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## THEORETICAL ANALYSIS OF CERTAIN TIME-TEMPERATURE FREEZING AND MELTING CURVES AS APPLIED TO HYDROCARBONS<sup>1 2</sup>

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### ABSTRACT

A method is described for determining analytically or graphically, from appropriate time-temperature freezing and melting curves obtained on hydrocarbons, the freezing point of a given substance, and within certain wide limits, the freezing point of that substance for zero impurity (liquid-soluble, solid-insoluble).

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### I. INTRODUCTION

In a recent paper [1]<sup>4</sup> dealing with time-temperature freezing and melting curves obtained on hydrocarbons, it was shown how, when significant undercooling occurs on freezing, the observations can be analyzed to yield, in proper relation to the subsequent equilibrium part of the curve, the "zero" time, that is, the time at which crystallization would have begun in the absence of undercooling. In that paper, visual extrapolation of the equilibrium part of the curve, to "zero" time on freezing and to the corresponding time on melting, was used to determine the freezing point, defined as the temperature at which

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<sup>4</sup> Figures in brackets indicate the literature references at the end of this paper.

an infinitesimal amount of crystals of the major component is in equilibrium with the liquid.<sup>5</sup>

The present paper describes a method, which may be used analytically or graphically, for extrapolating the equilibrium part of a time-temperature freezing or melting curve to give the freezing point,  $T_f$ , of the given hydrocarbon substance. There is also included a description of a method for deducing, within certain wide limits, from the same observations on the given substance if carried over a sufficiently large fraction of material crystallized or melted, the freezing point for zero impurity,  $T_{f_0}$ . When the heat of fusion is known or can be estimated, the value of  $T_{f_0} - T_f$  serves to give the amount of liquid-soluble, solid-insoluble impurity in the given substance.

## II. DERIVATION OF THE BASIC EQUATIONS

The definitions, abbreviations, and symbols used in this paper will be exactly the same as those of the previous paper [1], except that the subscript  $f$  attached to the time  $z$ , as in  $z_f$ , denotes the time corresponding to the freezing point,  $T_f$ . Some of the previous definitions and equations are repeated below for the sake of clarity and emphasis.

For an ideal, or a sufficiently dilute solution, the thermodynamic relation between the temperature of equilibrium and the composition of the liquid phase, for the equilibrium between a liquid phase consisting of a major component and one or more other components and a crystalline phase of the major component alone, is [2, 3]

$$-\ln N_1 = -\ln(1 - N_2) = N_2(1 + 1/2N_2 + \dots) = \\ (\Delta H_{f_0}/RT_{f_0}^2)(T_{f_0} - T)[1 + (1/T_{f_0} - \Delta C_{p_0}/2\Delta H_{f_0})(T_{f_0} - T) + \dots]. \quad (1)$$

In eq 1, the symbols are defined as follows:

- $N_1$  = the mole fraction of the major component in the liquid phase;
- $N_2 = (1 - N_1)$  = the sum of the mole fractions of all other components in the liquid phase;
- $R$  = the gas constant, per mole;
- $T_{f_0}$  = the absolute temperature of the freezing point of the major component when pure (that is, when  $N_1 = 1$  or  $N_2 = 0$ );
- $\Delta H_{f_0}$  = the heat of fusion, per mole, of the major component in the pure state at the temperature  $T_{f_0}$ ;
- $\Delta C_{p_0}$  = the heat capacity per mole, of the pure liquid less that of the pure solid, for the major component in the pure state at the temperature  $T_{f_0}$ ; and
- $T$  = the given temperature of equilibrium.

The assumptions involved in the derivation of eq 1 are the following:

- (a) The liquid solution is ideal, or sufficiently dilute, so that the fugacity of the major component in the liquid phase is proportional to its mole fraction.
- (b) The heat of dilution is negligible over the range of concentration from  $N_1 = 1$  to the given value of  $N_1$ .

<sup>5</sup> It is important to note that this temperature, when properly measured, must have the same value whether approached from a higher temperature as in cooling or from a lower temperature as in warming.

(c) The heat of fusion of the major component in the pure state at the temperature  $T$  may be represented by a power series expansion, as

$$\Delta H_f = \Delta H_{f_0} + \Delta C_{p_0}(T - T_{f_0})[1 + \dots] \quad (2)$$

Introducing the following additional abbreviations,

$$A = \Delta H_{f_0}/RT_{f_0}^2, \text{ and } B = 1/T_{f_0} - \Delta C_{p_0}/2\Delta H_{f_0}, \quad (3)$$

expanding  $-\ln(1 - N_2)$ , and rearranging, eq 1 becomes

$$T_{f_0} - T = \frac{N_2}{A}[1 + 1/2N_2 + \dots] - [B(T_{f_0} - T)^2 + \dots] \quad (4)$$

