 microvolt, corresponding to about 0.05° C. Most of this was in the potentiometer itself.

The first heating and cooling curves were obtained while making precision measurements of the natural rotation of polarized light at high temperatures. A marked slowing up of the rate of heating when passing through the inversion point (a to β quartz) was noticed although the heating current in the furnace was not changed. When the temperature of the quartz was plotted as ordinates against time as abscissas, this slowing up of the rate of heating, curves 1, 3, and 5 (fig. 2) was manifested by a sudden change in the direction of the curve. In curves 1 and 2 the couple was outside but touching the plate, and was influenced by the holder and furnace walls. In all subsequent experiments the couple was inserted in a hole drilled in

318

[Vol. 22

Bates Phelps

the quartz. When the experiment of placing the couple inside the quartz was made the effect was accentuated and the lowering of the temperature of the plate clearly shown, curve 3 (fig. 2), due to the heat absorption in passing from α to β quartz. After a few minutes the temperature of the specimen begins to rise more rapidly than before the inversion, and soon becomes what it would have been had there been no energy change at the inversion point. Obviously the heat capacity of the quartz is small in comparison with that of its surroundings. The reverse of this effect takes place when cooling from β to α , heat being liberated, curves 2, 4, and 6 (fig. 2). Curves 1, 2, 3, and 4 were made with a thin plate, No. 21, Table 1,



and a 0.6 mm thermocouple. Curves 5 and 6 were made on a large plate, E, Table 1.

The curves in Figure 3 are typical curves and are all for the same plate, No. 1. Curves Nos. 1 and 2 are relatively fast heating curves, and No. 3 slow heating. It will be observed that the rate of heating does not affect the temperature at which the inversion (α to β) starts. All the heating curves show a very abrupt change of direction when the inversion starts. This is in marked contrast to the cooling curves (Nos. 4 and 5). There is a rise in temperature during the inversion β to α , but it is not nearly so marked as in the drop in temperature during the reverse action. Neither is the temperature at which the action starts so reproducible when cooling as when heating.

The energy changes are more clearly shown by plotting temperature differences. In Figures 4 and 5 the curves show the difference between the temperature of the quartz crystal and the temperature at which the quartz would have been (furnace temperature) had there been no absorption or liberation of heat by the crystal. $(T_F - T_Q)$ is plotted as abscissae against (T_Q) as ordinates. To show the reproducibility of the phenomena and the order of accuracy obtained, the curves for a single plate of quartz are given in Figure 4. The temperature differences for the heating curves are plotted to the right and those for the cooling curves to the left of the zero line. The agreement shown by the heating curves as to the temperature at which the inversion starts is apparent, the highest and lowest tem-



FIG. 3.—Inversion of crystalline quartz

perature for this point differing by but 0.2° C. In contrast to this agreement, the cooling curves show a variation of 0.6° C. for the starting of the inversion temperature. This difference between the reproducibility of the two points is not due to experimental error, but to an actual variation of a few tenths of a degree in the temperature at which the transformation from β to a quartz begins.

Since the curves in Figure 4 were all obtained on a single sample of quartz, it becomes important to determine what differences would be found by using crystals collected from sources widely distributed geographically. Figure 5 shows for seven different crystals heating and cooling curves similar to those given in Figure 4. These crystals comprised dextro and levo quartzes as well as the twinned variety. Bates Phelps

It will be noted that the variations shown for the beginning transition temperatures are practically identical with those shown by Figure 4. These results indicate the remarkable reproducibility of the phenomenon regardless of the origin of the crystalline quartz used. A total of 40 determinations, Table 2, on 8 different crystals gives 573.3_0° C. as the temperature at which the inversion starts on heating. A



similar determination gives 572.3_8° C. as the temperature at which the inversion starts on cooling. So far as the experimental results may be interpreted, the temperature at which the inversion starts on heating is a well-defined fixed point, and the starting temperature on cooling varies with conditions obtaining in the crystal and not clearly understood.

