

## ERRORS OCCURRING IN THE DETERMINATION OF TEMPERATURE-HEAT CONTENT CURVES

by

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### INTRODUCTION

When melting or freezing curves are used as qualitative or quantitative criteria for purity it is usually assumed that the temperature functions represented by these curves are valid under thermodynamic equilibrium conditions.

However, it must be realized that during the experimental determination of these curves heat is transported (continuously or discontinuously) to or from the sample to be investigated. Thus permanent or temporary deviations from the thermodynamic equilibrium conditions will always occur and the obtained curves will represent the desired temperature-heat content curves only approximately.

To what extent the obtained curves differ from the desired ones depends on the rates of the occurring phase transitions, the rates of heat transport and the rates of diffusion (homogeneity of the occurring phases)

These rates as such, as well as their influences, depend on the sample and on the experimental conditions

The experimental conditions may differ widely and a quantitative treatment of the influence of all the factors mentioned soon becomes very complicated

We shall therefore restrict ourselves to some qualitative considerations concerning the rates of phase transitions and the rates of diffusion. Subsequently the influence of heat transfer will be discussed and an approximately quantitative discussion on the temperature differences occurring with the "thin film" method will follow.

Although it is realized that the following is far from complete, some conclusions can be drawn that are applicable to a wide variety of experimental methods.

### I. INFLUENCE OF RATES OF PHASE TRANSITIONS

When two phases are in thermodynamic equilibrium the amount of substance passing from phase 1 into phase 2 per unit time and unit surface area is equal to the amount of substance passing in the opposite direction. These rates cannot be measured and will be called absolute rates. The absolute rates will depend on temperature and some other factors which are not yet clearly understood. When no thermodynamic equilibrium exists the rate of the phase transition  $1 \rightarrow 2$  may be larger than the rate

in the opposite direction. The result will be an increase of the amount of substance contained in phase 2. This increase per unit time and unit surface area will be called the net rate of phase transition, which is zero when thermodynamic equilibrium occurs.

### 1.1 Solid-liquid transitions

Discussions and measurements on crystallization have been given by OSTWALD<sup>1</sup>, TAMMANN<sup>2</sup>, OHLMLER<sup>3</sup>, MEISSNER<sup>4</sup>, KRAHL<sup>5</sup>, JACKSON AND CHALMERS<sup>6</sup> and others.

Although the different authors do not agree completely it may be concluded from their papers that the net rate of crystallization may be low and depends on temperature.

The general picture is that the net rate of crystallization (being zero at the equilibrium temperature) initially increases at decreasing temperature and subsequently decreases after having passed through a maximum.

This somewhat peculiar behaviour of the net rate of crystallization may become more clear by considering the net rate of crystallization as the difference of the absolute rates of crystallization and melting (see Fig. 1).

This picture tallies qualitatively with the general theory on reaction kinetics. Without indulging in theoretical considerations on the kinetics of melting and crystallization we accept the drawn curve of Fig. 1 as a general representation of experimental experience. It is stressed that this curve obtains to systems in which both liquid and solid are present in *finite* quantities.

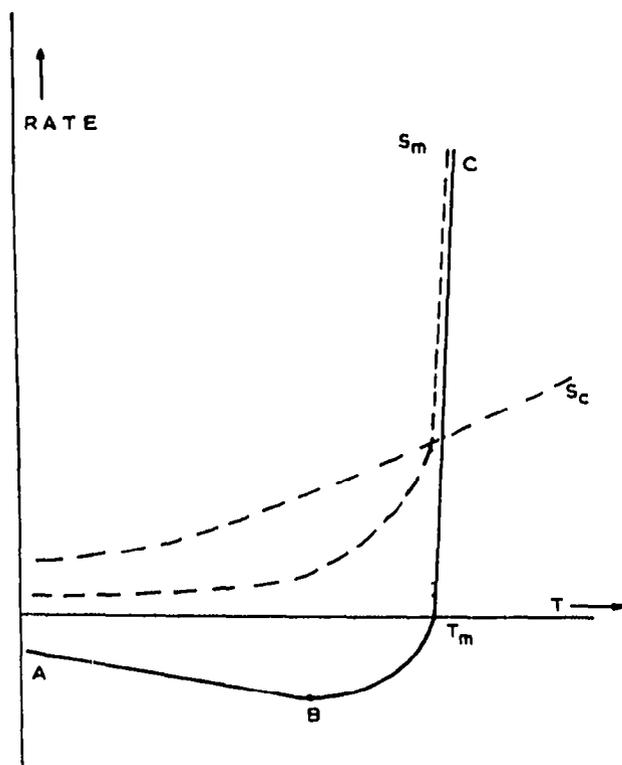


Fig. 1 Melting and crystallization rates as a function of temperature  
 Curve  $S_c$  (— · — · —) absolute rate of crystallization  
 Curve  $S_m$  (— — —) absolute rate of melting  
 The drawn curve represents the net rate of melting ( $S_m - S_c$ ).  
 (A negative net rate of melting means a positive net rate of crystallization)

As the net rate of melting may be considered as a measure for the rate of heat consumption, Fig. 1 leads to the following conclusions regarding a solid-liquid system consisting of one component.

