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A PROPOSED METHOD FOR CALCULATING THE MELTING POINT OF A PURE SUBSTANCE

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A method is proposed for calculating the melting temperature (T_0) of a pure substance by combining cryoscopic measurements of melting temperature (T_m) of various impure samples with differential calorimetric values of temperature differences $T_0 - T_m$ for the same samples. The proposed expression is:

$$T_0 = \frac{\sum_1^n T_m}{n} + \frac{\sum_1^n (T_0 - T_m)}{n}$$

where the right-side term denotes the average value of a sufficiently high number of experiments (n). The value of T_0 determined in such a way, may be much more reliable than that obtained by using graphical methods or preparing an extremely pure sample.

Knowledge of the exact melting point of a product may be very useful in order to characterize its purity. This is particularly true in the case of dimethylterephthalate (DMT) monomer used for polymerization; it is a perfectly crystalline compound and has a very sharp melting point.

The melting points T_m of a series of commercial samples of DMT were determined with a cryoscopic apparatus (a melting point T_0 of 140.683°C is admitted for the pure product).* Our cryoscopic technique is based on a slow *crystallization* of the sample (weighing ca 70 g), the temperature of which is measured by a platinum resistance thermometer. This method gives a reproducibility of ± 0.003°C, corresponding to ± 0.0068 molar per cent of impurity content.**

These determinations of T_m values were paralleled by measurements of the differences $T_0 - T_m$ on the same samples, by means of a Perkin Elmer Differential Scanning Calorimeter DSC-1. DSC-1 curves were obtained with a slow *fusion* of the sample by using the maximum sensitivity of the instrument, the minimum heating rate [1,2] and very tiny quantities of the substance (0.2—0.3 mg); very

* By American DMT producers.

** Formation of solid solutions between the principal product and its impurities is excluded.

regular peaks were obtained.* Moreover, experimental data were treated by a particular mathematical method which we will describe in detail; this method in our opinion considerably improves the accuracy of $T_0 - T_m$ difference.

The purpose of the applied procedure was to verify the reliability of the T_0 value which is obtained by adding the differential calorimetric values of $T_0 - T_m$ to the cryoscopic values of T_m.

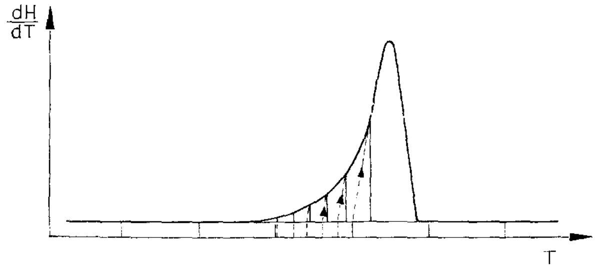

Fig. 1. An example of DSC-1 curve in the case of a purity determination

From the equation:

$$\frac{dq}{dT_s} = \frac{\Delta q(T_0 - T_m)}{(T_0 - T_s)^2} \quad (1)$$

(which gives the thermal capacity of a product during its fusion we can obtain, by integration,

$$F = \frac{T_0 - T_m}{T_0 - T_s} \quad or \quad T_s = T_0 - \frac{T_0 - T_m}{F} \quad (2)$$

where:

T_s = absolute temperature of the impure sample during the melting process in DSC-1
T_m = absolute melting temperature of the impure sample
T_0 = absolute melting temperature of the pure product
F = fraction of the impure sample which is melted at any particular temperature T_s (measured as the ratio of the partial area of the melting peak to its total area) (Fig. 1)
Δq = total heat of fusion of the impure sample

By plotting T_s vs. $1/F$ a straight line should be obtained; however, a branch of a hyperbola normally results (Fig. 2). Most probably the reason for this is not chemical but instrumental in character [3—6]: the sensitivity of the instrument is not capable of revealing the true beginning of the melting peak. As a con-

* Possible sampling errors due to the small amounts of substance should be taken into account.

sequence, the partial areas (α_i)[1] and the total area (A^*)[2] are underestimated by a quantity c. The problem is to find correctly this quantity c.

Sometimes plotting the baseline in a much lower position than the normal one compensates the above error exactly, and a straight line is obtained in Fig. 2. But this procedure is not a scientific one.

