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Differential Scanning Calorimetry

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1.1   INTRODUCTION

Whenever a material undergoes a change in physical state, such as melting or transition from one crystalline form to another, or whenever it reacts chemically, heat is either absorbed or liberated. Many such processes can be initiated simply by raising the temperature of the material.

Modern differential scanning calorimeters are designed to determine the enthalpies of these processes by measuring the differential heat flow required to maintain a sample of the material and an inert reference at the same temperature. This temperature is usually programmed to scan a temperature range by increasing linearly at a predetermined rate.

The apparatus can also be used to measure heat capacity, thermal emissivity and the purity of solid samples. In addition, it can be used to yield phase diagram information and to provide kinetic data.

In this chapter, we set out to show the precision and scope of differential scanning calorimetry (DSC), in the hope that it may be used more widely and with discrimination for the determination of basic thermodynamic and kinetic quantities. Attention will be focused on developments reported during the past four years. A bibliography[1] of literature on DSC, up to February 1970, has been compiled by the Perkin-Elmer Corporation.

Over 200 papers have appeared in the literature since early 1970, which report the use of differential scanning calorimetry. Although DSC yields data which are inherently more quantitative and more amenable to theoretical interpretation than the technique of differential thermal analysis (DTA), it does not seem to have been used as widely as the latter. The DSC technique has been applied, however, to diverse types of compounds, and reviews on the application of DSC to petroleum products[2], plastics[3], biological systems[4] and metal complexes[5] have appeared.

Most of the recent reviews[6-12] on DSC technique have been brief. However, Barrall and Johnson[13] have reviewed the subject in some detail, particularly on aspects relevant to polymer research. Wendlandt has surveyed the commercially available instrument for both DSC and DTA[14], and also reviewed thermal methods of analysis from an analytical viewpoint[15]. Redfern[16] has indicated some of the trends in the general field of thermal analysis.

1.2   THEORY

The somewhat indiscriminate use of the terms DSC and DTA has made it necessary for the IUPAC to offer definitions of these processes in a recent

(a) Classical DTA

(b) 'Boersma' DTA

(c) DSC
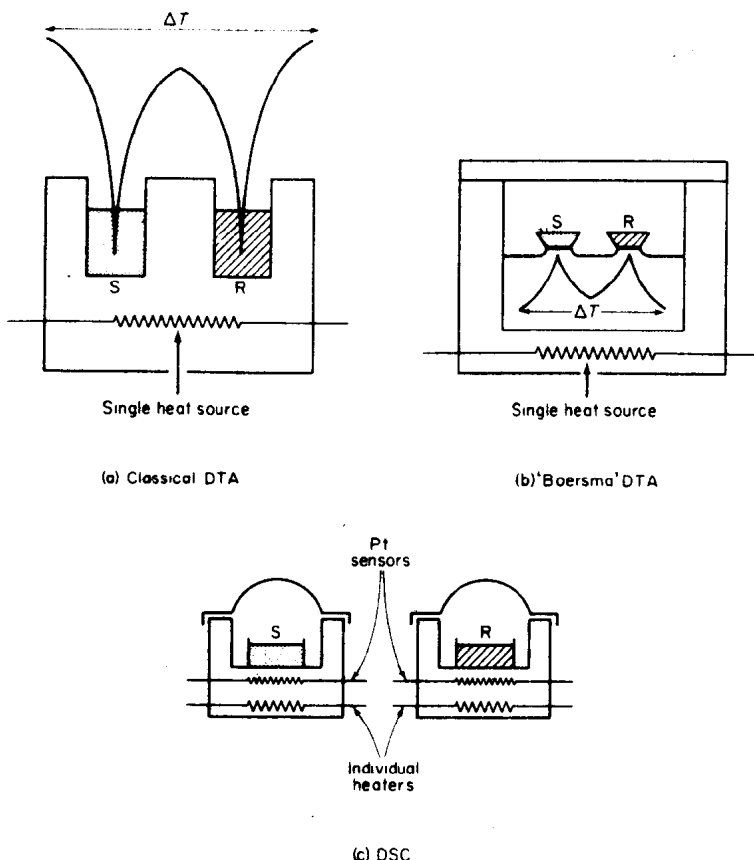
Figure 1.1 Schematic representation of the three principal thermal analysis systems. (From Ref. 18, by courtesy of the Perkin-Elmer Corporation.)

communication[17] on nomenclature. Our first task, therefore, is to describe, very briefly, the principles of differential thermal systems in general, and, in more detail, the theory of differential scanning calorimetry in particular.