When thermodynamic equilibrium exists the temperature of the system is  $T_m$ .

When heat is *supplied* to the system its temperature will increase until the net rate of melting meets the rate of heat supply. This is only possible at temperatures above  $T_m$ . Since the net rate of melting increases sharply at increasing temperatures (above  $T_m$ ) the deviation from the equilibrium temperature will be low (As a matter of fact, these deviations are imperceptible as far as is known\* )

When heat is *withdrawn* from the system its temperature will decrease until the rate of heat production (crystallization) meets the rate of cooling. This is only possible at some temperature below  $T_m$ . However, in this region the rate of heat production (crystallization) may be low and may increase only slightly at decreasing temperatures. Consequently the temperature finally obtained may differ appreciably from the equilibrium temperature

The temperature finally obtained remains constant as long as the rate of heat production of the system meets the rate of cooling. This is a steady state phenomenon and has nothing to do with thermodynamic equilibrium.

The type of undercooling mentioned above will be called two-phase undercooling. It should be distinguished from the undercooling of a liquid containing no perceptible amount of solid. The latter type of undercooling (to be called monophasic undercooling) demonstrates itself as the well known "undercooling peak" in a cooling curve. Monophasic undercooling depends on the rate of nuclei formation, whereas two-phase undercooling is more related to crystal growth.

In our experience two-phase undercooling is considerable with quite a number of substances even at cooling rates as low as 0.3 degree centigrade per minute (*ca. o.1 cal per gram minute*). This is illustrated by Figs 2 and 3

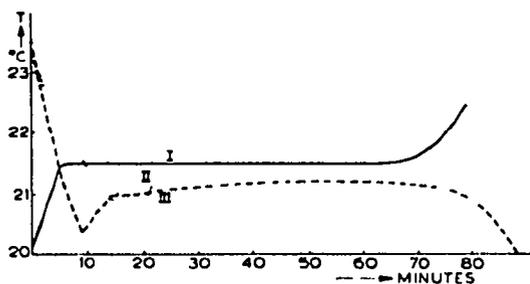


Fig 2 Heating and cooling curves of the eutectic mixture of  $\text{Na}_1\text{Hg}$  and  $\text{Hg}$   
Curve I heating curve, bath temperature  $25^\circ\text{C}$   
Curve II cooling curve, bath temperature  $20^\circ\text{C}$   
The curve is partly shown and is completed only after 150 minutes.  
Curve III cooling curve, bath temperature  $18^\circ\text{C}$

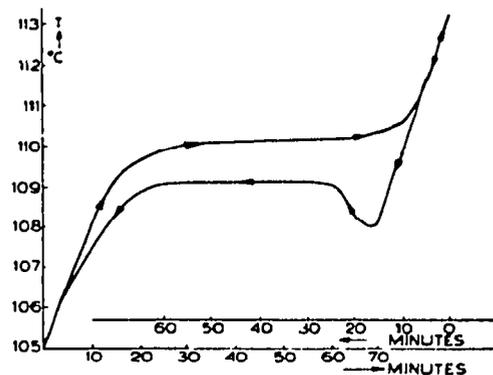


Fig 3 Heating and cooling curves of a sample of antipyrine, containing 0.1 mol% of acetanilide. The upper curve is the heating curve

\* The rare cases of "supermelting" mentioned in the literature should be scrutinized with great care, *e.g.* the conclusions drawn by VOLMER AND SCHMIDT (*Z physik Chem B*, 35 (1937) 467) regarding the supermelting of gallium must be treated with reserve

Fig. 2 shows heating curves and cooling curves of an exact eutectic mixture of  $\text{Na}_2\text{Hg}$  and  $\text{Hg}$ . The mixture was contained in a closed cylindrical tube provided with a thermometer well. The thickness of the cylindrical layer of metal was about 3 mm. The vessel was contained in a wide glass jacket and subsequently placed in a bath of constant temperature. The temperature of the vessel was recorded as a function of time. No stirring was applied to the sample. Curve I is a heating curve obtained after having cooled the mixture somewhat below  $18^\circ\text{C}$ .

The curve shows a constant temperature at  $21.49^\circ\text{C}$  for nearly 50 min. Complementary experiments carried out at bath temperatures as high as  $30^\circ$  or as low as  $22^\circ\text{C}$  all showed a range of constant temperature at exactly the same value of  $21.49^\circ\text{C}$ . As is obvious, the length of the constant range varied with the bath temperature.

On cooling, however, the constant range if present proved to be a function of the bath temperature (see Fig. 2, curves II and III).

The experiments could be repeated at choice, always yielding the same results. Additional experiments have been carried out with a sample that was partly melted. This sample was placed in a bath with a temperature either higher or lower than  $21.49^\circ\text{C}$ . The temperature registered fitted respectively to curve I (hot bath) or to the corresponding cooling curve (cold bath).

