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THERMAL GRADIENTS IN DIFFERENTIAL SCANNING CALORIMETRY

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A combined static and dynamic temperature calibration is described. The static calibration corrects the instrumental dial temperature reading. The dynamic calibration has instrumental and material components and therefore varies from specimen to specimen. It is obtained from individual DSC curves and so removes uncertainties in sample temperature due to varying mass, geometry, and heating rate. The instrumental performance is improved and specific heats may be obtained to an accuracy of ±1%.

List of symbols used

T_i, T_f	steady initial and final temperatures, respectively, in a calorimetric experiment;
$\Delta T = T_f - T_i$;	
T_D	dial temperature reading;
T	true temperature corresponding to T_D after all corrections have been made;
T_m	melting point;
δT_s	correction to T_D to give T under isothermal, 'static' conditions;
δT $(= \delta T_0 + \delta T_{mat})$	additional correction to T_D, due to thermal lag, to give T under programmed temperature conditions;
δT_0, δT_{mat}	contributions to δT originating in the instrument and sample material respectively;
δT_d $(= \delta T_s + \delta T)$	total correction to T_D to give T under programmed temperature conditions;
R	calorimeter heating rate;
$H(T_i)$, $H(T_f)$	enthalpy at T_i and T_f respectively;
$\bar{c}_p$	mean heat capacity over the temperature range T_i to T_f;
c_{p, T_f}	heat capacity at T_f.

Differential thermal analysis has long been a useful tool in the fields of geology and metallurgy [1]. The recent introduction of commercial apparatus, based on either differential thermal or differential enthalpic methods, has led to many applications far removed from these areas. In particular the technique has proved of immense value for determining the purity of organic compounds and for characterising polymers [2]. Both these applications involve materials of generally poor thermal conductivity. This paper will examine the effects of thermal lag which have been encountered in the development of a data treatment system and show how they may be eliminated by suitable use of the experimental data.

Experimental

All experiments were carried out using a Perkin Elmer Model 1B differential scanning calorimeter (DSC). The output signal from the DSC was monitored on a digital voltmeter and recorded on paper tape.

Calibration of the DSC has been described in detail elsewhere [3]. Here it is emphasised that the temperature calibration was carried out at a zero rate of heating by the slow stepwise melting (using temperature increments of ≤ 0.1 K) of pure materials. The correction δT_s which gives the true temperature T corresponding to any dial reading T_D is therefore free of thermal lag ('static', subscript 's') and $T = T_D + \delta T_s$; δT_s may be of either sign.

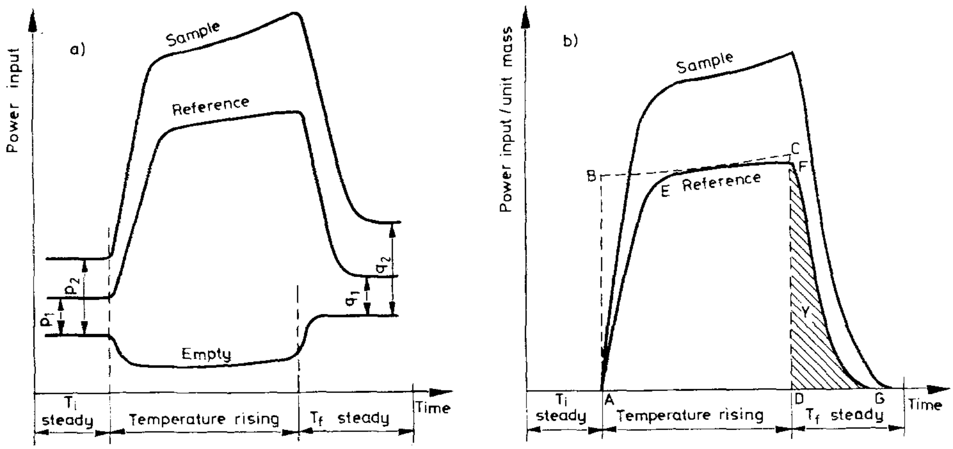

Fig. 1. Treatment of calorimetric data; (a) original curves (displaced for clarity), (b) material curves normalised to unit mass

