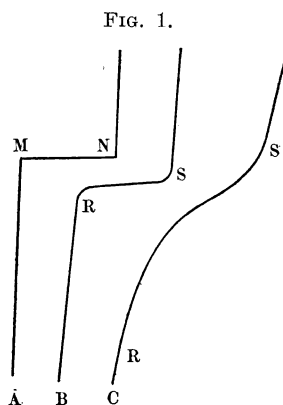


ART. XLIV.—*Melting Point Determination*; by WALTER P. WHITE.

[INTRODUCTORY.—The recent great advances in pyrometry, together with the development of the electric furnace, have given to many physical and physico-chemical determinations at high temperatures almost the ease and certainty attainable at ordinary temperatures. The appropriate special technic, however, being of very recent development, is not yet generally familiar; the importance, also, of the whole new and fertile high-temperature field is still growing in appreciation. It has therefore seemed wise that the methods developed at the Geophysical Laboratory be published from time to time for general information, aside from their immediate application to our own work. In pursuance of this idea, two special papers have already been published, treating of furnace construction and of temperature measurement up to $1600^{\circ}\text{C}.$ * The present two papers deal with the application of such measurements to those methods of physico-chemical thermal analysis which, best known through their revelations of the constitution of metallic alloys, are now being applied with equal success to the minerals and allied compounds. The first treats of melting phenomena in general, and its conclusions are not restricted to the high-temperature field. The second describes the furnace technic used to realise the conditions treated in the first.]



The preëminent value of melting ice as a temperature standard has made familiar the great constancy of the ideal melting point and its independence of external temperatures. The great majority of actual melting point determinations, however, fail to show this ideal constancy, and display a melting interval, rather than a point. If the temperature-time curve, A (fig. 1), represents an ideal

FIG. 1. Melting curves. A, ideal: B and C, actual curves for silver and anorthite, reduced from Day and Allen, *Isomorphism and Thermal Properties of the Feldspars*.

* Day and Allen, *Phys. Rev.*, xix, 177, 1904; W. P. White, *Phys. Rev.*, xxv, 334, 1907. Other papers from this laboratory incidentally treat of methods, but in this respect are largely summarized (as well as supplemented) by the present papers.

melting under uniform heat supply, with MN as the interval of constant temperature, the actual result with a substance melting at high temperature more nearly resembles the *oblique* curves B and C, where the temperature intervals RS may be as much as 60°.

When the melting curve is oblique, there is a much greater opportunity for both accidental and systematic errors. In our own work these have not been serious, considering the high temperatures concerned, and were for a long time far less uncertain than the extrapolated temperature scale itself. The greatest discrepancy in a set of determinations of the same point has seldom reached 3°.*

But other observers had found much larger and sometimes confusing irregularities, and had questioned the value of the thermal (Frankenheim) method of determining melting points; moreover, the causes for the obliquity of these melting curves were in themselves of interest; and finally, in investigations on some pyroxenes, a problem was encountered which called for much more accurate comparative measurements than we had been getting. A general investigation was therefore undertaken of the thermal method of determining melting points, with the twofold object of learning more about the properties of matter in the vicinity of the melting temperature and of improving our own technic. As a result, the agreement of our silicate determinations has been increased about five-fold,† along with an actual gain in case of experimental manipulation. An insight into the relations involved has also been obtained which has cleared up several questions once very puzzling, and has pointed the way to a further increase in accuracy whenever this seems necessary.

A number of substances, organic and inorganic, melting at temperatures from 0 to 1400°, were examined under various conditions. Most of these experiments were devised to test hypotheses and need not now be described in detail. The conclusions to which they led will perhaps also gain if presented in a different order from that of the actual investigation.

To fix the ideas, it may be well to recall at the outset the general plan of the experimental arrangement used in our regular work, to which this article more directly applies. The substance to be melted is contained in the crucible (fig. 2).

* It may make for clearness to emphasize at the outset that the errors considered in this paper, which the investigation here described sought to diminish, are errors of 5° or less, occurring in the regular work of this laboratory upon silicate fusions. With the systematic differences of 100° to 200° sometimes occurring in the literature, this paper has nothing to do.

† This improvement has already been illustrated in a paper on Diopside and its Relations to Calcium and Magnesium Metasilicates, this Journal (4), xxvii, 4, 1909.

In the middle of the charge is the thermometer, which in our case has always been a thermoelement of some kind. This is sometimes used bare, sometimes surrounded by porcelain and platinum jackets, as here represented. The crucible is heated by an electric resistance furnace, for which a storage battery furnishes a very regular source of heat. An additional control element, C, indicates the furnace temperature, and also, if desired, permits of regulating it.

FIG. 2.

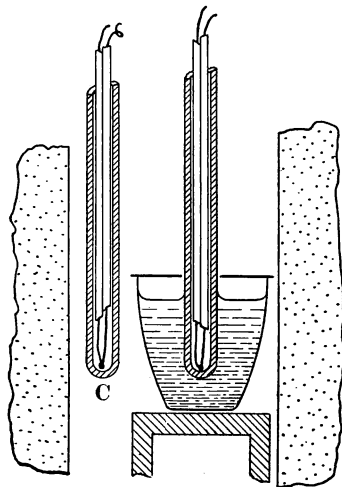


FIG. 2. Sectional view of ordinary melting point apparatus (half size).
C, control element.

