Journal of Thermal Analysis, Vol. 3 (1971) 229—246

TEMPERATURE MEASUREMENTS WITH A DIFFERENTIAL CALORIMETER

E. PELLA and M. NEBULONI

Carlo Erba Research Institute, Milan, Italy

(Received November 25, 1970)

A differential microcalorimeter was used for the reading of transition temperatures. The inherent factors in both the instrument and the sample which may introduce variables in temperature measurements carried out with the calorimeter were studied together with modifications of the reading methods. An accurate technique is described for the preparation of the sample and measurement of temperature. The proposed method, when applied to organic standards of very high and of decreasing purity, gives an accuracy of temperature reading in the order of ±0.1°, and confirms a relationship between experimental and theoretical values.

When a chemical compound is subjected to thermal investigation, certain physical and/or chemical transitions take place at characteristic temperatures. Knowledge of the transition temperature and the amount of energy involved enables one to investigate these changes and the nature of the sample in question. The solid → liquid transition of organic substances, i.e. the melting point, can be used for evaluating the degree of purity of these compounds. Precise measurements of the transition temperature using methods based on adiabatic calorimetry [1], time-temperature diagrams [2] and triple point measurements [3] is possible only if special instruments and large amounts of sample are available. However, it appeared possible to increase the reliability of temperature readings by using rapid calorimetric methods on smaller samples in the range of a few milligrams, provided that certain precautions were taken to eliminate the causes of the more common errors. For this purpose a Perkin Elmer DSC-1B differential micro-calorimeter has been used. This instrument [4, 5] permits one to measure quantitatively the energy involved in a physical or chemical transformation using a few mg of sample. The temperature of the source, from which energy is supplied to the sample, is simultaneously recorded.

The principle of differential calorimetric analysis consists in heating the sample under test and an inert reference material according to a predetermined programme. The energy is supplied to the sample in such amounts that its temperature is always equal to that of the reference. The energy supplied is measured in millicalories per second ($\Delta q/\Delta t$) and is recorded as a function of the programmed absolute temperature (°K).

The aim of this paper is to show that by studying the experimental factors influencing the measurement, and by using highly purified substances having known melting points as temperature standards, it is possible to use a differential calorimeter to obtain temperature readings reliable to ±0.1°.

Study of experimental variables

The precision of temperature measurements using a differential calorimeter is influenced by various factors [6]. Some of these are instrumental factors whereas others are determined by the properties of the sample. These factors must therefore be rigorously controlled to obtain reliable measurements. It is assumed that the commercial apparatus DSC-1B (Differential Scanning Calorimeter) and its operating technique are known and therefore further description will be omitted.

The instrumental factors are: (a) scanning speed, (b) external thermal resistance, (c) thermal capacity of the pan, and (d) nature of the flushing gas in the sample holder assembly; the factors inherent in the sample are: (e) weight, (f) purity, (g) internal thermal resistance, and (h) geometry.

(a) Scanning speed

Since the desired temperature is that of the equilibrium between the solid and liquid phases, heating should be such that conditions approaching thermodynamic equilibrium are achieved at all times. Due to the resistance of the sample to heat transmission, the heat required for melting cannot be supplied instantaneously but only over a certain time interval. If the change in the programmed temperature during this time interval is small, the error in the determination of the transition temperature will be reduced. Working under dynamic conditions therefore requires low scanning speeds and an expanded temperature scale (i.e. high recording chart speed) to get better resolution on the temperature axis.

The rate of heating must be constant. The DSC-1B calorimeter can provide very slow and linear scanning rates. The minimum rate of heating, 0.5°/min, is

Table 1

Influence of the scanning rate on the temperature indication

Substances	Melting temperature, °K		
	0.5°/min	1°/min	2°/min
p-Nitrotoluene	319.60	319.70	319.75
Naphthalene	350.25	350.50	350.60
Phenanthrene	371.30	371.55	371.75
Benzoic acid	394.70	394.75	394.85
Anisic acid	—	455.90	456.25

not useful in practice for temperature measurements with micro-quantities of organic substances, because it can cause the complete loss of the sample by sublimation. It is therefore not advisable to use rates lower than 1°/min, and, for high-melting compounds a heating rate of 2°/min may be necessary. Table 1 shows that the difference between the m.p. measured at rates of 1°/min and 2°/min is generally within ±0.1°.

(b) External thermal resistance

Under this heading are considered resistance factors which hinder the immediate transfer of heat from the heating element to the sample. The most significant of these, designated R_0, is that between the heating surface and the sample pan. The temperature recorded is not that of the sample (T_s) but that of the heating surface, i.e. the programmed temperature (T). A difference, or thermal lag, exists between these two temperatures which is related to the resistance R_0 and the rate of heat flow by Newton's equation: $T_p - T_s = R_0$ ($\mathrm{d}q/\mathrm{d}t$). (In practice the ratio between finite differences $\Delta q/\Delta t$ is used instead of the true derivative $\mathrm{d}q/\mathrm{d}t$.) The heat flow is proportional to the thermal lag of the signal and depends on the constant R_0. R_0 has not been eliminated by any existing instrument for thermal analysis, although it has been possible to reduce it within certain limits, by rigorous control of the pan geometry. The pan has a flat, circular base, which affords the largest possible area compatible with the diameter of the holder to assure maximum contact with the heating surface. This is only achieved if the pan bottom is flat and makes perfect contact with heating surface. R_0 and the thermal lag, $T_p - T_s$, are then reduced to a minimum, thus improving the measuring accuracy.