The calorimeter was always used in the "specific heat mode" [4]. The temperature was raised from one steady value T_i to another T_f in the sequence: (i) empty pan, (ii) reference material, (iii) sample (Fig. 1a). A computer programme subtracted results for the empty pan from those for the reference material and sample to give composite curves, normalised to unit mass (Fig. 1b), the areas of which were proportional to the specific enthalpy changes $H(T_f) - H(T_i)$ from T_i to T_f. The mean heat capacity $\bar{c}_p$ is $H(T_f) - H(T_i)/\frac{1}{2}(T_i + T_f)$. A feature of the programme was the ability to compensate for even gross mismatches in the isothermal portions of the curve (i.e. $p_i \neq q_i \neq 0$, where $i = 1$ or 2). Adequate balancing of the isothermal baselines is normally a difficult and time consuming operation.

Thermal lag

The response of an ideal calorimeter, with no thermal lag, to a linear increase in temperature from T_i to T_f is the composite curve *ABCD* of Fig. 1b. When there are no major thermal events, such as melting or phase changes, the ordinate is proportional to the specific heat c_p. In practice the onset of steady state conditions (*EF*) is delayed and a curve *AEFG* is obtained. The total area, *X*, of both curves is equal and is proportional to $\bar{c}_p \cdot \Delta T$, where $\Delta T = T_f - T_i$. *D* is the point where the final steady temperature, T_f, is attained at the sensor and the shaded "tail" area, *Y*, represents the additional energy needed to bring the temperature of the specimen and calorimeter to this value. *Y* is proportional to $c_{p, T_f}\, \delta T$, where c_{p, T_f} is the specific heat at T_f or, strictly, a mean value over the range δT, where δT is the temperature lag in the system. It is given by $Y \Delta T \bar{c}_p / X c_{p, T_f}$. The ratio $\bar{c}_p / c_{p, T_f}$ is normally only a few per cent less than unity and may generally be neglected. However it is important when a polymer passes from a glass to a rubber and there is a discontinuity in c_p. A good approximation is given by the ratio of the average value of the ordinate to the value when the programme temperature first reaches T_f.

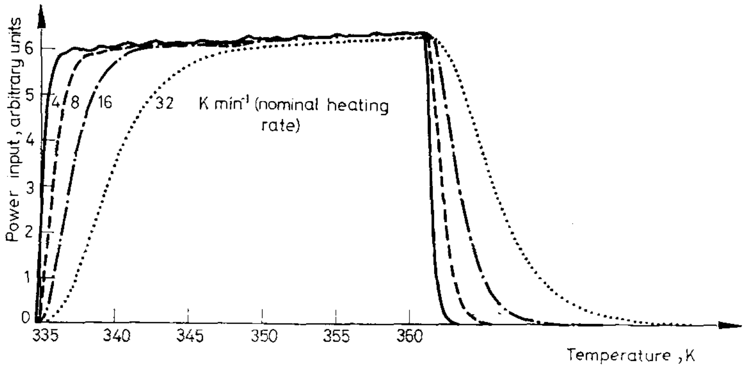

Fig. 2. Normalised curves for synthetic sapphire discs at several heating rates

The DSC output is basically a combination of time (abscissa) and voltage (ordinate). The former is easily transformed to the temperature scale shown in Fig. 2 (the heating rate, *R*, is a linear function of T_D). When this is done the ordinate must be correspondingly normalised. Without this, a doubling of *R* for a fixed temperature increment, ΔT, would leave the temperature axis unchanged (although halving the original *time* scale) but double the ordinate values. Display of the experimental data in this way allows a direct comparison of the effects of heating rate and of sample size and geometry.

Results for an alumina disc (synthetic sapphire 6 mm diam x 5 mm thick) are shown in Fig. 2. The alumina was placed directly on the DSC specimen holder. All areas agree to within $\pm 1\%$. The increased delay in reaching the steady state region (*EF*, Fig. 1b), as the heating rate is raised, is clearly visible. Calculated values of the thermal lag are shown in Fig. 3 which also gives results for a disc of the same diameter but approximately twice the thickness.