It is a familiar fact to workers in this field that freezing points are often sharper and show much better agreement than melting points. The reasons for this difference occupy much of the present paper. One result of it is that freezing point determinations are generally preferred, and most of the literature of the subject relates to observations made with falling furnace temperature. Freezing points, however, are uncertain or useless in substances where undercooling is marked or crystallization sluggish. Since this is nearly always the case in silicates, the melting point, in spite of its greater experimental difficulty, is the only one used in our silicate work, and is the point mainly in view in this paper. The special disadvantages of the melting curve would no doubt be largely overcome by stirring, but effective stirring is difficult in many cases, impossible in the rest, and has never been attempted here.

The principal causes of oblique melting curves appear to be the following:

- A. Primary, i. e., inherent in the substance itself.
 - I. Time lag in the melting process (with very viscous substances).
 - II. The presence of impurities.
- B. Secondary, i. e., due to a failure of the apparatus to register truly the behavior of the substance.
 - III. Inconstant heat supply.
 - IV. The normal temperature gradient between the outside and inside of the melting charge.
 - V. Accidental irregularities in temperature distribution.
 - VI. Flow of heat along the thermoelement.
 - VII. Electrical conductivity of the charge (in case the thermoelement is used bare).
 - VIII. Inhomogeneity of the thermoelement.
 - IX. Differentiation of the charge in crystallizing.
 - X. Radiation through the melting substance.

I. *Viscosity*.—Day and Allen* discovered that albite and orthoclase exhibit a sort of hysteresis in their melting, and the same thing has since been found true of quartz. It is connected with the great viscosity of the melted substance near its melting point. The change of state takes place gradually, even at temperatures many degrees (100 or more) above that at which it will also occur, if time enough is given. Theoretically, this effect must probably be regarded as characteristic of all substances, though of course it is too small to be perceived in most. That it might generally be large in silicates, however, did not at first seem at all unlikely, but such is not the case. Although considerable portions of a charge of albite or orthoclase may remain unmelted after several hours exposure at a temperature 150° or more above the point where melting begins, diopside (to take one instance) has been heated three times at rates varying from 4° to 13° per minute with results agreeing to .1°. (The distinguishing sign of the presence of this phenomenon is of course the variability of the melting temperature with the rate of heating.) Hysteresis in melting, therefore, is only an occasional cause of obliquity in melting curves.†

II. *Impurity*.—The effect of impurity in diminishing the sharpness of melting points is fairly familiar, especially to organic chemists. But the character of the effect on the temperature-time curve seems to have been little appreciated, and its importance and magnitude have often been underestimated.

* Isomorphism and Thermal Properties of the Feldspars, Publication No. 31, Carnegie Institution of Washington, pp. 50-54; this Journal (4), xix, pp. 119-125, 1905.

† If the hysteresis is large, however, the melting point procedure evidently needs radical modification. See the next article, p. 483.

It is, in fact, a direct result of the melting point lowering due to the impurity, and an expression for it can be derived from the law of the lowering. This takes a very simple form for the most common and important case, namely, that in which the depression of the melting point is proportional to the amount of impurity. A discussion of this case will serve to show the usual character of this important effect.

In order to define a melting point curve, two quantities are necessary, and usually sufficient—the temperature rise ($d\theta$) and the quantity of heat (dQ) required to cause it. Indeed, the true melting point curve is only the graphic expression of the relation between these two, that is, of the quotient $\frac{dQ}{d\theta}$. When the temperature rise is plotted against time, the time really serves only as an approximate measure of the added heat. $\frac{dQ}{d\theta}$ is,

however, by definition, the specific heat.* Hence a melting body as a rule is completely accounted for thermally if it is treated as a body of enormously variable specific heat, and this is often the simplest and easiest way of dealing with it.

The effect of impurity, then, on the melting curve is its effect on the quotient, $\frac{dQ}{d\theta}$, which is found as follows for the case where the melting point lowering is proportional to the amount of impurity present.

Let the melting point of the perfectly pure substance be taken as the temperature zero; (the temperatures during melting will then be negative and will decrease numerically as the substance becomes hotter.) Let θ_0 be the lowering of the melting point in the actual case. The temperature, θ_0 , is then the temperature at which the impurity present has just sufficient concentration to bring the whole mass of solvent into fluid condition. Next, let half the solvent be crystallized by lowering the temperature. The concentration of the impurity is now double what it was before, and the lowering of temperature by hypothesis also double, or equal to $2\theta_0$; similarly, one third of the solvent will remain liquid at $3\theta_0$. Or, if A is the fractional part of the solvent left in a liquid form, $A \propto \frac{1}{\theta}$.

This may be written $A = \frac{K}{\theta}$ where K is a constant to be determined.

* $\frac{dQ}{d\theta}$ may, of course, also be so measured as to equal the heat capacity.

As the two are proportional to each other for the same charge, the distinction is of no importance here.