According to the manufacturer's instructions [7], for accurate temperature measurements it was necessary to ensure the tight packing of the sample. A special punch was supplied to adjust the pan shape after closure but, unfortunately, it was not always possible to obtain sufficient pressure on the punch and it sometimes chipped the lip of the pan. Temperature values were therefore obtained which varied according to the position of the pan in the holder (Table 2). In the section "Measuring Procedure", a more accurate technique will be suggested for

Table 2

Dependence of the temperature indication from the pan position

Indium 99.9999% m.p. 429.75 °K	Melting temperature, °K		
	Starting position	Rotation of 120°	Rotation of 240°
Normal pan	429.70	430.05	429.95
Pan with rigorously standardized geometry	429.05	429.05	429.08

preparing the sample pan in such a way that a perfect contact with the holder surface is always obtained, and which prevents variations in the results irrespective of the position of the pan in the holder (Table 2).

The constant R_0 also appears in the equation representing the slope of the curve [7]:

$$\frac{d^2q}{dt^2} = \frac{1}{R_0} \frac{dT_p}{dt}$$

If R_0 could be reduced to a very small value, an increase in the slope of the ascending branch of the fusion diagram and thus a more regular diagram would be obtained. At the limit for $R_0 = 0$, a vertical line instead of a peak would appear in the diagram [8].

(c) Nature of the flushing gas

During measurement, the protecting chamber formed by the screw top of the sample holder assembly was flushed by an inert gas. The influence of the gas flow on temperature measurements was studied, and to obtain information on the influence of the nature of gas used, helium and nitrogen were compared under identical conditions. For the medium temperature zone, indium and benzanilide were chosen, while for higher temperatures tin and carbazol were used.

The results are shown in Table 3. Except at very high temperatures the gas flow has no substantial influence on the measurements.

Table 3

Influence of the flushing gas on the temperature measurements

Substances	Melting temperature, °K							
	Nitrogen cm^3/min				Helium cm^3/min			
	0	10	25	75	0	10	25	75
Indium m.p. 429.76	429.1	429.5	429.7	429.7	429.1	435.7	435.5	435.2
Benzanilide m.p. 436.36	437.6	436.4	436.5	436.5	437.6	443.7	443.2	442.9
Tin m.p. 505.06	508.9	504.8	505.0	505.3	508.9	515.1	514.9	514.6
Carbazole m.p. 518.46	520.9	517.7	517.7	517.9	520.9	528.7	529.1	529.6

The melting temperature of indium, with nitrogen at 25 cm^3/min, is taken as reference temperature for the calibration.

A difference of several degrees was found in the melting points of the compounds in Table 3 when nitrogen was replaced by helium as flushing gas; thus the attainment of equilibrium of the system depends on the nature of the gas used. In the present experiments nitrogen was better than helium.

The manufacturers mention errors that could be caused by the high thermal conductance of helium at temperatures above 350°, but in practice it has been found that it gave rise to errors even at lower temperatures. In fact:

(I) a difference of about 0.8 – 1.0° was observed between the readings for metals and pure organic compounds having close melting points;

(II) a difference was observed between the melting points recorded under static (gas flow 0 cm^3/min) and dynamic conditions; for indium this was as high as 6.4°;

(III) sublimation effects were increased and spurious endothermic peaks occasionally appeared.

(d) Thermal capacity of the container

During calorimetric analysis, the test sample was enclosed in an aluminium container or pan. If m_s is the mass of the sample, m_k the mass of the pan, and c_s and c_k their respective specific heats, the energy absorbed (ΔH_s) per degree is:

$$\Delta H_\text{s} = m_\text{s}c_\text{s} + m_\text{k}c_\text{k}$$

Its derivative with respect to the time is:

$$\frac{\mathrm{d}H_\text{s}}{\mathrm{d}t} = (m_\text{s}c_\text{s} + m_\text{k}c_\text{k})\,\frac{\mathrm{d}T}{\mathrm{d}t}$$

where the expression $(m_\text{s}c_\text{s} + m_\text{k}c_\text{k})$ represents the thermal capacity of the system. As the reading on the ordinate is $\mathrm{d}q/\mathrm{d}t$, it is seen that the contribution of the total thermal capacity results in a displacement of the base line [7]. The value $m_\text{s}c_\text{s}$ for 2 mg of organic sample is approximately 0.5 mcal/°K, while that of $m_\text{k}c_\text{k}$ is about 5 mcal/°K. Thus the total thermal capacity, and hence the displacement of the base line, is due almost entirely to the pan.

In measuring temperatures by the manufacturers' method [7], it must be remembered that the true base line is shifted from the interpolated base line as shown above. The true base line must be used to find the point of intersection for temperature reading. The effect of this factor on temperature measurements is very small and is entirely eliminated by using readings at the top of the peak.

(e) Sample weight

The amount of heat required for an endothermic transition is proportional to the weight of the sample. Although there is no difficulty in measuring either large or small amounts of heat, the thermometric indication is influenced by the total amount of energy involved. If high precision measurements are required, sample weights must be selected that will produce as little variation as possible in the recorded temperature. The observed temperature may be affected by thermal lags (weight of sample above 5 mg; high values of the ordinate dq/dt); variations in the ascending slope of the melting curve (different weights and different particle sizes in the sample); and by prolonged heating (different amounts of heat for different weights of the same sample cannot be supplied in equal periods of time).