Neglecting terms in  $N_2^3$  and higher, eq 4 becomes

$$T_{f_0} - T = \frac{N_2}{A}[1 + 1/2N_2 + \dots] - \left[ B\left(\frac{N_2}{A}\right)^2 + \dots \right] \quad (5)$$

or

$$T_{f_0} - T = \frac{N_2}{A}[1 + (1/2 - B/A)N_2 + \dots] \quad (6)$$

In a system of the type under investigation, in which the solid phase is restricted to the major component, let  $n_1^*$  represent the total number of moles of the major component (in both the liquid and solid phases),  $n_2$  represent the total number of moles of the other components (in the liquid phase), and  $n_1$  represent the number of moles of the major component in the liquid phase under given conditions. Then the number of moles of the major component in the crystalline phase under the same conditions is  $n_1^* - n_1$ . Let  $r$  denote the fraction crystallized of the total number of moles of all components, that is,

$$r = (n_1^* - n_1)/(n_1^* + n_2). \quad (7)$$

The mole fraction, in the liquid phase, of the sum of all components other than the major components is defined by

$$N_2 = n_2/(n_1 + n_2). \quad (8)$$

Let  $N_2^*$  represent the value of  $N_2$  when no crystalline phase is present, that is, when  $n_1 = n_1^*$ . Then

$$N_2^* = n_2/(n_1^* + n_2). \quad (9)$$

Combination of eq 7, 8, and 9 yields the following equation relating  $N_2$  and  $r$ :

$$N_2 = N_2^*/(1 - r). \quad (10)$$

Letting

$$a = N_2^*/A, \text{ and } b = (1/2 - B/A)(N_2^*)^2/A, \quad (11)$$

and combining eq 10 and 6, there is obtained

$$T = T_{f_0} - \frac{a}{1-r} - \frac{b}{(1-r)^2} - \dots = T_{f_0} - \frac{a}{1-r} \left[ 1 + \frac{b/a}{1-r} + \dots \right] \quad (12)$$

It is possible to further simplify eq 12 by using the general relation that, when

$$\left(\frac{b/a}{1-r}\right)^2 < 1,$$

$$\frac{a}{\left(1-\frac{b}{a}\right)-r} = \frac{a}{1-r} \left[1 - \frac{b/a}{1-r}\right]^{-1} = \frac{a}{1-r} \left[1 + \frac{b/a}{1-r} + \dots\right]. \quad (13)$$

Assuming that the unwritten terms in eq 12 and 13 are negligible, or may be substituted one for the other without significant error, then eq 12 may be written

$$T = T_{f_0} - \frac{a}{\left(1-\frac{b}{a}\right)-r}. \quad (14)$$

In general, the fractional error introduced by making the approximations leading to eq 14 will be of the order of  $1/12$  to  $1/3 N_2^2$ , depending upon the value of  $B/A$  (see eq 3 and 4). That is to say, fractional errors in  $N_2$ , or correspondingly in  $T_{f_0} - T$ , will be about  $1/3$  to  $1 \frac{1}{3}$  percent when  $N_2 = 0.2$ , and about  $1/12$  to  $1/3$  percent when  $N_2 = 0.1$ . Equation 14 therefore would appear to be practically useful only when the amount of solute or impurity is below several tenths in mole fraction.

The next step is to express  $r$ , the fraction crystallized or melted, in terms of the time. This is done by assuming that the experiment is one in which the rate of crystallization or melting of the major component is constant with time.<sup>6</sup> Denoting the time by the symbol  $z$ , and letting  $z = z_f$  when  $r = 0$ , one has the relation

$$r = k(z - z_f), \quad (15)$$

where  $k$  is a constant characteristic of the experiment, positive in sign for a freezing experiment and negative for a melting experiment. The time at which freezing begins, or melting is complete, is  $z_f$ , provided thermodynamic equilibrium is maintained throughout the experiment. The determination of  $z_f$  for an actual experiment has been discussed in reference [1].

Combination of eq 14 and 15 yields the following relation between the time and the temperature of equilibrium:

$$T = T_f - \frac{a'}{1 - k'(z - z_f)}, \quad (16)$$

where  $a' = a/(1 - b/a)$  and  $k' = k/(1 - b/a)$ .

Equation 16 relating  $T$  and  $z$  and eq 14 relating  $T$  and  $r$  are the equations of a rectangular hyperbola. The asymptote obtained by setting  $z = -\infty$  in eq 16 is  $T = T_{f_0}$ .

Since there are three constants in eq 16, it is clear that three points on a portion of the curve satisfying eq 16 are sufficient to determine the values of the three constants,  $T_{f_0}$ ,  $a'$ , and  $k'$ . However, if it is

<sup>6</sup> This is essentially the case in experiments performed with the apparatus described in reference [1] when the range of freezing (or melting) temperature is sufficiently small in comparison with the head of temperature.

desired to test the accuracy with which the data satisfies the equation, a greater number of points are necessary.

The following theorem concerning a rectangular hyperbola will be required. Consider any four points  $(T_1, z_1)$ ,  $(T_2, z_2)$ ,  $(T_3, z_3)$  and  $(T_4, z_4)$ , on the hyperbola defined by eq 16. There are three ways in which two chords can connect these points, each point being the terminus of only one chord. These are illustrated in figure 1, in which  $m_{12}$  denotes the slope of the chord connecting points  $(T_1, z_1)$  and  $(T_2, z_2)$ , and similarly for  $m_{13}$ ,  $m_{23}$ , and  $m_{14}$ . It is to be shown that the products of the slopes of the two chords is the same in each of the three cases

$$m_{12}m_{34} = m_{13}m_{24} = m_{14}m_{23}. \quad (17)$$

Using eq 16,

$$m_{12} = \left( \frac{T_2 - T_1}{z_2 - z_1} \right) = \frac{-a'k'}{[1 - k'(z_1 - z_f)][1 - k'(z_2 - z_f)]} \quad (18)$$

and

$$m_{12}m_{34} = \frac{(a'k')^2}{[1 - k'(z_1 - z_f)][1 - k'(z_2 - z_f)][1 - k'(z_3 - z_f)][1 - k'(z_4 - z_f)]} \quad (18a)$$

Equation 17 follows immediately, since the expression on the right-hand side of eq 18a is unchanged in value by any interchange of the subscripts 1, 2, 3, and 4.