The purpose of differential thermal systems is to record the difference between the enthalpy change which occurs in a sample and that in some inert reference material, when they are both heated. These systems may be classified[18] into three types as follows: (a) classical DTA; (b) 'Boersma' DTA; and (c) DSC. The most important differences between these three types are illustrated in Figure 1.1.

1.2.1 Classical and 'Boersma' DTA

In the classical and Boersma DTA systems, both sample and reference are heated by a single heat source. Temperatures are measured by sensors embedded in the sample and reference material (classical), or attached to the pans which contain the material (Boersma). A plot is made, usually by

means of a recorder, of the temperature difference, $\Delta T = T_s - T_r$, between sample and reference, as ordinate, against time as absicissa. The magnitude of ΔT, at a given time, is proportional to (a) the enthalpy change, (b) the heat capacities and (c) the total thermal resistance to heat flow, R. High sensitivity requires a large value of R, but unfortunately the value of R depends on the nature of the sample, the way it is packed into the sample pan and the extent of thermal contact between sample pan and holder; also, R varies with temperature. Attachment of the temperature sensors to the pans in the Boersma method is made in an attempt to reduce the effect of variations in the thermal resistance caused by the sample itself.

With neither of these DTA systems is it possible to make a simple conversion of the peak area, from a plot of ΔT against time, into energy units. This is because of (a) the need to know the heat capacities and (b) the variation of R, and hence the calibration constant, with temperature. Consequently, DTA systems are not very suitable for calorimetric measurements[19]. Brennan[20] has considered mathematical models of the two types of DTA (and also DSC), whilst Miller et al.[21] have carried out a statistical evaluation of the precision and accuracy with which enthalpic measurements can be made with indirect, Boersma-type DTA. Comprehensive reviews of DTA have been written recently by Mackenzie[22] and by Murphy[23, 24].

For the remainder of this chapter the technique referred to as DSC is specifically that described below* and any other thermal analysis method, in particular Boersma-type DTA, which may have been described as 'differential scanning calorimetry' in the literature will be referred to as 'indirect DSC', although we shall have little cause to comment extensively on such work.

1.2.2   Differential scanning calorimetry (DSC)

The important difference between the DTA and DSC systems is that in the latter the sample and reference are each provided with individual heaters.
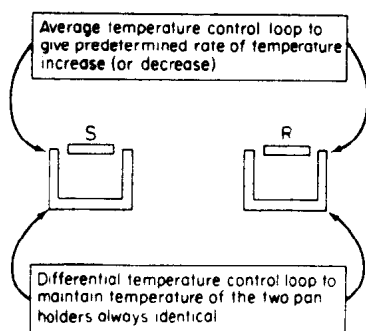

Figure 1.2 Schematic representation of the DSC control loops

* The theory of DSC and its use in thermoanalytical instrumentation is proprietary to the Perkin-Elmer Corporation (U.S. Patent 3 263 484).

This makes it possible to use a 'null-balance' principle. It is convenient to think of the system as divided into two control loops, shown schematically in Figure 1.2. One is for average temperature control, so that the temperature, T_p, of the sample and reference may be increased at a predetermined rate, which is recorded. The second loop ensures that if a temperature difference develops between the sample and reference (because of exothermic or endo-thermic reaction in the sample), the power input is adjusted to remove this difference. This is the null-balance principle. Thus, the temperature of the sample holder is always kept the same as that of the reference holder by continuous and automatic adjustment of the heater power. A signal, propor-tional to the difference between the heat input to the sample and that to the reference, dH/dt, is fed into a recorder. In practice, this recorder is also used to register the average temperature of the sample and reference.
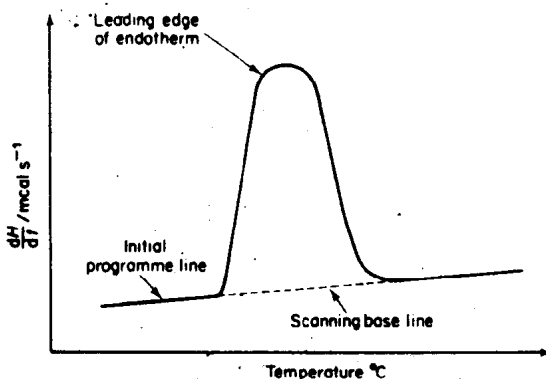
Figure 1.3 Idealised DSC thermogram

Figure 1.3 shows an idealised thermogram or record of the differential heat input, dH/dt, against temperature, T (or time, t, on the same axis). The most advanced commercial instrument, the Perkin-Elmer DSC-2, provides a maximum sensitivity of 0.1 mcal s^{-1} for a full-scale deflection, and is normally used with milligram quantities of sample. The operational tempera-ture range is from -175 to $+725°C$.