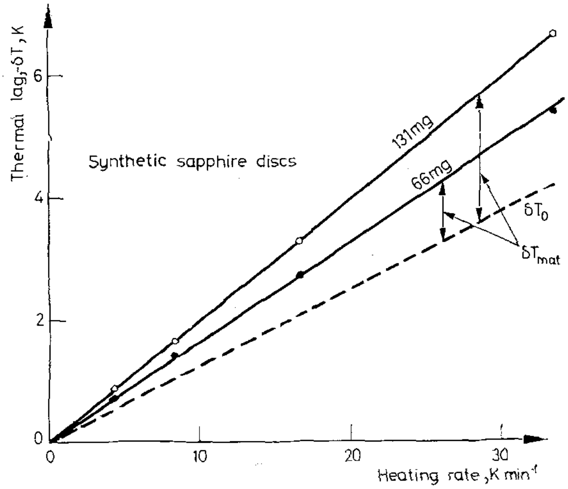

Fig. 3. Thermal lag as a function of sample mass and heating rate

The broken line of Fig. 3 (δT_0) was obtained by plotting δT, at a constant heating rate, against sample mass and extrapolating to zero mass (identical, reproducible thermal contact with the DSC is essential and a given extrapolation always involved discs of constant diameter). The broken line is an instrumental constant, the thermal lag between the bottom plane of the sample and the temperature sensor. It includes the thermal resistance between the sample and the DSC pan holder (all results so far refer to discs placed directly in the instrument). It is difficult to vary the sample mass (thickness) by more than a factor of about two and a given extrapolation to zero mass is based on only two or three points. The validity must therefore be judged by the values of δT_0 found using materials of very different thermal conductivities. Thus the following results were obtained using the substances shown in brackets: $\delta T_0 = .133\,R$ (silver), $.130R$ (lead), $.126R$ (sapphire), $.127R$ (benzoic acid). The extrapolation is clearly valid and gives a true instrumental constant.

Using an aluminium pan as a sample holder increases δT_0 by approximately 50%. The larger figure includes transfer of heat across two interfaces, pan holder to pan and pan to sample, and these are the conditions encountered in normal operation of the instrument. The simplified conditions noted earlier were desirable to reduce uncertainties due to differences in sample pans. Samples are usually far removed in form from that of ideal discs and δT may be considerably more than indicated above.

All runs with the DSC use synthetic sapphire discs as reference materials (they were chosen because high purity material is readily obtainable and the thermodynamic properties are well defined [5]). Many results are therefore available for δT as a function of heating rate, mass, and whether aluminium sample pans are present or not. For a given set of conditions δT is reproducible to ± 0.1 K for $R \leq 16$ K min^{-1} and ± 0.2 K for $R = 32$ K min^{-1}. The points of Fig. 4 give a good idea of the experimental scatter. Larger variations may be found when pans are used but these invariably involve increased values of δT and are due to the use of pans which are not perfectly flat. Similar remarks apply to other materials.

