

## Chapter 1

# A Practical Introduction to Differential Scanning Calorimetry

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## 1.1 Introduction

Differential scanning calorimetry (DSC) is the most widely used of the thermal techniques available to the analyst and provides a fast and easy to use method of obtaining a wealth of information about a material, whatever the end use envisaged. It has found use in many wide-ranging applications including polymers and plastics, foods and pharmaceuticals, glasses and ceramics, proteins and life science materials; in fact virtually any material, allowing the analyst to quickly measure the basic properties of the material. Many of the application areas are dealt with in greater depth within the chapters of this book, and the principles involved extend to many other materials that may not be mentioned specifically. It is in fact a fascinating technique and the purpose of this introduction is to provide an insight into this method of measurement, to provide the necessary practical guidance a new user will need to go about making measurements, and to give understanding about the information that can be obtained and how to interpret the data.

## 1.2 Principles of DSC and types of measurements made

### 1.2.1 A definition of DSC

A DSC analyser measures the energy changes that occur as a sample is heated, cooled or held isothermally, together with the temperature at which these changes occur.

The energy changes enable the user to find and measure the transitions that occur in the sample quantitatively, and to note the temperature where they occur, and so to characterise a material for melting processes, measurement of glass transitions and a range of more complex

events. One of the big advantages of DSC is that samples are very easily encapsulated, usually with little or no preparation, ready to be placed in the DSC, so that measurements can be quickly and easily made. For further details of instrumental design and basic equations, refer to Section 1.7 at the end of this chapter.

### 1.2.2 Heat flow measurements

The main property that is measured by DSC is heat flow, the flow of energy into or out of the sample as a function of temperature or time, and usually shown in units of mW on the  $y$ -axis. Since a mW is a mJ/s this is literally the flow of energy in unit time. The actual value of heat flow measured depends upon the effect of the reference and is not absolute. What matters is that a stable instrumental response or baseline is produced against which any changes can be measured. The starting point of the curve on the  $y$ -axis may be chosen as one of the starting parameters, and it should be set at or close to zero.

Two different conventions exist for the display of the heat flow curve: one shows endotherms in the downward direction, the other upward. The operator has a choice with most software packages. Traditionally, with heat flux systems (Section 1.7.2) endotherms are shown as going down, since endothermic transitions result in a negative temperature differential, whilst with power compensation systems (Section 1.7.1) they are shown as going up since with this principle endothermic transitions result in an increase in power supplied to the sample. In this chapter data are shown with endotherms up.

The value of measuring energy flow is that it enables the analyst to identify the range of different transitions that may occur in the sample as it is heated or cooled; the main transitions are described in Section 1.5.

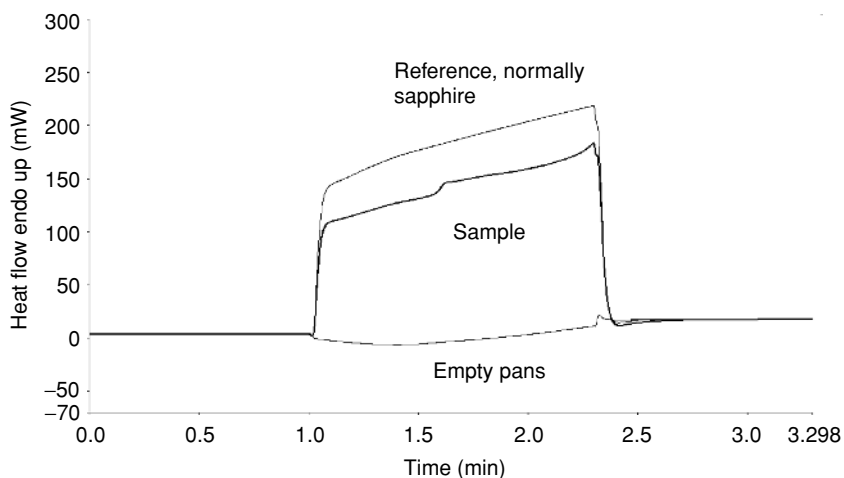
### 1.2.3 Specific heat ( $C_p$ )

The specific heat (heat capacity,  $C_p$ ) of a material can be determined quantitatively using DSC and is designated  $C_p$  since values are obtained at constant pressure. Traditionally, this is done by subtracting a baseline from the heat flow curve in the manner described below, but values may also be obtained using *modulated temperature* techniques, Section 1.6. The subtracted curve referenced against a standard gives a quantitative value of  $C_p$ , Figure 1.1. The accuracy that can be obtained depends upon the instrument and method in use.

In practice the traditional standard test method (see Appendix on p49) provides a fairly rapid method for determination of  $C_p$  and many manufacturers provide software specifically designed to comply with this. Three runs are required, each consisting of an isothermal period, temperature ramp and final isotherm. This method is applied identically to the succeeding runs:

1. First run: a baseline with uncrimped empty pans placed in the furnace.
2. Second run: as above but adding a reference (typically sapphire) to the sample pan.
3. Third run: replace the reference with your sample.

The three curves are brought up on the screen, isothermals matched, data subtracted and referenced against the standard. Most software packages will do this automatically, and if the



**Figure 1.1** Heat capacity of PET obtained using fast scanning techniques showing the three traces required for subtraction. The height of the sample compared to the empty pan is divided by the scan rate and the mass of sample to obtain a value for  $C_p$ . This is referenced against a known standard such as sapphire for accuracy. If small heating steps of, for example,  $1^\circ\text{C}$  are used the area under the curve can be used to calculate  $C_p$ . This calculation is employed as an option in stepwise heating methods.

differing weight and heat capacity of sample pans are taken into account then the baseline and reference runs may be used for subsequent samples, provided the DSC is stable. In fact, because the procedure is based on a subtraction technique between measurements made at different times, any drift will cause error. The DSC must be very stable and in practice it is best not to use an instrument at the extremes of its temperature range where stability may be compromised. The standard most often used is sapphire, and the mass used should be similar to the sample; in any event the sample should not be a great deal larger or errors will be increased. This method relies on the measurement of the heat flow of the sample compared to that of an empty pan. Whilst there may be a number of factors which dictate the scan rate of choice it should be noted that faster scan rates result in increased values of heat flow giving increased accuracy of measurement, and this also minimises the time of the run and potential drift of the analyser. It has been reported that fast scan rates used by fast scan DSC (Chapter 2) can give extremely accurate data [1].

A similar principle is employed in stepwise heating methods where the temperature may be raised by only a fraction of a degree between a series of isotherms. This is reported to give a very accurate value for  $C_p$  because of the series of short temperature intervals.

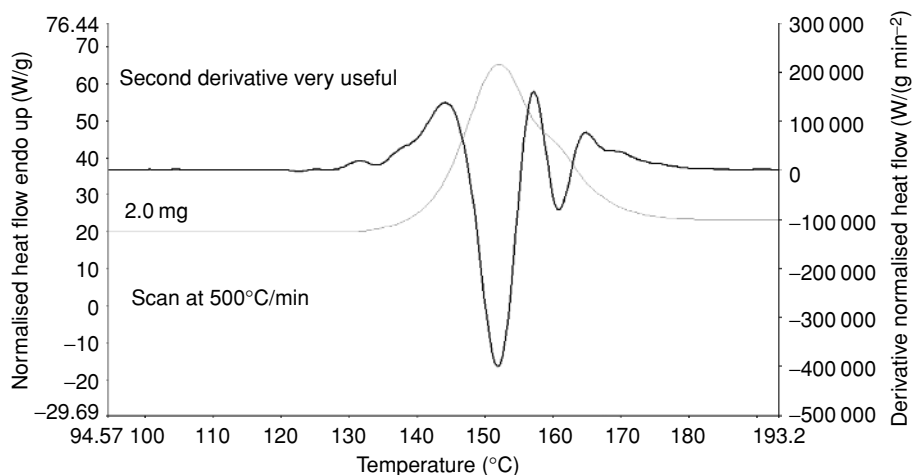
Specific heat data can be of value in its own right since this information is required by chemists and chemical engineers when scaling up reactions or production processes, it provides information for mathematical models, and is required for accurate kinetic and other advanced calculations. It can also help with curve interpretation since the slope of the curve is fixed and absolute, and small exothermic or endothermic events identified. Overall, it gives more information than the heat flow trace because values are absolute, but it does take more time, something often in short supply in industry.

### 1.2.4 Enthalpy

The enthalpy of a material is energy required to heat the material to a given temperature and is obtained by integrating the heat capacity curve. Again many software packages provide for the integration of the  $C_p$  curve to provide an enthalpy curve. Enthalpy curves are sometimes used for calculations, for example when calculating fictive temperature (see Glossary), and can help in understanding why transitions have the shape they do. In the cases where amorphous and crystalline polymer materials exhibit significantly different enthalpies, the measurement of enthalpy can allow an estimate of crystallinity over a range of temperatures as the polymer is heated [2].

### 1.2.5 Derivative curves

Derivative curves are easily obtained from the heat flow curve via a mathematical algorithm and aid with interpretation of the data. Typically they can help define calculation limits, and can aid with the resolution of data, particularly where overlapping peaks are concerned. The first derivative curve is useful for examining stepwise transitions such as the glass transition, and is very useful for thermogravimetric analysis (TGA) studies (Chapter 3) where weight loss produces a step. The second derivative of a peak is more easily interpreted than the first derivative. In this case the data are inverted, but any shoulders in the original data will resolve into separate peaks in the second derivative curve. It is particularly useful for examining melting processes to help identify shoulders in the peak shape due to multiple events. An example is shown in Figure 1.2. The second derivative produces a maximum or minimum for each inflection of the original curve. Shoulders in the original curve show up as peaks in the second derivative. The shoulder in this example is quite clear, but often the second derivative can pick out multiple events when the original data are much less clear.



**Figure 1.2** Indomethacin form 2 scanned at 500°C/min. The shoulder on the melt resolves into a separate peak in the second derivative, which shows a doublet pointing downwards.

The higher the derivative level the greater is the noise that is generated, so good quality data are needed for higher derivative studies. Curve fitting or smoothing techniques used on the heat flow curve before generating a derivative can also be very useful. In general, sharp events and inflections produce the best derivative curves. Studies at high rate also produce very good derivative curves since the rates of change are increased.

## **1.3 Practical issues**

### **1.3.1 Encapsulation**

Encapsulation is necessary to prevent contamination of the analyser, and to make sure that the sample is contained and in good thermal contact with the furnace. One of the most annoying sights after a DSC run is to find a pan burst with the contents all over the furnace, or unexpected peaks and bumps in the DSC trace with no real cause or meaning. Such errors can be due to poor sample encapsulation, which is one of the most important areas to be considered in order to obtain good data. Most manufacturers provide a range of sample pans for different purposes, with a range of different sizes, pan materials, and associated temperature and pressure ranges. Consideration should be given to the following issues when choosing pans and encapsulating your samples.

#### *1.3.1.1 Temperature range*

Make sure that the pan is specified for the desired temperature range and will not melt during a scan; remember that aluminium must not be used above 600°C. Pan materials such as gold (mp 1063°C), platinum or alumina can be used at higher temperatures.

#### *1.3.1.2 Pressure build-up and pan deformation*

Pressure build-up in an inappropriately chosen pan is a frequent cause of difficulties. It is important to determine whether the sample needs to be run in a hermetically sealed pan or not; dry samples unlikely to evolve significant amounts of volatiles below decomposition do not need to be sealed. Yet if run in a hermetically sealed pan then pressure will build up inside the pan as it is heated. Many hermetically sealed aluminium pans cannot withstand high internal pressure and will deform (not necessarily visible) and result in potential artefacts in the trace as heat transfer to the sample changes. Ultimately sample leakage and bursting can occur, which usually results in contamination of the analyser. The best solution for such systems is to work with crimped pans that do not seal, or use lids with holes in. If not available then it may be best to pierce the pan lid before encapsulation so that pressure does not build up. Sometimes one hole will block with sample (particularly if a hole is made after loading the sample) and back pressure will force sample out of the pan giving more artefacts, so it is better to have more than one hole in the lid.

In the case of foods and other water-containing materials hermetic sealing is important since volatile loss will mask other transitions and will dry out the sample. It is then necessary to use a pan system capable of withstanding the anticipated pressure. The maximum operating temperature of a sealed pan may vary but may be below 100°C. Some thicknesses

of aluminium and type of pan offer slightly higher temperature ranges but consideration should be given to 'O' ring sealed stainless steel pans which can hold pressures above 20 bar. These have been designed for use with biological materials or for systems involving condensation reactions, e.g. phenolics.

In the case of samples taken to very high temperature or pressure, capsules which hold internal pressures up to 150 bar should be used. Disposable high-pressure capsules which avoid the need for cleaning are available. For hazard evaluation, gold-plated high-pressure pans should be used, since these should be inert towards the sample.

#### *1.3.1.3 Reactions with the pan*

Samples that react with a pan can cause serious damage to an analyser since they may also react with the furnace beneath. Solder pastes and inorganic salts are typical of the type of samples where care must be taken. If in doubt check it out separately from the analyser, and then choose a pan type which is inert. Sometimes the effect of catalysis is of interest and copper pans may be used to provide a catalytic effect. Aluminium pans are normally made of very high-purity metal to prevent unwanted catalytic effects.

#### *1.3.1.4 Pan cleanliness*

Most pans can be used as received but sometimes a batch may be found to be slightly contaminated, possibly with a trace of machine oils used in pan manufacture. If so, pans can be cleaned by volatilising off the oil. Heating to 300 °C should be more than adequate for this. If using a hot plate, do not heat a lot of pans all together or they may stick together. The use of clean pans is also important for very sensitive work with fast scan DSC.

#### *1.3.1.5 Pans with very small holes*

Some pan and lid systems have been developed with very small holes, typically about 50 µm diameter that have found use with hydrate and solvate loss. They can be used with ordinary samples to relieve internal pressure, so long as the hole does not block, but are intended to improve resolution of mass loss from a sample. As volatiles do not tend to escape through such a small hole until the volatile partial pressure exceeds atmospheric pressure boiling point can be determined.

#### *1.3.1.6 Liquid samples*

Liquid samples must be placed in sealed pans of a type that can withstand any internal pressure build-up. Do not overfill the pan or contaminate the sealing surfaces, which will prevent sealing and cause leakage. When sealing a liquid, bring the dies together gently to avoid splashing the sample.