Details of the theory and design of differential scanning calorimeters have been given by Watson et al.[25] and by O'Neill[26]. Some of the more important points are the following.

In this technique the thermal mass of the sample and reference holders is kept to a minimum, the thermal resistances are reduced as much as possible and a high 'loop gain' in the closed loop of the differential power control circuit is used. These measures ensure that the response of the system is short. Consequently, the assumption that the sample and reference holders are always at the same temperature, T_p, is valid. The response of the system depends on the thermal resistance between the holders and surroundings, R (Figure 1.4), but this is unaffected by a change in the sample. Also, for a small

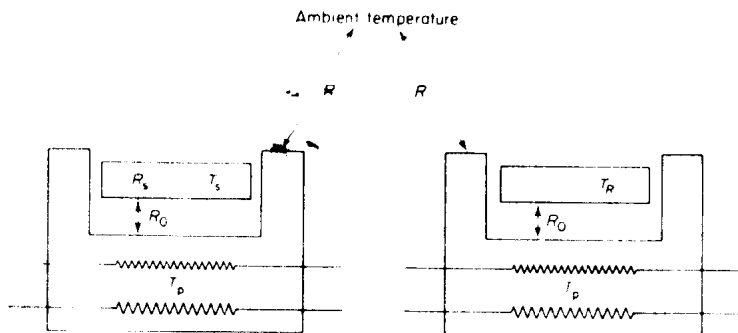**Figure 1.4** Thermal resistances in the DSC system. (From Ref. 18, by courtesy of the Perkin-Elmer Corporation.)

sample weight in close contact with its sample pan, the thermal resistance of sample and pan, R_s, is very small at a moderate scanning rate compared with the resistance between pan and holder, R_0.

Gray[19] has investigated the effect on dH/dt of the magnitude of R_0 in differential scanning calorimetry. He has shown that the slope of the leading edge of a melting endotherm of a pure sample is given by $(1/R_0)(dT_p/dt)$, where (dT_p/dt) is the programmed scanning rate. This relation is used subsequently to indicate how the true melting point of a sample may be obtained from a melting endotherm. Although variations in R_0 affect the peak shape, the peak area is unchanged. An infinitely sharp peak is obtained when R_0 is zero. (This is in contrast to DTA, where a variation in R_0 does affect the peak area, and the instrument sensitivity is proportional to the value of R_0).

1.3   OPERATION

Before any quantitative measurements are made the calorimeter must be calibrated to obtain a calibration constant in units of mcal (unit area)$^{-1}$ and to fix the temperature scale accurately. Correct sampling techniques must also be used. These aspects are now considered in some detail, with particular reference to the Perkin-Elmer instruments, which are the ones in most general use.

1.3.1   Sampling techniques

The method of encapsulation of samples most widely adopted is the use of an aluminium pan with a domed lid which may be crimped in position. The qualitative appearance of a thermogram will be affected by the sample configuration but there is no effect on the peak area. For optimum peak sharpness and resolution, the contact surface between pan and sample should be maximised, i.e. thin discs, or films, or fine granules should be used.

The normal lid-crimping procedure gives a tightly, but not hermetically, sealed pan. However, the introduction of a special volatile-sample pan, which may be completely sealed[27], has made possible the wider application of DSC to liquid samples and solids which have high vapour pressures. The limit of internal pressure which these hermetically-sealed volatile-sample pans can withstand is ca. 2–3 atm. Samples which are sensitive to oxidation in the temperature range of interest can be sealed in these special sample pans in an inert atmosphere. An ultra-high-pressure sample cell has been described[28], but its high mass causes less precision in the enthalpy data which can be obtained.

For materials that interact with aluminium sample pans, gold pans are available. An alternative method (and cheaper!) is described by Wendlandt[29], who proposes the use of glass capillary melting-point tubes for corrosive substances. When completely sealed, these could also be used for liquids and solutions. Taylor *et al.*[30] have described the use of a sealed, flint glass ampoule which enables DSC data to be obtained at high internal pressures and with highly corrosive compounds. Owing to the lower thermal conductivity of the flint glass relative to that of aluminium, the DSC peaks were broader, but good quantitative results were still obtained. Water-filled ampoules of this kind could withstand internal pressures greater than 30 atm before breaking.