Now the rate of absorption of heat by melting, that is, the portion of $\frac{dQ}{d\theta}$ required for the melting, is proportional to the amount melted per unit rise in temperature; that is, proportional to $\frac{dA}{d\theta}$, or, say, *equal* to $m\frac{dA}{d\theta}$, where m is merely the factor of proportion. But $\frac{dA}{d\theta} = -\frac{K}{\theta^2}$, and since the integral of $m\frac{dA}{d\theta}$, that is, the integral of $m\frac{K}{\theta^2}$, from θ_0 to ∞ , must equal the latent heat, L , therefore mK is equal to $L\theta_0$. Accordingly, if S is put for the true specific heat at any temperature, the total virtual, or apparent, specific heat, Σ , is

$$\Sigma = S + \frac{L\theta_0}{\theta^2} \quad (1)$$

for temperatures below and not too far from θ_0 . Through most of the interval where the equation can be used, S is relatively so small as to be usually negligible and the function may then be written simply,

$$\Sigma = \frac{L\theta_0}{\theta^2} \quad (2)$$

The form of the resulting melting curve can now be obtained by writing $\frac{dQ}{d\theta}$ for Σ and integrating from θ_0 to θ , giving

$$[Q]_{\theta_0}^{\theta} = \left(S + \frac{L}{\theta}\right) (\theta - \theta_0) \quad (3)$$

from which Q can be obtained in terms of θ . If (2) instead of (1) is used,

$$Q = L - \frac{L\theta_0}{\theta} \quad \text{whence} \quad \theta = \frac{L\theta_0}{L-Q} \quad (4)$$

from which θ can be plotted in terms of Q . Here θ is still measured downward from the true melting point, and Q is really the amount of heat given out as the body freezes. But of course this expression gives the form of the curve as well as any, and is simpler than one with positive temperatures and heat quantities would be.

Such a curve is the smooth curve of fig. 3. The circles mark a curve actually observed near 900° in a case where all other sources of obliquity were practically eliminated.

The recognition of the part played by impurity changes radically the ordinary conception of melting point phenomena.

Instead of a constant temperature, the observer has to deal with one varying continually from beginning to end.* The course of the phenomenon, so far from being independent of the furnace temperature, follows it closely and registers its

FIG. 3.

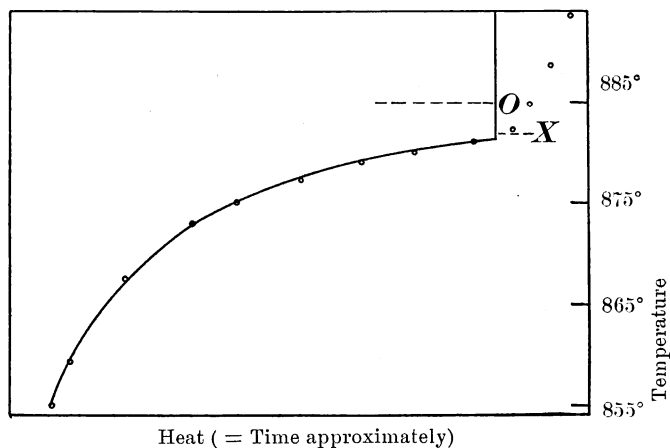


FIG. 3. Typical melting curve. Points taken from an observed curve for Na_2SO_4 containing $\frac{1}{4}$ per cent NaCl . X-O, melting point depression below pure substance. Smooth curve calculated by formula 3 for the depression, X-O. Data page 484.

every fluctuation.—Some consequences of this point of view deserve discussion.

1. *The accuracy of the thermal method.*—The obliquities of thermal curves have been cited by several observers as an evidence of the inaccuracy and untrustworthiness of the thermal method. Rather are they the very sign of its fidelity to the phenomena. If a method could be devised which gave perfectly sharp points in ordinary substances, it would by that very fact be convicted of misrepresenting the facts and of consequent untrustworthiness. And while the method, for instance, of locating the melting temperatures by watching for changes in the appearance of the charge shows in a way the gradual progress of the melting, its results are much further removed from the quantitative. There is no definite connection between the amount of material melted and the appearance of the charge to the eye. The thermal method alone at high

* The fact that a melting interval and not a melting point is really in question has been recognized by some observers, who regularly determine the upper and lower limits of this interval. It is clear, however, from the discussion above that the assignment of any lower limit is entirely arbitrary.

temperatures contains the possibility of tracing exactly the progress of a melting from beginning to end.

2. *Variation of the obliquity with temperature.*—In accordance with the familiar formula, $\Delta = \frac{0.2\theta^2}{L}$, the melting point depression, Δ , is proportional to the square of the absolute temperature and therefore (see equation (3) for instance) the melting curve obliquity must vary in the same way. Hence the large effect produced at high temperatures by amounts of impurity which would be quite negligible lower down. Thus, to take a roughly approximate illustration, .1 per cent of an impurity of molecular weight 80, say CaF_2 , dissociated to double the number of molecules, would by the formula lower the normal melting point (1392°) of diopside 1.3° , and would cause an apparent doubling of the specific heat 20° below that, while if the equation (1) held strictly, the beginning of the melting would be easily perceptible 50° lower still. A similar impurity would lower the melting point of ice only $.05^\circ$, and the doubling of the apparent specific heat would occur within 3° of the melting temperature.

These facts have a direct bearing on the question of the value of melting point determinations in natural minerals. While the impurities of natural minerals in rare cases run within a few parts per thousand, they are usually to be reckoned in percents. But one per cent of impurity may be expected to lower the melting point from 3° to 10° and extend the distinctly perceptible melting interval over some 100° . And silicates with 3 per cent of impurity usually show in most decided fashion the characteristic behavior of two-component systems.

3. *Experimental determination of the quantity of heat supplied to the charge.*—A quantitative knowledge of the heat supply is evidently essential to a correct melting curve. The use of time as a measure of it, which forms the basis of nearly all the common melting point methods, is recognized as merely a rough approximation,* and would not have answered at all in most of the cases here treated. Hence a more accurate method was employed. It rests on the use of the control element, C, fig. 2, which allows a determination of the temperature difference of furnace and charge, on which, and not on the temperature of either alone, the heat flow directly depends. This method is more fully treated in the second paper, p. 485.