#### *1.3.1.7 Sample contact*

Samples need to be in good thermal contact with the pan. Liquids and powders, when pressed down, give good thermal contact, other samples should be cut with a flat surface

that can be placed against the base of the pan. Avoid grinding materials unless you are sure it will not change their properties. If possible, films should not be layered to prevent multiple effects from the same transition, though this may be the only way to get enough samples. If so, take care to make sure that the films are pressed well together. Low-density samples provide poor heat transfer so should be compressed. Some crimping processes do this automatically; with others it may be of value to compress a sample between two pan bases or using a flat pan lid as an insert. Take care not to deform a pan and discard any pans that are obviously deformed before use. Sometimes pans of slightly thicker aluminium can give better heat transfer because they retain a flatter base.

#### 1.3.1.8 Spillage

A frequent cause of contamination is from sample attaching to the outside of the pan. Check and remove any contaminant sticking to the outside of the pan, particularly the base of the pan. A soft brush is good for removing powders.

#### 1.3.1.9 Use without pans

Occasionally, very stable samples may be run without pans, for example stable metals over a low temperature range. These benefit from increased thermal transfer to the sample. Thermally conductive pastes have also been used on occasion to try to improve thermal transfer, but such measures require great care, and the use of helium or other highly conductive purge gas may be a better alternative.

### 1.3.2 Temperature range

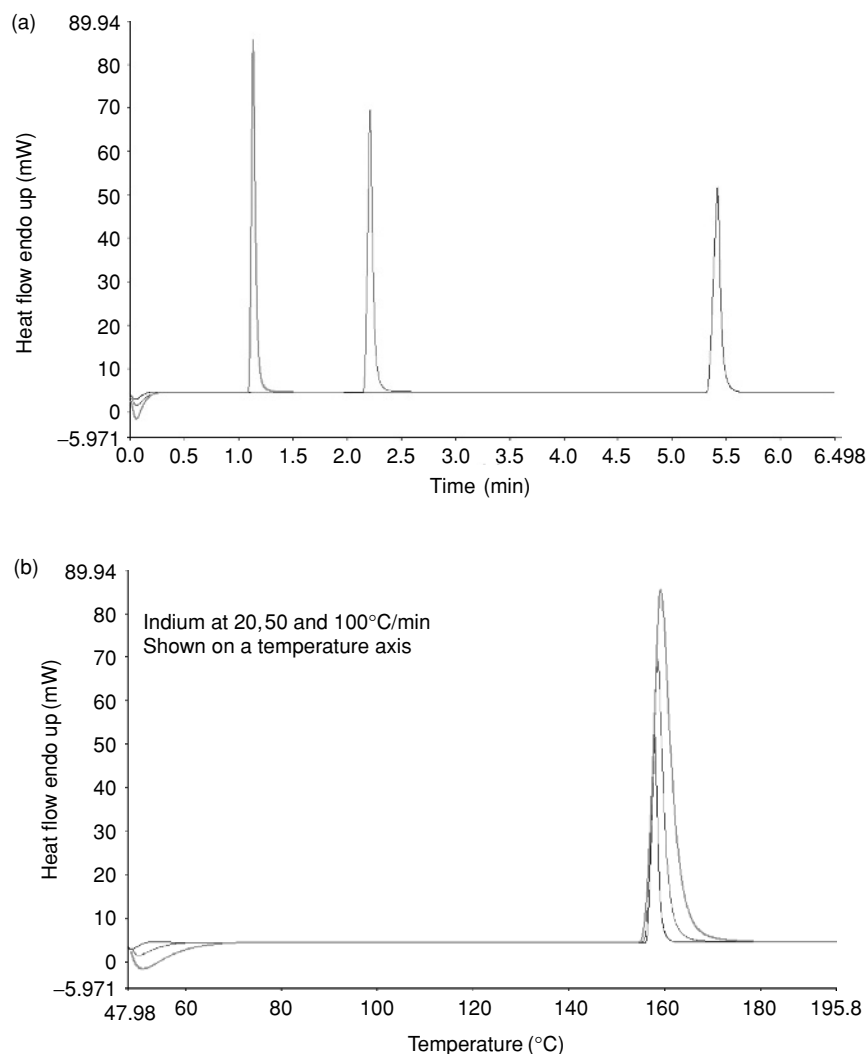
The starting temperature should be well below the beginning of the first transition that you want to measure in order to see it clearly following a period of flat baseline. This should take into account the period of the initial transient where the scan rate is not yet fully controlled and the baseline is not stable. With ambient DSC systems the starting temperature is often around 30°C. The upper temperature should be below the decomposition temperature of the sample. Decomposing a material in a DSC normally gives rise to a very noisy drifting response and the evolved volatiles will contaminate the system. It is good practice to establish the decomposition temperature first using a TGA analyser if available.

### 1.3.3 Scan rate

Traditionally, the most common scan rate used by thermal analysts is 10°C/min, but with commercially available instruments rates can be varied between 0.001 and 500°C/min, often to significant advantage. Choice of scan rate can affect the following areas:

1. *Sensitivity.* The faster the scan rate the greater the sensitivity; see the heat flow equation, Section 1.7. If a sample with a small transition is received where great care is thought necessary, there is no point in scanning slowly since the transition is likely to be missed altogether. Whilst the energy of any given transition is fixed and should therefore be the same whatever the scan rate, the fact is that the faster the scan rate,





**Figure 1.3** The effect of increasing scan rate on indium. Part (a) (upper curve) is shown with the  $x$ -axis in time; part (b) (lower curve) is shown with the  $x$ -axis in temperature. The same energy flows faster in a shorter time period at the faster rates, giving larger peaks.

the bigger the transition appears. Increasing scan rate increases sensitivity. The reason for this is that a DSC measures the *flow* of energy and during a fast scan the flow of energy increases, though over a shorter time period. A slow scan results in lower flows of energy over a longer time period, but since DSC data are usually shown with the  $x$ -axis as temperature, it simply looks like a transition is bigger at the faster rates; see Figures 1.3a and 1.3b. Hence an increased scan rate leads to an increase in sensitivity, so do not use slow rates for small difficult-to-find transitions, unless otherwise unavoidable.

2. *Temperature calibration.* Calibrations need to be performed prior to analysis to ensure that the scan rate of use is calibrated. Different instruments use different approaches to calibration and manufacturer's instructions should be followed.
3. *Resolution.* Because of thermal gradients across a sample the faster the scan rate the lower the resolution, and the slower the scan rate the sharper the resolution. Thermal gradients can be reduced by reducing sample size and improving thermal contact with the pan by good encapsulation.
4. *Transition kinetics.* Slow events such as a cure reaction may not complete if scanned quickly and may be displaced to a higher temperature where they can occur more rapidly. The kinetics of an event may need to be considered when choosing a scan rate.
5. *Time of analysis.* Speed of analysis is an issue in many businesses, and higher rates speed up throughput.

### 1.3.4 Sample size

The amount of sample used will vary according to the sample and application. In general, make sure that excessive amounts of sample are not added to the pan. Sample collapse when melting or softening can give rise to noise during or after the transition. Reducing sample size minimises the chances of this happening. Often just a few milligrams or less is sufficient, typically 1–3 mg for pharmaceutical materials, though for very weak transitions and for accurate heat of fusion measurements more sample may be needed. Note that when considering accuracy of energy measurements the accuracy of the balance should be taken into account. For most work a five-figure balance is needed, and six figures (capable of measuring to the microgram level) for more accurate heats of fusion. For polymers slightly larger samples of 10 mg are often used, but again this depends on the sample and the transition of interest. See the following chapters for practical discussion of individual application areas. As a general comment, if the sample is to be melted then choose a lower weight, though for accurate heat of fusion values typically 5 mg is needed in order to measure the weight accurately, possibly higher if the balance accuracy is not very great. Choose a pan that can cope with sample size needed. Note that one of the major causes of contamination is also from using too large a sample size.

### 1.3.5 Purge gas

Purge gases are used to control the sample environment, purge volatiles from the system and prevent contamination. They reduce noise by preventing internal convection currents, prevent ice formation in sub-ambient systems, and can provide an active atmosphere. They are recommended for use and essential for some systems. The most common purge gas is nitrogen, which provides a generally inert atmosphere and prevents sample oxidation and is probably the default choice. Air and oxygen are sometimes used for oxidative tests such as OIT (oxidative induction time) measurements. Helium is used for work at very low temperatures where nitrogen and oxygen would condense, and is recommended for fast scan DSC studies; see Chapter 2. Other gases such as argon have been used and this can be helpful when operating at higher temperatures, typically above 600°C. This gas has a lower thermal

conductivity, which results in lower heat losses but at lower temperatures results in decreased resolution and sensitivity. Air, nitrogen and oxygen have similar thermal conductivities and instrument calibration is unaffected if they are switched. The use of helium or argon requires separate calibrations to be performed. For totally inert performance use high-purity gases together with copper or steel gas lines, and give time for the sample area to be fully purged of air before beginning a run.

Gas flows are controlled either by mass flow controllers or by using a pressure regulator and restrictor. If you want to check for gas flows, do not put the exit line into a beaker of water. Suck back can occur, destroying the furnace, and bubble formation causes noise. A soap bubble flow meter can be used if needed, but any device used to measure the normally low purge gas flows should not in itself cause a restriction.

### ***1.3.6 Sub-ambient operation***

A variety of cooling systems are available for most instruments and these are now mostly automatic in operation. Issues of filling liquid nitrogen systems and of availability mean that refrigerated coolers (intracoolers) are often preferred and some systems can operate at below  $-100^{\circ}\text{C}$ . Intracoolers are preferred for use with autosamplers since there is no risk of the coolant running out.

### ***1.3.7 General practical points***

Cleanliness is next to godliness as far as DSC use is concerned. Contamination will occur if a pan is placed on a dirty surface and then transferred to the furnace, so keep the analyser and the working area clean and tidy, and discard used pans to avoid mixing them up. DSC furnaces should be kept clean; refer to manufacturers instructions for the most appropriate cleaning method. Avoid abrasives and be aware of the dangers of using flammable solvents. Take note of specific instructions for any particular type of furnace.

- Do not heat aluminium pans above  $600^{\circ}\text{C}$ .
- Do not operate furnaces in an oxidising atmosphere above their recommended limits.
- Do not use excessive force when cleaning a furnace.
- Discard used samples immediately after use before they become mixed up with fresh samples.

### ***1.3.8 Preparing power compensation systems for use***

With power compensation DSC analysers there are two small furnaces and some specific practices to be aware of.

Before starting and before turning on any sub-ambient accessories, inspect the furnaces to make sure that they are clean and the surrounding block is dry and free from condensation. Clean furnaces with a swab and suitable solvent, and complete this with a furnace burn-off in air at about  $600^{\circ}\text{C}$  or above. For this purpose, the furnace should be opened to allow air access

and volatiles to escape easily. Any pans should be removed. The furnaces are constructed of 95% platinum, 5% iridium, which will not oxidise within the temperature range of the analyser. Though organics will burn off, metal and inorganic content may burn in, so make sure that the furnaces are as clean as possible before a burn-off. The platinum furnace covers should also be clean; inspect the underside to make sure. The furnace covers should not be swapped about between sample and reference as they will have slightly different heat capacities which will affect instrument response run to run. They should fit easily, otherwise they may be incorrectly fitted. They can be reformed if needed using a reforming tool. Incorrectly fitting covers will lead to significant slope on the baseline. If a sample has leaked and stuck on the pan or a cover to the furnace, it is often helpful to heat the furnace to a point at which the sample softens and its adhesive properties are lost. The sample and pan can then be removed and the furnace cleaned.

The underside of the swing-away or rotating cover should be inspected from time to time to make sure that it is clean; particularly if sublimation is suspected. If the guard rings beside the furnaces are contaminated these can be removed and cleaned. They should be replaced with the slot facing the purge gas exit port, which is situated centrally behind the furnaces.

Turn on the purge gas and cooling system and allow them to stabilize; this applies to sub-ambient or ambient systems where water circulation is used. Stable background temperatures and purge gas flow provide a controlled environment from which stable and reproducible performance can be obtained. Dry purge gases must be used for the instrument air shield if operating below ambient. If the system has been left for any period of time it is good to condition the analyser by heating to 400–500°C before beginning your work.

## **1.4 Calibration**

### **1.4.1 Why calibrate**

There is potential for slight inaccuracy of measurements in all DSC analysers because sensors, no matter how good, are not actually embedded in the sample, and the sensors themselves are also a potential variable. Therefore in order to ensure accuracy and repeatability of data, a system must be calibrated and checked under the conditions of use. It is important to understand that calibration itself is just a tool or process designed by the manufacturer to adjust the analyser to give a slightly different temperature or energy response. The accuracy and acceptability of the system can only be judged by separately checking the system against accepted standards. A good overview of currently available standards for DSC with comments on accuracy and procedure is given in [3]. See also the details in this section.

### **1.4.2 When to calibrate**

When the system is out of accepted specifications! It is important to distinguish between the process of calibration and the process of checking specification. If a system is brand new, has undergone some type of service, or is to be used under new conditions, it may be in need of complete calibration, but a system in regular use should be checked regularly and calibrated when it is shown to be out of specification. Many systems, particularly in the pharmaceutical

industry, will be used under GLP (good laboratory practices) or other regulations and have established guidelines as to when and how often checks should be made.

### 1.4.3 Checking performance

In many industries frequency and method of checking, together with accepted limits, will be determined by the standard operating procedure (SOP) adopted and may well be done on a daily basis. Regular performance checks are common sense. If a system is only checked once every 6 months and then found to be in error, 6 months work is suspect.

The most common procedure is to run an indium standard under the normal test conditions and measure the heat of fusion value and melting onset temperature. These values are then compared with literature values and a check made against accepted limits. For many industries limits of  $\pm 0.5^\circ\text{C}$  for temperature or 1% for heat of fusion may be accepted, though tighter limits of  $\pm 0.3^\circ\text{C}$  and 0.1% may also be adopted. The choice of limits depends on how accurate you need to be. Indium is the easiest standard to use because of its stability and relatively low melting point of  $156.6^\circ\text{C}$ , which means it can often be reused, provided it is not heated above  $180^\circ\text{C}$ .