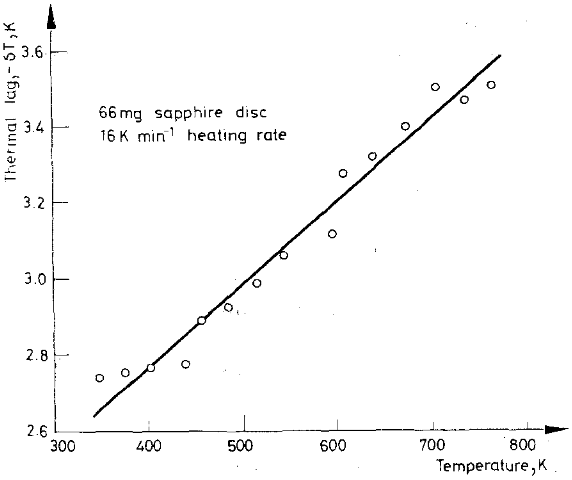

Fig. 4. Thermal lag as a function of temperature

Because δT varies from one specimen to another, temperatures determined from a calibration curve must only be fortuitously correct. The consequences of errors in the specimen temperature will be considered in the following section. First it will be shown how they may be removed. Before this is done the change of δT with temperature must be considered. Some results for sapphire are shown in Fig. 4. There is a slow increase with temperature but even at 700 K δT_0 is only about 30% greater than the value at room temperature. The overall variation of δT is a complex function of the several materials and interfaces encountered en route from the heaters to the specimen and it is not possible to derive any information about the thermal conductivity of the specimen.

The true temperature, T, of a sample in a DSC is obtained from $T = T_D + \delta T_s + \delta T$. δT_s is an instrumental constant; δT varies from sample to sample and, very strongly, with heating rate. The calculation of δT was described earlier and, as δT_s was determined in the "static" calibration it is mathematically a trivial operation to correct all dial temperatures, T_D. When a reference material and sample are run in successive experiments δT will in general be different for the two materials. The computer programme must interpolate ordinate values for both at common, corrected temperatures, T.

The treatment above refers to curves (Fig. 2) which are unperturbed by phase changes. When these occur the calculation for δT is invalid. Fortunately phase changes normally involve large quantities of heat (relative to specific heat) and only small samples are required, in this case δT may be replaced by δT_0.

Applications

(a) *Temperature calibration*

This section will consider some of the consequences of the thermal gradients discussed above. A problem of basic importance concerns the temperature scale of the instrument. This is normally [6] calibrated dynamically (subscript 'd') by observing the melting points, T_m, of pure metals at the required heat rate and using the relation $T_m = T_D + \delta T_d$ where δT_d is the dynamic correction to the dial reading T_D. The melting point is taken as the intersection of the leading straight edge (extrapolated) of the melting curve with the instrumental baseline. The procedure described in the present paper gives T ($= T_m$ at a melting point) $= T_D + \delta T_s + \delta T_0$ and the two methods of calibration should therefore be equivalent if $\delta T_d = \delta T_s + \delta T_0$. This relationship was found to hold to better than 0.3 K for the melting points of indium, tin, bismuth and lead for heating rates from 0.5 to 32 K $\min^{-1}$. Two aspects of the dynamic calibration should be emphasised: it is essential to use small samples and to use the melting point described above. With large samples δT_0 must be replaced by δT and the calibration is a function of sample mass; peak temperatures from a DSC curve are much more sensitive to heating rate and mass than is called for by the relation $\delta T_d = \delta T_s + \delta T_0$.

Although "static" and "dynamic" methods are equivalent the former must be used if an accurate calibration, covering the whole instrumental temperature range, is required. There are not enough metals with suitably spaced melting points. Other materials have to be used; their purity is generally orders of magnitude less than that of metals. The extraction of T_m from a "dynamic" DSC curve then becomes a rather subjective operation. A true melting point exists of course, albeit depressed, and this can be determined by conventional methods. The figure can then be unambiguously related to a "static" value found in the DSC – there are no uncertainties due to thermal lag at this stage. Finally, the instrumental correction δT_0 is applied. As seen above this is normally sufficient for the small (milligram) quantities of material required in fusion measurements.

Larger samples are needed for accurate determination of the heat capacity and thermal lag within the sample itself becomes important.