Sample weight should, therefore, be kept between 2 and 4 mg, but not so small as to impair the reading through sublimation. If different substances are examined, weights should be selected *that absorb the same amounts of heat on fusion.*

Table 4 shows the melting points obtained for different weight of the same substance. Variations in sample weight of ±1 mg alter the normal melting point reading by 0.2°.

Table 4

Influence of the sample weight on the temperature indication

Substances	Melting temperature, °K			
	1 mg	2 mg	3 mg	4 mg
p-Nitrotoluene	319.87	320.08	320.29	320.52
Phenanthrene	370.25	370.97	371.22	371.39
Benzanilide	435.82	436.07	436.15	436.26

(f) Sample purity

Only extremely pure compounds show sharply defined and constant melting points. When examined by the DSC technique, the calorimetric curves for these compounds show a straight line which rises steeply from the base line corresponding to the points of constant temperature of the solid → liquid transition. However this is only true in the case of exceptionally pure compounds, such as zone-refined p-nitrotoluene, whose melting curve is shown in Fig. 1. But with organic substances the sample is usually of limited purity. During the melting process there is always a difference in the compositions of the solid and liquid phases; i.e., the basic premise that the composition of the two phases must be the same for the temperature to remain constant throughout melting, does not hold. The result is that melting takes place over a range of temperature, rather than at a single, fixed temperature.

Due to premature partial melting (premelting) the DSC run (Fig. 2) shows an endothermal melting curve rising slowly from the base line. This curve has a changing slope and a rounded peak. The temperature recorded is, therefore, not well-defined but covers a range. It is usual to accept the end of this endothermal curve as the melting point [2]. This temperature, T_m, is lower than the melting point of the 100% pure substance, T_0, by a value, ΔT, which is related to the molar fraction of impurity, x_2, by the van't Hoff equation:

$$\Delta T = T_0 - T_m = \frac{RT_0^2}{\Delta H_f} x_2$$

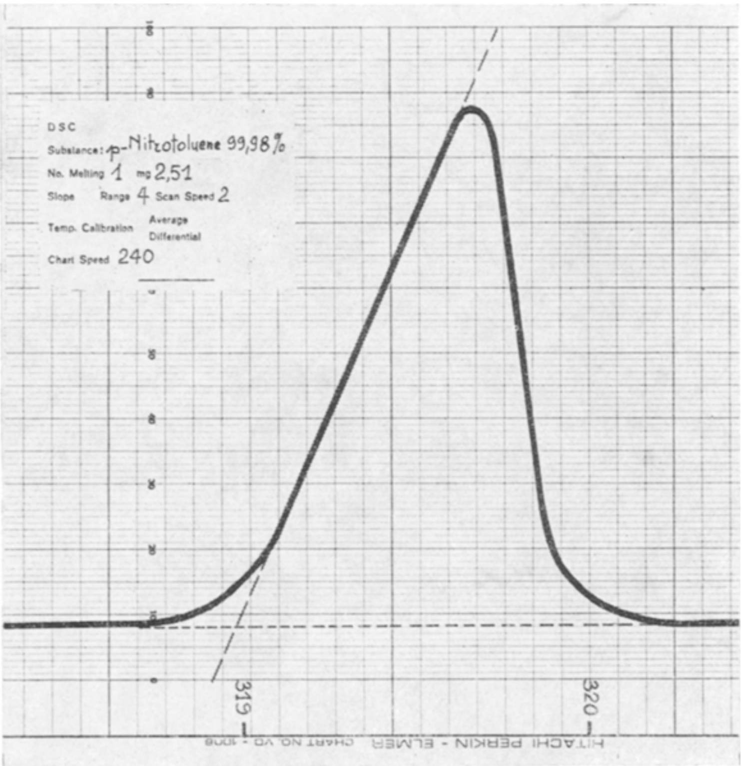


Fig. 1

Also in this case, the temperature recorded must be consistent with the theoretical temperature depression predicted in the equation, and only if this is true can the reading be accepted as valid.

(g) Internal thermal resistance

The heat supplied to the sample must not only overcome the external resistances but also the internal resistance of the sample itself. This resistance can be evaluated as being inversely proportional to the conductance: the less the conductance,

