Differential Scanning Calorimetry

Introduction

Differential scanning calorimetry (DSC) is a technique for measuring the energy necessary to establish a nearly zero temperature difference between a substance and an inert reference material, as the two specimens are subjected to identical temperature regimes in an environment heated or cooled at a controlled rate.

There are two types of DSC systems in common use (Fig. 1). In power–compensation DSC the temperatures of the sample and reference are controlled independently using separate, identical furnaces. The temperatures of the sample and reference are made identical by varying the power input to the two furnaces; the energy required to do this is a measure of the enthalpy or heat capacity changes in the sample relative to the reference.

In heat–flux DSC, the sample and reference are connected by a low–resistance heat–flow path (a metal disc). The assembly is enclosed in a single furnace. Enthalpy or heat capacity changes in the sample cause a difference in its temperature relative to the reference; the resulting heat flow is small compared with that in differential thermal analysis (DTA) because the sample and reference are in good thermal contact. The temperature difference is recorded and related to enthalpy change in the sample using calibration experiments.

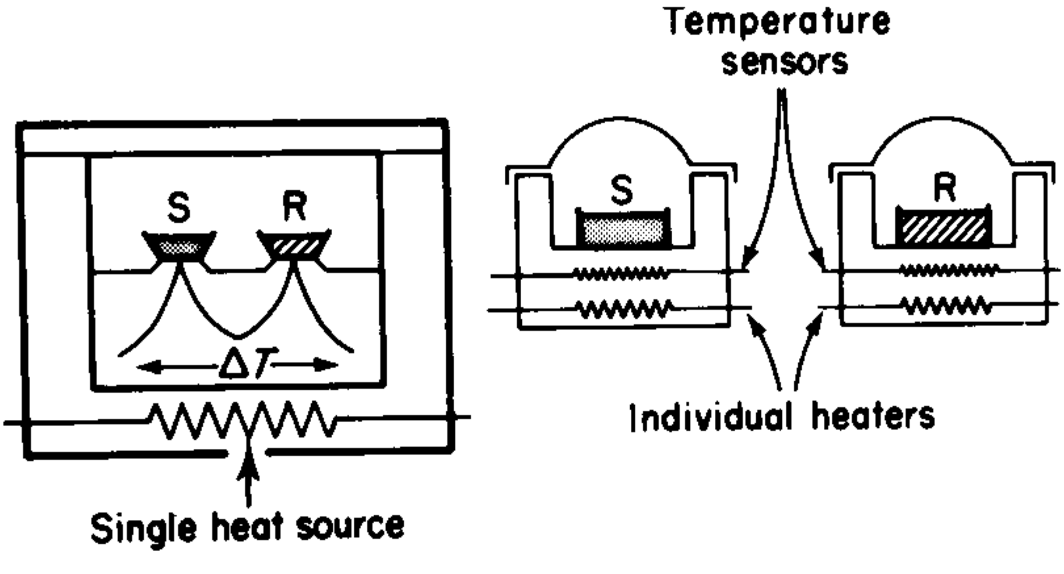

Fig. 1: (a) Heat flux DSC; (b) power–compensation DSC

Heat–flux DSC

This section is based largely on a description of the Dupont DSC system by Baxter and Greer. The system is a subtle modification of DTA, differing only by the fact that the sample and reference crucibles are linked by good heat–flow path. The sample and reference are enclosed in the same furnace. The difference in energy required to maintain them at a nearly identical temperature is provided by the heat changes in the sample. Any excess energy is conducted between the sample and reference through the connecting metallic disc, a feature absent in DTA. As in modern DTA equipment, the thermocouples are not embedded in either of the specimens; the small temperature difference that may develop between the sample and the inert reference (usually an empty sample pan and lid) is proportional to the heat flow between the two. The fact that the temperature difference is small is important to ensure that both containers are exposed to essentially the same temperature programme.

