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PURITY MEASUREMENT BY DIFFERENTIAL SCANNING CALORIMETRY: AN ALTERNATIVE METHOD OF COMPUTATION

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The established procedure for the estimation of purity from differential calorimetric melting range results involves empirical linearization of the data, which can be time consuming and may introduce a subjective element into the calculation. This is sometimes thought to be a disadvantage of the method. A modification of the procedure has been developed which avoids this difficulty and offers advantages in ease of data logging and of overall computer programming.

An important method of purity determination uses a differential scanning calorimeter to measure melting range, from which total molar impurity content can be deduced [1]. The method depends on the assumption of ideal solution behaviour, a condition usually met, since the amounts of impurity measurable by this means is small; and also on the assumption that the impurities form no solid solutions with the host component. This second assumption is less easily justified. However, the success of the extensive tests by Plato & Glasgow [2], and a continuing interest, particularly in industrial laboratories, suggests that despite limitations, the method is finding a wide field of application.

The procedure adopted for calculating molar impurity content from DSC melting curves is usually that first established by the Perkin-Elmer Corporation [1] for use with their differential scanning calorimeters. Some variants have been suggested and found to be useful [3–5]. In the present note, we describe a more extensive modification, which seems to us to offer certain advantages in objectivity and ease of computerization. We have not questioned the underlying assumptions of the method, nor the adequacy of the experimental technique, both of which seem to be satisfactory for many purposes.

General theory

Application of Raoult's Law to molten host component (component 1), in which is dissolved all the impurity present, shows that the temperature (T) at which pure solid (component 1) is in equilibrium with liquid containing dissolved impurity (component 2) is given by:

$$T_0 - T = \frac{RT_0^2}{q} \cdot x_2 \cdot \frac{1}{f} \tag{1}$$

where T_0 is the melting point of the pure solid, q is its heat of fusion, x_2 is the concentration of the impurity expressed as a mole fraction of the total solid + liquid, and f is the fraction of the substance melted. R, the gas constant, has its usual significance. In the commonly used Perkin-Elmer DSC method [1], f is measured at a series of values of T and a value of x_2 is calculated from the slope of a plot of $1/f$ against T; f is derived from the measured area "a" under a DSC peak of total area "A" (Fig. 1). If f is put equal to a/A it is found that the plot is rarely linear because considerable melting takes place at very low rates before the curve is observed to begin. The measured values of both "a" and "A" are too small by the same amount. An area Δ is therefore added to each and adjusted until the $1/f$ against T plot is substantially linear: i.e.

$$f = \frac{a + \Delta}{A + \Delta} \tag{2}$$

Since melting actually begins at the eutectic point, which may be 50°, or more, below the temperature of observation, the value of Δ may be quite large compared with the measured values of "a", especially at the beginning of the curve, where "a" is small. Values of Δ amounting to 30% of the total area "A" are not uncommon [5].

Adjustment of Δ is therefore an important part of the computation, which if done graphically can lead to subjective errors. Subjectivity can be avoided by statistical methods [3, 6]; nevertheless, there is an advantage in the following procedure which avoids adjustment altogether.

An alternative procedure

In the following treatment, existing theory is developed primarily with the object of eliminating Δ from the calculation. At the same time, this allows us to replace measurement of area under the melting curve, "a", with a measurement of its perpendicular height, P. An additional advantage of speed and accuracy in taking data from the curve is thereby achieved. Elimination of f from (Eq. (1) and Eq. (2) leads to

$$a + \Delta = \frac{C}{T_0 - T} \tag{3}$$

where

$$C = RT_0 \cdot x_2 \cdot \left(\frac{A + \Delta}{q}\right) \tag{4}$$

Differentiation of Eq. (3) yields:

$$\frac{\mathrm{d}a}{\mathrm{d}T} = \frac{C}{(T_0 - T)^2}$$

or

$$P\frac{\mathrm{d}L}{\mathrm{d}T} = \frac{C}{(T_0 - T)^2} \tag{5}$$

where P is the perpendicular height of the curve when the sample temperature is T, and L is a distance measured parallel to the time scale of the strip chart (Fig. 1).

To bring Eq. (5) into a practically useful form, we note that

$$T = \tau_0 + \gamma L - \gamma\alpha P \tag{6}$$

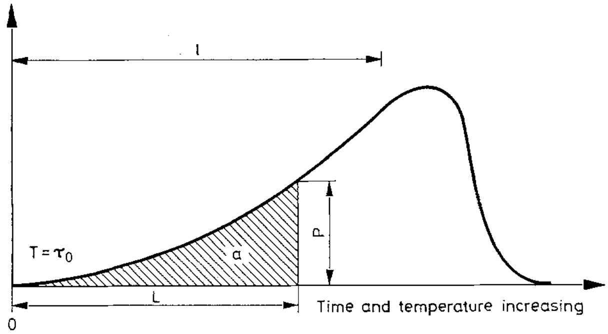

Fig. 1. Diagram of differential calorimetric melting curve of sample as recorded on strip chart, showing quantities P and L. The measured distance between one degree temperature marks is l, giving $\gamma = 1/l$. Actual measurement of τ_0 is not necessary

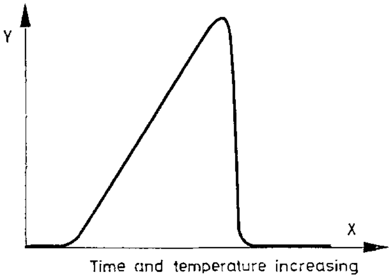

Fig. 2. Diagram of differential calorimetric melting peak of pure indium showing the linear rising front. The sample temperature lag correction factor α is given by X/Y

where τ_0 is the instrument-indicated temperature at the chosen (arbitrary) zero of L; $\gamma = d\tau/dL$; and α is the thermal lag factor, familiar to users of the Perkin-Elmer procedure. In our notation α is equal to the cotangent of the angle between the baseline and the linear rising front of a pure indium melting curve (Fig. 2), recorded at the same chart speed, scan-rate and instrument sensitivity as the sample. The factor α is determined chiefly by the thermal resistance between the sample pan and the calorimeter. It is kept constant from run to run by careful control of the experimental conditions.