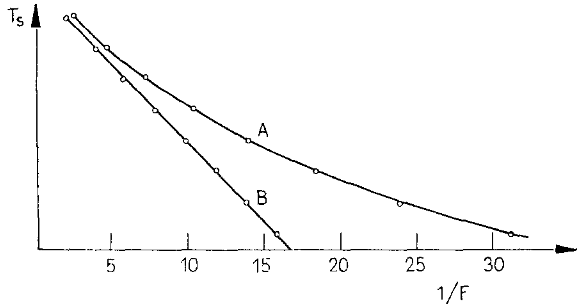

Fig. 2. A: experimental curve obtained from the melting peak; B: corrected curve (having slope a)

Our method is as follows: of all the experimental values $y_i\,\alpha_i$ (y_i = absolute temperature T_s of the sample during the fusion, α_i = partial areas of the melting peaks at the various T_s) let us consider the one with the minimum error: i.e. the point of minimum $1/F$ value in Fig. 2. Let us attribute a probability coefficient 1 to this particular pair of values, and different probability coefficients, progressively decreasing between 1 and 0, to the other pairs of experimental values y_i, α_i.

We shall have, therefore:

$$(y_1, \alpha_1, p_1);\ (y_2, \alpha_2, p_2);\ (y_3, \alpha_3, p_3);\ \ldots\ (y_n, \alpha_n, p_n) \text{ with } 0 < p_i < 1 \ (i = 2 \ldots n)$$

The following system is obtained, by taking into account Equation (2) and the definition of F,

$$\begin{cases} y_1 = a\dfrac{A^* + c}{\alpha_1 + c} + b & \text{with } p = 1 \\ y_2 = a\dfrac{A^* + c}{\alpha_2 + c} + b & \text{with } p = p_2 \\ \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots & \\ y_n = a\dfrac{A^* + c}{\alpha_n + c} + b & \text{with } p = p_n \end{cases} \tag{3}$$

[1] Let us recall that $F_i = \dfrac{\alpha_i + c}{A^* + c}$

[2] Planimetrically measured.

where:

a = slope of the straight line, that is $-(T_0 - T_m)$.[1]
b = intercept on the y axis
A^* = total area of the thermogram
c = corrective area

Or

$$\begin{cases} y_1 - b = a \dfrac{A^* + c}{\alpha_1 + c} & \text{with } p = 1 \\ y_2 - b = a \dfrac{A^* + c}{\alpha_1 + c} & \text{with } p = p_2 \\ \cdots\cdots\cdots\cdots\cdots\cdots & \\ y_n - b = a \dfrac{A^* + c}{\alpha_n + c} & \text{with } p = p_n \end{cases} \tag{4}$$

In the system (4), by dividing the 2nd, 3rd ... equation by the first one, we obtain:

$$\begin{cases} y_1 - b = a \dfrac{A^* + c}{\alpha_1 + c} & \text{with } p = 1 \\ \dfrac{y_2 - b}{y_1 - b} = \dfrac{\alpha_1 + c}{\alpha_2 + c} & \text{with } p = p_2 \\ \cdots\cdots\cdots\cdots\cdots\cdots & \\ \dfrac{y_n - b}{y_1 - b} = \dfrac{\alpha_1 + c}{\alpha_n + c} & \text{with } p = p_n \end{cases} \tag{5}$$

It follows from (5) that

$$\begin{cases} y_1 - b = a \dfrac{A^* + c}{\alpha_1 + c} & \text{with } p = 1 \\ (\alpha_2 y_2 - \alpha_1 y_1) - (\alpha_2 - \alpha_1)b + (y_2 - y_1)c = 0 & \text{with } p = p_2 \\ \cdots\cdots\cdots\cdots\cdots\cdots & \\ (\alpha_n y_n - \alpha_1 y_1) - (\alpha_n - \alpha_1)b + (y_n - y_1)c = 0 & \text{with } p = p_n \end{cases} \tag{6}$$

The function can be written:

$$f(b, c) = p_2 \left[(\alpha_2 y_2 - \alpha_1 y_1) - (\alpha_2 - \alpha_1)b + (y_2 - y_1)c\right]^2 + \cdots\cdots + p_n \left[(\alpha_n y_n - \alpha_1 y_1) - (\alpha_n - \alpha_1)b + (y_n - y_1)c\right]^2 \tag{7}$$

[1] In practice, a is the only important number, because it immediately furnishes $T_0 - T_m$, and then x_2, the molar fraction of impurity (see Equation 13).

