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USE OF THE "SHAPE FACTORS" AS AN EMPIRICAL METHOD TO DETERMINE THE ACTUAL CHARACTERISTIC TEMPERATURES OF BINARY PHASE DIAGRAMS BY DIFFERENTIAL SCANNING CALORIMETRY

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ABSTRACT

A typical problem with differential scanning apparatus used in thermal analysis is the determination of the actual characteristic temperatures of thermodynamic equilibrium states. An empirical method based on the notion of "shape factors" is given here. It allows the determination of all the characteristic temperatures of a binary phase diagram.

INTRODUCTION

Thanks to recent advances in technology, thermal process determination is now achieved by using differential scanning calorimetry analysers. Experiments are usually conducted by the exploration of temperature as a (generally linear) function of time: the sample to be analysed and the standard reference product are submitted to the same heating program. There are two different kinds of devices: (i) the thermal differential analyzer where the signal is proportional to the thermal flux between the sample and the reference and (ii) the power compensated enthalpy analyzer for which the signal is proportional to the energy needed to maintain both sample and reference at the same temperature.

In the case of an "isothermal" phenomenon (for instance the melting of a pure material at a temperature T) the dynamical aspect of these techniques raises the question of the interpretation of the experimental signal. In other words, how does one proceed to reach the "true" temperature T and with the greatest accuracy? This problem becomes even more difficult as one characterizes complicated phenomena that occur over a wide range of

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temperature, such as the melting of an alloy where a starting melting temperature (T_{solidus}) and an ending melting temperature (T_{liquidus}) are to be determined.

For each given phenomenon, there is a unique temperature which is always the same whatever the apparatus used and whoever operates the device.

In this paper we propose a simple method for the analysis of temperature signals and for the determination of the characteristic temperatures of the studied phenomena. This method is particularly effective for the determination of binary phase diagrams. At the beginning of this paper, we briefly recall the bases of the experimental approaches.

DETERMINATION OF THE CHARACTERISTIC TEMPERATURE OF AN ISOTHERMAL PHENOMENON

Starting from an experimental thermal signal, how do we determine, with the greatest possible accuracy, the temperature T of an isothermal phenomenon (e.g. a solid–liquid transition of a pure material)?

Temperature scale

The function of a scale is to spot the characteristic temperature of the encountered phenomena. The scale is defined by fixed points which are called defining fixed points and are related to perfectly reproducible thermal processes. We will not describe here the temperature scales that have been proposed so far; they are numerous and very well described elsewhere [1,2]. We will only recall that, according to the last decisions taken by the C.C.T. * meeting in 1975 [3], we have adopted the E.I.P.T.-68 **. This is based on the temperature values assigned to a certain number of reproducible equilibrium states (11 defining fixed points) and on specific instruments calibrated at these temperatures. These equilibrium states and the values of the Practical International Temperature that are assigned to them are given in ref. 3. The interpolation between defining fixed points is realized with the help of formulas that give the relation between the indications of the instruments and the values of the Practical International Temperature. Moreover, the E.I.P.T.-68 supplies an additional series of points called secondary reference temperatures [3]: they characterize more easily accessible thermodynamical equilibrium points.

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* Comité Consultatif de Thermométrie.

** Echelle Internationale Pratique de Temperature de 1968.

Thermal signal

The differential scanning thermal analysis yields the recording of two curves as a function of time (fig. 1): curve (1-a) which is the differential analysis curve (DTA or DSC curve) and curve (1-b) which corrsponds to the variation in the sample temperature. Although the phenomenon involved is isothermal, one notices that the experimental curve (1-b) rarely exhibits a strictly constant plateau during the recording of the thermal signal: a variation in temperature is observed which we will discuss later on. One knows that the transition occurs as soon as curve (1-a) leaves the baseline (point D). In fact, this point is often difficult to define and hardly reproducible. This is why we have adopted the following rule: the temperature T is taken at the onset temperature T_0. T_0 corresponds to the point of intersection between the tangent line drawn from the point of greatest slope on the leading edge of the peak with the extrapolated baseline. According to the ICTA's Committee of Standardization [4] this extrapolated onset temperature is a reproducible point of the curve (1-a).