The main assembly of the DSC cell is enclosed in a cylindrical, silver heating black, which dissipates heat to the specimens via a constantan disc which is attached to the silver block. The disc has two raised platforms on which the sample and reference pans are placed. A chromel disc and connecting wire are attached to the underside of each platform, and the resulting chromel–constantan thermocouples are used to determine the differential temperatures of interest. Alumel wires attached to the chromel discs provide the chromel–alumel junctions for independently measuring the sample and reference temperature. A separate thermocouple embedded in the silver block serves a temperature controller for the programmed heating cycle. An inert gas is passed through the cell at a constant flow rate of about 40 $\mathrm{ml\,min^{-1}}$).

The thermal resistances of the system vary with temperature, but the instruments can be used in the 'calibrated' mode, where the amplification is automatically varied with temperature to give a nearly constant calorimetric sensitivity.

Heat Flow in Heat–Flux DSC Systems

A variety of temperature lags develop between the specimens and thermocouples, since the latter are not in direct contact with the samples. The measured ΔT is not equal to $T_S - T_R$ where T_S and T_R are the sample and reference temperatures respectively. $T_S - T_R$ may be deduced by considering the heat flow paths in the system.

The following additional notation (due to Greer and Baxter) is relevant (Fig. 2):

T_{SP}, T_{RP} = Temperature of the sample and reference platforms, respectively, as measured by the thermocouples. T_{SP} is normally plotted as the abscissa of a DSC curve.

T_F = Temperature of the silver heating block.

R_D =Thermal resistance between the furnace wall and the sample or reference platforms (units $\mathrm{C\,min\,J^{-1}}$).

R_S, R_R = Thermal resistances between the sample (or reference) platform and the sample (or reference).

C_S, C_R = Heat capacity of the sample (or reference) and its container.

H = Imposed heating rate.

ΔT_R = Temperature lag of the reference platform relative to furnace.

ΔT_S = Temperature lag of the sample platform relative to furnace.

ΔT_L = Temperature lag of the sample relative to the sample thermocouple.

The following equations then hold:

$$\Delta T_R = H R_D C_R \tag{1}$$

$$\Delta T_S = H R_D C_S \tag{2}$$

$$\Delta T = H R_D (C_S - C_R) \tag{3}$$

$$\Delta T_L = H R_S C_S \tag{4}$$

$$\Delta T_S = \Delta T_R + \Delta T \tag{5}$$

$$\Delta T_L = R_S / R_D \Delta T_S \tag{6}$$

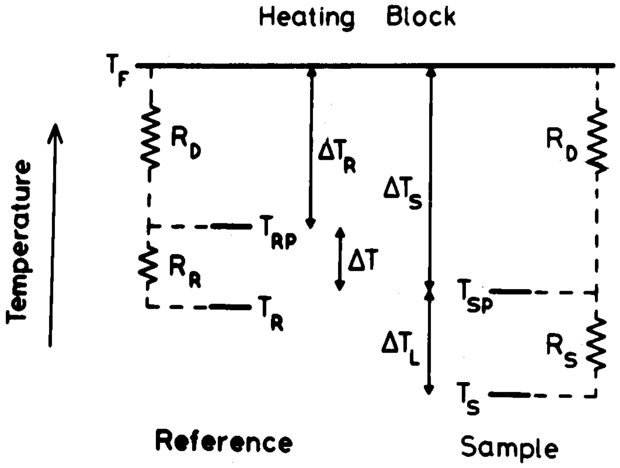

Fig. 2: Thermal resistance diagram representing a heat–flux DSC

Calibration: The Temperature Lag ΔT_L

ΔT_L is non–zero because the thermocouple is not in direct contact with the sample. When the transition temperature T' does not vary with heating rate, equation 4 indicates that a plot of the apparent T' versus H keeping the other quantities fixed, would at zero H extrapolate to the true value of T'; the apparent T' is the true value plus the lag.

A plot of the apparent T' versus C_S would also extrapolate to the true T' at $C_S = 0$, when H and R_S are kept constant.

Alternatively, the sample may be allowed to reach the temperature of the sample–platform by holding at a temperature just beyond T', and recording a DSC curve corresponding to the equilibration event. The area of this curve can then be used to deduce the temperature lag; this kind of an analysis requires more sophisticated equipment than is normally available.