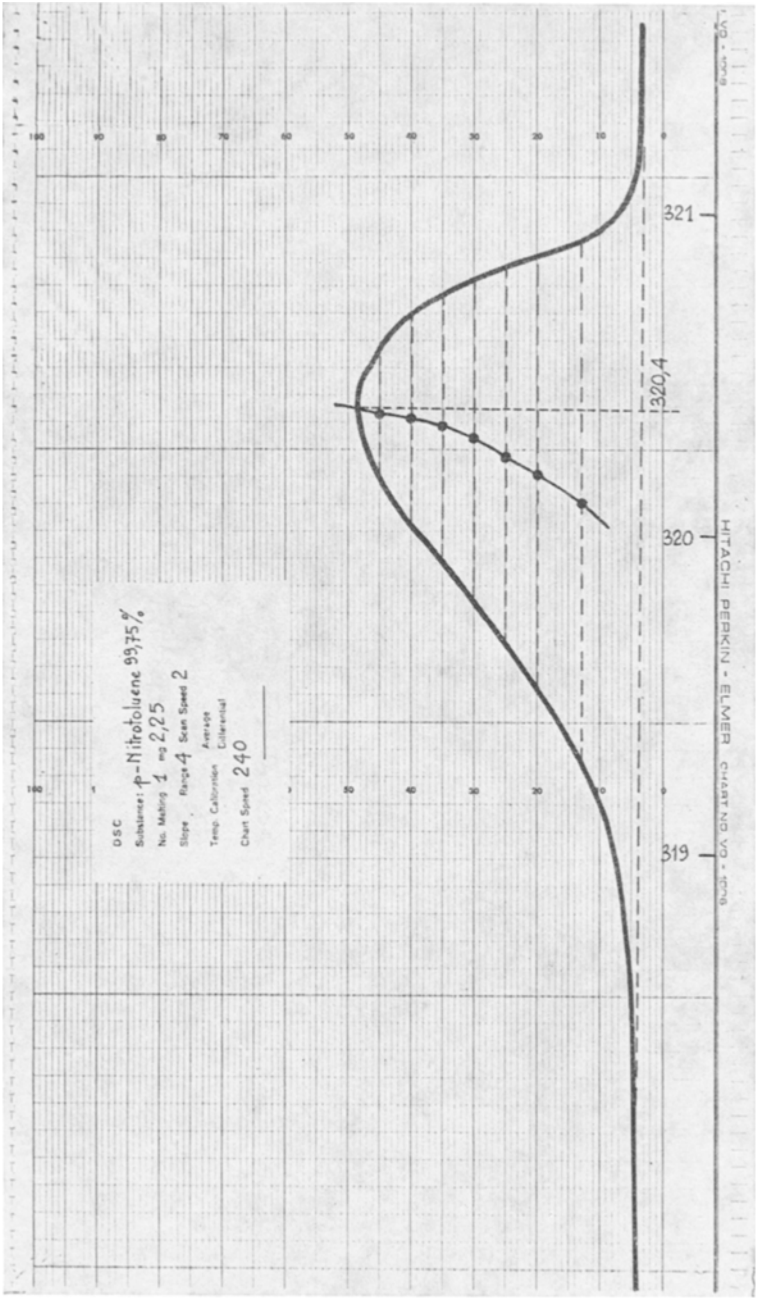

DSC
Substance: p-Nitrotoluene 99,75%
No. Melting 1 mg 2,25
Slope Range 4 Scan Speed 2
Temp. Calibration Average Differential
Chart Speed 240
100
90
80
70
60
50
40
30
20
10
0
321
320,4
320
319
HITACHI PERKIN - ELMER CHART NO VQ - 1006

Fig. 2

the larger the thermal lag and, therefore, the time needed to carry out transition. The conductance of a metal, expressed in $\text{cal} \times \text{s}^{-1} \times \text{cm}^{-1}$, is 250–300 times larger ($k_{\text{mean}} = 0.1$) than that of an organic compound ($k_{\text{mean}} = 0.0003-0.0004$). For this reason, if we examine a metal and an organic compound that theoretically melt at the same temperature, there will be discrepancies in the melting point readings measured outside the sample, as is the case with DSC. These differences have been clearly demonstrated in measurements with helium as flushing gas and, to a lesser extent, in those using nitrogen. To check this point, the melting points of some organic temperature standards were determined. Then, in order to increase the total thermal conductance of the sample and thus to eliminate the errors caused by the low heat conductance of the organic material, the measurements were repeated after mixing the substances with a metal powder (gold powder was used because other metals, such as silver and aluminium, may react with the sample). The data in Table 5 show a definite lowering of melting temperatures of substances when mixed with gold powder, resulting from increased conductance.

Table 5

Melting temperatures of organic substances mixed with metal

	Melting temperature, °K		
	Benzoic acid	Benzanilide	Anisic acid
Normal sample	395.56	436.46	456.16
Sample mixed with Au powder	393.26	396.11	455.71

The practical implication is that only organic reference substances may be used for calibrating the temperature scale when the instrument is to be used for studying organic compounds.

(h) Sample geometry

The sample geometry is determined by granulation, compactness, and distribution in the pan. The granulation influences the readings considerably, as can be seen in Table 6: generally, the smaller the particle size, the higher the melting point. According to literature [9], finer particles should facilitate the conduction of heat and promote a more rapid response to heating and hence a lower melting point. With the DSC technique the observed effect was the opposite. After the first melting and subsequent solidification, the sample was transformed into a compact thin layer, and further melting point readings became constant at a value somewhat below that originally found. In order to eliminate the influence of par-

Table 6

Influence of the geometry on the temperature indications

Sample geometry	Melting temperature, °K*		
	Naphthalene	Benzoic acid	Benzanilide
Particle size 350–250 μ	352.76	394.76	435.16
Particle size 200–100 μ	352.96	395.36	435.96
Particle size 50 μ	353.31	395.66	436.36
Particle size 10 μ	353.56	395.86	436.46
Thin layer (2nd melting)	353.46	395.56	436.46
Powder of 10 μ pressed at			
manual pressure	353.56	395.86	436.46
pressure of 5 atm.	353.61	395.76	436.41
pressure of 10 atm.	353.66	395.56	436.21

* The melting temperatures were corrected according the calibration curve

ticle size, the sample should be ground to a sufficiently fine powder and distributed uniformly; a preliminary melting run should be made, then the sample should be allowed to solidify and the m.p. retaken.

