

ZONE MELTING AS AN AID TO IMPURITY DETERMINATION BY THERMAL ANALYSIS

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When the temperature of a substance is plotted as a function of the amount of heat supplied to it, the resulting curve is indicated as a temperature-heat content curve. Such a curve comprising the melting range of the substance is called the melting curve. Almost every impurity soluble in the melt will influence the shape of the melting curve, and, in fact, the melting curve offers a very general sensitive and non-destructive criterion for purity. However, when attempts are made to state the data on purity in exact figures, difficulties are encountered. In other words, the quantitative interpretation of the melting curve so that the purity of a substance, or rather its impurity content, can be calculated, constitutes a problem that has not yet been completely solved.

In the interpretation of melting curves two categories of impurities must be distinguished, *viz.* solid insoluble impurities (impurities forming no mixed crystals with the main component), and solid soluble impurities (forming mixed crystals). When a substance contains only solid insoluble impurities, the determination of the melting curve and its quantitative interpretation presents no essential difficulties¹⁻⁵. Unfortunately, this is of restricted importance in dealing with "pure" substances. Very often substances are purified by means of crystallization or extraction. Both processes are very effective in removing solid insoluble impurities but are far less effective on solid soluble impurities and may even enrich the solid soluble impurities in the desired substance. Thus purified substances will often contain solid soluble impurities.

In the past distinct progress has been made in the determination of these impurities by means of melting curves. It appears possible to solve the problem completely when only one solid soluble contaminant is present⁶. When more than one solid soluble contaminant is present, it is possible to show that the concentration does not exceed a distinct value.

In the present paper, further progress in the development of impurity determination by the melting curve is reported.

When a sample is to be investigated, it must first be ascertained whether solid soluble contaminants are present or only solid insoluble ones. The shape of the melting curve of the sample may already be conclusive in some cases. However, a better test on mixed crystals is possible (see below). When this test shows the presence of mixed crystals and the system appears to be a multicomponent system, one melting curve will seldom give sufficient information for a complete analysis⁷.

It will be shown in this paper that the application of zone melting combined

with the measurement of several melting curves will often make it possible to obtain a complete analysis of all impurities with distribution coefficients different from 1. In the past, the application of zone melting for analytical purposes has been seriously hampered because zone melting was such a very time-consuming process. However, this difficulty has been overcome with the construction of a new apparatus which permits the passage of over 20 zones through a sample of 4 g within an hour⁸.

Test on mixed crystals

No mixed crystals are present when a slowly frozen sample gives a melting curve obeying the equation of WHITE¹:

$$Y^{-1}X = - \frac{Q}{RT_s^2} \Delta T \quad (1)$$

where Y is the fraction that has melted; X the total amount of the contaminants in mol fraction; Q the heat of melting in cal/mol; T_s the melting point of the substance in °K; ΔT the depression in °K; and R the gas constant in cal/degree · mol. Uncertainties in the value of Y may obscure eqn. (1). Thus, when a melting curve is not in accordance with the equation of White the conclusion that mixed crystals must be present may be incorrect.

A better test on mixed crystals is based on the differences between the melting curves of a slowly and a quickly frozen sample. In two previous papers^{8,9}, it has been shown that if mixed crystals occur a slow solidification of a sample results in an inhomogeneous distribution of the impurities analogous to the distribution after normal freezing. A quick solidification results in a more homogeneous distribution of the impurities. As a consequence of these differences a slowly frozen sample containing mixed crystals will melt at a lower temperature level than the quickly frozen sample, particularly at small values of Y . Moreover, the temperature differences along the melting curve of a slowly frozen sample are larger than those of a quickly frozen sample. When no mixed crystals occur the melting curves of the quickly and the slowly frozen sample will be identical.

The application of this very reliable test on mixed crystals requires certain precautions. The quick-freezing procedure often results in very imperfect crystals and sometimes in metastable modifications. In order to obtain perfect and stable crystals an annealing procedure is advisable. After solidification the sample must be kept at a temperature 3–5° below the melting range of the substance for at least 1 h.

Operations like slow solidification and annealing can be easily performed when the melting curves are determined by the thin film method^{6,10,11}.

THE INTERPRETATION OF MELTING CURVES OF A SAMPLE CONTAINING n CONTAMINANTS

The multicomponent system

When n contaminants are present in a sample and the distribution coefficients k_n of these contaminants can be considered as constants, the general T, Y relation for the melting curve of a slowly frozen sample is⁷:

$$\sum_1^n (1 - k_n) Y^{k_n-1} X_n = \frac{Q}{RT_s^2} (T_s - T) = - \frac{Q}{RT_s^2} \sum_1^n \Delta T_n \quad (2)$$

where n is the number of contaminants; k_n the distribution coefficient of the contaminant n ; Y the fraction that has melted; X_n the mol fraction of contaminant n ; T the temperature in °K when Y has melted; and ΔT_n the depression of the temperature caused by contaminant n .