Another method, due to Greer, is based on equation 6, and involves the evaluation of R_S/R_D. ΔT_R is measured for a particular reference, usually just an empty pan and lid. A heating run is first performed with an empty pan on both the sample and reference platforms. This provides a baseline, from which measurements of ΔT can be carried out. A second run is then performed, with two pans on the sample side, and one on the reference side. The difference between the first and second DSC curves is a measure of ΔT_R, as a function of temperature. This becomes evident from equations 1 and 3; for the first run, C_S and C_R are identical and hence $\Delta T = 0$, while for the second run $C_S = 2C_R$, so that $\Delta T = \Delta T_R$.

By repeating this procedure, ΔT_R can be obtained as a function of heating rate. To obtain the temperature lag ΔT_L, more tests are performed, bearing in mind that

$$\Delta T_R + \Delta T = \Delta T_S$$

Tests are conducted at a variety of heating rates, using a sample with a known transition temperature which is independent of heating rate, placed in the sample pan, with an empty pan on the reference side. These experiments give values of ΔT, and hence ΔT_S, as a function of heating rate; the gradient g_1 of the graph of ΔT_S versus heating rate is equal to $R_D C_S$, equation 2. Another set of experiments, based on equation 4 then gives a plot of the apparent transition temperature as a function of heating rate, and extrapolation to zero H yields the true transition temperature – hence a graph of $(T_L$ versus H can be plotted, whose gradient g_2 is equal to $R_S C_S$, equation 4. Hence, $g_1/g_2 = R_D/R_S$. The temperature lag may be calculated (since R_S/R_D and ΔT_R are known) for a given reference and at any heating rate or C_S, using equation 6.

Temperature Calibration

The temperature plotted on the abscissa of a DSC record is related to the emf generated at the thermocouple located under the sample. For standard thermocouple conditions, the emf may be reliably converted to temperature units using established calibration charts, but a variety of effects can cause the thermocouple to age and shift calibration. It is advisable to calibrate the abscissa using substances with precisely known melting points; most DSC instruments have facilities which allow calibration over limited temperature ranges. In changing the abscissa scale to a true temperature reading, allowances have to be made for the thermal lag effect (ΔT_L), but this can be avoided by using very low heating rates for the purposes of calibration.

Calorimetric Calibration

Calibration is carried out by measuring the changes in specific heat or in enthalpy content of samples for which these quantities are known. When the DuPont instrument is used in the calibration mode, the procedure related to equation 2 may be used to measure specific heat changes. The heat balance equation for the heat–flux DSC system can be shown to be as follows:

$$\frac{dH'}{dt} = \frac{T_{SP} - T_{RP}}{R_D} + (C_S - C_R)H + C_S \frac{R_D + R_S}{R_D} \frac{d(T_{SP} - T_{RP)}}{dt} \tag{7}$$

dH'/dt refers to the heat evolution of an exothermic transition; the first term on the right hand side is the area under the DSC peak, after correcting for the baseline. The second term on the right refers to the actual baseline, and it is this which is used in specific heat determinations. The last term takes account of the fact that some of the evolved heat will be consumed by the specimen to heat itself, and does not affect the are under the DSC peak, but may distort the peak shape. From equation 7 it is clear that when dH'/dt can be arranged to be zero, the second term can be used to determine specific heat. The method is involves a comparison of the thermal lag between the sample and reference; the system is first calibrated with a sapphire specimen, so that

$$C_{\text{sapphire}} = EqY/HM$$

where M is the mass of the specimen, E is a calibration constant, C_{sapphire}, the specific heat capacity of the sapphire, q Y–axis range ($\mathrm{J\,s\,mm^{-1}}$) and Y the difference in Y–axis deflection between sample (or sapphire) and blank curves at the temperature of interest.

Enthalpy changes can be determined by measuring the areas under peaks on the DSC curve, when the latter is a plot of ΔT versus time. A relationship of the form indicated in equation 1 then applies, again when the instrument is in the calibrated mode.