(b) *Heat capacity*

The ordinate displacement in a DSC is proportional to the heat capacity and heating rate. The highest accuracy will therefore be obtained from a large mass and/or heating rate. Increasing either of these increases the thermal lag in the system. Neglect of this affects c_p by amounts which depend on the relative magnitude of $\delta c_p/\delta T$ for the sample and reference material. Calculated values of c_p are in error because they refer to an apparent temperature, T_a, which is greater than the true sample temperature, T. The error is $c_p(T_a) - c_p(T)$, assuming that c_p is a constant for the reference material. This is normally a good approximation since the latter is deliberately chosen to be thermally inert – numerical values are given below for synthetic sapphire. The error will be negligible if $\delta c_p/\delta T$ is small but errors of several percent may occur when there is appreciable curvature as, for example, in the approach to a phase change. Here "lattice loosening" or "premelting" may lead to considerable increases in c_p over a temperature range which, for a polymer, may cover several decades prior to the actual melting point. Thus the percentage change in c_p, per K, for polyethylene crystals ($T_m = 401$ K) is [7] .47(240), .48(360), ..93(390), .14(410), .14(500 K). Corresponding figures for synthetic sapphire, the most usual reference material, are .47, .18, .14, .12, and .07%.

Conventional operation of the instrument assumes a sample temperature $T = T_D + \delta T_d$. It was shown above that $\delta T_d = \delta T_s + \delta T_0$. (Thermal lag is always a negative quantity, δT_s may be positive or negative.) For large samples δT_0 should be replaced by $\delta T = \delta T_0 + \delta T_{mat}$. The additional term is defined in Fig. 3 for sapphire discs. Organic compounds with this favourable shape give comparable values for δT_{mat}, say 1–2 K at a 16 K min^{-1} heating rate. This is because the generally higher heat capacities permit the use of thinner discs and this compensates for the poorer thermal conductivity. Calculated specific heats of the polymer crystals described above will be low by 0.5 to 1% 50 K below T_m. All are systematic errors and, although 1% is within the anticipated performance of the instrument, it was the low temperature data which first drew our attention to the problems of thermal lag. Polymer crystals were usd as control substances in a quite separate series of experiments in the range 330–360 K. The mean c_p from 10 runs was only trivially different from the value determined by adiabatic calorimetry [7] whereas the "dynamic" figure at $\frac{1}{2}(T_i + T_f)$ was 1.1% lower (curvature in the c_p–T curve is small and would not account for the difference). The internal inconsistency was completely removed when effects of thermal lag were considered.

The examples discussed above indicate that thermal lag generally has a fairly small effect on apparent values of c_p when samples of suitable geometry are used and the instrument has been calibrated at the relevant heating rate. The qualification with regard to geometry refers to idealised conditions. It is rare to meet with samples having regular shape, let alone thin discs. Indeed, a major advantage of the DSC is the ability to monitor the enthalpy change $H(T_f)-H(T_i)$ irrespective of sample size and shape. It is often possible to form polymers into discs by the application of pressure. Unfortunately, the morphology may be completely changed thereby and subsequent measurements will refer to an atypical sample. The values given above as possible errors in c_p for polymer crystals must therefore be regarded as minimum values, they may as much as double for unfavourable geometries. It is evident from Fig. 3 that doubling the sample mass gives a smaller increase in thermal lag than doubling the heating rate. As a general rule, therefore, specific heat determinations should be carried out with large samples at low heating rates.

(c) *Transition temperatures*

Reasons have been given above for preferring the "static" method of temperature calibration. When several heating rates are used the technique also involves the least effort in calibration. The only requirements in addition to the static correction δT_s are values of δT_0 at a few temperatures and heating rates. Few are required since δT_0 is effectively a linear function of both T and R of the form $\delta T_0 = (a + bT)R$. The true sample temperature is obtained from $T = T_D + \delta T_S + (a + bT)R$ and this is generally sufficient for small samples. However, even here a note of caution should be sounded. The melting temperatures of metals, although independent of sample mass in the range up to a few milligrams are not independent of geometry. For example, a 2.5 mg pellet of indium melted at $T_D = 437.8$ (leading edge) or 441.4 K (peak) for $R = 16$ K min^{-1}. These were reproducible values (the indium showed no tendency to wet the aluminium sample pan) which dropped to 436.4 and 438.0 K respectively when the pellet was flattened by an aluminium disc. Only the latter pair of temperatures were independent of sample mass.