4. *Single melting points.*—In most determinations on melting substances, the melting temperature is the sole object of

* G. K. Burgess, *Methods of Obtaining Cooling Curves*, Bull. Bur. Standards, v, 223, 1908; W. Rosenhain, *Observations on Recalescence Curves*, Proc. Phys. Soc. London, xxi, 183, 1908.

investigation. This temperature, θ_0 of the formula, is the upper end of the melting interval, the point X of figs. 3 and 4. The other characteristics of the curve, the values of the specific heat, etc., are then, at most, questions of minor interest. Nevertheless, in such cases the complications due to impurity are as important and as troublesome as anywhere. For in an impure substance the melting temperature desired is merely one value of a continually changing magnitude. Before it can be measured it must first be located on the oblique curve. But, coming as it does at the top of the melting interval, and therefore at the end of the melting, it falls where the temperature changes are most irregular, disturbed and uncertain of interpretation. The resulting difficulties occupy the rest of this paper. Meanwhile, a glance at fig. 1 shows the difficulty which may arise in locating the single melting point.

III. *Varying rate of heat supply.*—In determining the single melting point of an ideally pure substance, the character of the heat supply is a matter of indifference so long as it does not approach zero or infinity. For the exact determination of the melting curve of an impure substance, the heat supply must be well known, as has just been seen. For determining the single melting point of a rather impure substance an intermediate condition obtains. The heat supply need not be known and need not be constant so long as its variations are regular. That is, the "break" will show on almost any *smooth* curve. The determination of a melting point with a varying heat supply, however, often gives rise to a secondary phenomenon so striking and so apt to be misleading as to deserve mention here. This occurs when the furnace rate is kept nearly constant, as it usually is. As soon as the charge begins to melt, its temperature rise is checked, so that the continued advance of the furnace widens the gap between them; thus the constant rate of the furnace necessarily involves a very variable rate of heat supply to the charge. The result is to hurry up the latter end of the melting, apparently increasing its obliquity. The same happens at the end of a freezing curve, if such is taken. But the end of a melting curve is the top, of a freezing curve the bottom; hence the two kinds of curves are distorted out of all resemblance to each other, the melting curve appearing more, the freezing curve less, oblique in the upper part than it really is. The observer who, attempting to secure constant conditions, approaches his melting or freezing determinations at the same rate, and then maintains this rate constant in the furnace, is likely to go through the critical part of his melting curve five to ten times as fast as he realizes. If, however, the initial rate is then adjusted by trial so as to give satisfactory results at

the end of the melting, the only disadvantage will be the loss of time in taking the first part so slowly; and this may sometimes be less objectionable than the remedy—which is, to make separate observations on the furnace temperature and thus keep the external temperature gradient constant.

HEAT DISTRIBUTION WITHIN THE CHARGE.

The next three causes of obliquity constitute the chief practical problem in melting point work. They depend upon differences of temperature within the charge and could be avoided if thorough and effective stirring were possible. They are less detrimental in the determination of freezing than of melting points, and are less also in metals whose high thermal conductivity is in part a substitute for stirring. To them it is due that, other things being equal, the melting point of a salt usually cannot be determined quite as accurately as that of a pure metal or as its own freezing point. They may, however, be greatly diminished by proper experimental arrangements.

IV. *The regular and normal temperature gradient across the charge.*—The error and uncertainty resulting from the failure to stir has often been greatly overestimated. The charge as a whole may present great temperature differences, but the thermoclement does not record all these at once. It accounts only for the portion immediately surrounding it, and when this portion melts it will show a "break" in the temperature curve. Toward this small system of element and surrounding material, the outer portions of the charge act in many respects as so much foreign matter—though foreign matter which is particularly troublesome, on account of its own heat absorptions. Their effect can be investigated with quite enough exactness for the present purpose, by the device already used, of treating the melting charge as a body of variable specific heat.

1. *Expression for the temperature distribution in an ordinary charge.*—As a heated charge is brought toward its melting point, the supply of heat is usually constant, and then

the rate of temperature rise, $\frac{d\theta}{dt}$, soon becomes the same at all

points. The resulting temperature distribution at any instant may then be found to a sufficiently close approximation as follows: Suppose, first, that the body is spherical with a radius equal to R , and the heat flow is entirely along radial lines. Consider a spherical surface, A , at a distance, r , from the center of the sphere. Its area is $4\pi r^2$; the inclosed volume $\frac{4\pi r^3}{3}$. The

flow of heat across it may be expressed in two ways: (1) Directly, as the product of area, conductivity and tempera-

ture gradient, that is, as equal to $4\pi r^2 K \frac{d\theta}{dr}$; and (2) as the heat absorbed by the inclosed volume, or the product of volume, volume specific heat, and the rate of temperature rise, equal to $\frac{4\pi r^3}{3} S \frac{d\theta}{dt}$.

Equating these two and integrating, remembering that $\frac{d\theta}{dt}$ is here a constant, we have

$$\Delta\theta \Big|_r^R = \frac{S}{6K} \frac{d\theta}{dt} (R^2 - r^2) \quad (5)$$

If the charge is an infinitely long cylinder, we have the same expression with 4 substituted for 6 in the denominator of the second member. In general, we may say, therefore, that the temperature gradient within a uniform, solid, steadily heated charge approximates a parabola, and the difference of temperature between center and outside for bodies of the same shape is proportional to the *first power* of the rate of heating and to the *square* of the diameter.