### 1.4.4 Parameters to be calibrated

Areas subject to calibration are as follows:

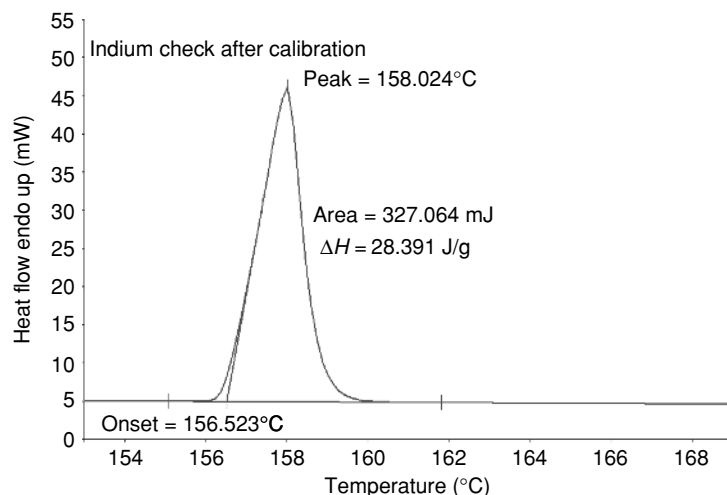
- (a) *Heat flow or energy.* This is normally performed using the heat of fusion of a known standard such as indium. As an alternative, heat flow may be calibrated directly using a standard of known specific heat.
- (b) *Temperature recorded by analyser.* This is performed using the melting point of known standards.
- (c) *Temperature control of the analyser.* Sometimes called furnace calibration.

Use the same conditions for calibration as will be used for subsequent tests. If a range of different conditions are to be used then a range of different calibrations must be performed, one for each different set of conditions. Some analysers/software make allowance for changes in scan rate, so simplifying calibration procedures, but the effectiveness of calibration should in all cases be checked and verified for each set of conditions and scan rates used.

Some instruments may require set default conditions to be restored before measurements are made. The manufacturers' instructions for calibration should in all cases be followed even if they deviate from the general principles outlined here. Use standard values obtained with the actual standards since different batches of standards may have different values.

### 1.4.5 Heat flow calibration

The y-axis of a DSC trace is in units of heat flow; this needs to be calibrated. This is usually performed via a heat of fusion measurement as shown in Figure 1.4. The area under the



**Figure 1.4** Indium run as a check after a calibration procedure has been completed showing the onset calculation for melting point, and area calculation for heat of fusion. This particular curve would benefit from a higher data point collection rate to remove the stepping effect of the data and improve overall accuracy.

melting curve is used since this reflects the heat flow as a function of temperature or time. Some software packages may also make provision for the  $y$ -axis itself to be calibrated and this is done against a heat capacity standard such as sapphire.

#### 1.4.5.1 Procedure

An appropriate standard is chosen and heated under the same conditions (e.g. scan rate, purge gas and pan type) as the tests to be performed. Measure the heat of fusion. This information is then entered into the calibration section of the software. Indium is probably the best standard to use but others may be available in order to check a wider temperature range. The weight of standard should be sufficient to be accurate, typically 5–10 mg and weighed with a six-figure balance for best accuracy. Inaccuracy of weight measurement will limit the accuracy of heat of fusion measurements. An inert purge gas should be used for calibration to minimise potential oxidation. Nitrogen can be used even if samples are to be subsequently run in air or oxygen since all these gases have similar thermal properties and can be used interchangeably as far as calibration is concerned. A clean melting profile is required, without irregularities such as spikes or a kink in the leading edge of the melt caused by sample collapse and flow. For this reason, the sample should be flattened when placed in the pan; most standard samples are sufficiently soft and they may be flattened using the flat part of tweezers before placing in the pan. It is also good practice to use indium on the reheat after it has been melted once, since this will improve the thermal performance. Indium may be reused provided it has not been overheated (see Section 1.4.8); other standards should be discarded after use, though metals such as lead, tin or zinc, which show irregularities on initial heating, may be used on the reheat since this is better than taking data from

a poor trace. In all cases stop the run once melting is complete, and if a standard is taken well above its melting point do not reuse it even if the initial heat is unsuitable. Heat of fusion values are more noticeably affected than temperature when a standard deteriorates.

If the  $y$ -axis scale is to be calibrated directly then the approach used for  $C_p$  measurement (see Section 1.2.3) should be employed. Values obtained for a  $C_p$  standard are then entered against standard values.

### 1.4.6 Temperature calibration

A typical temperature onset measurement is also shown in Figure 1.4. Note that melting point is determined from the onset of melt, not the peak maximum. Normally, at least two standards are needed to adequately calibrate for temperature, and ideally they should span the temperature range of interest, though if working in an ambient environment two widely spaced standards such as indium and lead or zinc are often sufficient. Temperature response is normally linear, so measurements outside of the standards range are normally accurate, but if in doubt then check against a standard. It is the verification process which is the critical aspect of calibration, not the actual procedure used with any specific system. For sub-ambient work a sub-ambient standard is advisable. Organic liquids do not make good reference materials but they are often the only available materials. Obtain as pure a material as possible. Cyclohexane is quite useful having two transitions, a crystal transition at  $-87^\circ\text{C}$  and melt at  $6.5^\circ\text{C}$ . Table 1.1 shows a list of standards.

**Table 1.1** Commonly used standards and reference materials

Standard	Melting point ( $^\circ\text{C}$ )	Heat of fusion (J/g)
Indium	156.6	28.42
Tin	231.9	
Lead	327.5	
Zinc	419.5	108.26
$\text{K}_2\text{SO}_4$	585.0	
$\text{K}_2\text{Cr}_2\text{O}_7$	670.5	
Substance	Transition	Transition temperature ( $^\circ\text{C}$ )
Cyclopentane	Crystal	$-151.16$
Cyclopentane	Crystal	$-135.06$
Cyclohexane	Crystal	$-87.06$
Cyclohexane	Melt	6.54
<i>n</i> -Heptane	Melt	$-90.56$
<i>n</i> -Octane	Melt	$-56.76$
<i>n</i> -Decane	Melt	$-29.66$
<i>n</i> -Dodecane	Melt	$-9.65$
<i>n</i> -Octadecane	Melt	28.24

#### **1.4.6.1 Procedure**

Use the same conditions as for the subsequent tests that you want to perform. Measure the onset values and enter them into the calibration software. Sample weights are not so critical if temperature measurement only is being made and typically a few milligrams should be used. The onset value of indium melt from the heat of fusion test is usually employed to save repeating the process.

#### **1.4.7 Temperature control (furnace) calibration**

In principle, calibration of the control of the analyser requires the same approach as temperature calibration: the information from temperature control should be compared with that of various standards. However, to save repeating the whole process again software often uses an automatic procedure to match the information already obtained with the control routines. Some parameters for this, e.g. the temperature range, may need to be chosen.

#### **1.4.8 Choice of standards**

Table 1.1 lists details of commonly used reference materials. Materials should be used once and then discarded. However, indium is one significant exception to this rule, since it can be reheated many times, provided it is not overheated. Indium fusion values repeat to very high precision (0.1%) provided it is not heated above 180°C. To ensure complete recrystallisation between tests it should be cooled to 50°C or below after each test. Since indium can be obtained to high purity, is very stable, and has a very useful melting point, it makes an ideal standard for most analysis and can be obtained as a certified reference material (CRM) (see below). Other metals listed should be discarded after use.

For temperature ranges where no metal transitions are appropriate other materials may be used as reference materials. These may not be certified materials but may be the best available. Use fresh materials of as high purity as possible.

##### **1.4.8.1 Certified reference materials**

These materials have a certificate giving values obtained after the material has been tested by a range of certified laboratories. This is not necessarily a certificate of purity but they are regarded as the ultimate in reference materials. They can be obtained from Lab of the Government Chemist [4]. Other materials may, for example, possess a certificate of high purity allowing use of theoretical melting and heat of fusion values. These types of materials are termed reference materials and are also widely accepted.

#### **1.4.9 Factors affecting calibration**

A number of factors are known to affect the response of a system and if varied may require different calibration settings. These include the following:



- Instrument set-up and stability
- Use of cooling accessories
- Scan rate
- Purge gas and flow rate
- Pan type

Varying any of these factors can affect calibration, though effects may be more significant for one instrument than another. Initially, ensure that the instrument is set up properly, all services turned on and stable. Most analysers will contain some analogue circuitry which will cause slight drift as they warm up, therefore make sure that instruments have been switched on for a while (typically at least an hour) before calibration. There may be other instrument settings in specific analysers that affect calibration, so users should have a good familiarity with the analyser being used before proceeding with calibration. Use of cooling systems can cause temperature values to shift whilst they are cooling down, so make sure that these are switched on and stable. If using different scan rates, particularly the very fast rates employed by fast scan DSC, you should ensure that the analyser is suitably calibrated for the scan rate of use. Purge gases such as air, oxygen and nitrogen have similar thermal effects and can be used interchangeably, provided scan rates are not altered. The higher conductivity of helium or lower conductivity of argon can have very significant effects on calibration and therefore systems must be calibrated with these gases, if they are to be used. Typically, helium is used at low temperatures or with high scan rates, whilst argon may give better performance at high temperatures. Differing pan types generally do not have too much effect but if thermal contact is changed, for example by the differing thickness or material type of a pan base, then calibration can be affected. If in doubt, then check.

#### 1.4.10 Final comments

Calibration is a process of check and adjustment. It is not complete until you have checked the analyser afterwards to ensure that values obtained are acceptable; see Figure 1.4. Verification ensures that the analyser is in good order, not the calibration procedure itself. A good overview of the calibration procedure together with recognised standards available is given in [3]. Note: Always follow manufacturers' recommended procedures when calibrating a system.

## 1.5 Interpretation of data

### 1.5.1 The instrumental transient

When the run begins, it takes a short period of time for energy to be transmitted to both sample and reference in order to produce the required heating rate, so there is always a slight period of instability at the start of a run before a stable heating (or cooling) rate is established. It often appears as an endothermic step but may vary run to run. This period is termed the *transient*. In Figures 1.3a and 1.3b where a complete trace can be seen the transient shows as the instability at the start of the run before a flat baseline is established.

The time taken by a transient will vary from instrument to instrument but will always be present. Values can be as low as a few seconds to well in excess of a minute, varying slightly with the mass in the furnace. After this period the baseline may show a slight slope. The heat flow curve reflects changes in heat capacity of the sample, compared to the reference, and this may result in a slight positive or negative slope. It is good to have a period of straight baseline before the first transition, so start well below the temperature of the first transition to allow for this and the transient. A transient will also occur when a scan is completed, for example when switching to an isotherm, and can on occasions mask measurements made during the isotherm. If this occurs it may be possible to minimise the effects by subtraction. For example, when performing an isothermal cure reaction the post-cured sample can be rerun under identical conditions and the transient portion can then be used for subtraction from the original trace.

## 1.5.2 Melting

A crystalline melt is one of the most commonly measured transitions, and appears as a peak on the heat flow trace (see Figure 1.4 for the melt of a single crystal such as indium and Figure 1.6 for the broader melt of a polymeric material). It is described as a first-order transition having a discontinuous step in the first-order derivative of the Gibbs free energy equation [5].

For first-order transitions

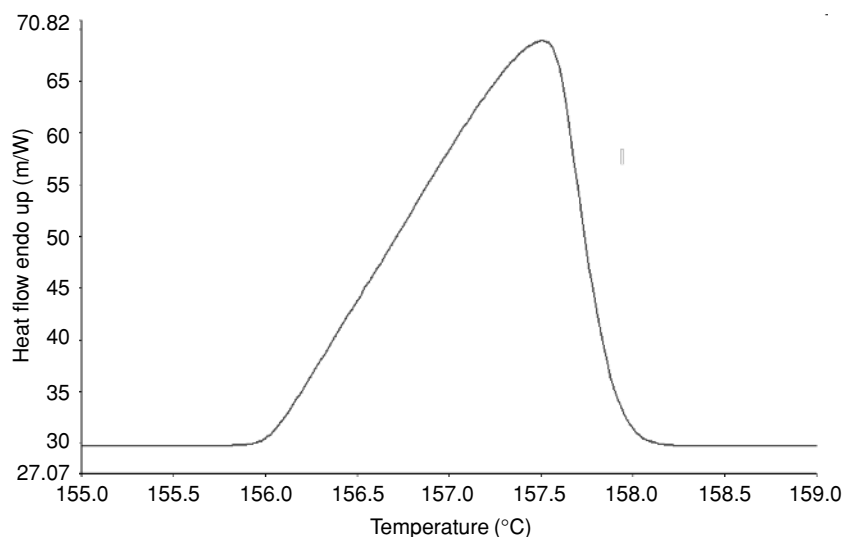
$$dG = -S dT + V dP$$

where  $S = -(dG/dT)_P$  and  $V = (dG/dP)_T$  discontinuities (steps) are observed in entropy, enthalpy or the volume. The first derivative of a step is a peak, so the heat flow curve, which is the first derivative of the enthalpy curve, shows a peak from a melt transition.

Melting is an endothermic process since the sample absorbs energy in order to melt. Integrating the peak area gives the heat of fusion  $\Delta H_f$  and this can be a simple process but often requires careful choice of cursor positions for the integration.

### 1.5.2.1 Single crystal melt

In principle, melting of a single crystal should not produce a symmetrical peak shape, though on occasion it may look so. When melting begins, the sample will essentially remain at the melting temperature whilst solid and liquid are in equilibrium and melting progresses. This results in a peak with a straight leading edge whose slope reflects the rate of energy transfer to the sample. The peak maximum represents the end of the equilibrium melt region and the trace then drops back to the baseline, the energy under the tail of the peak resulting from energy needed to heat the liquid sample to the temperature of the furnace. The resulting peak shape is not symmetrical and at slow rates looks more triangular (Figure 1.5). In a heat flux system it is the temperature difference between sample and reference that creates the signal that is reported as the heat flow. In a power compensation system, a temperature difference still occurs since solid and liquid in equilibrium will remain at the melting point until melting is completed. From this it will be seen that the melting point of a single crystal



**Figure 1.5** Indium heated at 5°C/min showing an almost triangular melting profile typical of single crystal melt at lower scan rates. The slope of the leading edge of the melt of a pure material such as indium gives a value for the thermal resistance constant  $R_0$ .