Compactness may either be natural, as determined by particle size, or artificial, i.e. increased by applying external pressure. The effect of compactness caused by the pressure applied to the pan was investigated by means of a press giving reproducible pressures. The data given in Table 6 show that there is no appreciable difference between melting points obtained with pans pressed either manually or at 5 atm, and the maximum difference observed between these and samples pressed at 10 atm is 0.2°.

The conclusion is that manual pressing is sufficient both to squeeze the sample into a thin layer and to obtain good pan geometry: higher pressures are not necessary and do not appreciably alter the temperature reading.

The distribution of sample material in the pan contributes to the sample geometry: if the distribution is not even, the peak will have an irregular shape and a broader base, with larger errors in temperature measurements.

This review of instrumental and sample factors shows that some of them are more important than others and need special attention to obtain precision and reproducibility of readings.

Undoubtedly the most important factor is pan geometry, as it determines the constant and minimum value of R_0. The pan should always be an aluminium rimless disc with a perfectly flat bottom. The geometry and purity of the sample are also important. Attention should be paid to the sample geometry, but preliminary melting reduces its influence to a negligible value. Sample purity does not interfere with the measurement unless a substance of insufficient purity is used as temperature standard. Other factors that may interfere with the uniformity of reading, such as the scan speed, the nature of the flushing gas, and the weight of the sample, are easily standardized; the influence of the thermal capacity of the sample pan may be lowered to a negligible amount.

In these studies another factor was also taken into consideration, viz. the thermal emissivity of the two cells, but as this factor proved to have no influence on temperature measurements no further attention was paid to it.

Reading criteria

Once a calorimetric record of a solid → liquid transition is obtained, a suitable criterion for temperature reading is necessary. A standard method recommended by the makers of the calorimeter [7] is as follows: from the top of the peak (Fig. 2) one draws a straight line having a slope equal to that of the ascending limb of the melting peak of indium, obtained by observing the same measuring parameters, and from the intersection of this line with the true base line, a perpendicular line is drawn to the abscissa, where the corresponding temperature is read.

This procedure corrects the temperature at the peak for thermal lag and gives a provisional value which must still be corrected for instrumental errors as derived from a calibration graph. The corrected value represents the melting temperature.

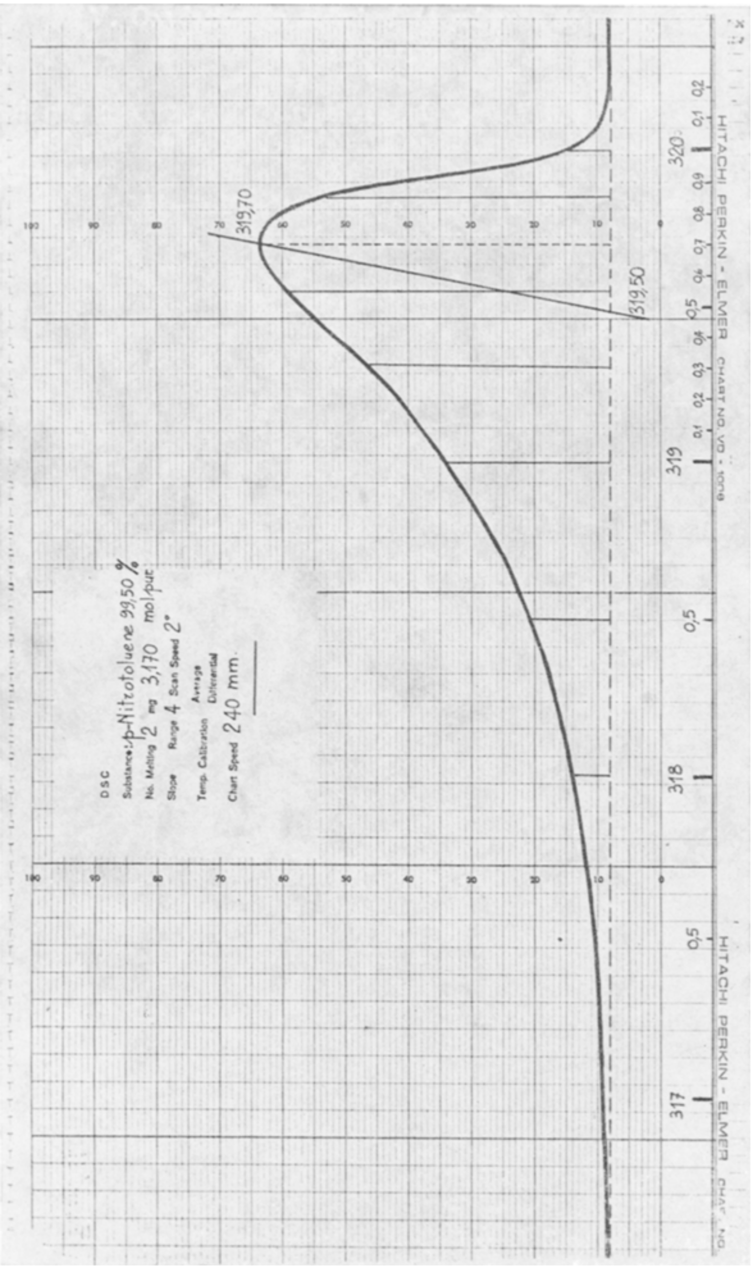
This method is based on the highest point of the peak, and introduces a correction for thermal lag, which lowers the accuracy of the initial reading.