1.3.2 Calibration

Use is frequently made of high-purity metals with accurately known enthalpies of fusion as calibration standards. The most commonly used calibrant is indium, ΔH(fusion) $= 6.80$ cal g^{-1}, m.p. 156.4°C. Between 5 and 10 mg are weighed in an aluminium sample pan on a microbalance and a thermogram of the melting peak is run at a selected heating rate, $(\mathrm{d}T_p/\mathrm{d}t)$, sensitivity (range) and chart speed of the recorder. The scanning base line (Figure 1.3) is drawn in from the point at which the trace begins to depart from the initial programme line to the point at which the trace returns to the programme line. The area between the interpolated base line and peak is integrated by some device, usually a planimeter. However, this gives a precision of only $\pm 1\%$ at best, so that as DSC instrumentation becomes more sophisticated more precise integrating techniques should be adopted[31]. The information is then used to calculate the calibration constant, k, in mcal (unit area)$^{-1}$ from the relationship

$$k = \frac{\Delta H(\text{fusion}) \times m_c}{A_c} \quad [\text{in mcal (unit area)}^{-1}]$$

where ΔH(fusion) is the enthalpy of fusion of the calibrant in mcal mg^{-1}, m_c is the mass of calibrant in milligram and A_c is the peak area of the calibration thermogram.

The value of k can be used to find enthalpy values, ΔH_s, for some other sample from the relationship

$$\Delta H_s = \frac{k \times C_s \times r_c \times M \times A_s}{C_c \times r_s \times m_s} \times 10^{-3} \ (\text{kcal mol}^{-1})$$

where C_c and C_s are the chart speeds used for calibration and sample run, respectively; r_c and r_s are the sensitivity (range) settings, in mcal s⁻¹ used for calibration and sample run, respectively; M·is the molecular weight of the sample; m_s is the mass of the sample in milligrams; and A_s is the peak area of the sample thermogram. It is important for precise work to ensure that the heating rates used for the calibrant and sample are the same to ensure that R_0 is kept constant.

Since the calibration constant for the earlier Perkin-Elmer DSC-1 and DSC-1B instruments is to some extent temperature-dependent, it should be determined at several temperatures by using various calibrating substances. Barrall and Johnson[13] have suggested that k may be ~20% greater at 330°C than it is at 60°C. This seems a very pessimistic conclusion and is not in agreement with observations by Schwenker and Whitwell[32], who suggest a calibration coefficient that varies by only ~4% over the temperature range 156–420°C. An indication of whether a multipoint calibration is needed can be obtained by checking enthalpy values for certain well-documented reactions occurring at temperatures far removed from the calibration temperature, as carried out by Mortimer and co-workers[33, 34]. However, the calorimetric response over the entire temperature range can be assumed constant for the most recent Perkin-Elmer DSC-2 instrument. This is shown in Table 1.1[35] by a comparison between literature values for ΔH(fusion) of metals which melt over a wide temperature range and those determined by DSC, using indium (m.p. 156.4°C) as a calibrant. The correlation is good even at high temperatures.

Table 1.1   Enthalpies of fusion (cal g⁻¹) of metals based on ΔH(fusion) of indium (6.80 cal g⁻¹)

	Tin	Lead	Zinc	Aluminium
M.p./°C	231.9	327.4	419.5	660.4
ΔH(fusion) [measured]	14.40 ± 0.01	5.45 ± 0.01	25.9 ± 0.1	94.9 ± 0.3
ΔH(fusion) [literature]*	14.24 ± 0.25	5.55 ± 0.14	26.6 ± 0.5	92.7 ± 1.1

* Kubaschewski, O. and Evans, E. L. (1958). *Metallurgical Thermochemistry*, 4th edn. (New York: Pergamon Press)

Errors can arise over the drawing in of the scanning base line, but for cases where the specific heat change during the transition is not very great the procedure described already is satisfactory.

1.3.3 Temperature correction

The endotherm corresponding to fusion of a compound may be used to determine the melting point of a substance. Two major corrections must be made to obtain these melting points to within ±0.2°C.

(a) If the calorimeter has been calibrated by the use of indium, then for samples which melt at temperatures significantly greater or less than
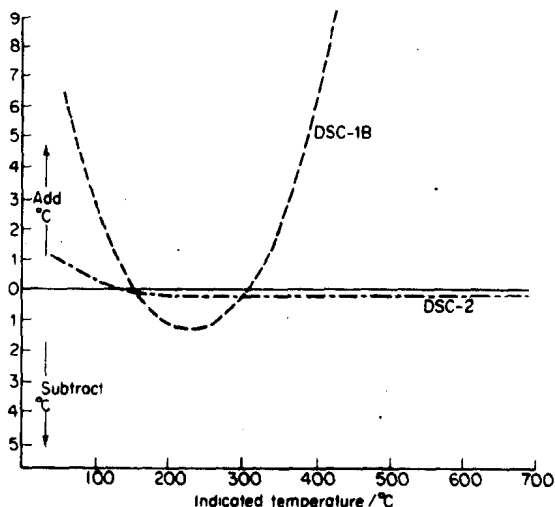
Figure 1.5 Temperature calibration correction curves for the Perkin-Elmer instruments DSC-1B and DSC-2. (From O'Neill and Fyans[36], by courtesy of the Perkin-Elmer Corporation.)