The differential of Eq. (6):

$$\frac{\mathrm{d}T}{\mathrm{d}L} = \gamma - \gamma\alpha\frac{\mathrm{d}P}{\mathrm{d}L}$$

combined with Eq. (5) and Eq. (6) leads to:

$$\left\{\frac{T_0 - \tau_0}{\gamma} - L + \alpha P\right\}^2 = \frac{C}{\gamma}\left\{\frac{1}{P} - \alpha\cdot\frac{\mathrm{d}\ln P}{\mathrm{d}L}\right\} \tag{7}$$

which relates C, and thence x_2, to the parameters of the run α and γ, and to the shape and dimensions of the melting curve [$P = F(L)$]. A convenient routine for applying Eq. (7) is as follows:

1. Measure 8 to 12 values of P and L on the rising concave part of the melting curve (Fig. 1).
2. Plot $\ln P$ against L. This plot has been found to be substantially linear giving a single value of $\frac{\mathrm{d}\ln P}{\mathrm{d}L}$ for each run.
3. Plot $L - \alpha P$ against $\left\{\frac{1}{P} - \alpha\frac{\mathrm{d}\ln P}{\mathrm{d}L}\right\}^{1/2}$ and take the slope, which is equal to $-\frac{C^{1/2}}{\gamma^{1/2}}$.
4. Calculate C from the slope, using a value of γ obtained as indicated in Fig. 1.
5. Calculate x_2 from

$$x_2 = \frac{C}{RT_0^2}\cdot\frac{Q}{B}\cdot\frac{w_i}{w_s}\cdot\frac{M_s}{M_i} \tag{8}$$

where Q is the molar heat of fusion of indium;

B is the measured area under the indium peak, which is subject to very little error, since melting of a pure substance begins sharply; w_s and w_i are the weights of sample and indium used;

and M_s and M_i the corresponding gram formula weights.

The heat of fusion of the sample, q, as well as the adjustable parameter (Δ) is eliminated from the calculation by using this procedure.

Note that Eq. (8) follows from Eq. (4) if the instrument sensitivity is the same for both sample and indium, since in this case:

$$\frac{q}{(A + \Delta)}\cdot\frac{w_s}{M_s} = \frac{Q}{B}\cdot\frac{w_i}{M_i}$$

Preliminary results

The method has been tried with samples of acetanilide and sulphanilamide, and on some of the data for pentaerythritol tetranitrate worked out by the Perkin-

Elmer method and previously reported [4]. Satisfactory and compatible results were obtained, and no anomalies outwith the estimated experimental and computational errors have been noticed.

We have not yet made a precise comparison between the new procedure and the Perkin-Elmer procedure since our results for pentaerythritol tetranitrate did not include data for the application of Eq. (8).

However, we have noticed that an application of Eq. (7) to these results, according to the above procedure, and a calculation of x_2 via Eq. (4) on the assumption that Δ was zero in all cases, gave values which were higher than the previous values by the expected "Δ error", namely 10 to 25%. A recalculation made on the assumption that "$A + \Delta$" was 1.2 times the directly measured value of "A" gave the following set of compatible values for percentage molar impurity. Previous values 0.27; 0.44; 0.50. Recalculated values 0.24; 0.40; 0.59, respectively. It may therefore be concluded that the procedure advocated here introduces no significant systematic errors and that results obtained thereby would be readily comparable with existing results.

Computer Programme

With Eq. (7) as a basis, a computer programme has been written using conventional statistical techniques. It is more straightforward than that devised by Fraser and reported by Hill and Rodger [4], requiring fewer data points and avoiding adjustment procedures, as explained above. A copy of the programme, which is in Basic language for the IBM 1130, is available on request.

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Résumé — Le procédé actuellement répandu pour estimer la pureté par analyse calorimétrique différentielle à partir de l'intervalle de fusion fait appel à la linéarisation empirique des données. Cette opération peut être longue et elle est susceptible d'introduire des éléments subjectifs dans le calcul. Ceci est parfois considéré comme un inconvénient de la méthode. Une modification de ce procédé est proposée dans le présent article pour éviter cette difficulté. Son avantage réside dans la facilité de conserver les données et d'effectuer la programmation générale sur ordinateur.

Zusammenfassung — Das für die Reinheitsbestimmung aus Ergebnissen differentialkalorimetrisch ermittelter Schmelzbereiche festgelegte Verfahren benötigt die empirische Linearisierung der Angaben, was zeitaufwändig sein kann und subjektive Elemente in die Berechnungen einführt. Manchmal wird dies als ein Nachteil der Methode betrachtet. Eine Modifizierung des Verfahrens wurde erarbeitet, welches diese Schwierigkeit beseitigt und bei Datenspeicherung und allgemeiner Computerprogrammierung vorteilhaft ist.

Резюме — Принятый метод определения чистоты, исходя из результатов дифференциальной калориметрической области плавления, включает эмпирическую линейность данных, что требует времени и может ввести субъективный элемент при вычислении. Считается, что это является недостатком метода. В связи с этим разработан модифицированный метод, который исключает эти трудности и дает преимущества в облегчении нивелирования данных и полного программирования на ЭВМ.