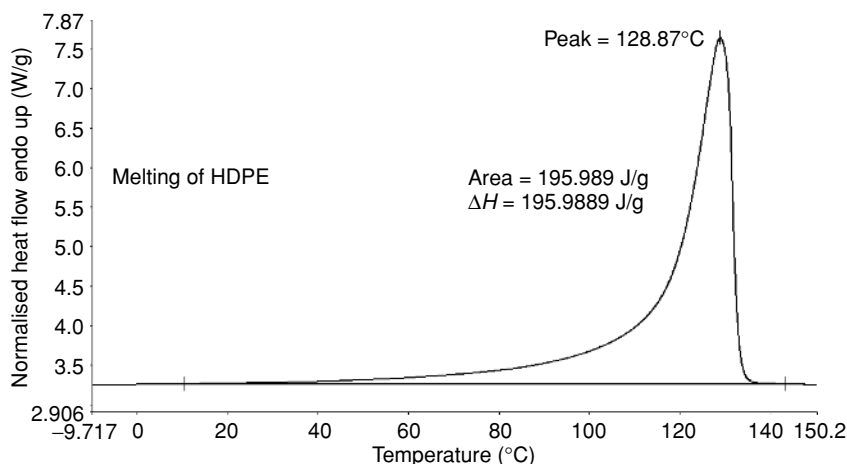
sample is reflected by the onset temperature, which is where melting begins, and not the peak maximum value. The peak maximum value and the peak height value will be influenced by sample weight and possibly by encapsulation procedure, since poor thermal contact will result in a broader peak with lower peak height. The two primary and most accurate pieces of information drawn from single crystal melt are therefore the heat of fusion (melting area) and melting point (onset temperature) Figure 1.4.

### 1.5.2.2 Thermal resistance constant ( $R_0$ value)

This is used in a number of calculations. In theory a 100% pure material should melt with an infinitely sharp and infinitely narrow peak if there were no thermal gradients across a sample (sometimes called thermal lags). However, because it takes time for energy to flow into a sample the peak is broadened and reduced in height. The slope of the leading edge of the melt profile of such a material (e.g. a pure indium standard) should therefore provide a measure of the maximum possible rate of absorption of energy into a material, or put another way, it is a measure of the thermal resistance to energy absorption. A value of  $R_0$  measured under the appropriate scan rate, pan type, and other experimental conditions is used to correct kinetic and purity calculations amongst others. It is easily measured, but note the units specified by any given calculation.

### 1.5.2.3 Broad melting processes

Many materials do not contain single crystals but a range of crystals of varying stability that melt over a broad temperature range. Typical of these are polymeric systems, including



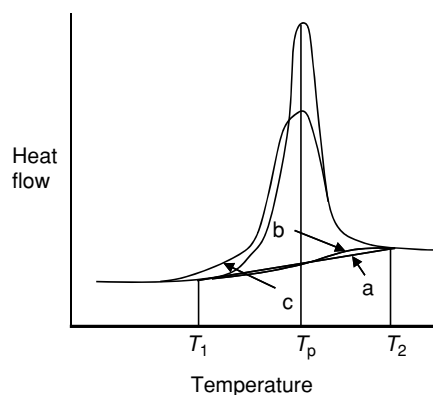
**Figure 1.6** Melting of high-density polyethylene showing calculation of the heat of fusion from the area under the curve, and melting point measured from the peak maximum, unlike single crystal melt. The accuracy of the heat of fusion needs to be assessed in conjunction with the sample weight and the balance used and is unlikely to extend beyond a decimal point.

thermoplastics, foods and biological materials. An example of a broad polymer melt is given in Figure 1.6. Trying to calculate an onset temperature for such a process is fairly difficult and possibly meaningless, since melting is too broad and gradual. The peak maximum temperature of a broad melt is the most meaningful and therefore used in practice. For many materials it represents the temperature where melting is complete, though it will be subject to variation with differing run parameters such as sample weight, so it is good practice when comparing samples to use the same weight and conditions for each analysis.

#### 1.5.2.4 Choice of peak integration baselines

Calculation limits need careful selection, particularly of broad peaks where the gradual start to melting may be hard to distinguish, and small changes can have a significant effect on the values obtained. The run may need to be started well below the melting region in order to distinguish the flat baseline from the gradual beginning of melt. Significantly expanding the data to see just the baseline area and where the transition begins can be very helpful, but it is down to the operator to decide the limits.

On some occasions, the heat capacity of a sample after melt may be noticeably different from that of the sample before melt, resulting in a peak with an obvious step underneath. In this situation, the actual baseline for peak integration is usually unknown but a number of different approaches may be made to the peak area calculation. The choice of a straight linear baseline is probably the most reproducible provided care is given to the selection of cursor positions. Sigmoidal baseline calculations provide another approach where the baseline extends linearly from before and after the melt and following a suitable mathematical algorithm provides a 'sigmoidal' shaped baseline for the calculation; see Figure 1.7. In practice these calculations look quite convincing, but as with all extrapolated calculations, they



**Figure 1.7** DSC peak and two possible baseline constructions (a and b). Also shown is the effect of impurity (curve c) which reduces the melting point and broadens the melting profile.

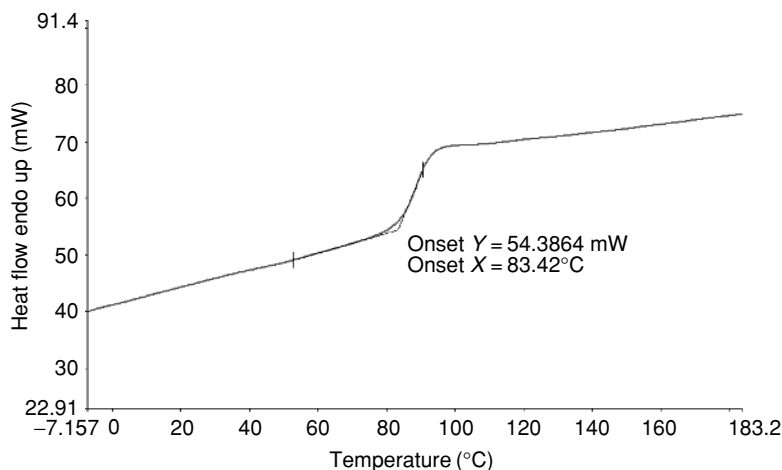
tend to be less reproducible. On other occasions, it may be preferred to extend horizontal baselines from the right or left, particularly if isothermal conditions have been used. Modern software now gives a wide choice of parameters for a range of different requirements, including partial area calculations for broad and multi-peaked processes.

#### 1.5.2.5 Effect of impurities

When comparing melting peaks it is important to remember the effect of impurities, which may vary between samples. This is particularly important in foods and pharmaceuticals where impurities both broaden the melting process and lower the onset temperature, as shown in Figure 1.7. Water can act as an impurity in materials such as starch [6], so effect of impurities should be considered when comparing melting processes. Examination of the peak shape can also allow an estimate of purity; see Section 8.2.4.

#### 1.5.2.6 Peak separation

On some occasions peaks may not be fully separated. To calculate the correct heat of fusion, it is best to separate the different events if possible. Because the actual peak shape does not follow any particular mathematical distribution it is not generally possible to perform an accurate mathematical de-convolution procedure, although where a particular peak shape has been well defined this may be a possible approach. The main approach to this situation is to try to improve resolution by reducing sample weight and by reducing scan rate. Employing helium as a purge gas has also been found to be beneficial in some systems, since its higher thermal conductivity leads to smaller thermal gradients. Depending on the kinetics of the differing events an increased scan rate may also improve separation. Bear in mind that if small samples are used very accurate weight measurement is needed for accurate results. If peaks cannot be separated, and some processes genuinely overlap, then partial area calculations provide a route to estimate the relative energies involved in the different parts of the transition.



**Figure 1.8**  $T_g$  of PET showing the step in the heat flow trace observed at  $T_g$  together with an onset calculation.

### 1.5.3 The glass transition

The glass transition ( $T_g$ ) is the temperature assigned to a region above which amorphous (non-crystalline) materials are fluid or rubbery and below which they are immobile and rigid, simply frozen in a disordered, non-crystalline state. Strictly speaking, this frozen disordered state is not described as solid, a term which applies to the crystalline state, but materials in this state are hard and often brittle. However it is a frozen liquid state, where molecular movement can occur albeit over very long time periods. Material in this frozen liquid state is defined as being a glass, and when above  $T_g$  is defined as being in a fluid or rubbery state. Materials in their amorphous state exhibit very substantial changes in physical properties as they pass through the glass transition and it is one of the most commonly measured transitions using thermal methods; see [7] for a review. Figure 1.8 shows the typical step shape of a  $T_g$  as measured by DSC. It is exhibited only by amorphous (non-crystalline) structure; fully crystalline materials do not show this transition, and it represents the boundary between the hard (glassy) and soft (rubbery) state.

It is described as a second-order transition, since it has a discontinuity in the second-order derivative of the Gibbs free energy equation with respect to temperature [5].

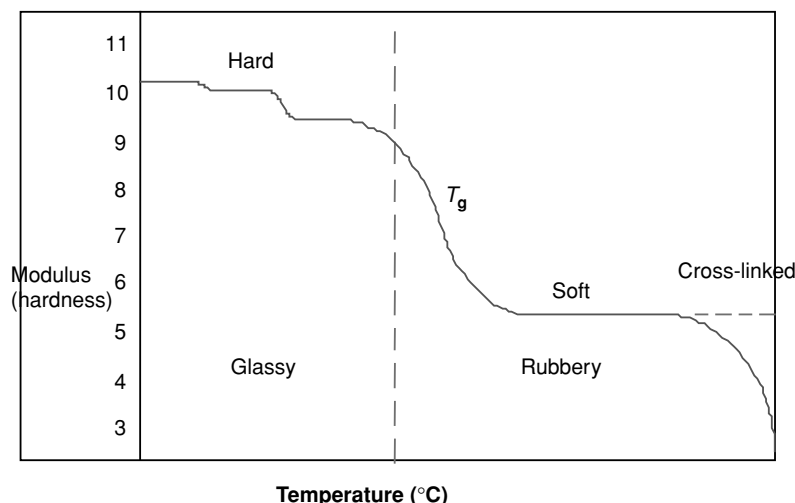
For second-order transitions

$$-(d^2G/dT^2)_P = -(dS/dT)_P = C_P/T$$

$$(d^2G/dP^2)_T = -(dV/dP)_T = -\beta V$$

$$d/dT(dG/dP)_T = -(dV/dT)_P = \alpha V$$

Therefore discontinuities would be observed in heat capacity (heat flow), isothermal compressibility and constant pressure expansivity; and such steps, over a finite temperature range, are indeed observed at the glass transition.

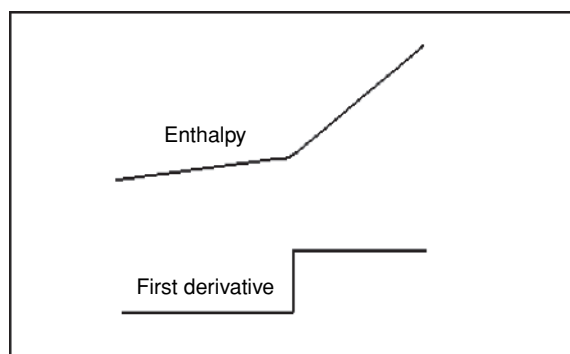


**Figure 1.9** Modulus (hardness) of an amorphous polymeric material as a function of temperature showing the dramatic change in hardness that occurs in the glass transition region. Small lower temperature events are termed  $\beta$ - and  $\gamma$ -transitions.

The glass transition is quite a complex event and has been explained in different ways. (See explanations given in Chapter 4 for mechanical issues and Chapter 10 as related to glasses and ceramics.) One approach involves consideration of the energy involved in movement. At very low temperatures, molecules have insufficient energy to move and materials are immobile and very hard. When gradually heated, a typical long-chain molecule will exhibit small transitions where rotations and vibrations of side groups or side chains can begin, and in some cases crank shaft type motions of the main chain itself. Eventually, a temperature is reached where one complete molecule of the structure can move independently of another resulting in significant softening of the material and this is designated the glass transition. Figure 1.9 shows a diagram of the modulus (hardness) of a material as it is heated through  $T_g$ . Above  $T_g$  fully amorphous materials are soft and fluid unless bonded together in some way. The  $T_g$  is the most significant of the transitions shown in Figure 1.9; transitions observed at lower temperatures are termed  $\beta$ - and  $\gamma$ -transitions respectively, and they too have their effects on materials properties, particularly toughness, since they provide a mechanism for the dispersion of energy from high-frequency impact.

After a molecule has passed through  $T_g$  it has greater ability to move in various molecular motions, described as an increase in degrees of freedom of movement. For a given molecule these various movements may not be well defined, but they represent additional ways of absorbing energy, which means that an increase in specific heat is observed. As a second-order transition this appears as a step in the heat flow curve, which reflects changes in specific heat, and as an inflection in the enthalpy curve; see Figure 1.10.

The significance of the  $T_g$  will depend upon the amorphous content. Some materials are fully amorphous and therefore  $T_g$  will have a very significant influence on material properties. For example, fully amorphous thermoplastics will become fluid above  $T_g$ , whereas partially crystalline materials will remain solid until the melting point is reached. Fully crystalline



**Figure 1.10** Diagram of an enthalpy curve as a sample is heated through  $T_g$ . A heat flow curve shows a broad step at  $T_g$  since it measures energy flow, which is a derivative of the enthalpy curve.

materials will not show a  $T_g$ , however, materials that are semi-crystalline will exhibit both a glass transition and a melt. The height of the  $T_g$  transition is dependent upon amorphous content and can provide a measure of it; further discussion of this can be found in Section 2.5.3. Partially, crystalline materials may also contain amorphous material which is not totally free to move because of its close proximity to crystals of the material, and some long-chain individual molecules may be part amorphous while a different section may be part of a crystalline structure. In Chapter 10 these have been referred to as tie points. Since such molecules are not totally free to move and may not undergo the glass transition this material has been termed the rigid amorphous fraction or RAF [8]. See Section 9.2.9 for further discussion of RAF, and possible multiple amorphous phases – polymorphism.