Calibration of the apparatus

The objective of calibration is to bind the response of the device with the temperature scale with the help of thermometric markers. It is a strictly compulsory operation without which a comparison of the results issued by different laboratories is not possible. We have worked essentially with the two following secondary reference temperatures: equilibrium between ice and water at 273.15 K (with water bi-distilled on colonne quartz) on the one hand, and the equilibrium between solid and liquid phases of indium at 429.784 K [1] (with indium supplied by the National Bureau of Standards). It is obvious that the method of the onset of T must also be used for these calibrations and that these must be realized and regularly checked for each of the heating speeds adopted for the experiments.

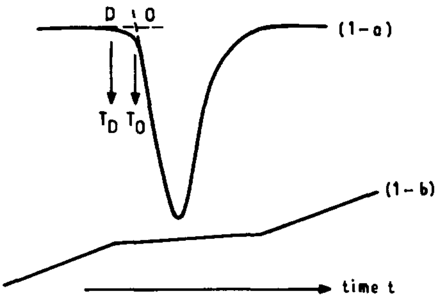

Fig. 1. Melting of a pure compound: curve (1-a), DTA curve or DSC curve; curve (1-b), sample temperature.

Measurement accuracy

It is well known that experimental errors are of two types: systematic errors and random errors. In our case, we believe that the first kind of errors can be considered as negligible since the calibration has been carried out very carefully ($\leqslant 0.3$ K). The calculation of random errors means that several independent experiments must be reproduced in order to check their random nature. For this purpose we have analyzed the results of more than 100 observations relative to the melting point of indium. The histogram has been divided into seven classes. The tests of χ^2 yield a sufficient probability. Calculation of the uncertainty of our measurements has been carried out using a statistical method: realization of n independent experiments ($n =$ 5–10) and use of the Student formula which allows the evaluation of the mean $\bar{\mu}$ of the population starting from the mean value $\bar{X}$ relative to the samples

$$\bar{\mu} = \bar{X} \pm t_c \frac{\sigma}{\sqrt{n}}$$

where σ is the population standard deviation deduced from s (the deviation relative to the sampling) by $\sigma^2 = n/(n-1)s^2$, and t_c is a factor tabulated by Student. We have adopted a confidence rate of 0.95.

SHAPE FACTORS

Our purpose here is to propose a convenient mean for the characterization of a simple experimental signal related to an isothermal process in order to be able to interpret more complicated thermal signals afterwards.

Let us go back to the signal relative to the melting of a pure material (Fig. 2). The peak spreads out from point D (departure of the differential curve from the baseline) to point R (return of the curve to the baseline). Both points D and R are in fact very hard to locate reproducibly and therefore

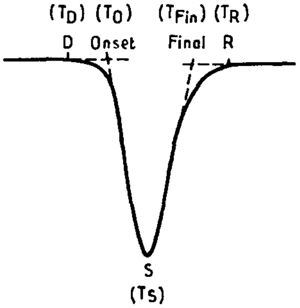

Fig. 2. Shape factors: $\Delta T_s = T_s - T_0$; $\Delta T_{\mathrm{fin}} = T_{\mathrm{fin}} - T_0$.

not appropriate for the definition of the phenomenon. For better characterization of the experimental signal we suggest [5,6] the use of the following three magnitudes that are easily attainable: (i) the T_{onset} temperature defined previously, (ii) the temperature T_s corresponding to the summit of the peak, and (iii) the temperature T_{fin} (intersection point of the peak extrapolated to the baseline and the tangent to the final part of the signal).

We can now introduce the two shape factors

$$\Delta T_s = T_s - T_0$$

$$\Delta T_{\text{fin}} = T_{\text{fin}} - T_0$$

It follows that the temperature T of the studied phenomenon will be attainable from three different paths

$$T \equiv T_0$$

$$T \equiv T_s - \Delta T_s$$

$$T \equiv T_{\text{fin}} - \Delta T_{\text{fin}}$$

provided that one knows values of the shape factors ΔT_s and ΔT_{fin}. Later we will see the advantage of this approach.

The reasons behind the broadening of an isothermal signal are numerous. They can be classified into two groups: those that are related to the device and its operating mode, and those that are related to the material to be analysed. The first group will contain, for instance, causes related to the type of device used, the quality of it, the position of the heat sensor, the form and the nature of the cells, the speed of the heating program, etc. In the second group one will find causes related to the sample mass and its nature, in other words all the factors that are supposed to create a temperature gradient inside the sample during the analysis. It goes without saying that thermal diffusibility, thermal conductivity and specific heat are directly involved here.