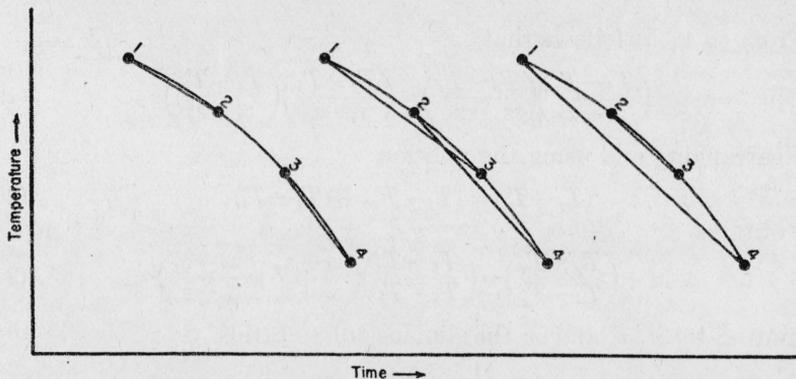


FIGURE 1.—Construction to show three ways of connecting four points on a curve with two chords, with each point being the terminus of only one chord.

### III. DETERMINATION OF THE FREEZING POINT

#### 1. ANALYTICAL

The procedure for determining the freezing point of the given substance analytically from the equilibrium portion of the time-temperature curve is illustrated by means of figure 2. Points  $G$ ,  $H$ , and  $I$  are on the equilibrium part of the time-temperature curve, as defined by eq 16. The zero time, at which crystallization would have begun in the absence of undercooling, has been determined [1]. It is required to determine on the ordinate through the zero time,  $z_f$ , the freezing point  $T_f$ .

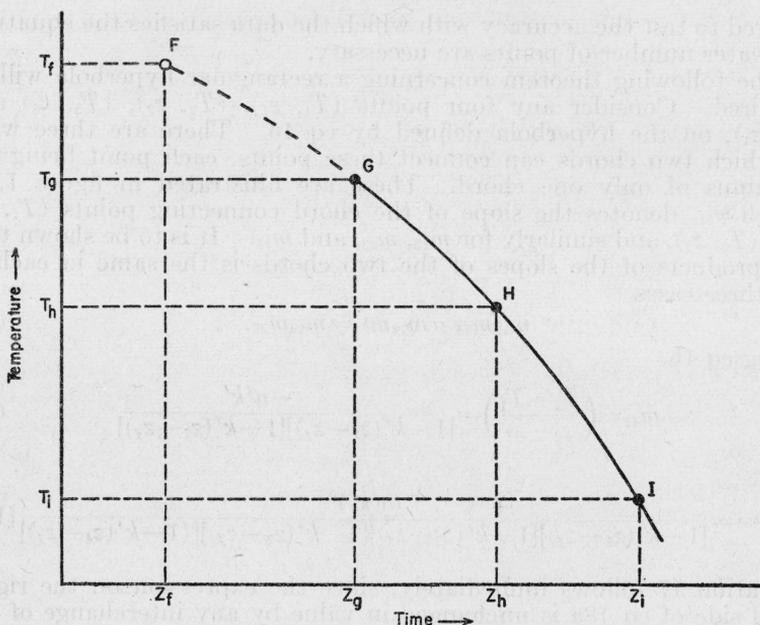


FIGURE 2.—Construction to show the analytical determination of the freezing point.

From eq 17, it follows that

$$\left(\frac{T_f - T_g}{z_g - z_f}\right)\left(\frac{T_h - T_i}{z_i - z_h}\right) = \left(\frac{T_f - T_i}{z_i - z_f}\right)\left(\frac{T_g - T_h}{z_h - z_g}\right). \quad (19)$$

Rearranging and using the relation

$$(T_f - T_i) = (T_f - T_g) + (T_g - T_i), \quad (20)$$

one obtains

$$1 + \left(\frac{T_g - T_i}{T_f - T_g}\right) = \left(\frac{T_h - T_i}{T_g - T_h}\right)\left(\frac{z_h - z_g}{z_i - z_h}\right)\left(\frac{z_i - z_f}{z_g - z_f}\right). \quad (21)$$

Denoting by  $u$ ,  $v$ , and  $w$  the dimensionless ratios

$$u = \left(\frac{T_h - T_i}{T_g - T_h}\right) \quad (22)$$

$$v = \left(\frac{z_h - z_g}{z_i - z_h}\right) \quad (23)$$

$$w = \left(\frac{z_i - z_f}{z_g - z_f}\right), \quad (24)$$

there is obtained, on substitution into eq 21, the relation

$$T_f = T_g + \left(\frac{T_g - T_i}{uvw - 1}\right). \quad (25)$$

Equation 25 gives the value of  $T_f$ , when there are known the temperature and time corresponding to three points (as  $G$ ,  $H$ , and  $I$ ) on the equilibrium curve (as defined by eq 14) and the "zero" time, the time

at which crystallization would have begun in the absence of undercooling.<sup>7</sup>

It is nearly always possible to select the point  $H$  equidistant in time between  $G$  and  $I$ , so that  $v=1$ . Furthermore, it will usually be possible to space the points  $G$ ,  $H$ , and  $I$  so that  $w$  is a simple ratio. Thus, if all three time intervals are equal

$$\left. \begin{aligned} (z_g - z_f) &= (z_h - z_g) = (z_i - z_h) \\ v &= 1 \\ w &= 3 \\ T_f &= T_g + (T_g - T_i)/(3v - 1) \end{aligned} \right\} \quad (26)$$

When the first time interval is twice as great as the other two intervals, then

$$\left. \begin{aligned} (z_g - z_f) &= 2(z_h - z_g) = 2(z_i - z_h) \\ v &= 1 \\ w &= 2 \\ T_f &= T_g + (T_g - T_i)/(2v - 1) \end{aligned} \right\} \quad (27)$$

It is obvious that a large value of  $w$  corresponds to a short extrapolation to  $T_f$ , and vice versa.