156 °C the temperature indicated on the instrument dial may be inaccurate. Hence, a correction curve to the indicated temperature should be constructed (Figure 1.5). In the latest Perkin-Elmer instrument, the DSC-2, this non-equivalence of programmed and observed temperature has been reduced. This is indicated in Figure 1.5, which shows the temperature calibration curve for two models of the instrument. For the highest accuracy in the determination of melting points, however, such curves should still be used.

' (b) Even having made this temperature calibration, the temperature of the vertex of the thermogram peak is not strictly the transition temperature. For a small sample and a slow heating rate, the resistance to heat flow between sample pan and holder, R_0, results in a lag between the temperature of the sample pan (which is taken to be the same as that of the sample) and the temperature of the pan holder. The thermal lag can be calculated by running a thermogram of the melting of a very pure compound in the temperature range of interest. The slope of the leading edge of the resulting endotherm is $(1/R_0)(dT_p/dt)$, as indicated in Figure 1.6[36]. Hence, the true melting point of a sample, say triphenylmethane, for which the melting thermogram is shown in Figure 1.7, is given by the point **B**, rather than A. Often the 'isothermal' true base line corresponding to a sample of zero specific heat is not constructed and the intersection with the scanning base line, B', gives a sufficiently accurate temperature value.

Obviously, if the value of R_0 varies during the work on measurement of a transition temperature owing to unclean sample pans or distortion of their bases which are in contact with the holders, then the data will not be reproducible. Also, for each different type of encapsulation, it is clear that
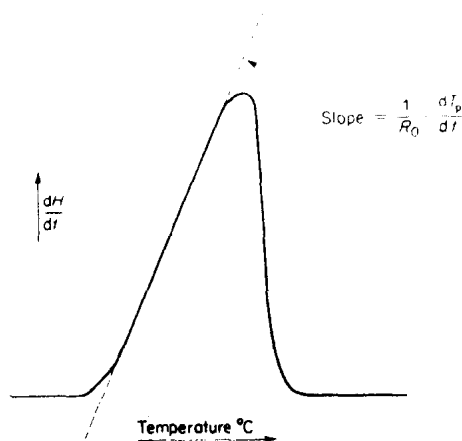
Figure 1.6 Thermogram for the fusion of 99.999 %
pure indium. (From Ref. 36, by courtesy of the
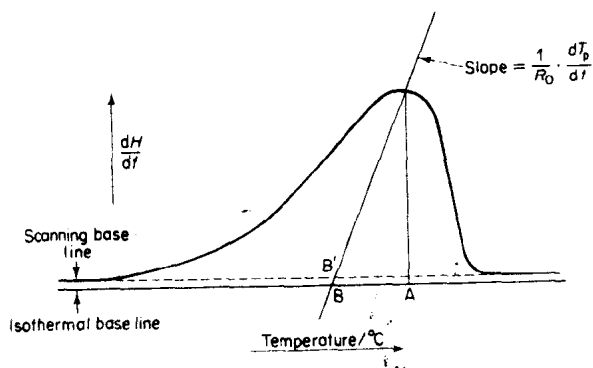Perkin-Elmer Corporation.)

Figure 1.7 Thermogram of the fusion of 99.9 % pure triphenyl-
methane. (From Ref. 36, by courtesy of the Perkin-Elmer
Corporation.)

a separate temperature correction for thermal lag (and temperature calibration) will be needed. Flynn[37] has reviewed the instrumental limitations upon the measurement of temperature and rate of energy production, dH/dt, by differential scanning calorimetry.

Pella and Nebuloni[38] discuss, in detail, the procedures by which DSC temperature data can be obtained to an accuracy of ± 0.1 °C. Many additional conditions must be adopted to ensure such a high degree of accuracy. Some of these are as follows.

(c) Standardisation of pan position in the sample holder.

(d) Use of nitrogen not helium as the flushing gas.

(e) Small and approximately constant sample weight for a given substance; where different substances are examined, sample weights should be chosen so that each absorbs the same amount of heat on fusion.