When nothing is known about the sample, the values of X_n , k_n , T_s and n are unknown. From one melting curve a number of relations between T and Y can be obtained but in general it is impossible to compute all unknown quantities accurately from one melting curve.

The problem may be simplified somewhat by substituting a distinct set of mean k_n -values covering the whole range of possible distribution coefficients. However, this approximation appears to be insufficient for adequate interpretation of a melting curve. The number of unknown quantities remains too large and moreover several combinations of X_n and k_n may exist giving approximately (within the accuracy of the measurement of Y and T) the same function of T . Only if the range of possible k_n -values is very restricted, can melting curves be interpreted accurately without making use of a computer.

It is therefore highly desirable to reduce the number of unknown quantities to a low figure. This can be done by subjecting the sample to zone melting. Before this subject is dealt with, some typical cases will be discussed.

The melting curve of a sample with apparently only one contaminant

When n can be reduced to 1 or when the sum of the depressions caused by all components but one is known, eqn. (2) can be reduced to:

$$(1 - k_1)Y^{k_1-1}X_1 = - \frac{Q}{RT_s^2} \Delta T_1$$

The value of k_1 and X_1 can be easily obtained by plotting $\log Y$ against $\log |\Delta T|$. The slope of the straight line obtained gives the value of $(k_1 - 1)$ and the intercept on the $\log |\Delta T|$ axis gives the value of $\log [(RT_s^2/Q) (1 - k_1)X_1]$ for $k_1 < 1$ and of $\log [(RT_s^2/Q) (k_1 - 1)X_1]$ for $k_1 > 1$. When T_s is unknown its value can be calculated from the melting curve as has been described in a previous paper⁶.

A sample containing n contaminants with only slightly differing k_n -values, will often behave like a sample with only one contaminant with a mean distribution coefficient \bar{k} . This is clear from the following considerations. When

$$\sum_1^n (1 - k_n)Y^{k_n-1}X_n = (1 - \bar{k})Y^{\bar{k}-1} \sum_1^n X_n,$$

\bar{k} must be a function of Y . This function can be written:

$$(1 - \bar{k}) = \sum_1^n (1 - k_n)Y^{k_n-\bar{k}}X_n / \sum_1^n X_n$$

When, e.g., $-0.1 < k_n - \bar{k} < 0.1$ and Y varies from 0.1 to 1, the value of $Y^{k_n-\bar{k}}$ will vary only from 1.25 to 0.8. Moreover, every $Y^{k_n-\bar{k}}$ value larger than 1 is opposed by a $Y^{k_p-\bar{k}}$ value smaller than 1. Thus the value of \bar{k} will vary only slightly with Y and the mean distribution coefficient \bar{k} will be close to:

$$\sum_1^n k_n X_n / \sum_1^n X_n.$$

The value of \bar{k} is found experimentally by drawing a straight line through the plot of $\log Y$ against $\log|\Delta T|$. The total amount of impurity calculated according to this approximation will be close to the value of $\sum_1^n X_n$.

The melting curve of a sample containing impurities with $k < 1$ and $k > 1$

Suppose that the system may be considered as a main component with two contaminants. Eqn. (2) reduces to:

$$(1 - k_1)Y^{k_1-1} + (1 - k_2)Y^{k_2-1} = \frac{Q}{RT_s^2} (T_s - T) = -\frac{Q}{RT_s^2} (\Delta T_1 + \Delta T_2) \quad (2b)$$

In this equation $k_1 < 1$ and $k_2 > 1$ may be the real distribution coefficients of the contaminants or the mean distribution coefficients of two sets of impurities having only slightly differing distribution coefficients within each set. At small values of Y the value of ΔT_2 may dominate over ΔT_1 .

When $\log Y$ is plotted against $\log|\Delta T_1 + \Delta T_2|$ a strongly curved line or a function in two portions is obtained (see Fig. 1). One or both ends of this line may be approximately straight.