A casual examination of the heating and cooling curves of the transformation is sufficient to establish the unique character of the phenomena involved. While it is evident that quartz is polymorphic and



FIG. 5.—Inversion of crystalline quartz (Plates Nos. 21, 1, A, B, C, D, E)

that the change is enantiotropic, yet here the similarity ceases when the change, $a \rightleftharpoons \beta$, is compared with the polymorphic properties of most substances, such as the well-known rhombic and monoclinic modifications of sulphur.

TABLE	2
-------	---

	Star	rting temp	perature (α→β inve	rsion of qu	uartz)	
No. 21	No. 1	A	в	С	D	Е	BL
573.3 .4 .3 .3 .2 .3 .() .1 .2 .4	573. 3 .3 .3 .4 .4 .4 .2 .4	573. 2 . 4 . 3	573. 3 . 4	573. 35	573.3 .2 .1 .2	573. 3 . 3 . 4 . 3 . 3 . 3	573. 3 .3 .3 .3 .3 .3

From a study of the heating and cooling curves and other physical phenomena accompanying the change it does not seem possible to ascribe an intermediate liquid or viscous stage between the α and β stages. There is no indication that the usual phenomena which accompany a solid-liquid transition are all present. What, then, is the mechanism whereby the matter in one crystal form passes over into another crystal form, and what is the rate of transformation? Crystallization presupposes the formation of crystal nuclei. The quartz transformation is further complicated by the fact, evident from the curves given above, that superheating and supercooling invariably accompany the transformation. Tammann⁷ in his classical work on the velocity of crystallization of supercooled liquids found that the velocity was a function of the rate of growth of the crystal nuclei and the rate of formation of new nuclei. From all existing data on the quartz transformation there seems to be no indication of the formation of definite crystal nuclei or of a definite rate of growth of nuclei. The transformation appears to be instantaneous when the critical temperature is reached on heating. It was found possible in the present investigation to control the furnace temperature so as to bring a crystal to the critical point with a sufficiently uniform temperature to have the transformation occur almost simultaneously throughout the mass of the crystal. A condition of strain exists in the new crystal for a definite period due to temperature gradients. It is, moreover, conceivable that when the transition starts, the process of recrystallization travels very rapidly throughout the entire mass, provided the temperature is sufficiently close to the critical temperature.

Repeated attempts to check the transformation after it had started were unsuccessful. The atomic forces are no longer in equilibrium in those portions of the crystal which are close to but have not yet reached the critical temperature. The crystal bends, and if the temperature of certain portions is not sufficiently close to the critical temperature, the crystal breaks in spite of its great tensile strength.

⁷ Kristallisierin und Schmelzen, Leipzig, 1903.

It has been shown by Bragg⁸ and Gibbs⁸ that the inversion consists of a shift in the relative positions of the silicon and oxygen atoms. When the initial transition temperature has been reached and the inversion starts, the condition exists that the α and β crystals have the symmetry planes of the silicon and oxygen atoms intersecting at the interface. A different set of forces will then exist at the points of contact. Superheating is necessary to supply the energy to release the atoms from their normal positions with regard to each other. Once formed the β atomic arrangement must travel very rapidly across the crystal as only by its formation can the stresses set up at the points of contact be relieved. The new β crystal comes to equilibrium with the disappearance of temperature gradients and is optically free from strain. This equilibrium temperature is the lowest reached on heating and conversely the highest on cooling. In the present investigation the temperature of the furnace changed so slowly that the entire crystal was so near the transition temperature that splitting did not occur. The same crystal could be carried from α to β and from β to α indefinitely.