(f) Organic calibrants should be used for calibrating the temperature scale when organic substances are being investigated, because of the much greater thermal conductivity of metal calibrants.

(g) Standardisation of sample geometry is necessary. Brennan *et al.*[39] have discussed the effect of the thermal resistance value, R_0, on the measurement of temperatures and on kinetic data from DSC. They conclude that the thermal resistance between sample and pan, R_s, though small may be significant. The adoption of only one standard calibrant to establish a thermal lag correction for use with other materials is not satisfactory, since the resistance, R_s, depends on the sample contact area.

It is clear, therefore, that to obtain reproducible and accurate temperature data to ± 0.1 °C extreme care is needed, mainly through the need to maintain the values of both R_0 and R_s small and constant for the duration of the experimental study. For reproducible and accurate enthalpy data, it is perhaps true to say that fewer conditions need be imposed since the area of integration of a plot of dH/dt against time is less dependent on the variation of R_0 (and R_s). Examples of the use of DSC to obtain enthalpy and temperature data are given in Section 1.4.9.

1.3.4 Specific heats

When a sample material is subjected to a linear temperature increase, the rate of heat flow into the sample is proportional to its instantaneous specific heat. By regarding this rate of heat flow as a function of temperature and comparing it with a standard material under the same conditions, we can obtain the specific heat, C_p, as a function of temperature. The procedure has been described in detail elsewhere[13, 40, 41]. O'Neill[40] claims a precision in specific heat determinations of 0.3% or better.

The procedure is briefly described as follows. Empty aluminium pans are placed in the sample and reference holders. An isothermal base line is recorded at the lower temperature and the temperature is then programmed to increase over a range. An isothermal base line is then recorded at the higher temperature as indicated in the lower part of Figure 1.8. The two isothermal base lines are used to interpolate a base line over the scanning section as shown in the upper part of Figure 1.8. The procedure is repeated
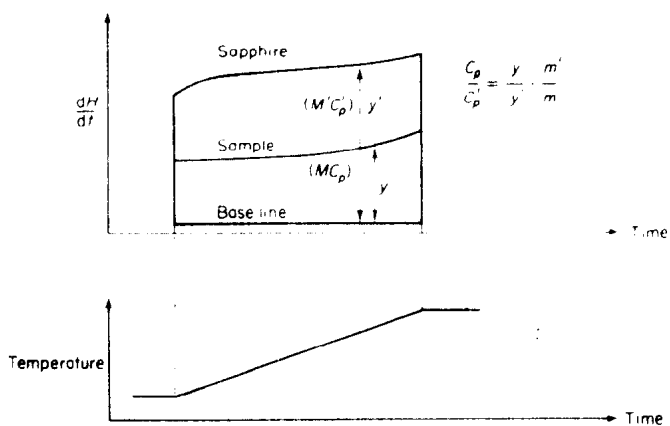
Figure 1.8   Specific heat determination by ratio method. (From O'Neill[40], by courtesy of the American Chemical Society.)
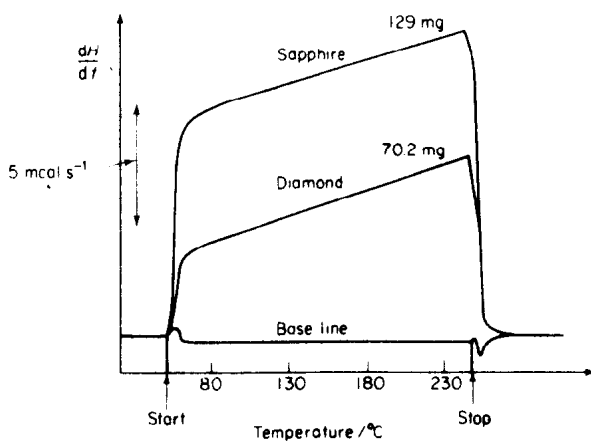

Figure 1.9   Base-line calibration and sample analysis. (From O'Neill[40], by courtesy of the American Chemical Society.)

with a known mass of sample in the sample pan and a trace of dH/dt against time is recorded. There is a pen displacement due to the absorption of heat by the sample, and we may write

$$\frac{dH}{dt} = mC_p \cdot \frac{dT_p}{dt}$$

where m is the mass of the sample in grams, C_p is the specific heat in cal g^{-1} and dT_p/dt is the programmed rate of temperature increase.