Comparable results have been obtained with *antipyrine*. The heating curves of this substance show a range of constant temperature at  $110.45^\circ\text{C}$ , which temperature appeared to be independent of the rate of heating. The cooling curves determined at a comparable rate of cooling show a small undercooling peak and subsequently the temperature rises up to a maximum at about  $109^\circ\text{C}$ . The height of the maximum is dependent on the rate of cooling and is always perceptibly below  $110.45^\circ\text{C}$ . The curves obtained are comparable with those of Fig. 3 showing heating and cooling curves of a sample of *antipyrine*, artificially contaminated by 0.1 mol% of acetanilide. The curves obtained have been determined with the thin film apparatus, described elsewhere<sup>7</sup>. With this apparatus no stirring is applied.

The cycle formed by the heating and cooling curve has been repeated several times without showing results essentially different from those represented by Fig. 3. Subsequently, experiments have been carried out with a sample that was partly melted. The temperature of this sample adapted itself to the upper or lower curve depending on whether heating or cooling was applied. All experiments were carried out with one and the same sample without removing it from the apparatus. The experiments could be duplicated with other samples.

Fig. 3 shows that a cooling curve of an impure substance may have a fairly flat part, giving the impression that the impure substance is extremely pure. The amount of contaminant calculated from the heating curve, on the contrary, tallied with the amount added.

Phenomena analogous to those represented by Figs. 2 and 3 have been obtained with *p*-xylene, benzyl benzoate and azobenzene. The literature gives evidence that quite a number of substances behave in the same way. We also observed less pronounced, though still noticeable differences between the heating and cooling curves of naphthalene. The heating and cooling curves of benzoic acid showed no differences exceeding our limit of accuracy.

### 1.2. Transitions in the solid phase

With a few alterations Fig. 1 may also be regarded as representing the transition rates between two solid phases which are coexistent at  $T_m$  (enantiotropy). It should be born in mind that transition rates in solids are often low. The curve  $S_m$  and consequently the part  $T_m-C$  of the drawn curve may be far less steep. In our experience this holds good for the odd fatty acids  $C_{13}$ ,  $C_{15}$  and  $C_{17}$ . A heating curve usually demonstrates clearly the occurrence of enantiotropic transitions. When melting occurs before the solid-solid transition is completed the melting curve obtained is obviously unreliable. It is therefore recommended that a sample be stored for some time at a temperature somewhat above the transition temperature before proceeding to the determination of the melting curve.

Other phase transitions in the solid may be due to monotropy. Monotropy is a typical non-equilibrium phenomenon. A monotropic solid may be compared to an undercooled liquid. When it is "seeded" with the stable modification, transition into the stable form should occur. However, the transition rate is often low. Extremely low transition rates have been met with in methyl esters of palmitic and stearic acid. Metastable crystals of these esters could be stored for one year in contact with stable crystals at a temperature only  $0.5^\circ$  below their melting point without completing the transition into the stable form<sup>8</sup>. Fats may show comparable phenomena

It may be useful to pay some extra attention to an effect caused by rapid cooling. Suppose a solid has been obtained by rapid cooling of a liquid. When a heating curve of such a solid is determined it may be unequal to the heating curve of a solid obtained from the same liquid at a moderate rate of cooling. We found this phenomenon occurring with a wide variety of substances including pure metals. This may be due either to (unknown) metastable forms of the solid or to the occurrence of imperfect crystals. The distinction is not essential; it is only mentioned as a reminder that (in order to obtain reliable melting curves) certain precautions to obtain a stable solid should not be omitted, not even when no metastable forms of the solid are known.

Storage of the solid at a temperature slightly below the melting point counteracts all the effects mentioned in this section. In many cases storage of the solid at elevated temperature for about an hour will do. Fatty acids appeared to need several days, and with fatty acid methyl esters no satisfying results could be obtained. It may be that many long-chain compounds display analogous difficulties.

On the strength of the facts mentioned above it may be advisable to submit an obtained heating curve to an internal check (see below), if necessary combined with duplicate measurements under different experimental conditions.

## 2. INFLUENCE OF THE RATES OF DIFFUSION

When the solid and the liquid of a multicomponent system are in thermodynamic equilibrium the composition of the solid will usually differ from that of the liquid. When such a system is submitted to further crystallization or melting, the composition of at least one of the phases will change *in the vicinity of the contact surface*.

Consequently, the bulks of the phases are not coexistent. Diffusion tends to equalize the concentration differences occurring both in the solid and in the liquid phase and should therefore be promoted. This can be done by spreading the phases in thin layers and/or by stirring.

### 2.1. The effect of stirring

It should be noted that stirring as such promotes the homogeneity of only the liquid phase. It does not affect inhomogeneities occurring in the solid. Thus even when stirring is applied thick layers may be disadvantageous. An advantageous effect of stirring is that it may cause disintegration of solid particles, thus producing a larger contact surface which also promotes the bulk rate of crystallization (see section 1).