The Baseline and the Transformation Curve

In DTA or DSC, it is expedient to conduct experiments either isothermally or with the temperature changing at a constant rate. In the former case, the ordinate value would be plotted against time at isothermal temperature, whereas in the latter case it could be plotted against time or temperature. The following discussion is based on the abscissa being a time axis; the height referred to is that beyond the baseline.

For DTA the height of the curve at any particular time t is a measure of the difference in temperature, ΔT, between the sample and the reference. For power compensated DSC, the height of the curve at some particular time t is a measure of the heat evolving from the sample per unit time, dH'/dt (this also applies to heat flux DSC, after suitable calibration). For either DTA or DSC, one can assume that ΔT is proportional to dx/dt or dH'/dt to dx/dt, respectively. Here, x refers to the volume fraction of transformation, t to the time measured from the point where the appropriate curve departs from the baseline, and H' to the enthalpy change. The constants of proportionality follow from the condition that the total area under the DTA or DSC corresponds to either $x = 1$, or to x equal to some constant value if the transformation terminates prematurely.

This assumes that a reliable baseline can be obtained from the experimental information. The baseline can be visually estimated for sharp peaks without entailing large errors; for broad peaks it is difficult to qualitatively establish the baseline. The problem is complicated by the fact that the DSC instrumental baseline on either side of the peak is not a no–signal line. Even in the absence of a transition, the instrument measures the effect of the heat capacity of the sample, which may vary with temperature. This variation is usually nearly linear, but the curvature becomes noticeable over wide temperature ranges.

One approximation to the baseline is a straight line connecting the start and finish of the transformation. Other methods involve the use of stepped baselines; the parent and product parts of the experimental curve are linearly extrapolated towards the centre of the experimental profile, and are connected by a vertical step at the position of the peak. Again, this method has no fundamental basis. The most reliable way of constructing the baseline is an iterative technique due to Scott and Ramachandrarao. The fractions transformed are first calculated approximately, using a linear baseline between the initial and final points of the reaction. The baselines of the parent and product are then extrapolated under the peak; this gives two separate baselines, since the heat capacities of the parent and pure product differ. The true baseline at any t is taken to be at a position between the extrapolated baselines. The exact positioning of the new baseline between the extrapolated parent and product baselines depends on an estimated value of the amount of product at any time t, using a lever rule type of a calculation. The new baseline generated in this manner can then be used as the starting point of another iteration and the process can be repeated to the desired accuracy. One iteration seems good enough for most purposes.

A subtle correction which has to be taken into account when constructing transformation curves from DSC curves is that the peak shape (rather than peak area) can be expected to be distorted, because some of any energy evolved may serve to the heat sample itself. In continuous heating experiments, the magnitude of this effect can be shown to be proportional to the heat capacity of the sample and to the rate of change of the differential temperature with time.

Autocatalysis and Recalescence

Calorimetric experiments can be adiabatic or isothermal. The temperature is maintained constant in an isothermal experiment, whereas heat is neither added nor removed from the system during an adiabatic experiment. In practice, experiments fall somewhere between the ideal isothermal and adiabatic conditions.

In an experiment where the rate of heat evolution is large relative to the capacity of the calorimeter to maintain isothermal conditions, the specimen temperature rises beyond the desired level, until a steady state is reached. This adiabatic rise in temperature will affect the rate of reaction, which may in term exaggerate the evolution of heat. This effect is known as autocatalysis. Recalescence describes the case where the release of heat reduces the transformation rate.

Kinetics of Glass Crystallisation

Both DSC and DTA have been used to study of the crystallisation of glasses. With few exceptions, the results have been analysed using Johnson–Mehl–Avrami equations with little attention to the mechanism of crystallisation. The general form of the equations is:

$$x = 1 - \exp\{-kt^n\} \tag{8}$$

where x is the volume fraction of transformation at time t, k is a function of transformation temperature, and n is a parameter which can in special cases give an indication of the mechanisms involved. The equation applies to isothermal transformations with the following assumptions:

1. It is assumed that the growth rate is constant, *i.e.* there is no composition change during transformation.
2. Modern calorimetric experiments use small quantities of samples; it is assumed the free surfaces of these samples do not affect the kinetics of transformation.
3. The extended volume concept on which the Avrami equation is based relies on random nucleation.