Now we look for its minimum by putting the first partial derivatives = 0

$$f'_b(b, c) = 0$$

$$f'_c(b, c) = 0$$

Then, by differentiating, we obtain:

$$\begin{cases} p_2(\alpha_2 - \alpha_1)[(\alpha_2 y_2 - \alpha_1 y_1) - (\alpha_2 - \alpha_1)b + (y_2 - y_1)c] + \cdots \\ \qquad + \cdots + p_n(\alpha_n - \alpha_1)[(\alpha_n y_n - \alpha_1 y_1) - (\alpha_n - \alpha_1)b + (y_n - y_1)c] = 0 \\ p_2(y_2 - y_1)[(\alpha_2 y_2 - \alpha_1 y_1) - (\alpha_2 - \alpha_1)b + (y_2 - y_1)c] + \cdots \\ \qquad + \cdots + p_n(y_n - y_1)[(\alpha_n y_n - \alpha_1 y_1) - (\alpha_n - \alpha_1)b + (y_n - y_1)c] = 0 \end{cases} \tag{8}$$

If

$$\begin{aligned} \alpha_i y_i - \alpha_1 y_1 &= A_i \\ \alpha_i - \alpha_1 &= B_i \qquad\qquad (i = 2 \ldots\ldots n) \\ y_i - y_1 &= C_i \end{aligned}$$

it follows that:

$$\begin{cases} p_2 B_2(A_2 - B_2 b + C_2 c) + \cdots + p_n B_n(A_n - B_n b + C_n c) = 0 \\ p_2 C_2(A_2 - B_2 b + C_2 c) + \cdots + p_n C_n(A_n - B_n b + C_n c) = 0 \end{cases} \tag{9}$$

from which:

$$\begin{cases} \sum\limits_{i=2}^{n} p_i B_i A_i - (\sum\limits_{i=2}^{n} p_i B_i^2)b + (\sum\limits_{i=2}^{n} p_i B_i C_i)c = 0 \\ \sum\limits_{i=2}^{n} p_i C_i A_i - (\sum\limits_{i=2}^{n} p_i C_i B_i)b + (\sum\limits_{i=2}^{n} p_i C_i^2)c = 0 \end{cases} \tag{10}$$

By putting;

$$A = \sum_{i=2}^{n} p_i B_i A_i$$

$$B = \sum_{i=2}^{n} p_i B_i^2$$

$$C = \sum_{i=2}^{n} p_i C_i^2$$

$$D = \sum_{i=2}^{n} p_i B_i C_i$$

$$E = \sum_{i=2}^{n} p_i A_i C_i$$

we have:

$$\begin{cases} Bb - Dc = A \\ Db - Cc = E \end{cases} \tag{11}$$

and

$$\begin{cases} b = \dfrac{-AC + DE}{-BC + D^2} \\ c = \dfrac{BE - AD}{-BC + D^2} \end{cases} \tag{12}$$

From the first equation of the system (5) we can obtain the value of a. The above procedure is an obvious application of the "least squares" method.

Calculations can be carried out by a computer: we used the General Electric "time sharing" system.

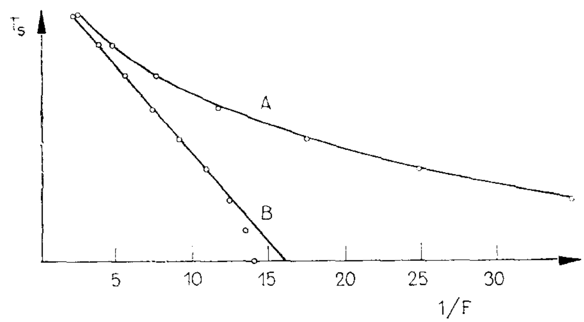

Fig. 3. The points of high abscissa, corrected by the quantity c, do not fit the straight line of slope a. A: experimental curve; B: corrected curve

Normally the experimental points, corrected for the quantity c, lie in a sinusoidal way on both sides of the line having slope a and intercept b: this means that experimental errors are well distributed along the melting peak. In contrast, the corrected points positioned as in Fig. 3 mean that the high experimental values of $1/F$ (and thus the small values of F) are the most affected by errors.