However, this advantage is somewhat dubious. First it should be noted that stirring is only applicable in a limited range of solid to liquid ratios. Further, the effectivity of stirring (when possible) depends on the amount of solid present. Thus an extra variable factor is introduced. Influence of the way and rate of stirring on the obtained curves may be demonstrated by examples derived from the literature.

When the effect of low *crystallization* rates is accounted for (see section 1) it is not surprising that cooling curves appear to be more dependent on the way of stirring than heating curves.

## 3. INFLUENCE OF THE RATE OF HEAT TRANSPORT

When heat is supplied to or withdrawn from a calorimeter, temperature differences will occur throughout all parts of the calorimetric system, including the wall, the substance contained in it, and even the thermometer. These differences again constitute a source of errors. The errors depend on the rate of heating, the sizes of the parts of the system and the heat conductivities of the composing materials.

An attempt will be made to obtain an impression of the size of these errors. We therefore give the calculations carried out to obtain the allowable dimensions of the thin film apparatus<sup>7,8</sup>.

With the thin film apparatus heat is supplied to a cylindrical measuring vessel schematically represented by Fig. 4. The substance to be investigated is contained in the annular space (2) between the outer wall of the thermometer (1) and the inner wall of the glass vessel (3). The heat supply (or withdrawal) is constant and occurs from the outside of the glass vessel (3).

The calculations necessary for evaluating the occurring temperature differences before melting sets in differ from those during the melting process. They will be presented subsequently.

The calculations are restricted to the cylindrical part of the system. The flow of heat through the top and the bottom of the system is disregarded.

The following symbols will be used:

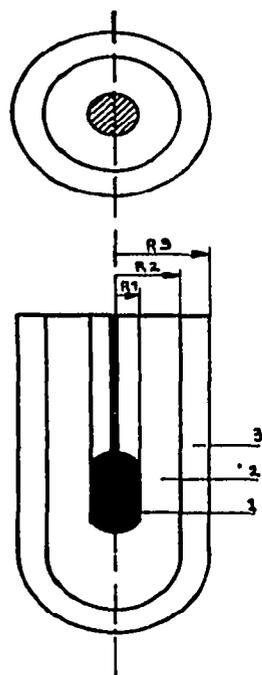


Fig 4 Measuring vessel with thermometer

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$a$  temperature conductivity ( $\lambda/h$ ) in  $\text{cm}^2/\text{sec}$   
 $C_1, C_2 \dots C_l, C_m$  constants

$d$	thickness of a layer
$\Delta$	temperature difference, defined by equation (5)
$f$	fraction of $\Delta$ such that $\Delta \cdot f$ is the temperature accuracy aimed at
$H_n$	heat content per unit length of a cylinder with radius $r_n$ (cal/cm <sup>2</sup> degree)
$h$	specific heat of a substance per unit volume (cal/cm <sup>3</sup> degree)
$K$	rate of heating or rate of heat supply per unit volume (degree/sec or cal/cm <sup>3</sup> sec)
$k$	integration constant
$l$	length of a cylinder
$\lambda$	heat conductivity (cal/cm <sup>2</sup> sec degree)
$n$	index referring to the $n$ th layer of substance
$p$	mol percentage of a contaminant present in a sample
$r$	radius
$S$	heat of fusion per unit volume (cal/cm <sup>3</sup> )
$T$	temperature (degree centigrade), $T_s$ , melting point of a pure substance
$t$	time (seconds), $t_s$ , total time necessary to melt a given sample at a rate of heat supply $K$
$Y$	fraction of sample melted
$Y_s$	fraction melted before a curve has become reliable

### 3.1. Temperature differences occurring before melting sets in

It is assumed that constant heat supply to the system has already been switched on for a sufficiently long time. Then the temperature of each part of the system will rise at a constant rate  $K$ .

According to Fourier

$$\left(\frac{dT}{dt}\right)_r = a_n \left(\frac{d^2T}{dr^2}\right)_t \quad (1)$$

where  $a_n$  stands for the temperature conductivity of the substance present at  $r$

Substitution of  $\frac{dT}{dt} = K$  and integration leads to

$$a_n \cdot \frac{dT}{dr} = Kr - k_{n1} \quad (2)$$

where  $k_{n-1}$  is a constant which is determined in the following way. Layer  $n$  is enclosed between two cylinders with radii  $r_{n-1}$  and  $r_n$ . The amount of heat passing per unit height and unit time through a layer of infinitesimal thickness  $dr$  at  $r_{n-1}$  equals the product of the rate of heating and the heat capacity ( $H_{n-1}$ ) of the cylinder with radius  $r_{n-1}$  and with unit height.