TABLE 1

Effect of sample nature and weight on shape factors ΔT_s, ΔT_{fin} (measurements were performed on a Du Pont de Nemours apparatus with $v = 2$ K min^{-1}; ΔT_s and ΔT_{fin} are in Kelvin)

Weight (mg)	In	1,3,5-TBB [a]	1,3,5-TCB [b]
2	$\Delta T_s = 0.30$ $\Delta T_{\text{fin}} = 1.00$	$\Delta T_s = 0.90$ $\Delta T_{\text{fin}} = 1.60$	$\Delta T_s = 0.90$ $\Delta T_{\text{fin}} = 1.60$
4	$\Delta T_s = 0.35$ $\Delta T_{\text{fin}} = 1.10$	$\Delta T_s = 1.10$ $\Delta T_{\text{fin}} = 2.00$	$\Delta T_s = 1.10$ $\Delta T_{\text{fin}} = 2.10$
6	$\Delta T_s = 0.40$ $\Delta T_{\text{fin}} = 1.30$	$\Delta T_s = -$ $\Delta T_{\text{fin}} = 2.40$	$\Delta T_s = -$ $\Delta T_{\text{fin}} = 2.40$

[a] 1,3,5-TBB = 1,3,5-tribromobenzene. [b] 1,3,5-TCB = 1,3,5-trichlorobenzene.

TABLE 2

Effect of the heating speed (on 1,3,5-dibromethylbenzene, $m = 2$ mg, Du Pont de Nemours apparatus)

0.5 K min^{-1}	2 K min^{-1}	5 K min^{-1}
$\Delta T_{\mathrm{fin}} = 0.60$	$\Delta T_{\mathrm{fin}} = 1.60$	$\Delta T_{\mathrm{fin}} = 2.80$

We have performed a thorough experimental study of the shape factors, in Bordeaux (on an AED Du Pont de Nemours, Model 910) and in Barcelona (on a DSC-4 Perkin Elmer). The results are reported elsewhere [7]. We recall here only the main points on which our method rests.

(i) ΔT_s and ΔT_{fin} are very sensitive to the nature of the material (see Table 1). They are both much weaker for the metal (indium which is a good thermal conductor) than for organic compounds (1,3,5-tribromobenzene and 1,3,5-trichlorobenzene).

(ii) The shape factors increase with the mass of analysed material (see Table 1); this mass influence affects particularly the summit of the peak which becomes difficult to define (the peak becomes slightly jagged) when m is large. However, there is no problem in plotting T_{fin}.

(iii) An increase in the heating speed leads to large increase in ΔT_s and ΔT_{fin} (see Table 2).

(iv) The ΔT_s and ΔT_{fin} factors can be considered identical for all the compounds of a given family provided that all the experimental conditions remain the same (i.e. device, measurement cells, atmosphere and heating speed).

One can eliminate the mass influence by using charts that are easy to draw experimentally. The word family may encompass a large number of compounds: the examples provided here show that for $m = 2$ mg and $v = 2$ K min^{-1}, $\Delta T_s = 0.9$ and $\Delta T_{\mathrm{fin}} = 1.6$ for all the 1,3,5-trisubstituted benzene derivatives and $\Delta T_s = 1.0$ and $\Delta T_{\mathrm{fin}} = 1.5$ for the *para*-bromochlorobenzene.

DETERMINATION OF THE CHARACTERISTIC TEMPERATURE OF A BINARY PHASE DIAGRAM

Now let us consider the case of the melting of an $A_{1-x}B_x$ alloy. We are not dealing with an isothermal phenomonenon any longer. Melting starts at T_{solidus}, the solidus temperature at which the first drop of liquid appears. It continues with the coexistence of the liquid and the solid until T_{liquidus} temperature is reached above which the last solid particle disappears. One has to define here T_{solidus} and T_{liquidus} from the experimental signal (exam-