Although the curve in figure 2 has been drawn to simulate a freezing curve, the above equations apply equally well to a melting curve, since, for the same substance, the melting curve is the mirror image of the freezing curve when the time rate of melting is made the same as the time rate of crystallization.

## 2. GEOMETRICAL

The manner of determining geometrically the freezing point,  $T_f$ , is shown in figure 3.

There are given the "zero" time,  $z_f$ , and the time and temperature corresponding to the three points,  $G$ ,  $H$ , and  $I$ , on the equilibrium part of the time-temperature curve defined by eq 16. It is required to locate the freezing point,  $T_f$ , on the ordinate at the time  $z_f$ .

The solution is as follows:

Draw  $\overline{AB}$  through  $I$  parallel to the time axis.

Draw  $\overline{AC}$  perpendicular to  $\overline{AB}$ , at the time  $z_f$ .

Draw a line through points  $G$  and  $H$ , intersecting  $\overline{AB}$  at  $E$  and  $\overline{AC}$  at  $D$ .

Draw a line through points  $I$  and  $H$ , intersecting  $\overline{AC}$  at  $J$ .

Draw  $\overline{JK}$  parallel to  $\overline{DE}$ .

Draw a line through points  $K$  and  $G$ , intersecting  $\overline{AC}$  at  $F$ .

$F$  is the desired point, representing the freezing point,  $T_f$ .

<sup>7</sup> It is worthwhile remarking that eq 25 is not limited to the determination of the freezing point,  $T_f$ .  $z_f$  in eq. 24 may be any given time, and eq. 25 then yields the corresponding temperature,  $T_f$ . It has been implied in the foregoing discussion that the cooling curve before crystallization begins (or the warming curve after melting is complete) is sufficiently steep so that  $z_f$  may be estimated exactly enough from a preliminary visual extrapolation to  $T_f$ . It is clear that if this is not the case,  $T_f$  may still be obtained with any required accuracy by successive applications of eq 25.

The proof, illustrated in figure 4, is as follows:

Draw  $\overline{FI}$ .

Draw  $\overline{NP}$  through  $H$ , parallel to  $\overline{AB}$ .

Then

$$\overline{NH}/\overline{NP} = \overline{ND}/\overline{NJ} \tag{28}$$

But

$$\overline{AI}/\overline{AK} = \overline{NH}/\overline{NP}. \tag{29}$$

Therefore,

$$\overline{ND}/\overline{NJ} = \overline{AI}/\overline{AK}. \tag{30}$$

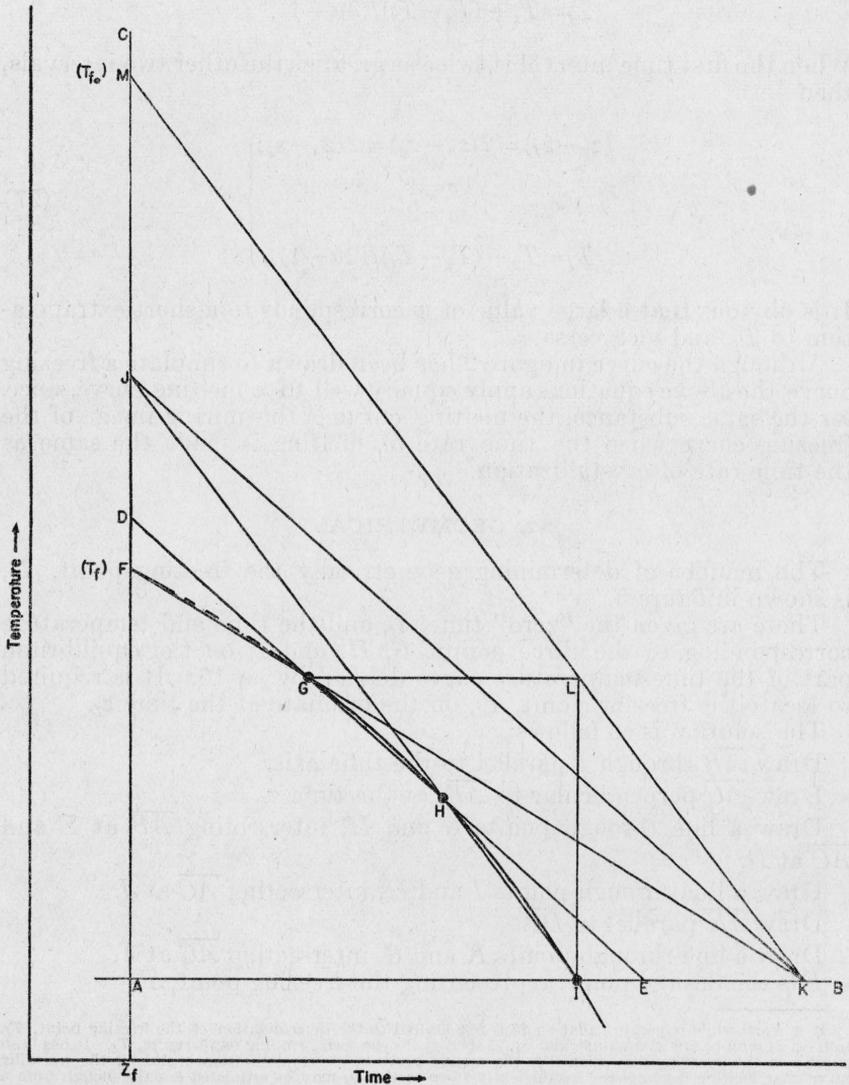


FIGURE 3.—Geometrical construction for determining  $T_f$  and  $T_{f_0}$ .