Thus:

$$KH_{n-1} = 2\pi r_{n-1} \lambda_n \left[\frac{dT}{dr}\right]_{r_{n-1}} \quad (3)$$

Combination of the equations (2) and (3) yields.

$$k_{n1} = K \left( r_{n-1} - \frac{H_{n-1}}{2\pi r_{n-1} h_n} \right) \quad (4)$$

Hence the constant  $k_{n-1}$  may be different in each layer of substance. Integration of equation (2) leads to:

$$a_n (Tr_n - Tr_{n-1}) = \frac{1}{2}K(r_n^2 - r_{n-1}^2) - k_{n-1}(r_n - r_{n-1}) \quad (5)$$

or

$$a_n (Tr_n - Tr_{n-1}) = \frac{1}{2}K(r_n - r_{n-1}) \left( r_n + r_{n-1} + \frac{H_{n-1}}{\pi r_{n-1} h_n} \right) \quad (5a)$$

In many cases the factor  $H_{n-1}/\pi r_{n-1} h_n$  approaches to  $r_{n-1}$  and the following equation holds good approximately:

$$a_n (Tr_n - Tr_{n-1}) = \frac{1}{2}K(r_n - r_{n-1})r_n \quad (6)$$

Thus it appears that the temperature difference occurring within the layer of material to be investigated is proportional to the rate of heating, to the thickness of the layer and roughly to the diameter of the cylinder. Equation (5) may also be used to calculate the lag of the thermometer.

An impression of the occurring temperature differences may be obtained from the following example. Let  $a_n = 7.5 \cdot 10^{-4}$  cm<sup>2</sup>/sec (which is an acceptable value for organic substances) and  $K = 0.01$  degree/sec,  $r_n - r_{n-1} = 0.1$  cm and  $r_n = 1$  cm, this yields when substituted in equation (6):

$$T_{r_n} - T_{r_{n-1}} = 0.67 \text{ degree centigrade.}$$

With the thin film apparatus  $r_n$  is about 0.3 cm and the rate of heating usually applied is 0.005 degree/sec (0.3° per min). This reduces the occurring temperature difference (before melting sets in) to 0.1 degree centigrade.

At the same rate of heating the temperature difference occurring through the glass wall of the measuring vessel (wall thickness 0.4 mm) amounts to about 0.01°, and the temperature difference through the mercury thermometer also amounts to about 0.01°.

These temperature differences remain constant until the substance shows a phase transition.

### 3.2. Temperature differences during the process of melting

The temperature differences discussed above reveal themselves when melting starts. Melting starts at the inner wall of the glass vessel and subsequently proceeds to the thermometer. As soon as melting starts the flow of heat to the thermometer decreases appreciably. It is not reduced to zero because the temperature of the thermometer is below the temperature of the melting zone. The difference between the temperature indicated by the thermometer and the temperature of the melting zone constitutes an error gradually decreasing with time. This error suggests non-isothermal behaviour of an isothermal process. The deviations will be large at the start of the "melting range" of the curve and gradually approach zero when the curve is continued. It is important to know within what time this error has decreased to a value not exceeding the limit of accuracy aimed at. (This limit may be given by the sensitivity of the thermometer.)

The exact calculation of this time constitutes a very complicated problem. The problem becomes somewhat more simple when the following additional assumptions are introduced:

The substance investigated is absolutely pure.

The thermometer has the same thermal properties as the substance. At the moment melting sets in the temperature throughout the solid cylinder of substance is  $T_s - \Delta$ , where  $T_s$  is the melting point of the substance and  $\Delta = T_{r_1} - T_{r_2}$  as obtained from equation (5).

The temperature at  $r_2$  remains constant and is equal to  $T_s$ .

This problem has been treated by WILLIAMSON AND ADAMS<sup>9</sup>. According to these authors the temperature  $T$  present at the core of the cylinder at a time  $t$  (being zero when melting starts) is determined by the following equation:

$$\frac{T_s - T}{\Delta} = 2 \sum_{m=1}^{\infty} \frac{1}{R_m J_1(R_m)} \exp \left[ \frac{a R_m^2}{r_2^2} t \right] \quad (7)$$

The values of  $R_m$  are the roots of the Bessel function  $J_1(x) = 0$ ,

where  $J_1(x) = 1 - \frac{x^2}{2^2} + \frac{x^4}{2^2 \cdot 4^2} - \frac{x^6}{2^2 \cdot 4^2 \cdot 6^2} + \dots$

For further details reference is made to the original paper<sup>9</sup>. For a number of cases WILLIAMSON AND ADAMS have calculated the value of  $\frac{T_s - T}{\Delta}$  as a function of  $at/r^2$ .

The first column of Table I gives the values of  $at/r^2$  and the other columns give the appertenant values of  $(T_s - T)/\Delta = f$  belonging to the bodies mentioned in the caption. With the aid of this table the time  $t_i$  necessary to reduce the original temperature difference to an allowable fraction ( $f$ ) of it may be determined for a given case.