It appears reasonable to read at the highest point of the peak, as it represents the end of the transition for both pure and impure compounds, but it is not logical to apply to organic substances a correction for thermal lag which has been obtained with a metal reference sample of different weight and conductance, without any certainty that the R_0 values are the same. This criterion may be considered useful for other purposes, but not for highly accurate temperature measurements.

The method of reading at the top of the peak should be used, because it is simpler and more accurate; this method has been adopted by other investigators [10]. The reading should always be corrected by reference to an independently determined calibration graph. However, these readings are only reliable if the peaks are definite and properly shaped; it the peaks are flat or irregular the reliability decreases. In these cases the method of reading based on the geometrical median line is recommended.

This is done by finding the midpoints of straight line segments connecting the two branches of the peak at various levels parallel to the abscissa (Fig. 3), then drawing a line through the midpoints and taking the intersection of this line with the calorimetric curve as its maximum value; the perpendicular projection of this point to the abscissa gives the temperature reading.

Another reading method, perhaps the best, is based on extrapolation of the curve obtained by plotting the fraction of melting heat as a function of tempera-



DSC

Substance: p-Nitrotoluene 99,50 %

No. Melting 2 mg 3,170 mol/pur

Slope Range 4 Scan Speed 2°

Temp. Calibration Average Differential

Chart Speed 240 mm.

Fig. 3

ture (Fig. 4). The melting curve of a substance is thus converted to a diagram of per cent melting heat against temperature: i.e., to a calorimetric melting curve. The total heat of melting is obtained by integration of the area of the melting curve, whereas the partial melting heats are obtained by integration of partial areas corresponding to selected temperatures within the peak (Fig. 2). The curve (Fig. 4), extrapolated to intersect the temperature axis, gives the final melting temperature. This method is more sophisticated than the single reading at the top of the peak, and should be reserved for special cases. Whichever method is adopted, the common and essential requirement is that all experimental errors be reduced to a minimum, and that the pan geometry be rigorously standardized.

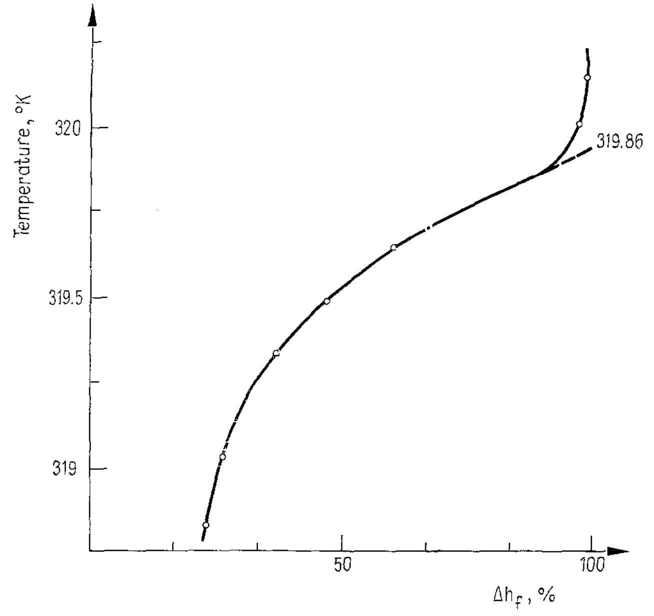


Fig. 4

Measuring procedure

The instrument used was the Perkin Elmer DSC-1B calorimeter. The sample holder assembly was washed with solvent and heated to 500° for 15 minutes before use. Temperature equilibration of the two cells was checked by using the "Differential" adjustment with pans of identical geometry containing a suitable metal. For the temperature range from 100 to 200° the most suitable standard was indium, and from 200 to 300°, tin.

The "Differential" and "Average" adjustments were sensitive to mechanical vibration and temperature changes; the reproducibility of measurements depended also on these parameters. The sample containers were the usual "leaking", or non-hermetic pans; hermetically sealed pans were not suitable because they had high, irreproducible R_0 values. All pans and covering discs were washed with solvents, rinsed with doubly distilled water, and dried at 110° before use. Organic samples were ground in an agate mortar and carefully dried over P_2O_5 under vacuum.

Equal amounts (between 2 and 4 mg) of the same sample were used, and calorimetrically equivalent amount when the substances were different.

The sample was carefully spread out in the pan and covered with the disc, and the pan closed with the crimping press and then transferred to a sharp-edged circular hole in a steel plate (6.8 mm diameter, 5 to 7 mm deep) placed on a flat, smooth steel surface; the capsule was vigorously pressed successively with two steel punches having diameters of 6.7 mm and 5.8 mm respectively. The sample and reference pans were then transferred to the holders. The pans were sometimes covered with aluminium lids to reduce heat emission and sublimation; this did not change the temperature readings. The sample holder assembly was closed by its cover, and dry nitrogen was passed through at 25 cm^3 per minute. It was important to maintain a constant gas flow, particularly at very high temperatures. The sample was then rapidly heated to melting temperature and after solidification and cooling, the pan was usually reshaped.

After these preparatory steps, the true calorimetric run was carried out using the following instrumental conditions. Chart speed 240 mm/min, range 4 mcal/s; the scan speed was kept at 4°/min up to a temperature approximately 10° below the melting point and then decreased to 1 or 2°/min.