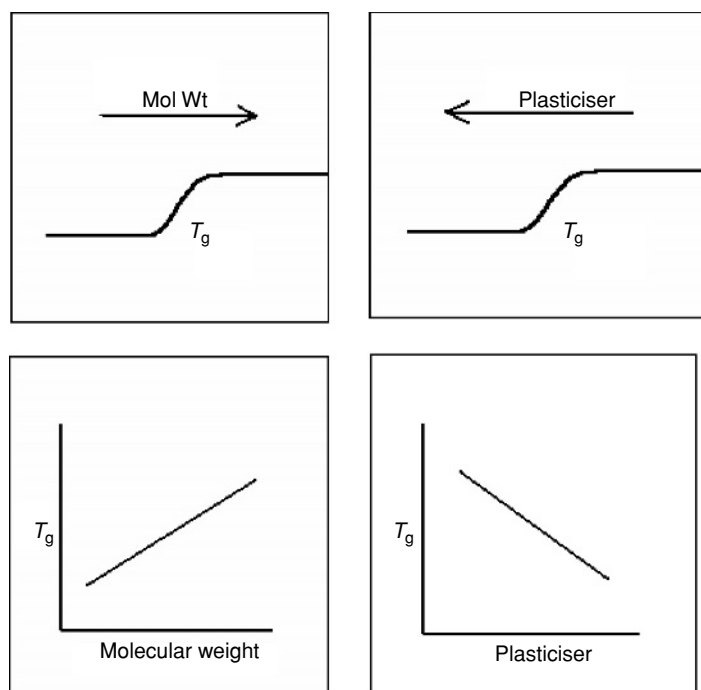
Materials in the glassy state are in general stable, and neither react or decompose very quickly because the molecules are immobile over short time periods. This feature is used to advantage in freeze-drying where materials are specifically produced in a glassy state to render them stable and yet easily used; see Section 1.5.8. Other materials such as epoxy resins need to be heated above their  $T_g$  in order for them to react and cross-link.

#### 1.5.4 Factors affecting $T_g$

The glass transition temperature is influenced by many parameters including effects of additives, for example plasticisers which are added to reduce the temperature of  $T_g$ ; see Figure 1.11. One of the most significant plasticisers is moisture. This is well known to affect the  $T_g$  of composites, pharmaceuticals and many other materials. It can lead to loss of strength or stability at a given temperature. Cornflakes are a typical example of a material which is hard and brittle when dry at room temperature, yet with the addition of water (milk) the  $T_g$  is reduced and the cornflakes become very soft and pliable. Reactions, such as a cure reaction, which increase the molecular weight of a material will increase the temperature of  $T_g$ , since molecules need more energy and a higher temperature to move independently of one another.

Another factor is the flexibility of the chemical bonds in the molecule itself. Materials with flexible bonds such as Si–O or CH<sub>2</sub>–CH<sub>2</sub> have low-temperature glass transitions whereas more rigid structures have higher temperature transitions.





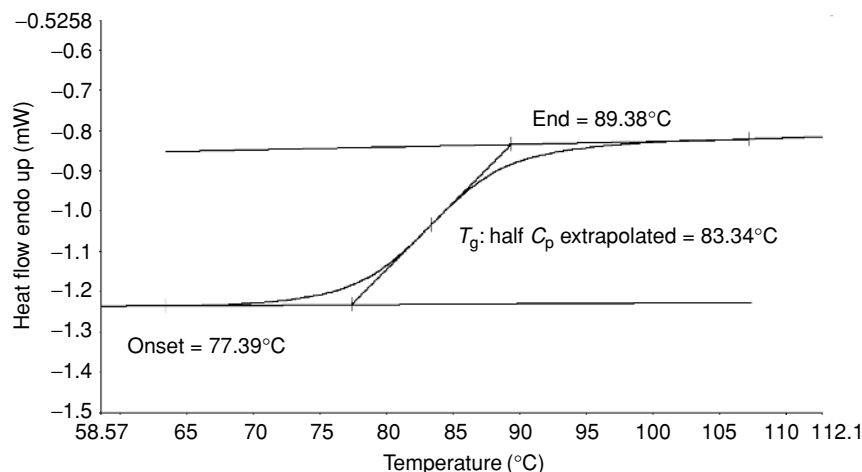
**Figure 1.11** Diagrams showing the effect of plasticiser or molecular weight on the glass transition temperature. Increasing molecular weight will increase  $T_g$  whereas the inclusion of plasticiser will reduce  $T_g$ .

### 1.5.5 Calculating and assigning $T_g$

The glass transition is not a single point and occurs over a region in temperature, in some cases many tens of degrees, therefore care is required when quoting a value for  $T_g$ . A choice can be made from the following calculations:

Onset	The intersection of tangents from the baseline and initial slope of the step; see Figure 1.12.
Midpoint	The middle of the step measured as half the step height; see Figure 1.12.
Endpoint	The intersection of tangents from the step and final baseline; see Figure 1.12.
Inflection point	The inflection point of the step.
Fictive temperature	This is a specific value and comes from the definition of the fictive temperature as being the temperature of the frozen glassy state at which a material is in equilibrium (see Section 1.5.6). The calculation is taken from the enthalpy curve and is the intersection of tangents taken from above and below the $T_g$ . The same value can be obtained by drawing tangents to the integral of the heat flow trace.

In practice, one of the most often used values is the midpoint calculation but there is no rule that says that this or any other value should be used, so the method of calculation



**Figure 1.12** Different calculations of  $T_g$ . The onset, midpoint and endpoint are shown. The method of calculation is best quoted with the  $T_g$  value.

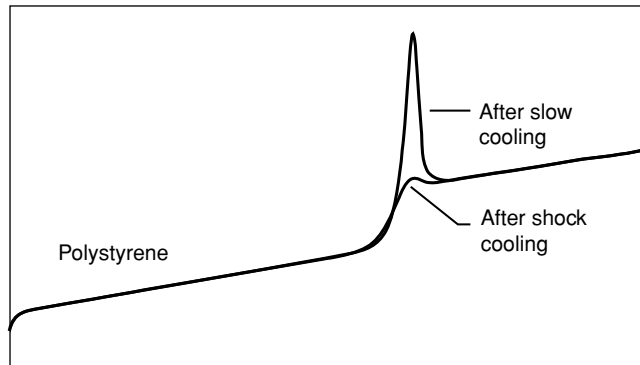
should be appropriate to the investigation at hand and should be quoted with the result. If a standard method is being followed then the procedure of calculation should be defined by the method, though the type of calculation used should always be quoted to avoid confusion.

### 1.5.6 Enthalpic relaxation

Sometimes a peak can occur on top of the glass transition which can affect the calculation of  $T_g$ . Large effects which entirely swamp the small glass transition event can sometimes be found, and these are possibly due to relaxation of mechanically induced stresses resulting from the production of materials such as films or fibres where mechanical pulling is used to orient molecules in one particular direction. Heating such a material results in a peak which is formed as previously stressed molecules are able to rearrange in the  $T_g$  region, absorbing energy in the process. If this occurs then a sample can be reheated to observe the glass transition, though care may be needed to ensure that the material is otherwise unchanged in the process.

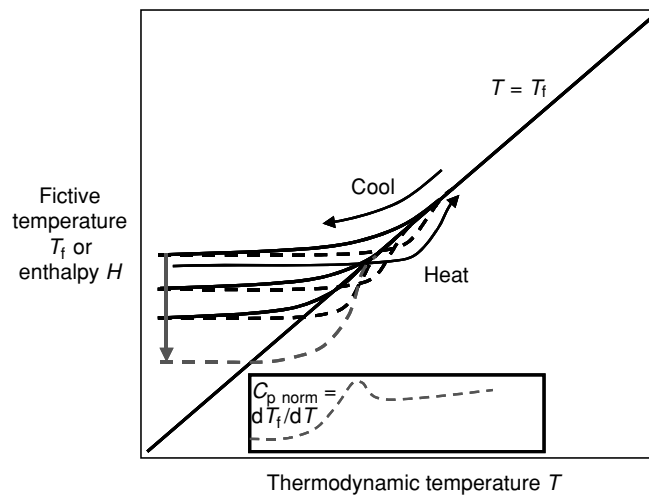
Enthalpic relaxation phenomena usually give rise to smaller peaks (see Figure 1.13) and often result when heating a material which has been cooled slowly through  $T_g$  or held just below the  $T_g$  for a period of time. This will allow the material to anneal (relax) into a lower enthalpic state; see Figure 1.14. A lower glass transition temperature is associated with a lower enthalpic state, since the glass transition of a material is not a fixed thermodynamic event, and the temperature of transition is dependent to some extent upon how it has been cooled, and the energy state into which it has been annealed.

On heating a polymer which has been annealed into a low enthalpic state a small peak may appear almost like an overshoot, referred to as an enthalpic relaxation event. If heated very slowly this peak may not appear and a true value of  $T_g$  is then obtained, but at normal



**Figure 1.13** Polystyrene heated at  $10^{\circ}\text{C}/\text{min}$ . This shows an example of a marked enthalpic relaxation peak which appears on top of the  $T_g$  on heating after the sample has been cooled slowly.

scan rates of  $10$  or  $20^{\circ}\text{C}/\text{min}$  a slight overshoot of the true  $T_g$  of an annealed material is often observed. The lower dashed line in Figure 1.14 shows an example. At this point, the material will pass into an energy state which is below the equilibrium energy state for the material, shown as the fixed line in Figure 1.14. When the material passes through  $T_g$  and the molecules become mobile they will also absorb energy in order to regain equilibrium, giving rise to a



**Figure 1.14** The enthalpy curve of a material in the  $T_g$  region. If cooled slowly through  $T_g$  or held isothermally (annealed) just below  $T_g$  a material can relax into a lower energy state as indicated. Heating an annealed material at normal heating rates is likely to produce a slight 'overshoot' of the true  $T_g$  onset resulting in a step as well as an inflection in the enthalpy trace. The resulting heat flow trace shown in the box is a step with a peak on top. The equilibrium line for the material is the solid line from bottom left to top right. It can be seen from the lower dotted line that an annealed sample heated at sufficient rate enters a non-equilibrium state of low energy before going through  $T_g$  at an elevated temperature and absorbing energy to regain equilibrium.

small endotherm. In consequence, a small enthalpic relaxation peak associated with the glass transition indicates that measurement has been shifted slightly from the true position. Since different  $T_g$  values are associated with the same material depending upon how it has been annealed, care needs to be taken not only with the measurement of the  $T_g$  but also with the conditioning of a material before measurement if a  $T_g$  value is to be quoted. The enthalpic relaxation peak will also affect the onset and midpoint calculations, since the shape of the transition is altered. If midpoint  $T_g$  calculations are to be performed it is normal to put the end cursor after the peak.

The true  $T_g$  value of such a material is then lower than that indicated by the normal DSC step calculation. Fast cooling is likely to prevent annealing and so remove any relaxation phenomena (one guideline is to first cool the polymer through  $T_g$  at the same rate or faster than it is to be heated), and this may be one preferred route prior to measurement; another is to use an enthalpic or fictive  $T_g$  calculations (see Section 1.5.5). This involves integration of the heat flow curve to give the enthalpy curve. A 'true' value of  $T_g$  can then be obtained using an extrapolated onset calculation of the enthalpy curve from above and below the  $T_g$  region; effectively, this seeks to reproduce the curve shown in Figure 1.14, though the results are likely to be less reproducible because it is an extrapolated calculation. This type of calculation can be done automatically with some software packages. However, it is worth noting that the  $T_g$  is neither a fixed point, nor does it occur at a fixed temperature as does a melt; it is dependent upon the thermal conditioning of the material. A very slow cooling rate, or slow heating rate, can permit annealing of a sample as can a modulated temperature method, so resulting in a lower  $T_g$  value. The change in  $T_g$  often associated with changing scan rate may in reality be due to annealing of a material.

The term 'ageing' or 'ageing peaks' has also been applied to the phenomenon of enthalpic relaxation, since it has been seen as an effect following storage. Many materials are not deliberately annealed but as they are stored the temperatures experienced over time may permit annealing, so the term ageing has been applied. It is observed in many amorphous food substances; starch, sugars and, less clearly, proteins are reported as being the prime examples (see Chapter 9).

See Section 10.2 and Figure 10.1 for further discussion of enthalpic relaxation of materials (glasses).

Enthalpic relaxation behaviour can be formalised in the TNM (Tool Narayanaswamy and Moynihan) description of ageing [9].

The equations describing this behaviour are as follows:

$$\tau_0 = A \exp[x\Delta H/RT + (1-x)\Delta H/RT_f]$$

$$T_f = T_0 + dT' \{1 - \exp[-(dT''/q\tau_0)^\beta]\} \quad \text{and} \quad C_p(\text{normalised}) = dT_f/dT$$

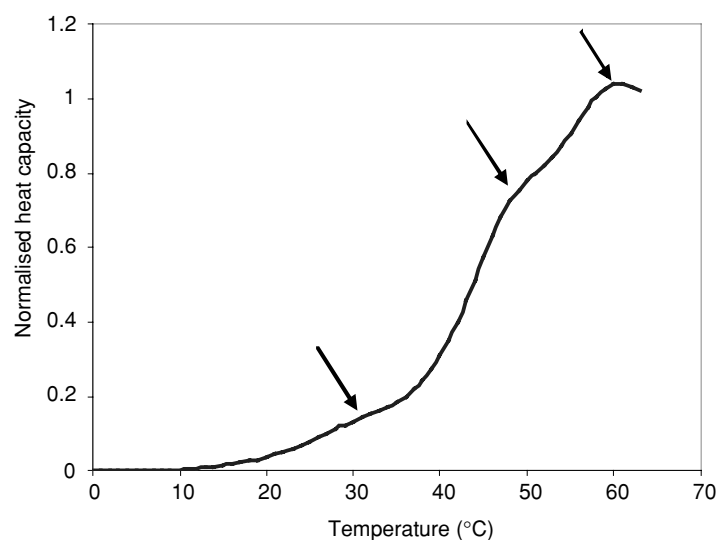
Where  $x$  and  $\beta$  are the non-linearity and non-exponential parameters respectively,  $A$  is the pre-exponential factor,  $\Delta H$  is the activation enthalpy,  $\tau_0$  is the time constant and  $T_f$  is the fictive temperature. The effects of changes in some of these parameters on the overshoot in heat capacity can be seen in Table 1.2.