This equation could be used to obtain values of C_p directly, but any errors in ordinate read-out, dH/dt, and in programming rate, dT_p/dt, would reduce the accuracy. To minimise these errors the procedure is repeated with a known mass of sapphire, the specific heat of which is well established[42], and a new trace is recorded. Thus, only two ordinate deflections at the same temperature (y and y' of Figure 1.8) are required to yield a ratio of the C_p values of sample and sapphire. Figure 1.9 shows the traces for diamond and sapphire relative to the trace for two empty aluminium pans.

Since we are necessarily dealing with small changes in heat content, then high sensitivity (1–4 mcal s^{-1}) and high scanning rates (5–20°C min^{-1}) are used, since both of these will increase the magnitude of the ordinates. O'Neill[40] has calculated that the weight variations of the aluminium pans are not likely to cause any significant errors. However, for precise work, Barrall and Johnson[13] recommend the running of a reference sapphire trace each time an unknown material is investigated in the same sample pan in which the unknown is to be contained.

The pen displacement results not only from the specific heat of the sample but also from the difference between the thermal emissivity of the sample and empty pan. This error is reduced markedly by the use of a metal cover on the pan holders and by locating the sample and reference material in the same relative positions inside the pans. Other errors likely to arise in specific heat measurements by DSC are as follows.

(a) Slow phase transformation caused by recrystallisation of the sample on heating.

(b) Poor thermal contact between the base of the sample pen and holder.

(c) Differences in the shapes of sample and sapphire standard.

(d) Errors in linearity of the dH/dt read-out. This can be obviated by choosing a sample size to give an ordinate deflection which is virtually the same for sample and standard.

(e) Errors in linearity of the temperature scale.

The figure of precision, 0.3%, is nearly that of data obtained by adiabatic calorimetry, but the advantage of the DSC method is the speed with which data can be obtained and the small sample size required. Excellent agreement between specific heat data obtained from DSC and from classical techniques has been reported[40].

The DSC technique for specific heat determinations is capable of detecting discontinuities in the heat capacity function, such as 'glass' transitions and Curie point transitions and the temperatures at which these occur. An example of this, for a polycarbonate resin, is shown in Figure 1.10.

The specific heat determination of liquids can be carried out in the same way if volatile-sample pans and the hermetic-sealing process are used.
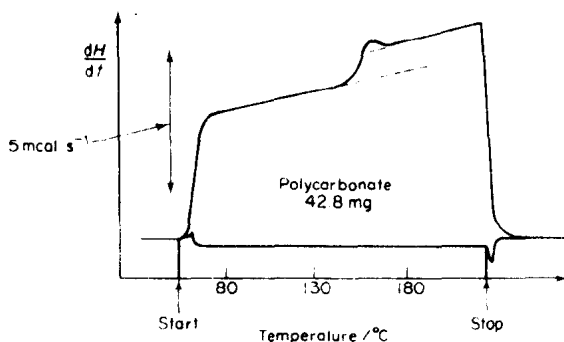
Figure 1.10 Specific heat discontinuity in a polycarbonate resin. (From O'Neill[40], by courtesy of the American Chemical Society.)

Corrections must be made for variations in the mass of the aluminium pans, as they are not re-usable for both the sample liquid and calibrant as are the standard aluminium pans.

Berlin et al.[43] have used DSC to determine the specific heats of the solid proteins ovalbumin and bovine β-lactoglobulin containing known amounts of adsorbed water, varying between 20 and 250 mg of adsorbed water per gram of protein. Hermetically sealed volatile-sample pans were used to prevent the adsorption or desorption of water vapour during the specific heat determinations

The identification and characterisation of plastic crystalline materials can be carried out directly by DSC. Rogers and Ortiz[44] have obtained the heat capacity as a function of temperature for such a compound, 2,2-dinitro-propane, over the temperature range -53 to $+127\,°C$, which clearly shows the appearance of a plastic crystalline phase.

1.3.5 Base-line correction in enthalpy measurements

In those cases where there is little change in heat capacity before and after a transition, the simple 'drawing-in' of a scanning base line (Figure 1.3) is sufficiently accurate. However, in cases where the change in specific heat is large, or where high scanning rates are used, a more rigorous method of establishing the base line must be used. This is also necessary to establish precise enthalpy and temperature data, or kinetic parameters.