Experimental measurements

As a final test, after investigation of all experimental variables and determination of the best experimental conditions, two series of calorimetric measurements were run: the first with highly pure organic substances, and the second with others of known decreasing purity.

The first series of measurements was intended to verify the limits of accuracy inherent in these temperature readings. Organic substances for which the literature provided either the exact melting point or the triple point temperature were used as standards. Such substances gave fixed reference points in the temperature range from 50 to 300°. All these substances were purified by zone refining to such a level of purity that they melted at practically constant temperature. Table 7 shows the substances used and their literature solid → liquid equilibrium temperatures.

The melting points of temperature standards used were determined by following the described "Measuring procedure" and reading temperatures at the top point of the peak. The Table also shows the temperature values found and the differences

Table 7

Temperature measurements with calibration standards

Substance	Reference melting temperature, °K	T_{read}, °K (mean value from 3 det. s)	ΔT exp.	ΔT theor.	Dev.
p-Nitrotoluene	324.70 [11]	320.70	−4.00	−4.04	0.04
Naphthalene	353.44 [12]	351.32	−2.12	−2.25	0.13
Phenanthrene	373.10 [13]	371.97	−1.13	−1.25	0.12
Benzoic acid	395.53 [14]	395.23	−0.30	−0.40	0.10
Dimethylterephthalate	413.84 [15]	413.75	−0.09	+0.07	0.16
Benzanilide	436.36 [16]	436.72	+0.36	+0.46	0.10
Anisic acid	456.14 [11]	456.55	+0.43	+0.57	0.14
2-Chloroanthraquinone	482.20 [11]	482.58	+0.38	+0.47	0.11
Carbazole	518.50 [11]	518.39	−0.11	−0.22	0.11
Anthraquinone	557.76 [11]	556.28	−1.46	−1.63	0.17
				Mean	0.12

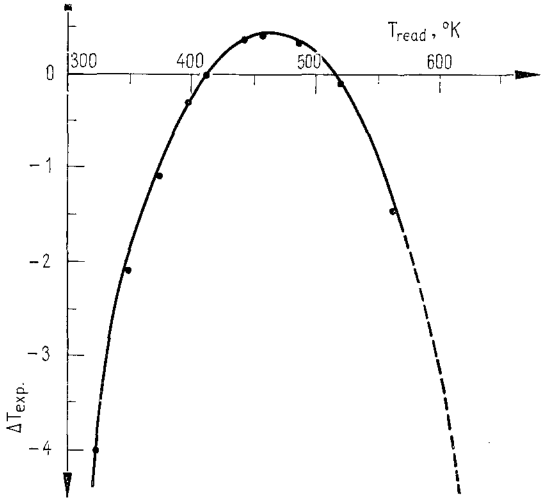


Fig. 5

between these and the literature values. By plotting differences versus measured temperatures, as recommended by the makers, the parabolic curve shown in Fig. 5 was obtained. The position of values on this curve provided adequate evaluation of the accuracy of temperature readings. However, the curve itself is represented by a quadratic equation that was calculated by the least squares method using the values $\Delta T_{\mathrm{exp.}}$ of Table 7.

$$y = -0.278 + 2.921x - 2.426\,x^2$$

where for mathematical conveniency $x = \frac{400 - T_{\text{read}}}{100}$

and $y = \Delta T_{\text{exp.}}$

From this equation, the theoretical correction values for the readings can be calculated and then compared with the experimental values (see also Table 7). This comparison shows that the average deviation of experimental from theoretical values is ±0.12°, which is therefore the order of accuracy of temperature readings afforded by the differential scanning calorimeter under optimum measuring conditons.

The second series of measurements was carried out to verify the suitability of the different reading and measuring techniques adopted. To make substances of known and decreasing purity, two of the ultrapure substances used in the first series of experiments were taken, namely *p*-nitrotoluene and phenanthrene, and weighed amounts of other standard substances were added to them as "impurities". By diluting these low-purity mixtures with ultrapure solvent (*p*-nitrotoluene or phenanthrene) in calculated amounts, mixtures of increasing purity were prepared. Samples of different purities were prepared as multicomponent and not binary mixtures, in order to control the molar fraction of added impurities by the method described for the differential calorimeter [7]. By means of preliminary

Table 8

Melting temperature of standards at decreasing purity

Substances	*M.T.* °K theoretical	ΔT theoretical	ΔT obtained from measured melt. temp.			
			Top reading	Mid-point reading	Extrapol. reading	Conventional reading
p-Nitrotoluene 100 % purity mol.	324.70					
p-Nitrotoluene 99.98% purity mol.	324.69	0.011	0.13			
p-Nitrotoluene 99.75% purity mol.	324.56	0.132	0.13	0.13	0.13	0.10
p-Nitrotoluene 99.50% purity mol.	324.42	0.286	0.31	0.30	0.27	0.39
p-Nitrotoluene 99.25% purity mol.	324.27	0.429	0.47	0.48	0.49	0.57
p-Nitrotoluene 99.00% purity mol.	324.13	0.572	0.70	0.69	0.71	0.87
p-Nitrotoluene 98.00% purity mol.	323.56	1.144	1.34	1.36	1.24	1.39
Phenanthrene 100 % purity mol.	373.10					
Phenanthrene 99.99% purity mol.	373.09	0.064				
Phenanthrene 99.75% purity mol.	372.94	0.160	0.19	0.16	0.17	0.11
Phenanthrene 99.50% purity mol.	372.78	0.320	0.34	0.38	0.36	0.36
Phenanthrene 99.25% purity mol.	372.62	0.480	0.55	0.50	0.50	0.60
Phenanthrene 99.00% purity mol.	372.46	0.639	1.04	0.98	0.96	0.99
Phenanthrene 98.00% purity mol.	371.82	1.278	2.25	2.16	1.84	2.03

runs, it was ascertained that the substances added as impurities did not form solid solutions with the solvent.