Moynihan gives an excellent description of the principles behind the TNM model. While the approach may at first appear complex, the behaviour of these equations is actually

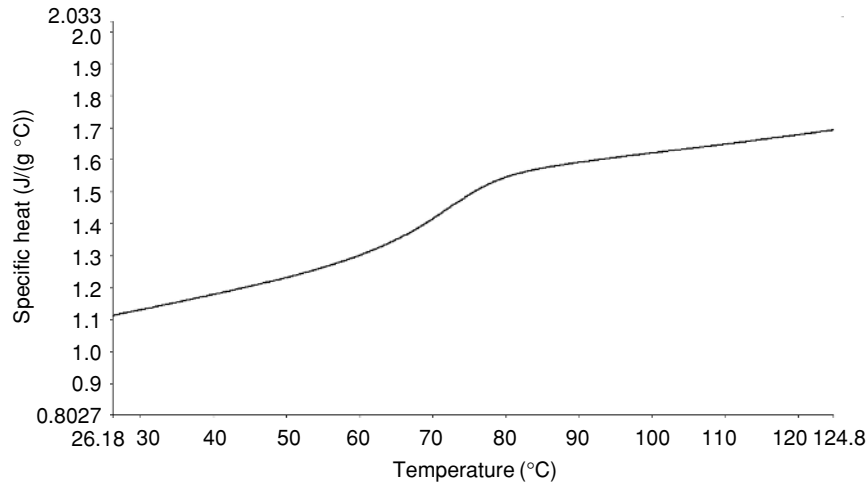
**Table 1.2** The effect of changes in the particular parameter on the ageing trace.  $T - T_\infty$  can replace the absolute temperature  $T$  if a WLF type treatment of the data is used

Parameter	$A$	$\Delta H$	$x$	$\beta$	$T_\infty$
Effect on trace	Position	Position and sensitivity	Peak development	Transition width	Compression

comparatively simple and represents an interplay between time and temperature effects. The whole formalism is based on superposition theory, which states that the current state of the material is the sum of all the responses to previous temperature steps, in the case of a temperature profile. It is vital that the system starts from an initial equilibrium temperature. The effects of different rates of heating and cooling, annealing steps where the time alone is allowed to increase and so relax the whole system, and multiple annealing steps can be included. The latter is particularly relevant to food products involving multiple processing at different temperatures and storage for different times at different temperatures. All these temperature histories can be simply accounted for by summing all the different steps involved according to superposition theory. Figure 1.15 shows a theoretical temperature profile and the corresponding heat capacity trace generated using superposition theory. The memory effect in these materials is particularly interesting; note the multiple peaks in Figure 1.15. Further discussion of this subject and the effects of scan rate in particular can be found in Section 2.4.6.



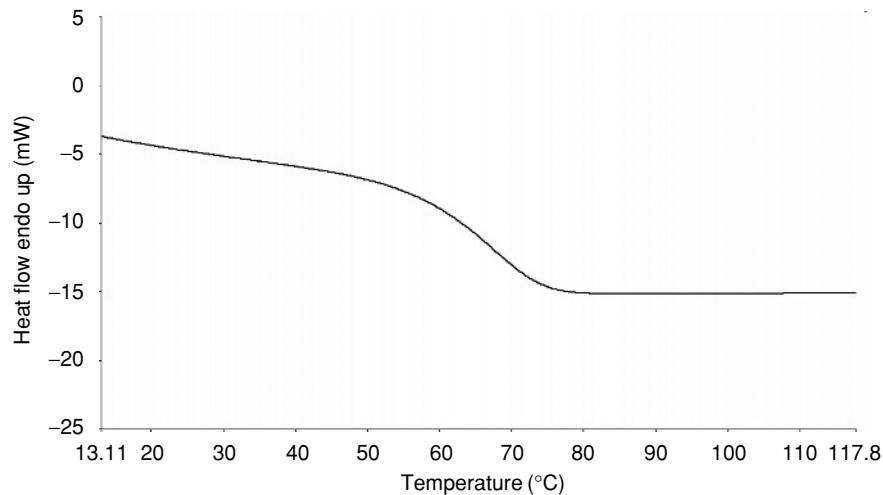
**Figure 1.15** The multiple peaks generated using the following TNM parameters. Temp high = 63°C, Temp low = -5°C, Temp anneal1 = 32°C, Temp anneal2 = 5°C, time anneal1 = 4800, time anneal2 = 480,000, all cooling rates = 20°C/min, heating rate = 10°C/min. Parameters were  $x = 0.632$ ,  $\beta = 0.355$ ,  $A = 6.57 \times 10^{-65}$ ,  $\Delta H = 97.1$  kJ/mol.



**Figure 1.16** The heat capacity trace of PET cooling at 200°C/min using fast scan DSC. The  $T_g$  is clearly shown as a step similar to that found on heating.

### 1.5.7 $T_g$ on cooling

If a sample is cooled through the  $T_g$  then a step in the DSC signal is again observed; see Figure 1.16. This shows the measurement of *heat capacity* on cooling, a step similar to that found on heating. However, the *heat flow* curve of  $T_g$  is quite different and apparently shows a step going in the other direction, as if there is an increase in heat flow on cooling as well as heating; see Figure 1.17. This is because the flow of energy on cooling is actually a negative



**Figure 1.17** Heat flow trace of PET cooled at 150°C/min showing the  $T_g$  which appears as an apparent step increase in heat flow as cooling proceeds, but in reality is a step decrease in negative heat flow.

heat flow, not always apparent because the  $y$ -axis is not absolute, and as the sample goes through  $T_g$  a step decrease in heat flow is measured, which appears as a step towards zero. Thus heat flow curves on heating and cooling should appear more like a mirror image of each other reflected against the zero heat flow line.

## 1.5.8 Methods of obtaining amorphous material

### 1.5.8.1 Rapid cooling

Many materials can exhibit a  $T_g$  if they are produced in a way that prevents crystallisation. One such method is rapid cooling at a rate that is sufficiently fast that the material does not have time for crystallisation. Even water if cooled sufficiently rapidly can exist in a glassy state with a  $T_g$  which has been reported in the region of  $-136^\circ\text{C}$  (see Table 9.3). Bear in mind that the value recorded will vary depending upon whether onset, midpoint, inflection point, etc. are being quoted (See Section 1.5.5). Depending upon the method of production not only polymers but also many small molecules can and do exist in a glassy state, and many mainly crystalline materials may well possess a small amount of amorphous material, particularly if the material has been ground to reduce particulate size. It is often useful if trying to find a  $T_g$ , to cool a material rapidly from the melt before reheating, so as to maximise the amorphous content and increase the size of the glass transition.

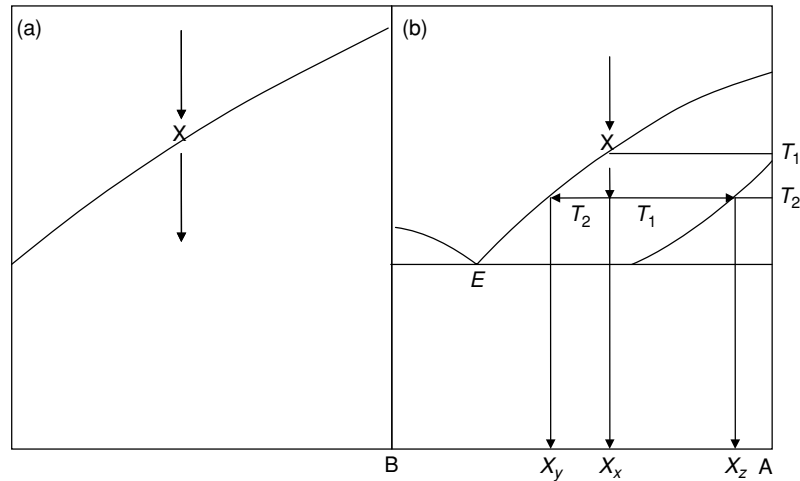
### 1.5.8.2 Spray-drying

One way of obtaining amorphous material is to dry rapidly from solution. In solution, the solute is in disordered state and if dried very quickly it does not have time to recrystallise, and so gives an amorphous product. The process of spray-drying is often used with pharmaceuticals and can therefore give an amorphous product, though some crystallisation may occur. Resulting products need to be kept dry to prevent the  $T_g$  from being reduced by plasticisation with water or the material may recrystallise.

### 1.5.8.3 Freeze-drying and phase diagrams

The term freeze-drying has become familiar to many people as foods that can be found on supermarket shelves, such as coffee, have been produced in a freeze-dried state. In fact, many foods and pharmaceuticals are freeze-dried and the aim is to produce a material which is stable and does not decompose, yet which can be rapidly reconstituted with the addition of water into a useable, desirable form. Since materials are effectively stable in the glassy state, freeze-drying is useful because it produces a glassy amorphous material with a  $T_g$  above room temperature so that it is stable and can be stored on the shelf, but is very porous and can be dissolved very easily. DSC is a valuable tool for measuring melting and freezing points to construct phase diagrams and to measure the  $T_g$  of freeze-dried materials, and the process is described below in some detail.

An appreciation of phase diagrams greatly aids the understanding of the principles of freeze-drying and the literature on mixtures and melting of materials such as fats. Figure 1.18a represents a trivial phase diagram and shows the condition of perfect mixtures of



**Figure 1.18** A phase diagram of a perfect mixture (a) and a eutectic mixture (b).

components in the liquid and solid phases. As the temperature is reduced the liquid solidifies at point  $x$  to a solid of exactly the same composition. In Figure 1.18b, if a mixture of ratio A/B is cooled from above the upper phase boundary, commonly referred to as the solidus line, the first thermal event occurs when this is crossed at position  $x$ . In fact this type of cooling method, coupled with accurate temperature measurement, was originally used to construct phase diagrams. At point  $x$ , temperature  $T_1$ , a phase enriched with A begins to crystallise out and the composition of the remaining material follows the curve towards point  $E$ . At any temperature, say  $T_2$ , the weight of the enriched phase and the remaining mixture can be calculated according to the length of the tie lines  $T_1$  and  $T_2$ .

Using conservation of mass

$$W = W_y + W_z$$

and conservation of component A

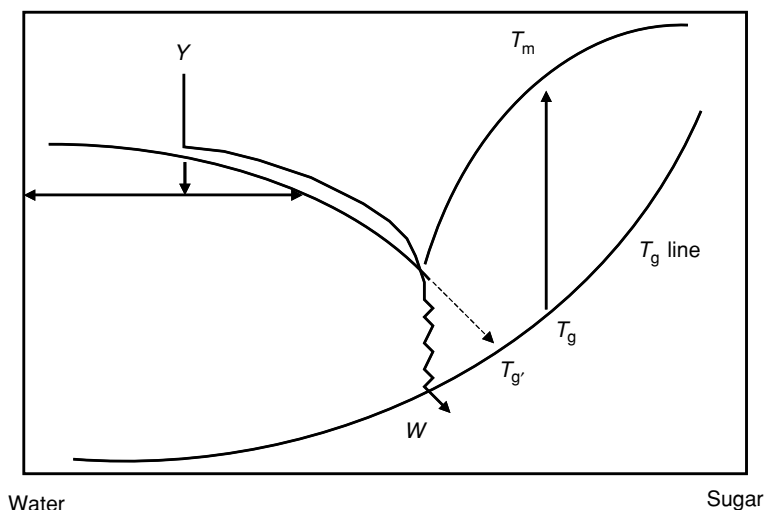
$$XW = X_y W_y + X_z W_z$$

therefore

$$W_y/W_z = \{X_z - X_x\}/\{X_x - X_y\} = T_1/T_2$$

Here  $W_n$  is the weight of phase  $n$  and  $X_n$  is the mole fraction of component A in phase  $n$ . This process continues until the remaining mixture reaches the point  $E$  where a solid mixture of composition  $E$  (eutectic) crystallises out. Naturally, the same arguments hold if the eutectic point is approached from the opposite side where B is the crystallising component.





**Figure 1.19** Supplemented state diagram for a sugar–water mixture.

Phase diagrams similar to the above, but where a pure compound crystallises out, apply to compounds such as benzene and naphthalene. However, if we consider a different system where A is assumed to be sugar and B water, an interesting observation is made.

By similar arguments and starting from position Y in Figure 1.19, pure ice would be expected to crystallise out until a point is reached where pure sugar and pure water would crystallise separately to form a solid mixture at point  $T_g'$ . However, the viscosity of the material is such that equilibrium behaviour is prevented and a material is formed having a raised concentration of water (point W in Figure 1.19). The material formed is a non-equilibrium uniform glass. The sample has been cooled at a rate where equilibrium can no longer be maintained, and it is commonly held that any material showing this behaviour will form a glass. The moisture content of a glass can subsequently be altered by relative humidity adjustment and the transition temperature  $T_g$  studied as a function of the concentration of the components. There are several equations, which describe the resultant  $T_g$  as a function of the concentration of the components. Perhaps the most common is the Gordon–Taylor equation [10]

$$T_g = \{x_1 T_{g1} + K x_2 T_{g2}\} / \{x_1 + K x_2\}$$

This can be seen to be equivalent to the Couchman–Karasz equation where  $k$  is equal to the ratio of the specific heats instead of  $\rho_1 \Delta\alpha_2 / \rho_2 \Delta\alpha_1$  as in the original paper [11].  $P$  and  $\Delta\alpha$  are the density and thermal expansivity respectively:

$$\ln T_g = \frac{\sum x_i \Delta C_{p_i} \ln T_{g_i}}{\sum x_i \Delta C_{p_i}}$$

This equation can also be expressed in a linear approximation.

The Ten Brinke modification of the Couchman–Karasz equation was proposed to describe the lowering of the glass transition temperature of a cross-linked polymer network by a low molecular weight diluent [12].

This results in the following equation:

$$T_g = -\Delta C_{p2}/\Delta C_{p1}(T_{g1} - T_{g2})x_2$$

All these equations describe to a greater or lesser degree of accuracy the variation of the glass transition temperature with composition.