If we let $\delta\theta = \Delta\theta$, then δt is the time required for a given temperature value to pass from R to r,—that is, it is the *time lag* of r behind R. It equals

$$\frac{S}{6K} (R^2 - r^2) \quad (6)$$

It is independent of the rate and is thus important as a property of the charge alone.

2. *Effect of the melting on the temperature distribution.*—In an actual melting point determination one fundamental hypothesis of the preceding no longer holds. The temperature rise of the charge is not regular after melting begins. We may, however, still proceed for the case of a small charge, for which the time required to reach an equilibrium temperature distribution will be relatively small, so that the divergence from such a distribution may be neglected in making the first approximation. Mathematically, the problem then reduces simply to finding the effect of a change in the specific heat, the rate of heat supply, $\frac{dQ}{dt}$, remaining constant. This is easily done as follows: Since

$$\begin{aligned} dQ &= Sd\theta \\ \frac{d\theta}{dt} &= \frac{dQ}{dt} \cdot \frac{1}{S} \end{aligned} \quad (7)$$

If, therefore, the specific heat S increases n times, becoming nS , the rate, $\frac{d\theta}{dt}$, will evidently *diminish* n times. The time lag (equation (6)) will *increase* n times. The temperature distribution can be found by substituting from (7) in (5). The result is:

$$\Delta\theta] \frac{dQ}{dt} \text{ const} = \frac{dQ}{dt} \frac{1}{6K} (R^2 - r^2) \quad (8)$$

In this expression the specific heat does not appear at all. The equilibrium *temperature* distribution, therefore, is not altered by a change in the specific heat. Among these results of a change in specific heat the increase of the time lag is of most immediate interest. Occurring under constant heat supply to the whole charge, it involves a retardation in the supply to the center, and one which is proportional to the square of the radius. The formulæ thus express in a roughly quantitative way the otherwise obvious fact that as the melting begins the inner layers fall behind, since the outer layers for a time absorb large quantities of heat, passing very little to the interior. Expressed in terms of temperature, the retardation will be $n-1$ times the (original) time-lag times the rate.

This result, however, as already indicated, applies strictly only to an infinitesimal charge, since it assumes a complete homogeneity, which the melting itself destroys. In the actual case, while the body is melting the outer layers will have a higher temperature and therefore a greater specific heat than the inner. This, it can readily be shown, will diminish the temperature difference between center and surface and therefore the time lag, while an increase of conductivity due to melting will probably act in the same direction. The retardation of the center will thus really increase less rapidly than the square of the radius, and for a very large crucible will not even approach the formulæ just given.

As soon as the outward layer of the charge is fully melted, the whole course of the phenomena changes. The virtual specific heat of the substance while melting is usually from 50 to 100 times what it is before or after, hence the heat capacity of the whole depends for a time almost entirely on the still unmelted core. As this diminishes the *relative* heat supply to it increases, increasing the obliquity of the critical end-portion of the curve. Nor is the resulting distortion, like that from uneven heat supply, above described (page 461), merely a general increase in steepness at the end. It is a rapidly accelerated increase, changing the form of the curve in that region. In large crucibles, it often masks entirely the break at the end of the melting, substituting for it a premature break a degree

or two *lower down*, due to the rapid increase in heat supply before the melted layer has touched the thermoelement at all.

In brief, then, the inevitable heat distribution in an unstirred charge has this effect on the center, where the thermoelement is located. It retards the normal temperature rise at the beginning of the melting and partly makes up the loss by accelerating it at the end, thus increasing the obliquity of the curve just where such increase is most undesirable. This effect increases somewhat less rapidly than the rate of heating and than the square of the diameter. The difference of temperature between center and surface remains nearly constant for small crucibles, but diminishes during melting for large diameters and rates.

3. *Magnitude of the distortion.*—Diopside, a well-crystallizing silicate, melting at 1392° , showed a time lag of 24 ± 6 seconds for a crucible of 1^{cm} radius before melting began. The charge was in shape a short cylinder. The latent heat was enough to raise the solid over 300° , but was so distributed that the maximum value of the virtual specific heat was only about fifty times the true specific heat.

If, now, this substance is heated in a crucible of 1^{cm} radius with a constant heat supply, giving a temperature rise before melting begins of 8° per minute, the melting will last (roughly) thirty-five minutes. The time lag (surface to center) would by formula (6) reach twenty minutes for a charge all at the maximum specific heat, but in this case, as experiment shows, will be not much over half that. Even so, however, the period of accelerated heat supply to the center will last ten minutes, so that the last third (or more) of its melting will be distorted. This third covers an interval of 2 to 3° . The resulting uncertainty in the melting point would be less than that, and, therefore, not very serious, but with a crucible of 4^{cm} diameter the uncertainty would be much increased.

If the crucible has 1^{cm} diameter (·5^{cm} radius), the maximum lag by formula (6) is only five minutes, or one-seventh the melting interval, and the whole accelerated interval is not over half a degree. If this smaller crucible, however, contains a substance of greater purity, say sodium chloride, melting through a 1° interval, the virtual specific heat might reach 400 times the true, and the accelerated interval would again cover a third or more of the melting.