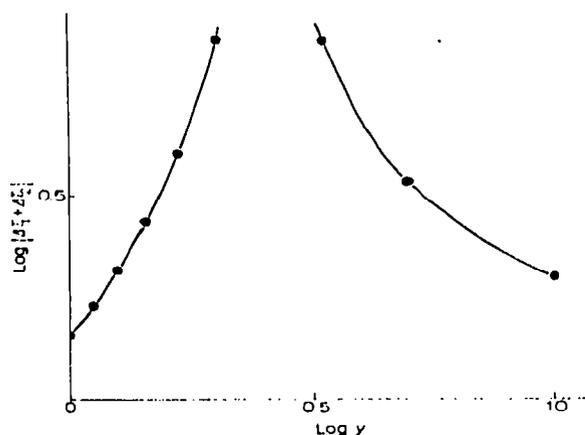


Fig. 1. Plot of $\log|\Delta T_1 + \Delta T_2|$ against $\log Y$ for two impurities with $k = 0.7$ and $k = 2$ present in equal concentrations (the scale of ΔT -values is arbitrarily chosen).

The following method of successive approximation can now be followed. The tangents at one or both ends of the line (e.g. $Y = 0.1$ and $Y = 0.9$) are drawn. It is assumed that these lines represent as a first approximation the functions

$$\log(-\Delta T_1) = (k_1 - 1)\log Y + \log[(RT_s^2/Q)(1 - k_1)X_1] \quad (2c)$$

and

$$\log(\Delta T_2) = (k_2 - 1)\log Y + \log[(RT_s^2/Q)(k_2 - 1)X_2] \quad (2d)$$

From the first tangent the depressions ΔT_1 are calculated in the range $Y = 0.5-1$ and from the second tangent the elevations ΔT_2 in the range $Y = 0.1-0.5$. Now the ΔT_1 -values are corrected with the calculated ΔT_2 -values and the ΔT_2 -values are corrected with the calculated ΔT_1 -values. The logarithms of these corrected values are

plotted again against $\log Y$. The graphs through these plots will show a much smaller curvature than the original curve. The correction of ΔT_1 and ΔT_2 may be repeated using the new corrected graphs until the obtained lines are perfectly straight. These lines will represent the functions (2c) and (2d) from which k_1 , k_2 , X_1 and X_2 can be calculated.

ZONE MELTING AS AN AID IN THE DETERMINATION OF IMPURITY CONTENT BY MEANS OF MELTING CURVES

When a substance is subjected to zone melting the impurities are redistributed along the ingot depending on the distribution coefficients of the impurities. To a certain extent a classification of the impurities according to their distribution coefficients will be obtained. In some parts of the ingot the concentration of several impurities may be reduced beyond a detectable value while other impurities are less reduced or enriched. After a sufficient number of zone passes the first part of the ingot will only contain impurities with k close to 1 or >1 . In most cases the first part of the ingot will give interpretable melting curves.

The actual determination of the impurity content of a sample can thus be performed in the following way. The substance is subjected to zone melting and after an arbitrarily chosen number of zone passes, the melting curves of several parts of the ingot are determined. From the set of melting curves obtained, those melting curves are selected that can be interpreted as described in the previous section of this paper. When the concentration and the distribution coefficient of a contaminant (or a group of contaminants) can be determined in a part of the ingot, the concentration in every part of the ingot and the mean concentration can be computed. This means that for every melting curve the ΔT_n -values caused by this contaminant can be calculated.

The melting curves are corrected for these ΔT_n -values; and from these corrected melting curves again those melting curves are selected that can be interpreted. The remaining curves are corrected again and the whole process is repeated until all impurities and the distribution coefficients are determined. In general, every determination of the impurity content of a sample is a new problem and rules concerning the number of zone passes and the parts of ingot that will give interpretable melting curves cannot be given. Much depends on the number, kind and concentration of the contaminants.

Often the number of impurities giving mixed crystals with the main component is restricted and in most cases the value of n is only 3 or less. In these cases the rather cumbersome procedure described above is not necessary. From the melting curves of several parts of the ingot, the distribution coefficients of the impurities can be easily determined. The obtained set of distribution coefficients is used in the interpretation of the melting curve of the original sample.

An important value in the interpretation of melting curves when impurities with $k > 1$ and $k < 1$ are present is the melting point of the pure main component. By zone melting a relatively pure main component can be obtained from which the value of T_B can be determined more accurately.

SUMMARY

The determination of the impurity content of a sample by means of the melting-

curve method (calorimetric analysis) is often seriously hampered when solid soluble contaminants are present. Solid solutions often occur in substances purified by crystallization or extraction. A simple test on mixed crystals is described. When three or more impurities are present the relations obtainable from a melting curve are insufficiently accurate for computing the unknown concentrations and distribution coefficients to an acceptable extent. Only melting curves obtained from samples containing one or two impurities permit an exact, simple interpretation. A complex of impurities may be analysed when the sample is subjected to zone melting and a set of melting curves is obtained for parts of the ingot.

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