It follows that a material which is to be prepared by freeze-drying is first cooled, allowing the formation of pure water crystals and increasingly concentrated solution of the solid which eventually enters into the region of the glassy state. Pressure is then reduced and the pure water crystals sublimed away, a process which requires the input of energy. The process can be controlled so that the fraction of water remaining is low, and the consequent  $T_g$  of the final material is above ambient. This allows the material to be stored in a stable dry state which can be easily reconstituted by the addition of water.

It is important to keep these materials dry because an ingress of moisture into the material will lead to a reduction in  $T_g$  and in the resulting stability of the material. It is therefore important to know the  $T_g$  of these materials. One difficulty encountered is that the material may dry out if being heated slowly, so changing the measured value. An alternative route is to measure the  $T_g$  of the dried material and then with knowledge of the moisture content back-calculate the  $T_g$  of the material using the Gordon–Taylor equation. High scan rates can also be used to measure the  $T_g$  of moisture-containing materials before they have chance to dry out; see Section 2.3.3.

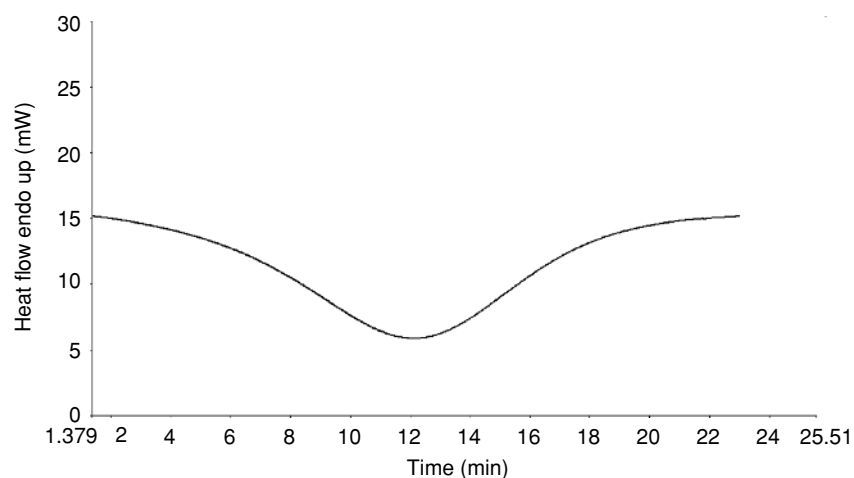
When heating amorphous materials through the  $T_g$  region the expected  $T_g$  step can be followed by recrystallisation as the system seeks to reestablish its equilibrium state. Some materials, particularly low-density freeze-dried materials, are prone to physical collapse once heated through  $T_g$  and this can also result in significant transitions in the  $T_g$  region or following  $T_g$ . These are usually not very reproducible because they result from sample movement, and faster scan rates can benefit the analysis since the  $T_g$  can be measured before the sample has had time to move.

#### 1.5.8.4 Non-Arrhenius behaviour

When considering glasses, it would be surprising if the issue of non-Arrhenius behaviour did not arise. It is found in rheological studies that the effective zero temperature where mobility ceases should be greater than zero kelvin, which is the implicit assumption in the Arrhenius equation. Certain rheological plots can be linearised by assuming a value of  $T_\infty = T_g - 50$ . It is this term which appears in the WLF equation (see Chapter 4), and is thought to be the limiting underlying glass transition temperature at infinite time. By adding 50°C to this value, the rheological glass transition can be given a more real-world value but is effectively a reference value. A similar procedure has been carried out in annealing studies [13].

### 1.5.9 Reactions

The most common reaction that is measured is the cure reaction found in rubbers and composites and which appears as a broad exothermic peak; see Figure 1.20. In general, any



**Figure 1.20** A cure reaction measured by DSC showing a broad exothermic peak. Slow scan rates (or isothermals) are normally preferred for such measurements to allow time for the reaction to occur prior to decomposition.

exothermic response comes from some type of reaction, be it decomposition, crystallisation or chemical interaction.

### 1.5.9.1 Cure reactions

Cure reactions in composites and other materials are normally slow events compared to typical scan times, and in order to measure them slow scan rates need be used so that the cure reaction can be measured fully before decomposition temperatures are reached. The alternative is to heat to an isothermal temperature where time can be given for the reaction to come to completion. This is also helpful when making calculations since a flat line extrapolated from the reacted portion of the sample provides an accurate baseline for peak integration. Note that subsequent heating to a higher isothermal temperature may permit further reaction to occur, since the extent of reaction may be limited by increasing viscosity and the material becoming hard. (Effectively, the  $T_g$  increases towards the isothermal temperature and upon reaching it the material becomes a stable glassy structure.) Often a  $T_g$  can be observed prior to a cure reaction, in a pre-mixed system the material will be stable below  $T_g$  so it needs to be heated above this temperature for reaction to begin. Modulated methods have also found value for the measurement of cure since the underlying heat capacity of the material can be measured as a function of increasing temperature, during the cure reaction. This can provide a more accurate peak baseline for the measurement of energy during a temperature scan.

From a slow scan, the onset and energy of reaction can be measured which can be of value in itself and can also give some idea of the potential hazard involved. These curves can be further investigated using kinetic analysis. Data can be fit to a variety of mathematical models, yielding activation energy and other information. Arrhenius-type models are the most common and are often available as part of the instrument software. Whilst data can be obtained from a single scan, the accuracy of the data is open to question since the software

will generally be able to fit the data and produce values for activation energy, order of reaction and rate constant, whether accurate or not. Data obtained from isothermal reactions is to be preferred. This is taken from a series of isothermal curves run at different temperatures, and results can be compared from different isothermal values. If data from a temperature scan are used they should first be checked against isothermal data to assess their accuracy.

In any kinetics work the control of the sample temperature is important, and if isothermal measurements are taken from an analyser with heat flux principle it should be noted that the heat flow measurement is obtained from the deviation of the sample temperature from the cell temperature. It is the furnace temperature that is controlled, not the sample temperature, so true isothermal measurements cannot be made using this approach. Once the basic kinetic parameters have been established predictions can be made as a function of temperature, time, and extent of reaction, though the accuracy depends upon how well the data fit to the model used.

### 1.5.9.2 Arrhenius kinetics

Most kinetics start with the assumption that the rate of reaction is a function of degree of conversion and sample temperature.

The degree of conversion is given by

$$d\alpha/dt = k(T) f(\alpha)$$

where  $k(T)$  is described by the Arrhenius expression

$$k(T) = Z \exp(-E_a/RT)$$

Here  $Z$  is the pre-exponential constant,  $E_a$  is the activation energy of the reaction,  $R$  is the universal gas constant, and  $T$  is the absolute temperature in kelvin.

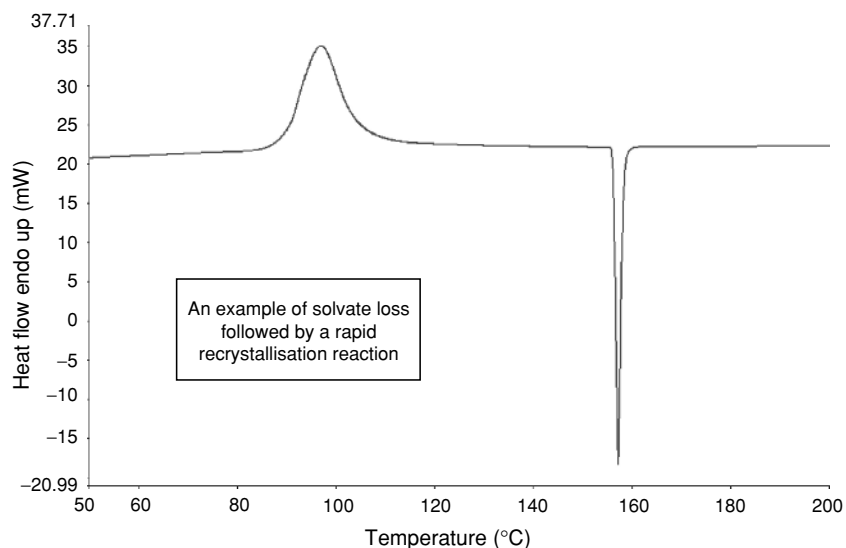
Combining the above equations in logarithmic form gives

$$\ln[d\alpha/dt] = Zf(\alpha) - E_a/RT$$

A plot of  $\ln[d\alpha/dt]$  versus the reciprocal of temperature should then give a straight line of slope  $-E_a/R$ .

This is the so-called Arrhenius plot. Since the slope is dependent upon activation energy, plots of these types are often displayed within kinetics software to allow the operator to check the consistency of the data. This is of particular value where isothermal data are obtained at a series of different isothermal temperatures. A similar expression can be derived for kinetics based on a series of different scan rates, and results in an Arrhenius plot of scan rate versus reciprocal temperature. These plots are then checked at a series of desired conversions.

Once obtained, the kinetic parameters can be used to predict reaction and storage times at times and temperatures not so conveniently measured, and may also give an indication of hazard.



**Figure 1.21** An example of solvate loss, the initial endothermic peak, followed by rapid recrystallisation of the destabilised crystalline structure.

### 1.5.9.3 Recrystallisation reactions

Many pharmaceuticals and foods are prone to polymorphism, where exist a number of distinct crystal structures, and recrystallisation between polymorphs can occur. These are usually fairly rapid events compared to the cure reaction, particularly if resulting from desolvation or dehydration where a solvent or water molecule has been ejected from a crystal leaving it unstable. A typical example is shown in Figure 1.21.

Loss of solvate and hydrate are both observed as endothermic events resulting from the loss of mass from a pan; in a sealed high-pressure pan no transition may be observed. The loss of moisture from a sample can therefore be a significant issue since it can obscure smaller events occurring in the same region, for example the glass transition in a polyamide or a freeze-dried material such as heparin (Figure 2.7).

Thermoplastic polymers are also prone to recrystallisation processes, particularly after rapid cooling employed in many manufacturing processes. Sometimes these are very evident as with PET (Figure 2.5), though sometimes the overall annealing effect does not show an overall exothermic event. The kinetics of recrystallisation processes are usually described by the Avrami equation discussed below.

### 1.5.9.4 The Avrami equation

The Avrami equation is crucial in the description of crystallisation and other processes. The equation has been applied to areas as diverse as corrosion, reaction kinetics and the growth of micro-organisms. If applied correctly, it can give information on the type of nucleation (homogeneous or heterogeneous) as well as the geometry of crystallisation, for

example whether crystals are growing spherically (in three dimensions), or linearly with a needle-shaped form.

Crystallisation can be thought of as the expanding waves when raindrops fall on a pond. The probability that  $n$  circles will pass over a point  $P$  is given by the Poisson distribution  $\lambda^n \exp(-E)/n!$ , where  $E$  is the expected value.

To obtain  $E$ , the contribution of each annulus of width  $dr$  centred at a distance  $r$  from  $P$  is calculated and integrated for all values of  $r$  from 0 to  $vt$ , where  $v$  is the radial velocity of the wave. The integration is permissible because expectation is additive. Nuclei at distances exceeding  $vt$  will not reach  $P$ . The annulus has an area  $2\pi r dr$  and during a time  $(t - r/v)$ , a point within the annulus will be capable of sending out a circle that will cross  $P$  before time  $t$ . If  $\Omega$  is the 2D nucleation rate then

$$dE = \Omega(t - r/v)2\pi r dr \quad \text{and} \quad E = 2\pi\Omega \int_0^{vt} (tr - r^2/v) dr = 1/3\pi\Omega v^2 t^3$$

and the chance that no circle passes over point  $P$  is

$$P_0 = \lambda^0 \exp(-E)/0!$$

or

$$\alpha = \exp(-\pi\Omega v^2 t^3)$$

The crucial point is that the formula is derived for the chance that  $P$  escapes being covered by a circle, i.e.  $n = 0$ . In other words, this expression is for the uncrystallised material.

If the nuclei are pre-existing, the number of circles is represented by a nucleation density  $\omega$  and the number present in an area  $dA$  is  $\omega dA = \omega r dr$ . The function to be integrated contains no time terms, such as  $(t - r/v)$  as all the nuclei are present at the start and none are added. Therefore,

$$E = 2\pi\omega \int_0^{vt} r dr = \pi\omega v^2 t^2 \quad \text{and} \quad \alpha = \exp(-\pi\omega v^2 t^2)$$

These two previous functions have the forms

$$1 - \exp(-kt^3) \quad \text{and} \quad 1 - \exp(-kt^2)$$

Note in particular the value for  $n$ .

Similarly, for expanding spheres from nuclei appearing sporadically in time, the annulus is now a spherical shell and the differential of expectation is

$$dE = \Omega'(t - r/v)4\pi r^2 dr$$

**Table 1.3** The different exponents and expressions for the rate constant in the Avrami equation for different crystallisation morphology

Mechanism of crystal growth	Sporadic nucleation (primary)		Predetermined nucleation (seeded)	
	$n$	$K$	$n$	$k$
Polyhedral	4	$\pi G^3 I/3$	3	$4\pi G^3 I'/3$
Plate-like	3	$\pi dG^2 I/3$	2	$\pi dG^2 I'$
Linear	2	$\pi d^2 GI/r$	1	$\pi d^2 GI'/2$

The Avrami equation here is  $\phi = 1 - \exp(-kt)^n$ .

where  $\Omega'$  is the volume or 3D nucleation rate. This gives a higher power of  $n$  in the expression for the crystallising fraction  $(1 - \alpha)$

$$1 - \exp(-kt^4)$$

This can be summed up in Table 1.3, which shows that fits of these sigmoidal curves to crystallisation data give information on the rate constant as well as the geometry.

The Avrami equation is frequently applied directly to isothermal DSC data where the heat output of the crystallisation process is thought to describe exactly the crystallisation. It can also be applied in modified form to non-isothermal data such as the crystallisation of PET on cooling. It should be noted that there is a certain ambiguity in the exponent value. For example, a value of 3 can mean either 2D nucleation from nuclei appearing randomly in time, or 3D nucleation from pre-existing nuclei.

The issue of induction time is important. Frequently, in order to obtain sensible values for the exponent  $n$ , it is necessary to subtract the induction time, or the time taken for the formation of a stable nucleus. The equation is then

$$\text{Rate} = 1 - \exp[-k(t - t_{\text{ind}})^n]$$

Similarly, the value of the rate constant is frequently put inside the brackets in order to have constant dimensions. The Avrami equation has found increasing application in the foods area, for instance, in the crystallisation of fats as well as more traditional polymer areas.