By considering the probability coefficients, it can be observed that, for example, if

$p_1 = 1$
$p_2 = 0.95$ (the first and the last terms are exceptionally far)
.
.
.
$p_n = 0.05$

c increases by about 5%, but a and b are practically unaffected: this means that the slope of the straight line (therefore the difference $T_0 - T_m$) does not depend on the particular values of the coefficients. Therefore, it is generally correct to put all the probability coefficients = 1.

On the other hand, due to the increase of c with decreasing probability coefficients, it is advisable to plot the baseline of the thermogram in a rather low position.

A number of T_m cryoscopic values, $T_0 - T_m$ calorimetric values and T_0 calculated values are reported in Table 1.

Table 1

T °C	$T_0 - T_m$	T_0 °C
140.648	0.0561	140.7041
140.650	0.0255	140.6755
140.613	0.0560	140.6690
140.644	0.0480	140.6920
140.644	0.0304	140.6744
140.645	0.0567	140.7017
140.645	0.0367	140.6817
140.645	0.0302	140.6752
140.645	0.0288	140.6738
140.650	0.0588	140.7088
140.650	0.0588	140.7088
140.650	0.0287	140.6787
140.650	0.0237	140.6737
140.649	0.0410	140.6900
140.649	0.0250	140.6740
140.613	0.0589	140.6719
140.613	0.0750	140.6889
Note: Temperatures are assigned by IPTS-68		Average value = 140.6850

As can be seen, the deviations of the T_0 temperatures are very small, and the average T_0 value is in an almost perfect agreement with the initially admitted T_0 value.

In conclusion, we believe that the combination of a cryoscopic measurement and a differential calorimetric one must be taken into account when one wants to determine the T_0 melting point of a pure product. For this it is necessary to work with very pure sample, because it is the absolute error in $T_0 - T_m$, and not the relative one, that is important.

If T_0 is known for a substance, the molar % of impurity can be obtained by a cryoscopic measurement of T_m:[0]

[0] This measurement is much more accurate than a calorimetric one of $T_0 - T_m$.

$$T_0 - T_m = \frac{R T_0^2}{\Delta H_f} x_2 \cdot 100 \qquad (13)$$

x_2 = mole fraction of impurity
ΔH_f = molar heat of fusion of sample, cal/mole.

*

We are greatly indebted to Dr. Mario Menconi (General Electric-Milan) for the mathematical development of the problem.

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Résumé — On décrit une méthode pour calculer la température de fusion (T_0) en utilisant à la fois la détermination cryoscopique de la température de fusion (T_m) d'échantillons impurs et la détermination de la différence de température $T_0 - T_m$ par calorimétrie différentielle des mêmes substances:

$$T_0 = \frac{\sum_1^n T_m}{n} + \frac{\sum_1^n (T_0 - T_m)}{n}$$

où n représente le nombre d'expériences qui doit être assez grand. La valeur T_0 déterminée de cette manière semble être plus sûre que celle obtenue par voie graphique ou en préparant un échantillon extrêmement pur.

Zusammenfassung — Es wurde über eine Methode zur Errechnung der Schmelztemperatur (T_0) einer reinen Substanz durch Verbindung von kryoskopischer Messung der Schmelztemperatur von unreinen Proben (T_m) und differentialcalorimetrischer Bestimmung der Temperaturdifferenzen ($T_0 - T_m$) derselben Proben berichtet:

$$T_0 = \frac{\sum_1^n T_m}{n} + \frac{\sum_1^n (T_0 - T_m)}{n}$$

Hierbei ist in die rechte Seite der Mittelwert einer ziemlich hohen Zahl (n) von Versuchen zu setzen. Der so bestimmte T_0-Wert ist verläßlicher als derjenige den man auf graphischem Weg oder durch Bereitung extrem reiner Proben erhält.

Резюме. — В настоящей работе описан возможный метод для расчёта температуры плавления (T_0) чистых веществ с использованием данных криоскопического измерения температуры плавления (T_m) некоторых различных образцов и дифференциального колориметрического измерения разницы температур (T_0—T_m) для подобных образцов.

$$T_0 = \frac{\sum_1^n T_m}{n} + \frac{\sum_1^n (T_0 - T_m)}{n}$$

где правая сторона уравнения представляет обобщенное выражение результатов достаточно большого числа экспериментов.

Величина T_0, определённая таким путем, гораздо больше недёжна, чем та, которую полйчают графическим методом или пйтем приготовления образца наивысшей степени чистоты.