The distorting effect produced on the melting curve by the normal gradient through the charge is, then, practically important only in large charges, and though serious in them, can be rendered negligible by a reduction of dimensions which is easily attainable in practice. The distortion is also relatively greatest in the purest substances, where the total obliquity is least detrimental.

For naphthaline, the time lag was about three times that for diopside. For metals, the conductivity is so great that distortion of the kind just considered is probably always negligible in practice.

4. The above seems to justify the following practical conclusions: (1) *For determinations of single points*, the essential thing is to reduce the interval of accelerated heat supply. This calls for small crucibles or slow rates. And when they are used, the difficulties arising from the regular temperature gradient across the charge can be rendered negligible compared to other sources of error. The requirements of a given case depend on the accuracy desired and on the purity of the substance, and can be determined well enough for all practical purposes from the length of the melting interval in conjunction with the approximation just given for the relation of time lag to radius in different substances. (2) *For determining the form of the whole melting curve*, the time lag must be kept small, and this again calls for the narrow crucible but not the slow rate, for a reason given in the following paper (p. 485). (3) Whether rate or radius, or both, shall be diminished will depend mainly upon the apparatus and conditions at the disposal of the investigator. The whole time required to complete the melting varies nearly as V , the rate of heating. The distortion varies as R^2V , but V varies as G/R , where G is the external gradient, hence the distortion varies as GR also. And, therefore, for the same distortion by diminishing R , V and G are both increased. So if R is made, say, one-third, the run may be finished in one-ninth the time, and the effect of variation or uncertainty in the furnace temperature also diminished three times, with little increase in distortion.

V. *Irregular variations in heat distribution.*—The preceding section has dealt with an ideal case. It assumes a charge in which the heat travels uniformly toward an infinitesimal thermoelement situated exactly at the center. Of course these conditions are never completely realized.

Sources of irregularity may lie in the furnace, in the charge itself, or in imperfect centering of the thermoelement. Aside from these, there is nearly always a tendency for melting to start at one end of the charge, either top or bottom. In any case, the difficulty comes mainly from the fact that the melted area reaches some parts of the thermoelement before others, so that the temperature of the junction depends on different portions of the charge, some of which are melted while others are not. This converts the ideally sharp break (X, fig. 3) into a gradual rise, of uncertain interpretation. To avoid this difficulty, two things are necessary. The thermoelement itself should conduct heat as little as possible, and the melting should

approach it from the side and not from the end. This calls for a thermoelement of fine wire, and for a charge narrow but not too short. Failure to center the thermoelement is evidently a minor fault. A thermojunction inclosed in a porcelain tube is from the present point of view undesirable, since its temperature is dependent on a considerable portion of the charge. A resistance thermometer is evidently still worse. In fact, the difference in sharpness is very marked between melting points measured with an inclosed and a bare thermoelement. But a bare element of platinum wire $\cdot 6^{\text{mm}}$ in diameter, immersed 8^{mm} in a cylindrical charge of $9 \times 14^{\text{mm}}$, has been found to give (from 800° up) points quite as sharp as can be obtained with wire much smaller. Since finer wire than this and narrower and higher charges can be easily used, there seems to be no difficulty in avoiding the effect of irregular temperature distribution for substances in which a bare element is admissible. A few experiments indicate that at lower temperatures charges narrower in proportion to their height may perhaps be needed, but at lower temperatures they can also easily be employed.

VI. *Conduction of heat along the thermoelement.*—The thermal conductivity of most substances is much less than that of the metal thermoelement, so that the junction often receives heat along the wires. This causes a gradual additional rise of temperature toward the end of melting, thus increasing the obliquity, and it also tends to make the final break come high. The effect is little altered by change of rate, since this acts in the same way upon the heat, whether coming through the charge or down the wire. It increases with the diameter of the charge, since this increases the time of melting for the same external gradient. It is diminished by thinness of the thermoelement, and by depth of immersion in the charge. The avoidance of this cause of obliquity, then, demands the same conditions as for the preceding, namely narrow and high charges and fine thermoelement wires. And the experience just now cited to show that the one cause of obliquity can be easily avoided is equally conclusive with respect to the other. On the other hand, an enclosed element, immersed 3^{cm} in a crucible of sodium chloride, gave a melting point 7° too high. This error is much greater than that found with some other substances melting at higher temperatures,* but it shows that melting point results obtained with inclosed thermoelements must be interpreted with care. A sufficient estimate of the error resulting from heat conduction down the thermoelement can in general be easily reached by varying the depth of

* See, e. g., *Isomorphism and Thermal Properties of the Feldspars*, pp. 23-25; *Diopside and its Relations to Calcium and Magnesium Metasilicates*, pp. 3-4, loc. cit.

immersion. This method applied to 2.5 gram silicate charges indicates that there was no perceptible error of this sort with the element immersed 6 to 8^{mm}, thus confirming the results obtained by varying the size of wire.

VII. *The use of bare thermoelements.*—From the foregoing it is clear that in several ways a very great advantage results if the thermoelement can be inserted directly in the charge. But an error may then be introduced, due to the electrical conductivity of the charge itself, which can not be altogether neglected. At high temperatures, practically everything conducts electricity to some extent.