Activation Energy

The term k is temperature dependent since it is a function of the nucleation and growth rates of the transformation product; for most solid–state transformations both of these processes can be expected to be thermally activated. Consider a transformation in which nucleation is random, the nucleation and growth rates are constant and where growth is isotropic. Equation 8 becomes:

$$x = 1 - \exp\{-Y^3 I t^4/3\} \tag{9}$$

where Y is the growth rate and $I$is the nucleation rate per unit volume. Hence,

$$\begin{aligned} k &= Y^3 I/3 \\ &= C_1(C_2 \exp\{-G_Y/RT\})^3(C_3(\exp\{-GI/RT\}) \\ &= C_4(\exp((-3G_Y - G_I)/RT\}) \end{aligned} \tag{10}$$

where G_Y and G_I are the activation free energies for growth and nucleation, respectively, and both are assumed to be independent of temperature (R is the gas constant). A further assumption is that the growth and nucleation events are both singly activated processes. The activation energies of equation 10 may be lumped together into a single effective activation energy given by G', which is the term really obtained from an analysis using equation 9. G' cannot be isolated using this analysis since x depends on more than just the growth rate.

For isothermal transformation experiments, G' can be obtained plotting the time taken to achieve a fixed amount of transformation (*i.e.* t_x) versus $1/T$, a plot based on equation 11 below, which is derived from equation 10:

$$t_x = C_5 \exp\{G'/nRT\} \tag{11}$$

It is difficult to determine the activation energy from anisothermal experiments. For any thermally activated process, the DTA or DSC peaks will shift with heating rate; Kissinger derived a relationship between the peak shift and the effective activation energy, assuming homogeneous transformation:

$$dx/dt = C_6(1-x)^m \exp\{-G'/RT\} \tag{12}$$

where m is the order of the reaction, and the other terms have their usual meanings. Kissinger showed that

$$\frac{d(\ln\{H/T_p^2\})}{d(1/T_p)} = -\frac{G'}{R} \tag{13}$$

where H is the heating rate used and T_p is the sample temperature at which the maximum deflection in the DTA or DSC curve is recorded. The equation requires that T_p equals the temperature at which the maximum reaction rate occurs.

Most solid–state reactions are not homogeneous, but proceed by nucleation and growth events. Hence the G' value obtained through equation 13 must not be compared with that obtained from isothermal experiments which obey the Johnson–Mehl–Avrami equation. Henderson has shown that for reactions that obey equation 8, a plot of $\ln\{H/T_p^2\}$ versus $1/T_p$ should have a slope of $-G'/nR$ rather than the $-G'/R$ of equation 13.

Marseglia has suggested that the activation energy G' for anisothermal experiments can be deduced from a plot of $\ln\{H/T_p\}$ versus $1/T_p$. The difference between Marseglia and Henderson arises because the former takes account of the variation of k with time, whereas the latter does not. However, the manner in which the dependence of k on time is taken into account is not rigourous:

$$\frac{dk}{dt} = \frac{dk}{dT}\frac{dT}{dt} = \frac{dk}{dT}H$$

Thus, the variation in growth rate with time is not fully accounted for.

Phase Transitions

Thermal analysis techniques have the advantage that only a small amount of material is necessary. This ensures uniform temperature distribution and high resolution. The sample can be encapsulated in an inert atmosphere to prevent oxidation, and low heating rates lead to higher accuracies. The reproducibility of the transition temperature can be checked by heating and cooling through the critical temperature range.

During a first order transformation, a latent heat is evolved, and the transformation obeys the classical Clausius–Clapeyron equation. Second order transitions do not have accompanying latent heats, but like first order changes, can be detected by abrupt variations in compressibility, heat capacity, thermal expansion coefficients and the like. It is these variations that reveal phase transformations using thermal analysis techniques.

