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TEMPERATURES IN DIFFERENTIAL SCANNING CALORIMETRY

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ABSTRACT

A recently described method is used to characterise thermal gradients in a DSC-2 and the results are compared with a conventional temperature calibration. Under certain circumstances the latter may be in error by several degrees with consequent adverse effects on calculated heat capacities. The errors are removed when allowance is made for variations in thermal lag from sample to sample.

INTRODUCTION

The calibration of a differential scanning calorimeter (DSC) under isothermal conditions is a straightforward operation and temperatures can be specified to ±0.1 K. Unfortunately, under normal dynamic conditions (a linear change of temperature with time), the position is far less clearly defined because temperature is measured by a platinum resistance thermometer located in the base of the cell, so that actual sample temperatures lag behind the indicated values. Attempts to compensate for this lag are normally made by constructing a calibration curve, using the melting points of a series of standard substances observed at the relevant heating rate. However, a great advantage of the DSC lies in the wide variety of materials and geometries which may be examined and thermal lag will clearly be less for, say, a copper disc than for a pan full of polyethylene chips. This is the problem; the normal calibration makes no allowance for differences from one sample to another.

A method has recently been described which overcomes the above difficulties[1]. An isothermal temperature correction is first applied; to this is added a lag correction which is derived from individual thermograms and so compensates for variations from sample to sample.

In the present paper a modification to ref. 1 is introduced and used to define conditions in a DSC. These results are then compared with a conventional temperature calibration and it is shown how a sample-related calibration removes systematic errors when a DSC is used to measure heat capacity.

EXPERIMENTAL

Details of the experimental technique and data treatment have been given earlier[1-3] except that a more versatile program, described in the next section, is now used to calculate thermal lag. In the present work attention has been confined to the melting of a pure organic compound (acetanilide, Aldrich 99.9%, m.p. 387.4 K) and a metal (indium, Koch-Light 99.9999%, '6N', m.p. 429.8 K). A Perkin-Elmer DSC-2 was used. With this instrument it is, in principle, possible to remove the isothermal temperature correction[1]—that is, the instrument reading under isothermal conditions is the true temperature. In practice it is impossible to achieve this desirable goal over the whole 900 K range of the instrument and we have merely reduced it to a few tenths of a degree and made the final small, static correction as described earlier[1].

Prior to the runs using acetanilide or indium, thermograms were obtained for the empty pan and a series of synthetic sapphire reference materials—discs of identical diameter but varying thickness. These were used both as calibrants for enthalpy changes[2,3] and also to calculate thermal lag in the instrument[1].

Acetanilide and indium were melted in normal aluminium sample pans without crimping the lids since this tends to deform the base, thereby giving a geometry and thermal contact that is no longer the same as that of the reference material. Acetanilide readily distributed itself symmetrically in the pan on melting; with indium the aluminium lid had to be pushed gently down on the molten sample (in a stream of nitrogen) to give a thin film of indium. In the form finally used both samples had stable geometries as shown by the reproducibility of the initial experiment and a repeat after all other runs were complete. Both samples were cooled from the melt at 10°C min^{-1} prior to all experiments. There was a very slight loss (ca. 0.1%) of acetanilide by sublimation during each experiment and it was therefore weighed after each run. When all dynamic experiments were complete the reproducibility of the isothermal temperature calibration was checked by slow stepwise melting of the samples[1,4].

RESULTS

Thermal lag, δT, was obtained from the thermograms of sapphire discs heated from 400 to 430 K. δT was calculated using the equation $mc_p\delta T = F\delta A$ where m and c_p are the weight and heat capacity of the sample, respectively, δA the area of the thermogram remaining after the final programmed temperature has been attained, and F is the enthalpy conversion factor obtained from any of the runs using sapphire. Literature values[5] were used for c_p (when there is an "unknown" sample, c_p may be estimated using the conventional ratio of sample/reference amplitudes. This makes no allowance for thermal lag but the error thus introduced is trivial as it occurs in a correction to a correction). The calculation of δT according to ref. 1 gives erroneous results when samples undergo a phase change, the above method removes this drawback.