The possibility that there may be two different and, perhaps, independent transformation temperatures can not be ignored. Nevertheless careful consideration of the curves in Figures 4 and 5 leads to the conclusion that the phenomena involve two solid phases and that it is possible for the two forms to exist in equilibrium at the true transition temperature, which, however, is not quite reached in these experiments. The transition temperature must, therefore, as shown in Figures 4 and 5, lie between the average low temperature reached on the heating curves and the average high temperature reached on the cooling curves. It is evident from Figures 4 and 5 that after the inversion starts on cooling, the average temperature of the quartz, as indicated by the thermocouple, continues to drop for a brief interval after which it begins to rise and approach the equilibrium temperature. The temperature of the furnace was always steadily falling, with the exception of a single curve which is shown as a straight line. The initial drop in temperature with an average value of 0.13° C. must be caused by heat flowing from the quartz to the furnace more rapidly than the heat of transition is being released. The highest temperature reached on the cooling curves should, therefore, be increased on the average by at least 0.13° C. to obtain as closely as may be possible the average high temperature actually reached. From Table 3 the true inversion temperature is therefore 572.67° C. Obviously, on both heating and cooling a small transfer of heat occurred not shown by the curves. The average curve, therefore, falls short of reaching the true equilibrium

⁸ See footnotes 2 and 3, p. 315.

New Base Point on the Thermometric Scale

temperature by 0.10°, Table 3. It is evident from Figure 4 that the true inversion temperature can not well differ from 572.6_7° C. by more than 0.1° C. However, this 0.1° looms large in the consideration of the nature and character of the inversion. For practical purposes it is significant to note from Table 3 that the value of the transition temperature obtained by averaging the beginning temperatures is 572.8_4° C., a difference of only 0.16° C.

	Heating			Cooling			Inversion
-	Figure 4	Figure 5	Average	Figure 4	Figure 5	Average	tempera- ture
Inversion starts	° C. 573. 33 572. 80	° C. 573. 27 572. 72	° C. 573. 30 572. 70	° C. 572. 35	° <i>C.</i> 572. 40	° C. 572. 38	° <i>C</i> .
Maximum temperature Temperature change	51	54	52	572. 59 +. 24	572.50 +.10	572. 55 +. 17	} 572. 67

 TABLE 3.—Quartz inversion temperatures

If the specific heats of α and β quartz at the inversion temperature were accurately known it should be possible from a consideration of Figures 4 and 5 and Table 3 to calculate the unknown heat of transition of the quartz inversion. White ⁹ and Wietzel ¹⁰ have studied the energy changes in quartz. White gives a table of mean atomic heats determined experimentally from zero to 1,000 degrees, from which it is possible to make an estimate of the specific heats of α and β quartz at the inversion temperature. In this manner by extrapolation, $C_{\alpha} = 0.4$ to 0.7 and $C_{\beta} = 0.262$. Unfortunately White did not obtain a value for C_{α} above 550° or for C_{β} below 700°. Since C_{α} evidently increases in value rapidly as the inversion temperature is approached, the value 0.4 to 0.7 can be nothing more than a crude approximation. The value of $C_{\beta} = 0.262$, however seems much more accurate. Let

 t_1 = the temperature at which the $\alpha \rightarrow \beta$ inversion begins,

 t_2 = the temperature to which the crystal drops, due to the latent heat of inversion, during the $\alpha \rightarrow \beta$ inversion,

 t'_1 = the temperature at which the $\beta \rightarrow \alpha$ inversion begins,

 t'_2 = the temperature to which the crystal rises, due to the latent heat of inversion, during the $\beta \rightarrow \alpha$ inversion,

H = heat change in calories per gram during the $\alpha \rightleftharpoons \beta$ inversion, $C_{\alpha} =$ the true specific heat of α quartz, and

 C_{β} = the true specific heat of β quartz. Hence

 $\begin{aligned} H_{t_1} &= C_{\beta} \ (t_1 - t_2) \\ H_{573.30} &= 0.262 \ (573.3_0 - 572.7_8) \\ &= 0.136 \ \text{g cal.} \end{aligned}$

• Am. J. Sci., 47, p. 19; January, 1919.

¹⁰ Z. anorg. u. allg. Chem., **116**, p. 71; 1921.