TABLE I

$\frac{at}{r^2}$	$(T_s - T)/\Delta = f$		
	cylinder with $r = \infty$	cylinder with $r = 2r$	sphere
0	1 0000	1 0000	1 0000
0 032	0 9990	0 9988	0 9975
0 080	0 9175	0 8947	0 8276
0 100	0 8484	0 8054	0 7071
0 160	0 6268	0 5301	0 4087
0 240	0 3991	0 2802	0 1871
0 320	0 2515	0 1453	0 0850
0 800	0 0157	0 0028	0 0007
1 600	0 00015	—	—

This time as such is important, e.g. when a static calorimetric method is used.

With dynamic methods it is more important to know the ratio ( $Y_1$ ) of this time and the total time of melting  $t_s$ . This ratio  $Y_1$  determines which fraction of the substance has already melted before the obtained curve has become reliable.

With the thin film apparatus the total time of melting is determined by the following equation

$$t_s KH_{n+1} = (r_n^2 - r_{n-1}^2)S \tag{8}$$

$KH_{n+1}$  represents the heat supplied per unit time and per unit length to the calorimetric vessel and its contents. As  $S$  is the heat of fusion per unit volume the right hand member of the equation represents the total heat necessary to melt the contents of an annular space with radii  $r_n$  and  $r_{n-1}$  and unit height.

Solving  $t_s$  from equation (8) and bearing in mind that  $t_i/t_s = Y_1$  we may put

$$Y_1 = t_i KH_{n+1} / (r_n^2 - r_{n-1}^2)S \tag{9}$$

This equation will now be discussed.

As already stated, the time  $t_i$  may be derived from Table I. Looking at Table I we see that  $f$  is only 0.00015 at a value of  $at/r^2$  equal to 1.600. When  $at/r^2$  decreases only 50% (to 0.800) the value of  $f$  is multiplied by a factor 100.

As  $\Delta$  may vary between about 0.1 and 1 degree centigrade we are quite on the safe side of the temperature accuracy ( $f \cdot \Delta$ ) by choosing a value of  $at/r^2 = 1.6$  (or

larger), this value is not much too large because of the rapid increase of  $f$  as compared to the decrease of  $at/r^2$ . Consequently we take  $t_2 = 1.6 r^2/a$

In order to obtain a more convenient expression than equation (9) the following approximations are introduced.

The heat of fusion  $S$  is made equal to 100 times the mean specific heat of the calorimetric vessel and its contents

Thus:

$$H_{n+1} = 10^{-2} \pi r_{n+1}^2 S$$

Further  $r_n^2 - r_{n-1}^2$  is made equal to  $2r_n d$  where  $d = r_n - r_{n-1}$  and quotients of  $r_n$  and  $r_{n+1}$  or  $r_{n-1}$  are assumed to be equal to unity.

Allowing these approximations and substituting the values of  $t_1$ ,  $S$  and  $H$  chosen leads to

$$Y_1 = 8 \times 10^{-3} Kr^3/ad \quad (9a)$$

Equation (9a) constitutes a more simple relation between  $Y_1$ , the radius of the vessel, the thickness of the layer, the rate of heating and the temperature conductivity. The temperature conductivity of a pure organic substance may be put as  $7.5 \cdot 10^{-4}$  cm<sup>2</sup>/sec. Choosing the rate of heating  $5 \cdot 10^{-3}$  degree/second,  $d = 0.2r$  and  $r = 0.3$  cm yields  $Y_1 = ca. 2\%$ . The dimensions mentioned refer to the thin film apparatus. The formulae show that large errors may occur when deviations of the conditions occur. It may be useful to remember that an impure substance showing a wide melting range may be considered as a substance with an apparently increased specific heat, which results in a lower temperature conductivity.

### 3.3. Influence of contact between layers

With the above derivation it has been assumed tacitly that a perfect contact exists between the glass wall, the substance and the thermometer. Actually this contact is never completely perfect, thus causing extra temperature differences. Since the contact improves as soon as some liquid has been formed peculiar effects may result. Two cases may be distinguished: The first case concerns an ideal dynamic calorimeter showing no other flow of heat than from the outside to the core. When the substance is still entirely solid and imperfect contact exists (between the wall of the measuring vessel and the substance) a rather high temperature difference will occur between wall and substance. When melting starts the contact is improved and a higher flow of heat will result. Thus when an impure substance is investigated the initial range of premelting will be passed with a variable flow of heat, making the first part of the melting traject of the curve unreliable.