in which the time-temperature observations extend over a sufficiently large fraction (probably of the order of  $\frac{1}{4}$  to  $\frac{1}{2}$ ) of material crystallized. Furthermore, since that portion of the curve which is required for determining  $T_{f_0}$  is also the portion in which departures will most likely occur in the relations upon which eq 16 is based, it is seen that the determination of even an approximate value of  $T_{f_0}$  will frequently be impossible for many experiments. However, for completeness, the description of the procedure for evaluating  $T_{f_0}$  by this method is given here so that it may be available for application to those experiments which do conform to the requirements.

### 1. ANALYTICAL

An equation for the freezing point for zero impurity,  $T_{f_0}$ , may be arrived at as follows. Returning to eq 16, it will be noted that  $T$ , as defined there, approaches  $T_{f_0}$  as  $z$  approaches  $-\infty$ . This may be regarded simply as an analytical property of eq 16, so far as the present argument is concerned.<sup>8</sup>

Since eq 25 applies to any point on the curve defined by eq 16, we may imagine  $z_f$  and  $T_f$  in eq 24 and 25 to be replaced by  $z$  and  $T$ , respectively, corresponding to any point on the curve. Then as  $z$  approaches  $-\infty$ ,  $w$  approaches unity, and eq 25 becomes

$$T_{f_0} = T_g + \left( \frac{T_g - T_i}{uv - 1} \right). \quad (33)$$

Since  $w$  has been eliminated from eq 33,  $T_{f_0}$  does not depend on the location of  $z_f$ . As pointed out following eq 25, it is nearly always possible to select the point  $H$  equidistant in time between  $G$  and  $I$ , so that  $v=1$ .

The precision of the determination of the freezing point for zero impurity rests heavily upon the value of the product  $(uv)$ , which can be seen from eq 22 and 23 to be the ratio of the slope of the chord  $\overline{HI}$  to the slope of the chord  $\overline{GH}$ .

### 2. GEOMETRICAL

The manner of determining geometrically the freezing point for zero impurity,  $T_{f_0}$ , is shown in figure 3.

After having determined the freezing point,  $T_f$ , as indicated in the preceding section, the procedure is as follows:<sup>9</sup>

Draw a line through  $G$  parallel to  $\overline{AB}$  and a line through  $I$  parallel to  $\overline{AC}$ , the two lines intersecting at  $L$ .

Draw a line through points  $K$  and  $L$ , intersecting  $\overline{AC}$  at  $M$ .

$M$  is the desired point, representing the freezing point for zero-impurity,  $T_{f_0}$ .

<sup>8</sup> The extension of the time in eq 16 to  $-\infty$  may be easily pictured by considering a corresponding melting curve, which may be prolonged indefinitely in time by the continued addition of the pure major component in the solid phase to the existing solid phase as melting proceeds. This procedure serves to produce a liquid phase in which the number of moles of the major component approaches infinity, the composition of the liquid phase approaches  $N_l=1$  or  $N_s=0$ , and the temperature approaches the freezing point for zero impurity,  $T_{f_0}$ .

<sup>9</sup> The method of obtaining  $T_{f_0}$  described here has the advantage that  $T_{f_0}$  is obtained on the same vertical axis as  $T_f$ , so that the initial freezing point lowering  $(T_{f_0}-T_f)$  is immediately apparent. However, it should be pointed out that the value of  $T_{f_0}$  obtained depends only on the points  $G$ ,  $H$ , and  $I$ , and not at all on the time chosen for  $z_f$ .

The proof is as follows:

Draw  $\overline{GI}$ .

Since point  $F$  is on the curve, eq 22, 23, and 33, for  $T_{f_0}$ , may be rewritten with the three points  $G$ ,  $H$ , and  $I$  replaced by  $F$ ,  $G$ , and  $I$ .

$$T_{f_0} = T_f + \left( \frac{T_f - T_i}{u'v' - 1} \right), \quad (34)$$

where

$$u' = \left( \frac{T_g - T_i}{T_f - T_g} \right) \quad (35)$$

$$v' = \left( \frac{z_g - z_f}{z_i - z_g} \right) \quad (36)$$

Equation 34 may be put in the form

$$\left( \frac{T_{f_0} - T_i}{T_{f_0} - T_f} \right) = u'v'. \quad (37)$$

But from figure 4,

$$\left( \frac{T_{f_0} - T_i}{T_{f_0} - T_f} \right) = \frac{\overline{AM}}{\overline{FM}} = \frac{\overline{IL}}{\overline{RL}}. \quad (38)$$

Also, from eq 35 and 36 and figure 4,

$$u'v' = m_{GI}/m_{FG}, \quad (39)$$

where  $m_{GI}$  and  $m_{FG}$  are the slopes of the chords  $\overline{GI}$  and  $\overline{FG}$ , respectively. Combining eq 37, 38, and 39,

$$\frac{\overline{IL}}{m_{GI}} = \frac{\overline{RL}}{m_{FG}}. \quad (40)$$

But both sides of eq 40 are equal to  $\overline{GL}$ , from figure 4.