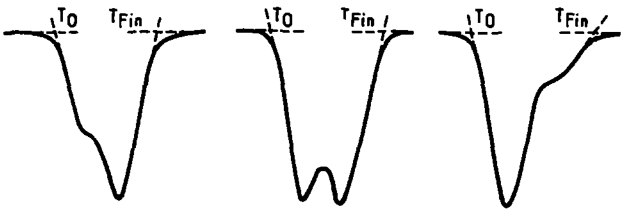

Fig. 3. Melting of an alloy: $T_{\text{solidus}} = T_0$; $T_{\text{liquidus}} = T_{\text{fin}} - \Delta T_{\text{fin}}$.

ples of the signal are given in Fig. 3). There is no problem in defining T_{solidus}; it is the first phenomenon that occurs, so

$$T_{\text{solidus}} = T_0$$

However, one detects the end of T_{liquidus} through T_{fin}; so we propose to take

$$T_{\text{liquidus}} = T_{\text{fin}} - \Delta T_{\text{fin}}$$

ΔT_{fin} is determined from the study of the two compounds A and B. In most cases, $(\Delta T_{\text{fin}})_{\text{A}} = (\Delta T_{\text{fin}})_{\text{B}}$ * and one can then use this value for the different alloys A_{1-x}B_x.

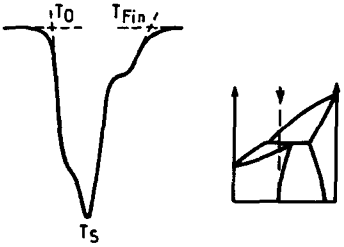

Fig. 4. $T_{\text{solidus}} = T_0$; $T_{\text{perit}} = T_s - \Delta T_s$; $T_{\text{liquidus}} = T_{\text{fin}} - \Delta T_{\text{fin}}$.

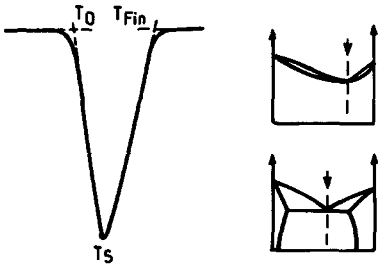

Fig. 5. $T_0 = T_s - \Delta T_s = T_{\text{fin}} - \Delta T_{\text{fin}}$; $T_{\text{solidus}} = T_{\text{liquidus}} = T_0$.

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* If not, a linear interpolation is taken.

At the composition x, the width between the solidus and liquidus curves is given by

$$l_x = (T_{\text{fin}} - \Delta T_{\text{fin}})_x - (T_0)_x$$

Thanks to this method, the invariant points such as the Gibbs points or eutectic points may be determined easily. They correspond, of course, to $l_x = 0$ (Fig. 4). In Fig. 5 we give a more complicated example of the use of shape factors: it is the melting of an alloy with a peritectic transformation, where the characteristic temperature determination requires the use of both ΔT_{fin} and ΔT_s.

CONCLUSION

Although it is empirical, the method we present here has many advantages. First, it is a simple one, since one has only to determine precisely ΔT_s and ΔT_{fin} for the two compounds A and B, under the same experimental conditions as those that will be used in the analysis of the alloys, i.e. same device, same heating speed, etc. After that, it becomes easy to determine the characteristic magnitudes needed for the definition of the equilibrium phase diagram A–B.

It should also be noted that it may be useful, eventually, to determine the shape factors under two or more sets of experimental conditions, for instance, two different heating speeds. It is often the case for binary phase diagrams with peritectic phenomena that the solid–liquid two-phase domain is generally narrow near the two pure compounds and very wide in the center regions. For these domains, one should increase the heating speed slightly in order to obtain a sharper signal which is easier to analyse. The use of the shape factors method allows a good agreement between the two sets of data.

This method is useful for the determination of narrrow phase domains, for the accurate definition of the position of invariant points, and for the analysis of polymorphic materials. However, in our opinion, its most important advantage is that it allows factors related to the type of device used to be overcome (the influence of which should not be neglected as is shown

TABLE 3

Effect of apparatus (experiments were performed on *para*-bromochlorobenzene with $m = 2$ mg, $v = 2$ K min^{-1}

Du Pont de Nemours	Perkin Elmer
$\Delta T_s = 1.00$	$\Delta T_s = 0.80$
$\Delta T_{\text{fin}} = 1.50$	$\Delta T_{\text{fin}} = 1.10$

in Table 3). It is therefore a good means of obtaining directly comparable results from different laboratories. Consequently it is liable to publication in data bases.

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