Bates Phelps 0.136 g cal. is less than the true value of H because a small amount of heat must have been absorbed from the furnace by the crystal during the inversion.

The temperature interval lying between the temperature at which the inversion starts on heating and cooling is (from Table 3) 0.92°. Since, from the curves $(t_1-t_2)+(t'_2-t'_1)=0.69^\circ$, the heating and cooling curves do not reach the equilibrium temperature. If it is assumed that the heating and cooling curves, when corrected for heat interchange, would just reach the equilibrium temperature, 572.67°, then $(t_1-t_2)=0.63$ and $(t'_2-t'_1)=0.29$. Therefore

$H_{573,30} = 0.63 \times 0.262 = 0.165$ g cal.

Because of the uncertainty regarding the value of $H_{572 \cdot 3_8}$, it seems inadvisable to estimate the value of C_{α} . However, a relatively large value for the specific heat of α quartz at the transition point appears reasonable in view of the fact that it makes the acceleration in the specific heats of the α crystal comparable with the acceleration of other physical properties, such as the optical rotation, at this point.

The dissimilarities in the heating and cooling curves (fig. 4) seem consistent with the above facts. The outstanding dissimilarity is the flatness of the cooling curves at the inversion temperature in contrast to the marked drop in the heating curves in passing from α to β . Since the density of 2.65¹¹ of α quartz is the highest of all the quartz modifications, there is a volume change with a corresponding increased energy content to correspond to a density 2.518¹² for β quartz. The abstraction of this additional energy results in the marked drop in the temperature of the new β crystal. On cooling, the rise in temperature does not correspond in magnitude with this drop.

While it is evident that the condition obtaining in the crystal at the inversion temperature is gradually brought about as the temperature approaches the inversion temperature, the change from trigonal to hexagonal form—that is to say, the shift in the relative positions of the silicon and oxygen atoms when it does occur—occurs instantaneously on both heating and cooling. The important thing is, however, as shown by the heating and cooling curves, that the condition obtaining in the crystal is different as the inversion point is approachedon cooling from the condition obtaining in the crystal as the inversion point is approached on heating. There is a definite hysteresis effect. The inversion takes place in a different manner on heating from what it does on cooling. The curves showing the rotation of plane polarized light corresponding to the heating and cooling curves, which will

326

¹¹ Tammann-Wehl, States of Aggregation, p. 183.

¹² Day, Sosman, and Hostetter, Am. J, Sci., 37, p. 1; 1914.

Bates Phelps

appear in a subsequent paper, throw additional light on the mechanism of the transformation.

It is evident from what has preceded that the start of the inversion of α quartz to β quartz occurs at 573.3° C. and that this is a sharply defined fixed temperature. It is not a function of the origin of the crystal or of its morphological character. The energy change is of sufficient magnitude to be readily detectable by the thermocouple. In addition, clear crystalline SiO₂, in considerable masses, is one of nature's most common and widely distributed fine structure forms. The idea at once suggests itself that here is a nearly ideal material to provide a new base point on the thermometric scale. In the present temperature scale¹³ there are six base points covering the range from liquid oxygen to the freezing point of gold. The region from steam, 100° C., to silver, 960.5° C., is covered by sulphur, 444.60°, and antimony, 630.5°. The temperature 573.30° comes between the boiling point of sulphur and the melting point of antimony. In view of the many advantages connected with the quartz inversion for temperature scale purposes, it is suggested that the antimony point might be abandoned as a base point. In addition, the wide distribution of α quartz and the ease with which it can be utilized for initial thermocouple standardization and subsequent periodic verification gives what is, perhaps, the most convenient and simple method for the calibration and control of thermocouples in the average laboratory. It is sufficient to select a small piece of clear crystalline quartz and if not convenient to drill a small hole for the insertion of the thermocouple, merely place it in contact with the quartz.

WASHINGTON, May 25, 1927.

¹³ Mueller, I. C. T., **1** p. 53.

A