## V. UNCERTAINTY OF THE DETERMINATION OF THE FREEZING POINT AND OF THE FREEZING POINT FOR ZERO IMPURITY

An expression may be derived for the error of  $T_f$  or  $T_{f_0}$ , as calculated from eq 25 and 33, for any given experiment. For simplicity, one may assume that there is no error in  $z_f$ ,  $z_g$ ,  $z_h$ , and  $z_i$ , but that a uniform random error,  $\sigma$ , is to be attached to  $T_g$ ,  $T_h$ , and  $T_i$  (fig. 2). The error in  $T_f$ ,  $\sigma_f$ , may then be calculated from the usual propagation of error equation

$$\left( \frac{\sigma_f}{\sigma} \right)^2 = \left( \frac{\partial T_f}{\partial T_g} \right)^2 + \left( \frac{\partial T_f}{\partial T_h} \right)^2 + \left( \frac{\partial T_f}{\partial T_i} \right)^2. \quad (41)$$

Equation 41 assumes that the errors in  $T_g$ ,  $T_h$ , and  $T_i$  are, on the average, uncorrelated, and gives the error for  $T_f$  in terms of the average of these errors,  $\sigma$ .

The derivatives in eq 41 may be obtained by differentiation of

eq 25, noting that  $u$ , but not  $v$  and  $w$ , is a function of  $T_g$ ,  $T_h$ , and  $T_i$ . They may be put in the following form (with the aid of eq 22):

$$\left(\frac{\partial T_f}{\partial T_g}\right) = \frac{u^2 v w (v w + 1)}{(u v w - 1)^2} \quad (42)$$

$$\left(\frac{\partial T_f}{\partial T_h}\right) = -\frac{v w (u + 1)^2}{(u v w - 1)^2} \quad (43)$$

$$\left(\frac{\partial T_f}{\partial T_i}\right) = \frac{(v w + 1)}{(u v w - 1)^2} \quad (44)$$

When eq 42, 43, and 44 are substituted into eq 41, there is obtained the relation:

$$\left(\frac{\sigma_f}{\sigma}\right)^2 = \frac{(v w + 1)^2 (u^4 v^2 w^2 + 1) + v^2 w^2 (u + 1)^4}{(u v w - 1)^4}, \quad (45)$$

which expresses  $(\sigma_f/\sigma)$  as a function of  $u$ ,  $v$ , and  $w$ . Equation 45 may be put in a more useful form as follows:

For any given segment of an equilibrium curve, the greatest accuracy in  $T_f$  (minimum  $\sigma_f$ ) will be obtained by choosing  $z_g$  and  $z_i$  at the beginning and end of the segment in question (corresponding to a maximum value of  $w$ ). With  $z_g$  and  $z_i$  fixed, the following relation then holds:

$$u w = c, \quad (46)$$

where  $c$  is a constant characteristic of the given segment of the curve, and independent of the choice of  $z_h$ . Equation 46 may be derived in the following way.

It is evident from eq 22 and 23 that the product  $(u w)$  is the ratio of the slope of the chord  $\overline{HI}$  to the slope of the chord  $\overline{GH}$  (fig. 2). From eq 18  $c$  is then given by

$$c = \left( \frac{1 - k' z_g}{1 - k' z_i} \right), \quad (47)$$

which is independent of  $z_h$ .

If one eliminates  $u$  from eq 45 and 46, there is obtained the relation

$$\left(\frac{\sigma_f}{\sigma}\right)^2 = \frac{(v w + 1)^2 (c^4 w^2 + v^2) + w^2 (c + v)^4}{v^2 (c w - 1)^4}. \quad (48)$$

A numerical investigation of eq 48 shows, as would be expected, that, for the range of conditions encountered in practice, the optimum value of  $v$  is in the neighborhood of unity (corresponding to  $z_h$  equidistant between  $z_g$  and  $z_i$ ). When  $v=1$ ,  $u=c$ , and eq 48 becomes

$$\left(\frac{\sigma_f}{\sigma}\right)^2 = \frac{(w + 1)^2 (u^4 w^2 + 1) + w^2 (u + 1)^4}{(u w - 1)^4}. \quad (49)$$

The error in  $T_{f_0}$ ,  $\sigma_{f_0}$ , may be obtained immediately by setting  $w$  equal to unity in eq 48 or 49. When  $v=1$ ,

$$\left(\frac{\sigma_f}{\sigma}\right)^2 = \frac{4(u^4 + 1) + (u + 1)^4}{(u - 1)^4}. \quad (50)$$

From eq 49,  $(\sigma_f/\sigma)$ , for  $v=1$ , has been calculated for  $w=1, 1.5, 2, 3, 5$ , and  $\infty$ , and for  $u=1, 1.25, 1.5, 2, 3, 4$ , and  $\infty$ . The results are presented in figure 5, in which the abscissas represent  $(1/u)$ , and the ordinates represent  $(\sigma_f/\sigma)$ , on a logarithmic scale. The curve for  $w=1$  represents  $(\sigma_{f_0}/\sigma)$ , and rises to infinity at  $(1/u)=1$ , which corresponds to a freezing curve of constant slope. The other curves, representing  $(\sigma_f/\sigma)$  for various values of  $w$ , are finite for all values of  $(1/u)$ .