The above effects can be recognised and treated in metals but the problem is more intractable when considering the melting point of a polymer. These must often be scanned through the melting region at a high rate (to avoid irreversible annealing effects). Since there is no well-defined "leading edge" (polymers melt over a wide range of temperature) it is normal to take the "peak" temperature as the melting point. This is not valid even for pure metals – especially when in an unfavourable geometry. Polymeric samples are usually of irregular shape and the small differences in melting point which are frequently described in the literature and attributed to subtle structural differences should be treated with some reserve.

When larger samples are used δT_0 is replaced by δT which is computed for each run and thus automatically compensates for any specimen peculiarities. It was found, for example, that the uncorrected glass temperature, T_g, of a polystyrene disc dropped from 380 to 379 K ($R = 8$ K min^{-1}) after leaving overnight at 450 K. The polymer had the same thermal treatment prior to each measurement and no change in molecular weight was detectable by gel permeation chromatography after holding at 450 K. The original disc was cut from a moulded sheet to fill the aluminium specimen pan as well as possible but there was still the 1° change in T_g as the sample effectively flowed and made better contact with the pan. (The weight-average molecular weight was 310,000 and the long treatment time at 450 K was needed because of the high viscosity.) This "instrumental" effect was entirely removed when the correction δT was applied and the two curves could be superimposed with no temperature shift. This example illustrates the care which must be taken in analytical treatment of thermal lag using the flow of heat through thin slabs [8]. No allowance can be made for differences in thermal contact between specimen and calorimeter.

Conclusions

An experimental analysis has been made of the factors which affect the sample temperature in a differential scanning calorimeter. The importance of both instrumental and material parameters has been shown. The former include the non-linear response of the platinum resistance thermometer (which accounts for the parabolic shape of the normal dial temperature correction curve) and thermal lag within the instrument. The latter encompass sample size, geometry and packing in addition to the physical constants characteristic of the material itself; all combine to give a response for which an a priori calculation is impossible.

A procedure has been described which considers all the above variables and gives accurate sample temperatures. Initially a calibration gives the true temperature corresponding to any static dial temperature. A second correction is applied which gives thermal lag within the instrument as a function of heating rate and temperature. The final correction is obtained from individual thermograms and so automatically compensates for the several material variables.

Examples have been given which show how the instrumental accuracy is improved by the above treatment.

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Résumé — On décrit un mode d'étalonnage de la température pour les essais statiques et dynamiques. L'étalonnage statique permet de corriger la valeur de la température lue sur le cadran de l'instrument. L'étalonnage dynamique varie avec les échantillons étudiés car il utilise des accessoires instrumentaux et des matériaux adapté aux études particulières. Il est fourni par des enregistrements individuels qui éliminent les incertitudes dues aux variations de masse, de géométrie et de vitesse de chauffage. Les caractéristiques instrumentales sont ainsi améliorées et les chaleurs spécifiques peuvent être obtenues avec une exactitude de ±1 p.c.

Zusammenfassung — Eine kombinierte statische und dynamische Temperatureichung wird beschrieben. Die statische Eichung korrigiert die Temperaturablesung an der Instrumentenscheibe. Die dynamische Eichung besteht aus instrumentellen und Stoff-Komponenten und ist deshalb in verschiedenen Fällen unterschiedlich. Sie wird aus individuellen DSC Kurven erhalten und beseitigt somit Unsicherheiten der Temperatur des Musters, welche durch Änderungen der Masse, der Geometrie und der Aufheizungsgeschwindigkeit bedingt sind. Die Leistung des Instrumentes kann erhöht werden und die Bestimmung spezifischer Wärmen ist mit einer Genauigkeit von ±1% möglich.

Резюме — Описана комбинированная статическая и динамическая калибровка температуры. Статическая калибровка вносит поправку в чтение температуры по шкале прибора. Динамическая калибровка включает приборный и материальный компоненты и поэтому изменяется в зависимости от образца. Она проведена на основе индивидуальных термических кривых и, следовательно, устраняет колебания в температуре образца, обусловленные изменениями массы, геометрии и скорости нагрева. Инструментальное выполнение улучшено и удельную теплоемкость можно определять с точностью до ± 1%.