The second case deals with a non-ideal calorimeter in which an extra flow of heat occurs along the "stem" of the thermometer to or from the environment. When heat flows from the environment along the "stem" to the "bulb" of the thermometer and subsequently to the substance the temperature of the thermometer will be high when imperfect contact exists between substance and bulb. When after some melting has occurred the contact is improved the temperature of the bulb will adapt itself to that of the substance. The result will be a curve comparable with that represented in Fig. 5. Such curves have been actually obtained with some metals and organic materials

that have a tendency to form large crystals. The curve represented has been obtained with sodium as substance and a tenfold thermocouple as thermometer. It could be

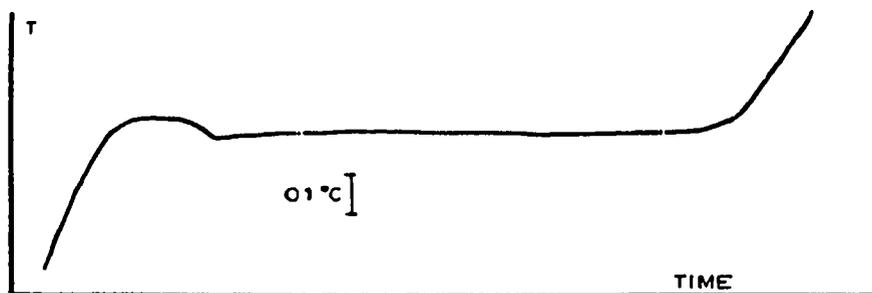


Fig 5 Anomalous heating curve

shown that the "hill" occurring in the curve depended on the flow of heat through the couple wires.

With mercury thermometers comparable results may be obtained. In this case the "hill" may also be due to pressure on the thermometer bulb initiating from the way of fitting the apparatus. When the substance melts the pressure is released and the bulb will resume its original volume.

#### 4. INTERNAL CHECK ON HEATING CURVES

Realizing that quite a number of errors may have affected the obtained curve it may be very useful to apply a check on the obtained results. This may be done by duplication or triplication of the measurements under different experimental conditions.

Apart from these experimental checks one may examine to what extent a curve or a series of curves obeys the following equation.

$$T_y = T_a - \frac{C_f C_m}{C_f + Y(C_m - C_f)} p \quad (10)$$

where  $T_y$  is the temperature at which a fraction  $Y$  of the substance has melted.  $T_a$  is the (unknown) melting point of the absolutely pure substance.  $C_f$  and  $C_m$  are constants and  $p$  is the mol percentage of a distinct contamination present in the sample. This equation has been derived previously<sup>7</sup> and will not be discussed now.

Equation (10) may be rewritten.

$$T_y = C_1 - \frac{C_2}{C_3 + Y} \quad (11)$$

where  $C_1$ ,  $C_2$  and  $C_3$  are constants.

These constants may be resolved algebraically by selecting three pairs of corresponding values of  $T_y$  and  $Y$ . (With the curves obtained with the thin film apparatus it proved to be advantageous to select values of  $Y$  lying closely together near  $Y = 0.15$ , e.g.  $Y = 0.10$ ,  $Y = 0.15$  and  $Y = 0.20$ .)

Now  $T_y$  values of the melting curve are plotted as a function of  $\frac{1}{C_3 + Y}$ . The plotted points should fit to a straight line with slope  $C_2$ . The ranges of  $Y$  where the plotted points deviate from the straight line should be considered as less reliable. (When the contaminant is immiscible with the main component in the solid state  $C_3$  reduces to zero.)

## 5. DISCUSSION AND RECOMMENDATIONS

The methods for determination of temperature-heat content curves may be divided into *static* and *dynamic* ones

When a static method is applied each period of heat supply to the substance is followed by a period of "adiabatic conditions" sufficiently long to approach equilibrium to a desired extent.

When a dynamic method is applied a continuous flow of heat occurs through the substance during the determination.

With a static method the errors previously mentioned may be reduced to any desired extent provided sufficient time is available. However, it has to be realized that the longer the time necessary to approach equilibrium, the more severe are the demands on the adiabatic properties of the calorimeter. The considerations and calculations given in the preceding sections may be useful for estimating the time necessary for an accurate determination.

More simple apparatuses can be used and much time can be saved by applying a dynamic method. With dynamic methods certain precautions are imperative, however.

On the strength of section 1 it is recommended that heating curves be preferred to cooling curves.

Before starting the measurement of a heating curve the solid should be preferably kept at a temperature slightly below the initial melting point for at least one hour.

Accepting that heating curves should be preferred to cooling curves leads to doubts concerning the advantages of the stirrer method.

As the thin film method may be applied to small samples (even as small as 20 mg, which constitutes an important advantage) a comparative investigation concerning the stirrer method and thin film method is recommended.

On the strength of section 3 it is recommended that more attention be paid to the adaptation of the dimensions of the apparatuses and the rate of heating to the accuracy aimed at.

If necessary, the rate of heating should be decreased when substances with low heats of fusion have to be investigated

With dynamic methods lack of equilibrium cannot be avoided at the very beginning and at the very end of the melting range. Even with static methods it is difficult to avoid comparable errors. Moreover, both methods may yield less reliable results when unforeseen slow processes of recrystallization occur. Therefore one is advised to subject any obtained curve to an internal check and to select a reliable part for purity determination. The internal check given in section 4 might be improved.