The slightly conducting charge acts like a battery of very high resistance connected in shunt across the junction.* The effect on the galvanometer reading of such a battery is easily

shown to be practically equal to $E_s \frac{T}{S}$, where E_s is an E.M.F.,

T , the (very low) resistance of the shunted portion of the thermoelement, S , the (very high) resistance of the shunt. It follows, first, that the leakage error increases with the depth of immersion of the thermoelement and the fineness of its wires, and second, that by dipping into a charge portions of a thermoelement far from the junction the effect can be magnified, and so a very delicate test made for it. Indeed, for this test there need be no junction at all; if there is one, either it can be kept at room temperature, or its E.M.F. can be measured by making it also the junction of two other wires which do not dip in the charge. In these ways it has been shown that the error due to this effect, under the conditions of our work, is not over one or two-tenths of a degree, either in sodium chloride near 801° or in diopside near 1400°. It was also shown, in the case of sodium chloride melted in a crucible over a Bunsen burner, that the E.M.F. is thermoelectric and is directed (in this case) from the electrolyte to the colder of the two wires. Hence the error increases with the temperature differences present in the charge. The convection currents of a large charge frequently reveal their presence through the slight unsteadiness of the galvanometer, and in one case the leakage disturbance from melt conductivity was increased a hundred-fold by bringing a charge too near the furnace top.†

The conditions making for small leakage error are therefore: Uniformity of external temperature, smallness of charge, and thickness and shortness of the immersed portion of the thermo-

*The effect would of course be the same if it were connected across any other portion of the circuit.

†It is therefore clear that the results just quoted as to the very small error from conductivity of the melt should be applied with great caution in extreme cases.

element. These are in part antagonistic to those required for diminishing effects V and VI, but with apparatus of the dimensions given above, page 467, all these errors are reduced to one or two-tenths of a degree or less.

MINOR CAUSES OF OBLIQUITY.

VIII. *Contamination of the thermoelement.*—If the furnace is heated continuously and more or less regularly throughout the melting interval, the temperature of the furnace end relatively to the charge steadily rises, and if the thermoelement is not homogeneous between these two, its reading will rise also.* In the case of a badly contaminated element at 1400° , this apparent increase of obliquity was found seldom to exceed 1° . It practically vanishes if a constant temperature difference is maintained between furnace and charge, as also of course if the element is in good condition; hence, while not to be overlooked, it should never constitute a serious difficulty.

IX. *Differentiation in the charge.*—The portions of an impure charge which crystallize last may have more impurity in them, hence there may be a tendency for that part of the charge immediately around the thermoelement to melt at a lower temperature than the outside. This would tend to increase the obliquity of the observed curve. Thus far, we have not been able with certainty to distinguish this effect from the other accompanying causes of obliquity.

X. *Radiation through the charge.*—If the charge which is being melted is diathermanous, direct radiation from the crucible wall to the thermoelement will heat the latter, causing a temperature rise which is greatest at the beginning of the melting and which depends upon the fluctuations of the furnace temperature. This effect, also, has not yet been distinguished with certainty.

PRESENT STANDING OF THE PROBLEM.

Fig. 4A shows the typical melting curve of a fairly limpid silicate (diopside). That the obliquity in the lower part of this and similar curves is due to the substance itself (and therefore to impurity) can be easily shown as follows: The obliquity always precedes the melting, wherever that may occur, hence it is due to the melting in some way or other, and not to the furnace; that is, it indicates a true heat absorption accompanying the melting. When the heat absorption begins, the thermoelement in the charge reads about 30° lower, and a bare element exposed directly to the furnace outside the charge reads (usually) 25° lower than the final melting point. Hence

* Phys. Rev., xxvi, 535, 1908.

no part of the very small charge can then be at or near the melting point itself. And therefore some heat absorption due to melting must occur at least 20° below the melting point. The obliquity is also, within the experimental error, such as would be expected from the known impurity, and can be increased in silicates, and produced in substances originally pure, by the addition of impurity.

FIG. 4.

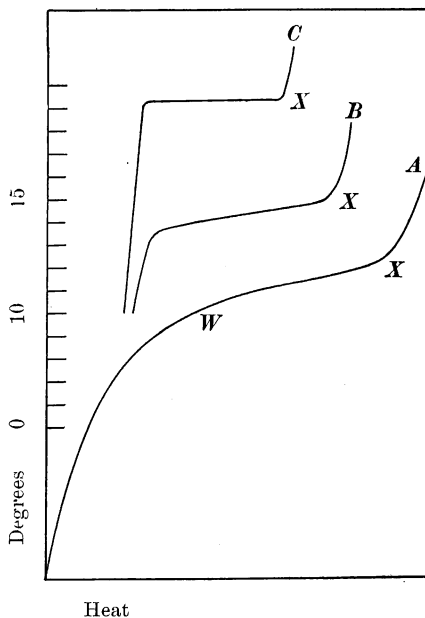


FIG. 4. Actual melting curves. *A*, Diopside (melting point 1392°). *B*, NaCl (melting point 801°). *C*, Na_2SO_4 (melting point 885°) (see text pp. 469–471).

The slope of the curve at the top from *W* to *X* is inconsistent with equations (1) to (4) and is not easily accounted for by any other known impurity effect. An attempt was made to determine its cause. Variations in rate of heating, in the depth to which the thermoelement was immersed, and in the size of the wire, did not materially alter this part of the curve, thus showing that neither distortion (effect IV) nor conduction down the thermoelement (VI) was responsible.