Brennan et al.[45] have suggested a method which allows the enthalpy changes, ΔH, to be isolated from the heat capacity changes. Figure 1.11 illustrates the principle behind their correction. It shows a thermogram for the thermal pyrolysis of a sample of cotton. The observed trace follows curve 1, i.e. AMB. The point A is displaced upwards from A' on the base line A'B' because of the specific heats of cotton and pans, while the point B is displaced upwards from B' because of the specific heat of the pyrolysis
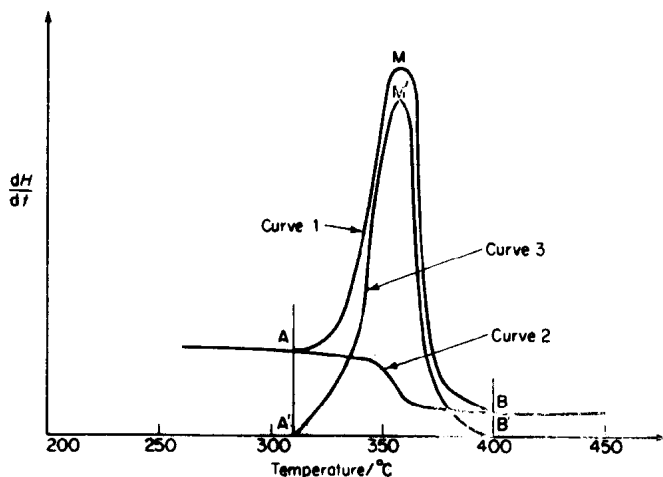
Figure 1.11 Correction of observed enthalpy data for the change in heat capacity. (From Rogers and Ortiz[45], by courtesy of the American Chemical Society.)

products and pans. If the enthalpy of pyrolysis had been zero (a thermo-neutral reaction), then the trace would have followed curve 2, joining A and B, which shows the varying specific heat of cotton and pyrolysis products. The points on the observed thermogram, AMB, are corrected for the specific heat effect and the result is the thermogram A'M'B' (curve 3). The area of the peak A'M'B' above the base line A'B' represents the enthalpy change for reactants and products for which $\Delta C_p = 0$.

This method of correction of the observed enthalpy data for a change in specific heat specifically assumes that there is no thermal lag in the system, so that it can be applied rigorously only to transitions which occur over a wide temperature interval. For the most precise determination of the base line, Heuvel and Lind[46] have developed a theory which takes into account not only the heat capacity difference between initial and final states but also the thermal lag. They have incorporated their theory into a computer program which also performs a correction for non-linearity of the temperature calibration.

Guttman and Flynn[47] suggest that the base line can be obtained by extra-polating the initial and final base lines to the thermodynamic transition temperature (determined by the method indicated in Section 1.3.3). The enthalpy of the transition is then given by the area under the curve of dH/dt against time, using this new base line. Their method is by no means as general as that of Brennan et al.[45] or Heuval and Lind[46], but it is easy to use.

1.4   APPLICATIONS

Differential scanning calorimetry has been used to determine physical constants of substances and also to measure the enthalpies of both chemical

reactions and phase changes. The examples which follow are chosen to
illustrate these applications.

1.4.1 Thermal conductivity

Brennan[20] has described the adaptation of DSC to measure the thermal
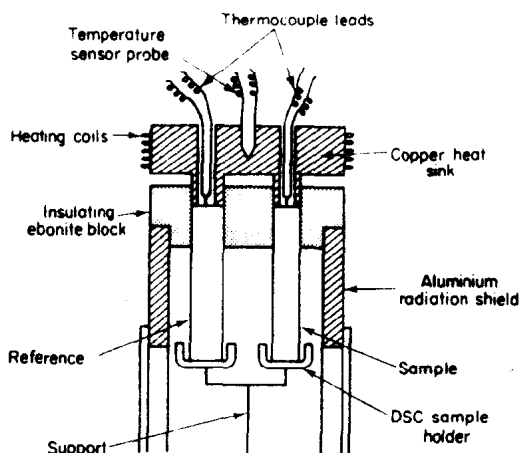conductivities of cylindrical specimens placed upright in each sample holder.

Figure 1.12 Thermal conductivity apparatus. (From
Brennan[20], by *courtesy of Princeton University, New
Jersey*.)

The arrangement is shown in Figure 1.12. The temperature, T_0, of the pan
holders and the copper heat sink is made the same and a steady-state base
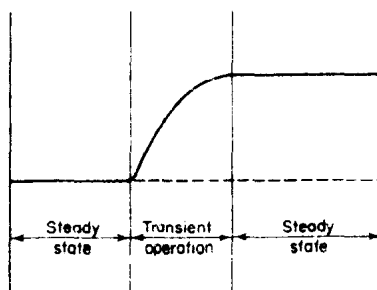line is recorded (Figure 1.13). Under these circumstances there is no heat

Figure 1.13 DSC output for thermal conduc-
tivity measurements. (From Brennan[20], by
courtesy of Princeton University, New Jersey.)