Results are shown in Fig. 1. The broken line shows the extrapolation to zero thickness (weight) of sapphire. Experimental points at 5 and 10°C min^{-1} have values that are almost exact fractions of those at 20°C min^{-1} and these provide a check on the consistency of the extrapolation. The dotted line, δT_0 is the "zero thickness" line when no sample pan is used, that is, the sapphire discs are placed directly on the DSC cell. $\delta T_0'$ is the corresponding quantity when sample pans are used.

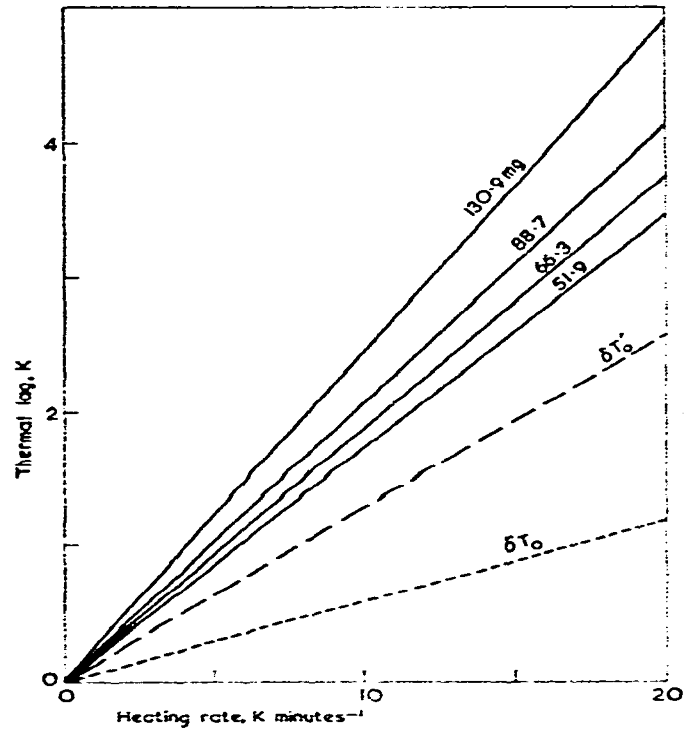

Fig. 1. Thermal lag in sapphire discs, weights as shown (mg). Broken line: extrapolation to zero thickness in pans. Dotted line: extrapolation to zero thickness with no pans.

Figures 2 and 3 show melting curves for indium and acetanilide, respectively. Duplicate experiments using similar amounts of either indium (12±1 mg) or acetanilide (4.5±0.5 mg) were in very good agreement. Because of the common axes of the several curves of Figs. 2 and 3 a reversal of the normally accepted shapes has occurred. Fast heating rates are generally thought of as producing sharp endotherms, slow rates giving broad diffuse values. That the reverse is true is easily seen even in the uncorrected recorder trace. Displacements from isothermal conditions are usually proportional to the heating rate, but in the melting region the peak amplitude only increases by a factor of 1.4 to 1.5 on doubling the heating rate so that c_p, which is proportional to the ratio of sample to reference displacements, appears to decrease

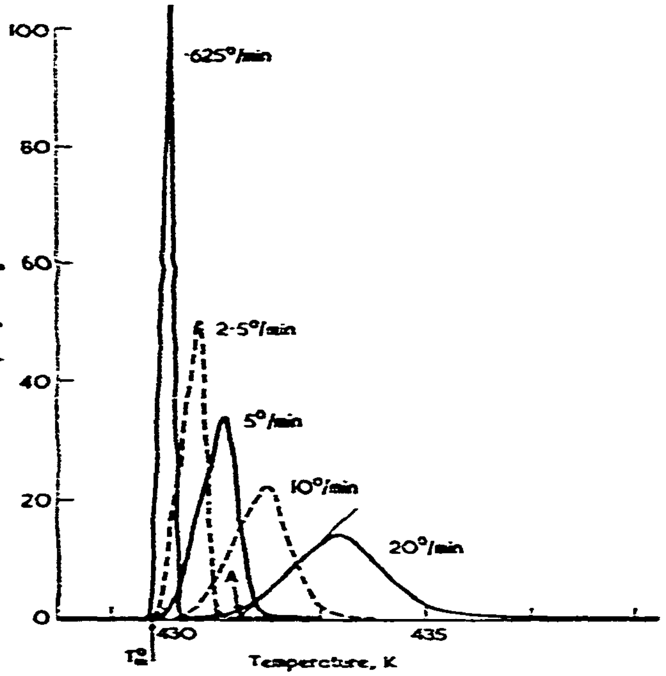

Fig. 2. Melting curves for indium. Point A defines the "leading edge" temperature at a heating rate of 20°C $\min^{-1}$.