An easily crystallizing substance was next tried. Sodium chloride (freezing point $801^{\circ} \pm 1^{\circ}$)* gave the curve *B* in fig. 4, which shows the same peculiarity. Variation of rate and of

* This is a new determination.

size of thermoelement wire did not affect it perceptibly. The freezing point here lay below the melting point as determined from the curve. Hence in this case, the slope of the upper end of the curve is due to the temperature measurement and causes the melting point to come a little high. Presumably the same thing is true of the silicates giving curves like A of fig. 4. In fact, the results obtained by adding different amounts of impurity to one of these silicates are much more consistent with each other and with equation (1) if the melting points are taken a degree or so lower than indicated by the curves.

Sodium sulphate† (melting point $885^{\circ} \pm 1^{\circ}$)* was then tried. The resulting curve is C of fig. 4. The whole melting interval was 1° in one charge, 3° in another, which probably became slightly contaminated in handling. For a temperature so high, this is a remarkably sharp curve. Taken with the preceding it indicates that the false rise at the end of the melting may be avoided, and that a clue to its cause may be found in the physical differences between sodium sulphate and sodium chloride at their melting points. A further investigation of the problem seems to require apparatus not now at hand. Meanwhile, the systematic error for the melting point determination in a limpid silicate has been reduced to a degree or so, and the accidental variation to half a degree, and this accuracy is obtained with exceedingly simple and convenient apparatus. The error in the true melting point of these silicates due to impurity is (in our case) quite as great as (and opposite to) the experimental error. An attempt to realize greater accuracy, probably attainable only through more elaborate experimental arrangements, has not seemed necessary at present.‡

The addition of impurity to the sodium sulphate of fig. 4, C, gave the typical oblique curve of fig. 3.

* This is a new determination.

† From J. T. Baker Chemical Company, who gave the following analysis: Ca, .005 per cent; Mg, none; Fe, .0006 per cent; Cl, trace.

‡ In the work on Diopside, etc. (this Journal, xxvii, 8, 1909), the melting points of the eutectic in different mixtures of pseudowollastonite and diopside are not quite the same, as by theory they should be, but rise with the percentage of eutectic present, varying about 6° . The variation, though far within the limits of error of most previous determinations at this temperature, is consistently greater than the accidental variations of our results. Two causes for it are indicated by the present article: (1) Where the percentage of eutectic is larger and the time of melting, therefore, longer, the false rise at the end of the melting curve is greater. These results are therefore a little too high. (2) Where the amount of eutectic is small the total impurity present bears to it a larger ratio, and there is thus a tendency for the melting point lowering to be increased—these results are thus a little too low. It is probable that both causes are operative.

Hüttner and Tammann* point out the connection between impurity and the obliquity of the melting curve, here developed in equations (1) to (4), and suggest that the form of the curve may be a convenient means of estimating non-isomorphous impurities. They give a numerical computation for the last half of the melting interval (or the first half of the freezing interval), but appear to have overlooked the result which would be obtained by carrying their calculation farther down the curve, for they have no other explanation of the large obliquity usually found there than conduction of heat along the (bare) thermoelement, which they assign as the principal source of obliquity. Their view as to the practical cause of such obliquity is thus decidedly opposed to that reached in the present investigation.

Summary.

1. Actual melting and freezing point curves are nearly always oblique—that is, they show, not the constant temperature called for by elementary theory, but instead, an interval within which the temperature continuously rises or falls.

2. The prime cause of obliquity in melting curves is the obliquity of the melting itself, due to impurity. The true melting point is the high end of the oblique melting interval.

3. The melting hysteresis of some very viscous substances (mostly compounds of boron and silicon) is also an occasional (and then serious) cause of obliquity.

A number of causes of obliquity lie in the experimental determination of the behavior of the melting and freezing substance.

4. The determination of a melting curve necessarily involves two factors: temperature rise, and heat supply; the latter depends on the temperature difference of furnace and melting charge; if this varies, the curve is distorted in a way striking but easy to correct. The most common and conspicuous example is where the furnace temperature is allowed to rise or fall continuously, while the substance, melting or freezing, remains nearly stationary.

5. The freezing point, coming at the beginning (in time) of the interval, where temperature distribution in the charge is relatively uniform, is easier to observe than the melting point, but is inadmissible in substances where undercooling is marked.

6. The melting point, coming at the end (in time) of the interval, is liable, where stirring is not practiced, to obliquities resulting from uneven temperature distribution: First, due to the inevitable temperature difference between inside and out-

* K. Hüttner and G. Tammann, Über die Schmelzpunkte und Umwandlungspunkte einiger Salze. *Zeitschr. f. Inorgan. Chem.*, xliii, 218, 1905.

side of the charge, troublesome with large charges, negligible with small. Second, due to various irregularities in heat flow, less with narrow charges and small thermoelements, hardly ever over a degree or two. Third, due to conduction of heat down the thermoelement, also less with narrow charges and small thermoelements, for which it is usually negligible; but possibly amounting to several degrees with inclosed elements.

7. Electrical conductivity in the melt produces an error in the reading of bare thermoelements, thus far negligible in small charges of salts.

8. Contaminated elements, besides reading false, read so as to increase obliquity.

9. Differentiation and diathermancy of the charge probably increase obliquity.

10. Meltings have been made above 800° agreeing with each other to $\cdot 05^{\circ}$. In most cases an experimental obliquity remains of from $\cdot 5^{\circ}$ to $1\cdot 5^{\circ}$ (at high temperatures) whose cause is still to be definitely determined.

Geophysical Laboratory, Carnegie Institution of Washington,
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