Because of the sensitivity of liquid–vapour transitions to pressure, additional precautions are called for when testing for boiling points or enthalpy changes. The ambient pressure is required; the peak area no longer corresponds to the latent heat of vaporisation in any simple way. The transition temperature T' is related to the pressure P by the Clausius–Clapeyron equation

$$\ln\{P\} = L/RT' + C$$

where L is the molar heat of vaporisation and C is an integration constant. L can be obtained using the Clausius-Clapeyron equation and a set of measured P, T' values, assuming L is independent of temperature, that the volume of the vapour phase far exceeds that of the liquid, and that the vapour behaves as an ideal gas.

Greater care is needed when studying solid–solid transitions where the enthalpy changes are much smaller than those associated with vaporisation. Stored energy in the form of elastic strains and defects can contribute to the energy balance, so that the physical state of the initial solid, and the final state of the product, become important. This stored energy reduces the observed enthalpy change.

Polymer Crystallinity

It is assumed that a volume fraction V of the polymer consists of perfectly crystalline material which melts *i.e.* becomes amorphous, over the course of the experiment. The matrix which is not crystalline is assumed to be perfectly amorphous. The transition from the crystalline to the amorphous state is accompanied by a heat of "fusion", written H_{FO} when it occurs at the pure crystal "melting" point T_0. The fraction V of crystalline phase can be determined for a partially crystalline specimen by comparing the measured heat of fusion with H_{FO}. Imagine a DSC experiment in which a partially crystalline polymer is heated from a temperature T_1 to T_2 where the polymer becomes completely amorphous ($T_1 < T_0 < T_2$). The enthalpy changes can be analysed in the following phenomenological sequence (Fig. 3):

a) Both the crystalline and amorphous phases are first heated, without transformation to T_0. The enthalpy change for this process is

$$H_a = V(H_{C,1-0}) + (1 - V)(H_{A,1-0})$$

where the last two terms simply represent the change in heat content of the crystalline and amorphous components, respectively on heating form T_1 to T_0. H_a can be deduced from the DSC curve by measuring the area between the section of the DSC curve obtained before any change in V, linearly extrapolated over the range T_1 to T_0, and the instrumental baseline (*i.e.* the no-sample baseline).

b) At T_0 the crystalline component is allowed to become amorphous. The enthalpy of fusion for this is

$$H_b = VH_{F0}$$

c) The now completely amorphous material is permitted to rise in temperature from T_0 to T_2, so that the enthalpy change is

$$H_c = H_{A,0-2}$$

H_c thus corresponds to the area between the DSC curve and the instrumental baseline, between the temperatures T_0 to T_2.

If the total enthalpy change calculated from the separation of the DSC curve from the instrumental baseline is given by H_{1-2}, then

$$H_{1-2} = H_a + H_b + H_c \qquad \text{and} \qquad V = (H_{1-2} - H_a - H_c)/H_{F0}$$

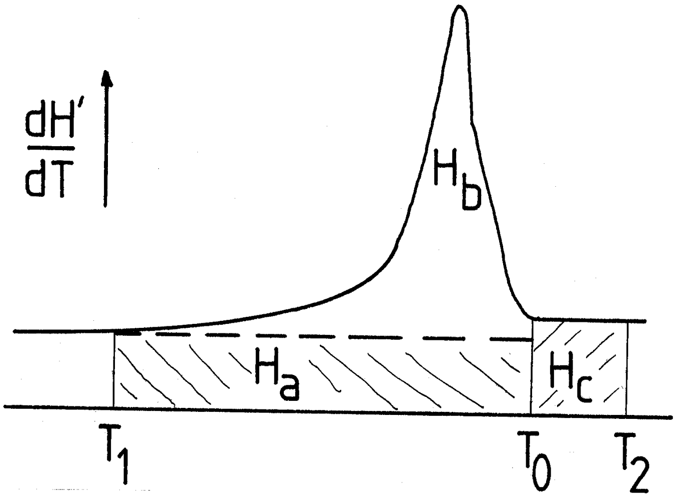

Fig. 3: Analysis of a DSC peak.