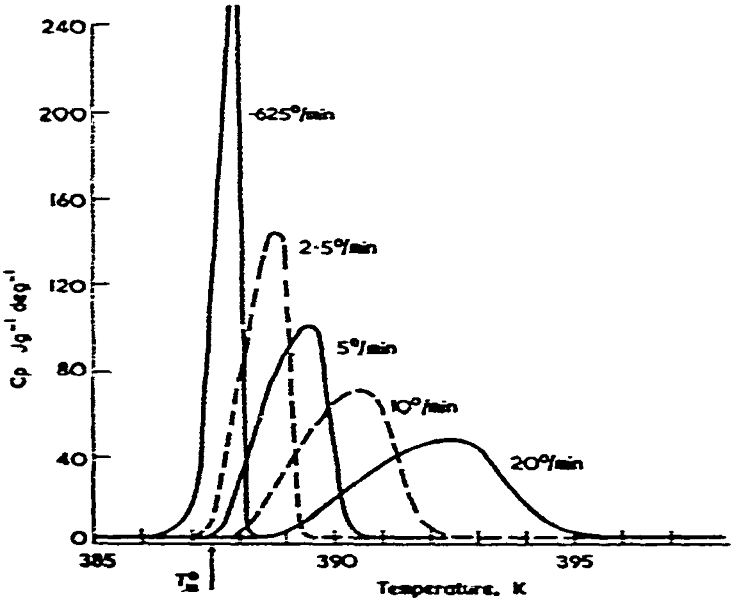

Fig. 3. Melting curves for acetanilide.

and the required heat of fusion must be obtained by a broadening of the melting curve.

DISCUSSION

In this section we use the above results to consider sample and instrumental effects in a DSC-2. The conventional calibration is then examined so that the errors caused by using a fixed calibration can be clearly identified. Unless otherwise stated unqualified values of thermal lag refer to heating rates of 20 °C min^{-1}.

Thermal lag in the DSC-2

The true average temperature, T, of a sample in a heated DSC cell is given by

$$T = T_i + \delta T_i - \delta T_0 - \delta T_{mat} \quad [1]$$

where T_i is the indicated temperature, δT_i the isothermal temperature correction, δT_0 is the instrumental lag and δT_{mat} the additional, material, lag in a loaded cell. Since δT_0 and δT_{mat} are invariably negative they are shown thus, δT_i may be of either sign. All temperatures given in this paper have had δT_i applied so that differences between T_m^0 and the observed melting curves are exclusively due to the kinetic problems (both instrumental and sample) of a dynamic experiment.

The several interfaces in a loaded DSC cell are major obstacles to efficient heat transfer. The normal arrangement is (i) cell; (ii) sample pan; (iii) sample; (iv) sample pan lid (Fig. 4). The dotted line, δT_0, of Fig. 1 is derived from a simplified system, (i)+(iii) only, and refers to the thermal lag at a surface in contact with the cell itself (A, Fig. 4); it includes any instrumental lag within the cell. When determined by the methods described here δT_0 is a very reproducible quantity and a variety of different materials agree to ±0.1 °C. The low values of δT_0 are noteworthy: there is only a 1 °C lag between the temperature at the sensors and a face in contact with the cell. This should be compared with the earlier model DSC-1B for which δT_0 is more than

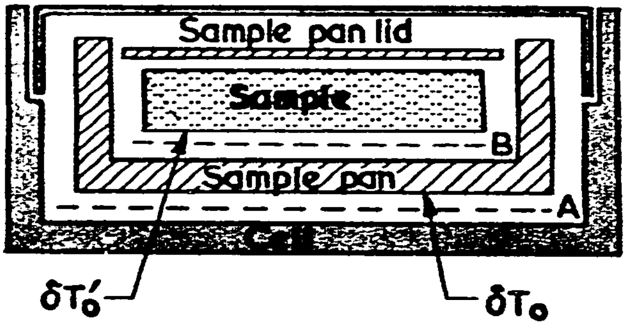

Fig. 4. Schematic diagram of a loaded DSC cell showing the surfaces to which the instrumental constants δT_0, $\delta T_0'$ refer.