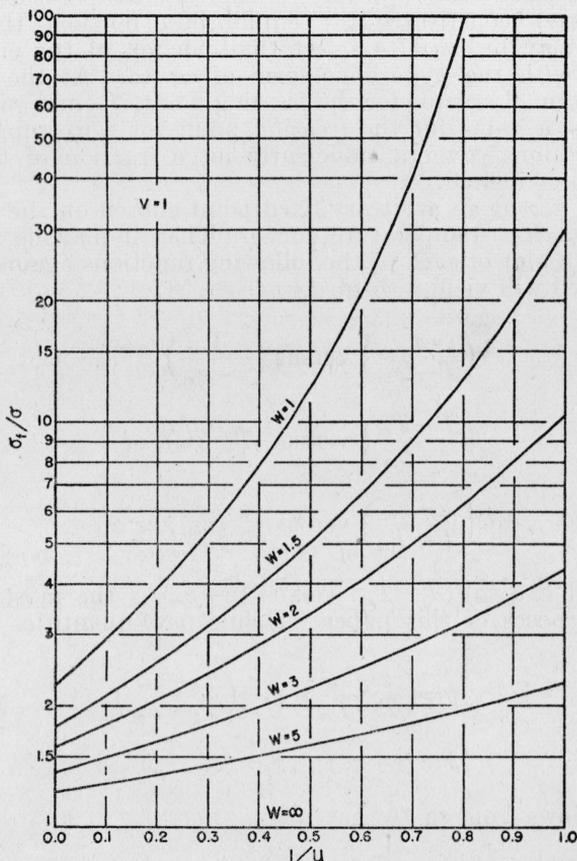


FIGURE 5.—Chart to show the uncertainty of the determination of  $T_f$  and  $T_{f_0}$ .

Figure 5 is expected to be convenient for estimating the uncertainties of  $T_f$  and  $T_{f_0}$  in practice. In calculating  $T_f$  and  $T_{f_0}$  from eq 25 and 33,  $u$  and  $w$  are first evaluated from eq 22 and 24 ( $v=1$ ). The values of  $(\sigma_f/\sigma)$  and  $(\sigma_{f_0}/\sigma)$  may then be read immediately from figure 5. It remains for the experimenter to estimate a reasonable value for  $\sigma$ . In any case, figure 5 indicates relative errors for various values of  $u$  and  $w$ .

The errors discussed above do not include those arising from departures from the ideal solution laws or from lack of constancy of the rate of crystallization or melting (see appendix, page 212.)

## VI. ALTERNATIVE METHOD FOR DETERMINING THE FREEZING POINT (AND THE FREEZING POINT FOR ZERO IMPURITY)

The foregoing methods for determining  $T_f$  (and, where appropriate,  $T_0$ ) may be used when the experimenter is able from previous experience to select with some assurance the equilibrium portion of the time-temperature freezing or melting curve. When there is some doubt as to what portion, if any, of the time-temperature freezing or melting curve constitutes the equilibrium portion, the following procedure may be used to select that portion of the curve that is consistent with the hyperbolic form of eq 16. At the same time, there is obtained a value for the freezing point,  $T_f$ , and within certain wide limits, a value for the freezing point for zero impurity,  $T_0$ , if the observations cover a sufficiently large fraction of the material crystallized or melted.

Let  $(T_m, z_m)$  be an arbitrary fixed point chosen on the equilibrium portion of a time-temperature curve. Then it may be shown from eq 16 that a plot of each of the following functions against the variable indicated will yield a *straight line*:

$$\left(\frac{1}{T-T_m}\right) \text{ versus } \left(\frac{1}{z-z_m}\right)$$

$$\left(\frac{T-T_m}{z-z_m}\right) \text{ versus } (T-T_m), \text{ or } T$$

$$\left(\frac{z-z_m}{T-T_m}\right) \text{ versus } (z-z_m), \text{ or } z$$

The plot of  $(z-z_m)/(T-T_m)$  versus  $(z-z_m)$  is the most convenient for the purposes of this paper. Define new quantities  $y$  and  $x$  as follows:

$$y = \left(\frac{z-z_m}{T-T_m}\right); \quad y_f = \left(\frac{z_f-z_m}{T_f-T_m}\right) \quad (51)$$

$$x = (z-z_m); \quad x_f = (z_f-z_m) \quad (52)$$

Then it follows from eq 16 that

$$y = y_0 + sx; \quad y_f = y_0 + sx_f \quad (53)$$

where

$$s = \left(\frac{1}{T_{f_0}-T_m}\right) \quad (54)$$

$$y_0 = -\left(\frac{(\alpha'/k')}{(T_{f_0}-T_m)^2}\right) \quad (55)$$

Thus a plot of  $y$  against  $x$  yields a straight line for that portion of the curve, presumably the equilibrium portion, which is consistent with eq 16. Extrapolation of the straight line to  $x=x_f(z=z_f)$ ,

yields  $y_f$ ;  $T_f$  may then be calculated from the equation

$$T_f = T_m + \frac{x_f}{y_f}, \quad (56)$$

similarly,

$$T_{f_0} = T_m + 1/s = T_m + \frac{y_f - y_m}{x_f}, \quad (57)$$

since  $x_m = 0$ . The smoothed temperature at any other time is given by the relation

$$T = T_f - \frac{x_f}{y_f} + \frac{x}{y}. \quad (58)$$

The point  $(T_m, z_m)$  should be selected near the middle of that portion of the time-temperature curve which the experimenter regards as most likely to represent equilibrium. The linearity of the  $y$  versus  $x$  plot is then an indication of the range on either side of  $(T_m, z_m)$  in which equilibrium has apparently been maintained. It should be noted that the error in the calculated value of  $y$  increases rapidly as  $x$  decreases. In plotting  $y$  it is better to plot circles, of radii inversely proportional to  $x$ , than points. This will insure approximately the correct weighting of the points in drawing the straight line. It should also be noted that a slight displacement of  $(T_m, z_m)$  from the true curve will have a negligible effect on the location of the straight line, provided  $(T_m, z_m)$  is about in the middle of the equilibrium portion of the curve.