The results of these experiments are shown in Table 8, together with the values found using various reading methods and the theoretical values calculated by applying the van't Hoff equation. It can be seen that the measured variations in melting temperatures at various levels of impurity are consistent and in agreement with the theory. Naturally, due to the limitations inherent in the use of the DSC technique for measuring temperature the agreement is not very good, but it is sufficient. At low levels of purity (99 and 98 %) the agreement with theory is less good probably due to the deviation from the ideal behaviour of dilute solutions.

As regards reading criteria, the best results were those obtained by graphical extrapolation; there was no difference in temperatures which were read visually at the top of peak or extrapolated from geometrical midpoints.

There was a difference between the results obtained using these methods and those obtained with the method recommended by the manufacturers, the former being more accurate. Finally, concerning the technique and sample preparation, it is emphasized that the instructions must be followed closely, as otherwise the temperature indications obtained will be at variance in contrast to those deduced theoretically by the application of the van't Hoff equation.

*

The authors wish to thank Prof. G. Milazzo of the Istituto Superiore di Sanità (Rome) for assistance in the work.

References

1. A. Weissberger, Physical Methods of Organic Chemistry, Vol. I. Interscience, New York, 1949, pp. 74, 747.
2. Houben-Weyl, Methoden der organischen Chemie, Band II, Analytische Methoden. G. Thieme-Verlag, Stuttgart, 1953, pp. 803–814.
3. F. W. Schwab and E. Wichers, J. Res. Nat. Bur. Stand., 34 (1945) 3, A. R. Glasgow, N. C. Krouskop and F. D. Rossini, Anal. Chem., 22 (1950) 1521.
4. E. S. Watson, M. J. O'Neill, J. Justin and N. Brenner, Anal. Chem., 36 (1964) 1233.
5. M. J. O'Neill, Anal. Chem., 36 (1964) 1238.
6. F. W. Schwab and E. Wichers, Temperature, its Measurement and Control in Science and Industry. Rheinhold, New York, 1941.
7. Thermal Analysis Newsletter, No. 5 (1966), Analytical Division, Perkin Elmer Corp., Norwalk, Conn.
8. A. P. Gray, in Analytical Calorimetry, Ed. R. S. Porter and J. F. Johnson, Plenum Press, New York, 1968, p. 209.
9. R. W. Grimshaw, E. Heaton and A. L. Roberts, Trans. Brit. Ceram. Soc., 44 (1945) 87. Kofler, Thermomikromethoden zur Kennzeichnung organischer Substanzen. Verlag Chemie GmbH, 1954, p. 17.
10. C. Fouquey and J. Jacques, Bull. Soc. Chim., France (1966) 165.
11. V. G. Colarusso and M. A. Semon, Anal. Chem., 40 (1968) 1521.
12. J. P. McCoullough, H. L. Finke, J. F. Messerly, S. S. Todd, T. C. Kincheloe and G. Waddington, J. Phys. Chem., 61 (1957) 1105.
13. See following article in this journal.

14. A. C. WERNER and S. V. P. MASTRANGELO, J. Am. Chem. Soc., 75 (1953) 5244.
15. P. SANMARTIN and N. REGINE, J. Thermal Anal., (1969) 403.
16. H. HILBCK, Pharmaz. Ztg., 112 (1967) 74.

RÉSUMÉ — On a utilisé un microcalorimètre pour la détermination des températures de transition. On a étudié les facteurs inhérents à la fois à l'instrument et à l'échantillon, susceptibles d'introduire des variations dans les mesures thermométriques et l'on a proposé des modifications. On décrit une technique précise pour préparer l'échantillon et mesurer la température. La méthode proposée, appliquée à des étalons organiques de très haute pureté, ainsi que de pureté moins élevée, donne une précision de l'ordre de ±0.1° dans la lecture de la température et confirme une relation entre les valeurs expérimentales et théoriques.

ZUSAMMENFASSUNG — Ein Differentialmikrokalorimeter wurde zur Bestimmung der Übergangstemperaturen angewandt. Man untersuchte die Faktoren sowohl seitens des Instruments wie der Probe, durch welche Variablen in den mit dem Kalorimeter ausgeführten thermometrischen Messungen eingeführt werden können, weiterhin wurden Modifikationen der Ablesemethoden vorgeschlagen. Ein sicheres Verfahren zur Probebereitung und Temperaturmessung wird beschrieben. Die Methode gab bei der Anwendung von organischen Standardstoffen sehr hoher und minderer Reinheit eine Genauigkeit von ±0.1°.

Резюме — Описано использование микрокалориметра дифференцирующего типа для определения температур перехода. Разработана надежная методика для приготовления образца и измерения температуры. Если предлагаемый метод использовать для органических стандартов высокой чистоты, то это дает возможность определять температуры с точностью порядка ±0.1° и подтверждает соотношение между экспериментальными и теоретическими величинами.