double the present values[1]. The full lines of Fig. 1 are for sapphire samples in conventional aluminium pans and the broken line, $\delta T_0'$, is the extrapolation of these results to zero sample weight, that is, to the configuration (i)+(ii)+(iv) (B, Fig. 4). The relative magnitude of δT_0 and $\delta T_0'$ clearly shows that interfaces (A, B, Fig. 4) external to the cell dominate heat transfer in the DSC-2. It is possible to reduce thermal lag still further by coupling the sample and/or its container to the cell by, say, a drop of silicone oil. Using this technique Barrall and Dawson[6] have recently reported shifts of 2.1 °C in a DSC-1B heated at 5 °C min^{-1}, although such a change seems excessive at this relatively slow scanning rate. Unfortunately it is difficult to maintain reproducible conditions and the technique cannot readily be adapted to routine operation.

Using the methods of calculation described above, it is found that thermal lag in a given sample is reproducible to better than 0.1 K. It has already been shown[1] that a variety of very different materials give consistent (±0.1 K) values of δT_0, introduction of sample pans increases the scatter for $\delta T_0'$ to ±0.2 K. Systematic errors, mainly associated with slight differences between "full" and "empty" conditions, are unlikely to contribute more than 0.1 K and we believe the absolute error in δT is less than ±0.3 K.

Results for polystyrene show the sensitivity of the above technique to material parameters. At the glass transition temperature, T_g, of this polymer, there is a decrease in both thermal conductivity and diffusivity[7] and the observed δT values are indeed greater above T_g than at lower temperatures provided the molecular weight is large enough (> 100,000) to prevent flow in the high temperature form. This assures no change in the sample/pan interface (B, Fig. 4) on passing through T_g. At lower molecular weights molten polymer can flow and wet the sample pan and a decrease in lag is frequently found. This example clearly illustrates the difficulties facing any attempt at a general a priori calculation of δT.

The conventional temperature calibration

So far we have discussed thermal lag in a set of well-defined samples and used the results to calculate the "instrumental" parameters δT_0, $\delta T_0'$. We now consider melting curves as in Figs. 2 and 3, the conventional route to temperature calibration, and see whether the results fall in the already wide range of values shown in Fig. 1.

Well-defined points on the melting curves are the peak temperature and "extrapolated leading edge", one of which is defined by A in Fig. 2. Differences between these values and the isothermal melting temperature T_m^0 are shown in Fig. 5 (T_m^0 is defined as the temperature where all crystallinity vanishes in a stepwise, isothermal melting experiment). Peak temperatures show gross deviations from linearity and there is no improvement when a logarithmic scale is used. The finite width of the melting curves is a combination of instrumental and sample effects (especially weight) and the peak temperature has no particular significance. Occasionally, as with polymers, they may be the only well-defined points on a melting curve and here it is permissible to use them as characteristic temperatures. Differences in a set of samples of similar geometry are meaningful but no attempt should be made to endow them with thermodynamic respectability.

Unambiguous results are only obtained by using "leading edge" data for very pure materials. 6N indium gives the straight line δT (Fig. 5), which passes through the origin. Indium of this purity has a melting range of less than 0.1 K and it is permissible to identify the onset of melting with the actual melting temperature. In this case the quantity $\delta T = T_{\text{onset}} - T_m^0$ gives a direct measure of thermal lag in indium contained in an aluminium sample pan. In the notation of eqn [1] $\delta T = \delta T_{\text{mat}} + \delta T_0$, δT is the lag at the thin (12 mg ≡ 0.06 mm) film of indium contained in the pan, the latter is only 0.1 mm thick and with good thermal contact we would anticipate an additional, material, term, δT_{mat}, of less than 0.1 K. As it is the observed value of 0.5 K, although small, suggests a conductivity boundary at the interface B. This is probably because, although the molten component is constrained to form a thin film, it does not wet aluminium. Thermal contact is still, of course, much better than obtained by merely placing a solid disc on the pan—$\delta T_0'$ of Figs. 2 and 5.