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### SUMMARY

In the determination of temperature-heat content curves errors may occur which are due to low transition rates, low diffusion rates and low rates of heat transfer. These errors are subsequently discussed. Liquid to solid transitions may be slow even when liquid and solid are in contact with each other at finite ratios. This causes appreciable differences between melting temperatures and solidification temperatures. The phenomenon is called two-phase undercooling. When

two-phase undercooling occurs the cooling curve obtained may lead to erroneous conclusions, *e g.* an impure substance may seem to be extremely pure This is illustrated by experiments

As far as is known two-phase superheating appears to be negligible under normal conditions Therefore heating curves are preferred to cooling curves

As stirring cannot promote diffusion in the solid phase it is doubted whether the stirrer method has advantages over the thin film method

Errors due to limited heat transfer and occurring with the thin film method have been calculated Formulae have been given relating the dimensions of a thin film apparatus and the rate of heating to the accuracy aimed at

Application of an internal check on heating curves is recommended

### RÉSUMÉ

Lors de la détermination des courbes température enthalpie des erreurs peuvent se produire, erreurs dues à de faibles vitesses de transition, de diffusion et de transmission de chaleur Ces erreurs sont discutées Les transitions liquide-solide peuvent être lentes même lorsque liquide et solide sont en contact dans des proportions finies Ce fait cause des différences considérables entre les températures de fusion et de solidification Ce phénomène est indiqué comme surfusion à deux phases Lorsqu'il y a surfusion à deux phases, la courbe de refroidissement obtenue peut conduire à des conclusions erronées, elle peut par exemple faire juger extrêmement pure, une substance impure Des expériences illustrent ce phénomène

Tant que l'on sache, le surchauffage à deux phases semble être négligeable dans des conditions normales C'est pourquoi les courbes de chauffage sont préférées aux courbes de refroidissement.

Comme une agitation ne peut pas promouvoir la diffusion dans la phase solide, il est douteux que la méthode à agitation présente des avantages par rapport à la méthode à film mince

L'auteur a calculé les erreurs dues à une transmission de chaleur limitée et qui ont lieu lors de l'emploi de la méthode à film mince Il donne des formules reliant les dimensions d'un appareil à film mince et la vitesse de chauffage à la précision désirée

L'application d'une méthode de contrôle par corrélation aux courbes de chauffage est recommandée

### ZUSAMMENFASSUNG

Bei der Bestimmung von Temperatur-Wärmeinhalt-Kurven können Fehler auftreten, die auf niedrige Übergangs-, Diffusions- und Wärmeübergangsgeschwindigkeiten zurückzuführen sind Diese Fehler werden erörtert Übergänge vom flüssigen in den festen Zustand können langsam stattfinden, auch wenn Flüssigkeit und fester Stoff in endlichen Verhältnissen miteinander in Kontakt sind Dies verursacht merkliche Unterschiede zwischen den Schmelz- und Erstarrungstemperaturen Die Erscheinung wird Zweiphasenunterkühlung genannt Bei Zweiphasenunterkühlung kann die Abkühlungskurve zu fehlerhaften Schlüssen führen, wie, zum Beispiel, dass eine unsaubere Substanz für äußerst rein angesehen wird Dies wird durch Versuche dargelegt

Soviel man weiss, scheint die Zweiphasenüberhitzung unter normalen Bedingungen vernachlässigbar zu sein Darum sind Erhitzungskurven den Abkühlungskurven vorzuziehen

Da man durch Rühren die Diffusion in der festen Phase nicht befördern kann, wird bezweifelt, dass die Ruhrmethode gegenüber der Dunnfilmmethode Vorteile bietet

Fehler die auf beschränkten Wärmeübergang zurückzuführen sind und bei der Dunnfilmmethode auftreten, wurden berechnet Formeln welche die Dimensionen eines Dunnfilmapparates und die Erhitzungsgeschwindigkeiten mit der erwünschten Genauigkeit in Verbindung bringen werden mitgeteilt

Die Anwendung einer Korrelationskontrolle auf die Erhitzungskurven wird empfohlen

### REFERENCES

- 1 W OSTWALD, *Z physik Chem*, 21 (1897) 289
- 2 G TAMMANN, *Z. physik Chem*, 23 (1897) 326, 25 (1898) 472, 26 (1898) 306, 29 (1899) 52; 81 (1912) 171
- 3 P OTHMER, *Z physik Chem*, 91 (1915) 209
- 4 F MEISSNER, *Z anorg Chem*, 110 (1920) 169
- 5 M E KRAHL, *J Am Chem Soc*, 55 (1933) 1425.
- 6 K A JACKSON AND B CHALMERS, *Can J Phys.*, 34 (1956) 473.
- 7 W M SMIT, *Rec trav chim*, 75 (1956) 1309
- 8 W M SMIT, *A tentative investigation concerning fatty acids and fatty acid methyl esters*, Thesis, Vrije Universiteit, Amsterdam, 1946
- 9 E D WILLIAMSON AND L H ADAMS, *Phys Rev*, 14 (1919) 99.