Equation 57 relates  $T_{f_0}$  to the slope,  $s$ , of the  $y$  versus  $x$  plot. However, it is clear that  $s$  is a sort of second derivative of the time-temperature curve. It is to be expected, therefore, that the value of  $T_{f_0}$  calculated from eq 57 may be quite inaccurate. It is possible to reverse the procedure, if  $T_{f_0}$  is known, and calculate the value of the slope of the  $y$  versus  $x$  plot to be expected on the basis of eq 16.

The  $y$  versus  $x$  plot is principally of use in extrapolating to obtain  $T_f$ , by eq 56, and also in obtaining smoothed values of the temperature at any other time, by eq 58. The smoothed values of the temperature may be used in conjunction with the other methods of obtaining  $T_{f_0}$  as described [1].

[1].

## VII. DISCUSSION

In connection with the practical application of the foregoing methods for determining from time-temperature freezing and melting curves the freezing point,  $T_f$ , and the freezing point for zero impurity,  $T_{f_0}$ , the following points are important:

(a) The experimenter must assure himself that the time-temperature relations substantially follow eq 16 over that part of the experiment which represents thermodynamic equilibrium between the liquid and solid phases. (See section VI and the appendix of this paper.)

(b) The precision of determining the freezing point,  $T_f$ , will be nearly as good as the determination of temperatures along the equilibrium part of the curve, except when the time and temperature

covered by undercooling are very large. In terms of the uncertainty in the temperatures along the equilibrium part of the curve, the uncertainty in  $T_f$  is given by eq 49 and illustrated in figure 5.

(c) The precision of determining the freezing point for zero impurity,  $T_{f_0}$ , by the method described, will be much less precise than the determination of the freezing point. In terms of the uncertainty in the temperatures along the equilibrium portion of the curve, the uncertainty in  $T_{f_0}$  is given by eq 50 and illustrated in figure 5 by the curve for which  $w=1$ . The practical utility of determining  $T_{f_0}$  by this method depends entirely upon the equilibrium portion of the curve covering a sufficiently large range of  $r$  (fraction crystallized, or melted) so that the product  $w$  in eq 33, the ratio of the slopes of the two chords, will have a value appreciably greater than unity. If the observations of the given experiment do not cover a sufficiently large fraction of material crystallized or melted, no useful determination of  $T_{f_0}$  may be made by this method. For any given experimental procedure, it is desirable to check the value of  $T_{f_0}$  obtained by this method with the value obtained by the method previously described [1], which has been shown to give reliable results.

### VIII. REFERENCES

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### IX. APPENDIX

In the foregoing discussions, it has been assumed for simplicity that the rate of crystallization is a constant, or that  $r$  is linear in  $z$ , as given by eq 15. It is of interest to consider the effect of a varying rate of crystallization. Two types of variation may be distinguished:

(a) The rate of crystallization varies initially, but approaches a constant value as the experiment proceeds.

(b) The rate of crystallization varies progressively as the experiment proceeds, and does not tend to approach a constant value. Supercooling should give rise to a variation of type (a). Variations of type (a) will destroy, for a certain time, the rectangular hyperbolic relation between  $T$  and  $z$ , eq 16, on which the linearity of the  $(z-z_m)/(T-T_m)$  versus  $(z-z_m)$  plot depends. It may therefore be assumed that in the linear region of this plot such variations have decreased sufficiently to be neglected.

Variations of type (b) are of more importance, since they increase throughout the experiment. Such variations would be caused, for example, by any factor, such as a decreasing (or increasing) head of temperature, that alters the rate of heat transfer and hence the rate of crystallization (or melting).

If the variation is of type (b),  $r$  may be represented by a power series in  $(z-z_f)$ :

$$r = k(z-z_f)[1 - e(z-z_f) + \dots]. \quad (59)$$

Now consider the following expansion, valid for  $[e(z-z_f)]^2$  less than unity:

$$\left[ \frac{k(z-z_f)}{1+e(z-z_f)} \right] = k(z-z_f)[1 - e(z-z_f) + \dots]. \quad (60)$$

Therefore, when the higher order terms in eq 59 and 60 may be neglected,  $r$  may be written:

$$r = \frac{k(z-z_f)}{1+e(z-z_f)}. \quad (61)$$

Equation 61 is a rectangular hyperbolic relation between  $r$  and  $z$ . Furthermore, eq 14 is a rectangular hyperbolic relation between  $T$  and  $r$ . It is easily shown that the relation between  $T$  and  $z$  obtained by substitution of eq 61 in eq 14 is also rectangular hyperbolic. Specifically, eq 16 is replaced by the equation:

$$T = \left( T_{f_0} + \frac{a'e}{k' - e} \right) - \frac{a'k'/(k' - e)}{1 - (k' - e)(z - z_f)}. \quad (62)$$

Equation 62 reduces to eq 16 for  $e$  equal to zero.

It is clear from eq 62 that all the results previously derived on the basis of eq 16 are unchanged, provided  $k'$  is replaced by  $(k' - e)$ ,  $a'$  is replaced by  $[a'k'/(k' - e)]$ , and  $T_{f_0}$  is replaced by  $[T_{f_0} + a'e/(k' - e)]$ . Of the previous results which are unaffected, there may be mentioned the theorem concerning the slopes of the chords, eq 17, and the linearity of the  $(z - z_m)/(T - T_m)$  versus  $(z - z_m)$  plot. The calculated value of  $T_f$  will not be in error. However, the calculated value of  $T_{f_0}$  will be in error by the amount  $[a'e/(k' - e)]$ , corresponding to the fact that the asymptote of the hyperbola is shifted.

WASHINGTON, January 6, 1944.