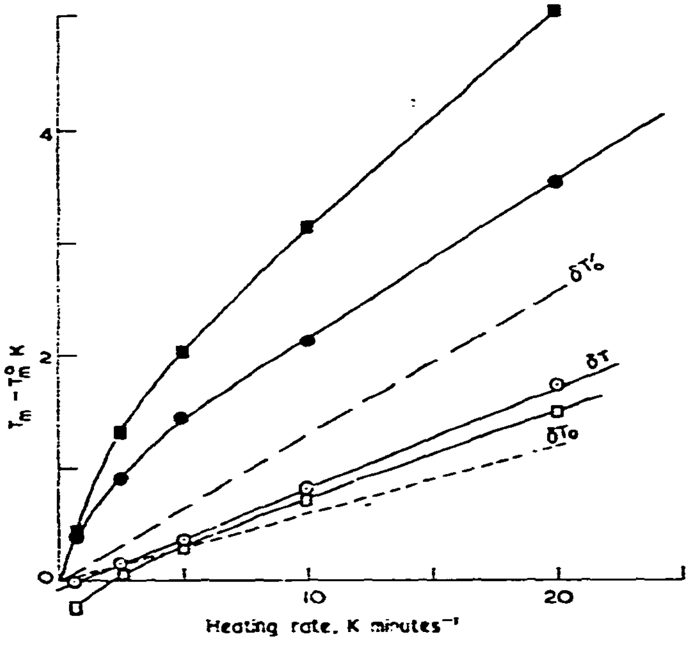

Fig. 5. Instrumental and material parameters for several heating rates. Broken and dotted lines as in Fig. 1. T_m is the melting point defined by the extrapolated leading edge (○, □) or the peak temperature (●, ■). ○, ● indium; □, ■ acetanilide.

Very pure materials are essential for the dynamic melting calibration as emphasised by the results for 99.9% acetanilide. Although orders of magnitude less pure than the indium, this figure is high for an organic compound. Premelting distorts the leading edge data and the onset temperatures in Fig. 5 are seen to dip well below the origin.

Specific heats

Errors in sample temperatures due to the inflexibility of conventional methods of calibration are given by the difference between any of the full lines of Fig. 1 and the line δT of Fig. 5. Values range from 2 to 3.5 K for the particular sapphire discussed. For smaller samples the calibration given by δT will tend to δT_0 and temperature errors will be unimportant with the weights normally used for, say, heat of fusion determinations. We are more concerned with the relatively massive amounts used in the measurement of heat capacity. Here it is by no means uncommon to find that temperatures in poorly packed organic samples are 7 or 8 K lower than indicated by δT. Fortunately errors of this magnitude do not automatically imply corresponding errors in calculated c_p values, this is because the technique is such that errors tend to cancel when the sample and reference materials have similar values of thermal lag and $\partial c_p/\partial T$. The greater the deviations from these conditions the larger the errors become. Typically, c_p will increase by a few tenths of a percent per degree and systematic errors of 1 or 2% are by no means uncommon. In exceptional cases the error may be much greater, near a magnetic transition, for example, where the equilibrium specific heat temperature curve has a large negative slope[8].

It is clear from the above that, depending on circumstances, DSC determinations of specific heat are subject to a broad spectrum of systematic errors when a fixed temperature calibration is used. Judicious choice of sample size and geometry can minimise errors but a major advantage of the DSC is lost thereby—an ability to accept any type of sample. This versatility need not be sacrificed when sample temperatures are corrected by the method described in this paper.

CONCLUSIONS

Heat transfer within a DSC-2 cell is very efficient. The main causes of lag in a heated instrument are the several interfaces, which are unavoidable when a cell is filled with a loaded sample pan, and the finite size of the specimen itself. The conventional temperature calibration, using the known melting points of a set of pure materials, refers to what is essentially a "zero weight" condition so that in the large samples used in specific heat determinations temperatures may lag several degrees behind those suggested by such a calibration. Calculated specific heats can thus be in error by several percent. These problems may be overcome by using the calibration discussed in this paper which uses individual thermograms and so makes allowance for variations from sample to sample.

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