### 1.5.9.5 Explosives and decomposition reactions

Explosives are a particular class of exothermic reaction where the size of the exotherm is very large. Using small sample sizes of 1–2 mg in the DSC allows the reaction to be controlled and measurements can be made without damage to the analyser. The DSC can be considered as a screen for hazardous materials; usually high-pressure pans are used to encapsulate the sample, and a kinetic evaluation produced. If potential hazard is indicated then samples of larger size can be run on other equipment, for example isothermal/adiabatic calorimetry, to obtain more exact information.

### 1.5.9.6 *Oxidative Induction Time (OIT test)*

In general, sample decomposition should be avoided when using a DSC. They are usually noisy, dirty interactions of exothermic decomposition energy and of endothermic volatile loss and often result in the contamination of the analyser. However, one type of test that does measure decomposition is OIT test, used frequently with oils, polymers and foods. Often production and manufacturing conditions are quite extreme compared to storage and usage conditions, and it is necessary to know whether a material can stand these production conditions. The OIT test is an isothermal test which involves heating the material to the desired test temperature under inert conditions (make sure that the cell is purged of all oxygen before heating). Once holding isothermally at the test temperature the atmosphere is switched to an oxygen atmosphere, and the run continued until the material begins to exotherm, which indicates the start of oxidative decomposition. The run is then stopped. The time from the gas switch to the onset of decomposition is calculated and is known as the oxidative induction time. It is usual to employ automatic gas switching for this test and software will usually employ an OIT calculation which automatically calculates from the gas switching time. Oxygen is normally specified for this test rather than air and it is normal to use a small sample size, e.g. 1–2 mg, and use a completely open pan. When using oils the surface area is all that matters and sample sizes may be smaller; however, the loss of volatiles from oils and similar materials will affect the results. It is for this reason that external pressure cells have been developed and typically operate to about 40 bar, though some may go higher. These suppress the loss of volatiles from open pans and allow measurements to be made with volatile materials. A good example of the use of the OIT test is given in Section 5.2.1.

### 1.5.10 *Guidelines for interpreting data*

First of all optimise the data. Data should be expanded to a scale where transitions of interest can be clearly seen in the context of the trace. It may be helpful to slope the data so that areas of flat response are shown as flat. The eye can interpret more easily from the horizontal. The process of sloping simply pivots the data graphically; it is not a curve fitting or smoothing process so has no effect on transitions or calculations performed. Sometimes transitions are missed simply because they are very small compared to a major transition. Inspect the whole trace carefully if looking for small events. Remember, if a transition cannot be repeated it is unlikely to be real. If in doubt repeat the analysis.

In addition, find out as much about the sample as possible, it is difficult to set up a good method or to give clear interpretations of a trace when working without full information. The sort of information commonly needed is an idea of melting point or decomposition temperature, but more fundamentally it is better to have some idea of what transitions to look for and why. For example:

1. What type of sample is it?
2. What type of transitions can it undergo?
3. What would any changes appear as?
4. What is the temperature range of interest?
5. What data are available from complimentary techniques, e.g. TGA?
6. Has there been any previous analysis?



Then examine the data:

1. Is the event an endotherm or exotherm?
2. Is the event repeatable on a fresh sample or on a reheat?
3. What happens on cooling?
4. Is the event the same in a sealed and unsealed pan?
5. Is the transition sharp or gradual, large or small?
6. Does the event look real? Thermal events are not normally excessively sharp.

Examine the sample pan and look for sample leakage, decomposition or bursting which may have influenced the trace. In some cases, it may be useful to reweigh the pan to see if sample has volatilised and escaped.

The following general comments may help with the assignment of peaks:

#### *Large well-defined endotherms*

1. Pure crystal melting
2. Liquid crystal
3. Solvate/hydrate loss
4. Stress relaxation

#### *Shallow broad endotherms*

1. Moisture loss
2. Residual solvent/monomer loss
3. Sublimation
4. Range of molecular weights melting

#### *Large well-defined exotherms*

1. Crystallisation in/from the liquid state
2. Degradation of highly unstable material
3. Crystal structure rearrangement

#### *Shallow and broad exotherms*

1. Cure reaction
2. Degradation/oxidation

Calculations performed may require careful placement of cursors so that extrapolated tangents and baselines give sensible intercepts. Few software packages offer any automatic calculations, so individual interpretation is required. Often the derivative can help, and with peaks it can be useful to expand the trace to a high level to see where the transition actually began, reverting to a smaller scale once the calculation is performed.

#### *1.5.10.1 Baselines, subtraction, and averaging*

Ideally, the baseline recorded from a DSC with no pans should be flat. A truly flat response is not expected when there is a sample in a DSC since the heat flow data should reflect the

heat capacity of the sample, which will increase as a function of temperature. In practice, if the thermal mass of the sample and reference are not exactly matched a positive or negative slope may arise; often more clearly seen with power compensation systems which measure differential heat capacity directly. The slope of a DSC curve is not an issue, unless extreme, since data can be resloped as required using data handling at the end of a run. Difficulties arise when the baseline is curved or contains anomalies as a result of contamination. It may be that simple cleaning is required but if the instrument itself cannot be adjusted then it may be preferable to run an instrument baseline and subtract it from the data. It should be established first that the baseline is totally stable and reproducible; if it is not then the cause of any instability should be identified.

Where a baseline is to be subtracted it should be run under the same conditions as the sample, and software may permit real-time or post-run subtraction. Real time is preferred since the data set is then permanently saved, though it is helpful if both the subtracted data and un-subtracted data are available for view.

Subtraction routines can also be useful to view differences between materials. A lot of thermal analysis work involves comparison of one material with another. Subtracting curves allows differences to be seen in a more exact way.

When a transition is very small it is possible to improve the sensitivity of the analysis by an averaging process. Just as with techniques such as FTIR (Fourier transform infrared spectroscopy) where the signal improves with the number of scans, repeated DSC scans of the same material can be averaged to improve the final response, though at slow scan rates this can be time consuming. Algorithms for this may be included in the instrument software.

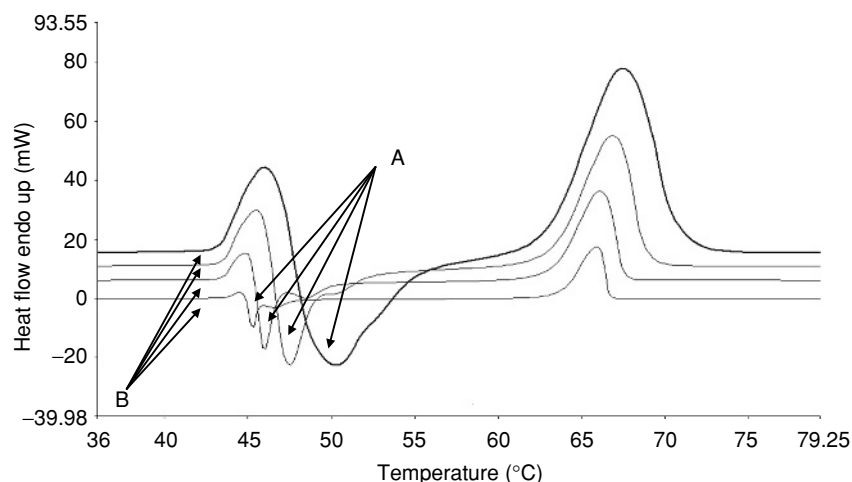
## 1.6 Oscillatory temperature profiles

When a cyclic temperature profile is applied to a sample the heat flow signal will oscillate as a result of the temperature program, and the size of the oscillation will be a function of the heat capacity of the sample. Therefore, the amplitude of the heat flow signal allows a heat capacity value to be obtained. This is similar to DMA (see Chapter 4) where the amplitude of the oscillation allows a modulus value to be obtained. Whilst other methods already exist to provide heat capacity, the value of this method is that the heat capacity measurement is separated from other potentially overlapping events, such as reactions or stress relaxations and can also be obtained with increased sensitivity compared to the slow linear scan rates of traditional DSC.

The sinusoidal approach by Reading [14, 15] introduced the terminology of *reversing heat flow* for what is essentially the heat capacity trace, *total heat flow* for the average of the modulated heat flow trace, which is the conventional DSC trace, and *non-reversing heat flow* for the kinetic response. Since the  $T_g$  is observed as a step in the heat flow trace the reversing heat flow signal has been used to make measurements of  $T_g$ . This curve should show events that are truly reversing in the sense that the same event can be observed upon reheating or recooling.

### 1.6.1 Modulated temperature methods

In many DSC traces, there is evidence of a 'kinetic signal' being present in addition to the usual changes in heat capacity such as those due to the glass transition and melting. This is



**Figure 1.22** The recrystallisation event in this fat sample is shifted as a function of scan rate whereas the melting events remain unaffected.

often hinted at by the kinetic signal being sensitive to the scanning rate while other signals appear to be relatively unaffected (Figure 1.22). Essentially, the kinetics of slow events such as reactions and recrystallisation events are influenced by the scan rate and so shifted to higher temperatures as a function of increasing scan rate. Modulated temperature DSC (MTDSC) techniques allow the reversing heat flow (heat capacity) signal which is measured over the short time period (the period of the modulation) to be separated from slower transitions that occur over a much longer time period. Thus the glass transition can be separated from relaxation, recrystallisation and other events that might obscure it and make the measurements clearer. Relaxation and other non-reversing events should then appear on the non-reversing curve. With appropriate parameters the sensitivity of measurement can be enhanced by the increased rate of scanning that occurs during part of the cycle, which results in an increased heat flow signal. Hence difficult-to-find glass transitions can become more obvious when using modulated methods. MTDSC can also be used in quasi-isothermal mode such that no overall temperature ramp is induced and allows measurement of  $C_p$  values at a single point. This can allow improved resolution of events where a change in  $C_p$  is observed. During melting, energy is continually absorbed by a material and a steady state is not maintained, making analysis of the data more complex.

For many applications a qualitative analysis of the resulting data will be all that is necessary, for example giving values for the glass transition temperature. If a fully quantitative analysis is required it is important to decide on the limits of applicability. Schawe and Hohne [16, 17] have given clear guidelines as to when the reversing and non-reversing signals may be accurately separated from each other. They have stated that only in the case where the reaction is fast, such that the system is always in equilibrium relative to the temperature change and the enthalpy is independent of temperature, will the reversing and non-reversing signals be reliably separated. In addition, the amplitude of temperature modulation must be sufficiently small that the term  $bT_a$  in the temperature-dependent expansion of the reaction

rate can be neglected. This is equivalent to a reaction, which although clearly time dependent has a weak temperature dependence and so will be in equilibrium for small temperature steps. This can be summed up in the following equations.

The degree of reaction can be expanded as

$$\alpha(T) = a + bT + cT^2 + \dots$$

where  $\alpha$  is the degree of reaction,  $a$ ,  $b$  and  $c$  are constants, and  $T$  is the temperature. The scanning rate is

$$\beta = \beta_0 + \omega_0 T_a \cos \omega_0 t$$

where  $\beta_0$  is the linear rate of temperature increase, and  $\omega_0$  and  $T_a$  are the frequency and the amplitude of modulation respectively.

The heat flow into the sample =  $C \times$  scanning rate, where  $C$  is a generalised heat capacity

$$C = C_p + H_r d\alpha/dT$$

Therefore the heat flow into the sample is

$$(C_p + H_r d\alpha/dT) \times (\beta_0 + \omega_0 T_a \cos \omega_0 t)$$

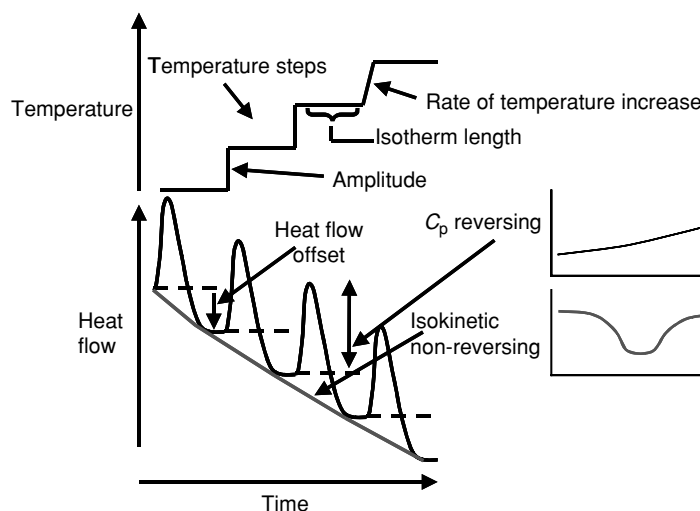
$T_a$  can be chosen such that the effect of modulation on the reaction is small and so a linear approximation to the effect of the temperature profile on the reaction can be used.

Therefore, the heat flow into the sample is  $[C_p \beta_0 + H_r d\alpha/dT \beta_0] + C_p \omega_0 T_a \cos \omega_0 t$  where  $H_r$  is the enthalpy of reaction. It can be seen that in this case the reversing signal can be obtained from the second term in the periodic heat flow, as there is no complication of other contributions such as the energy of reaction appearing in this term. The conventional DSC trace can then be used as a background for subtraction to obtain the energy of the kinetic transition, provided the frequency dependence of the reversing signal is weak relative to the modulation frequency. This is a rather stringent test, even the well-known cold crystallisation of PET fails to completely meet these criteria, except at the very lowest of modulation amplitudes and underlying heating rates.

If the modulation amplitude is higher, such that  $T_a$  cannot be neglected or it causes the reaction to behave non-linearly, i.e. requires higher terms in the expansion for  $\alpha(T)$ , then a simple separation can no longer be made. Further, if the signal is delayed in time from the stimulus, in this case the temperature rate, then the treatment of the data cannot be analysed in the previous way and needs to be treated in a linear-response framework along the lines of rheology and dielectric data to obtain in-phase and out-of-phase components. Interpretation of data can then become very complex and difficult to relate to events in the material.

### 1.6.2 Stepwise methods

Using a stepwise approach, the method of calculating thermodynamic (reversing) and iso-kinetic baseline (non-reversing) signals is different from the methods given in the previous

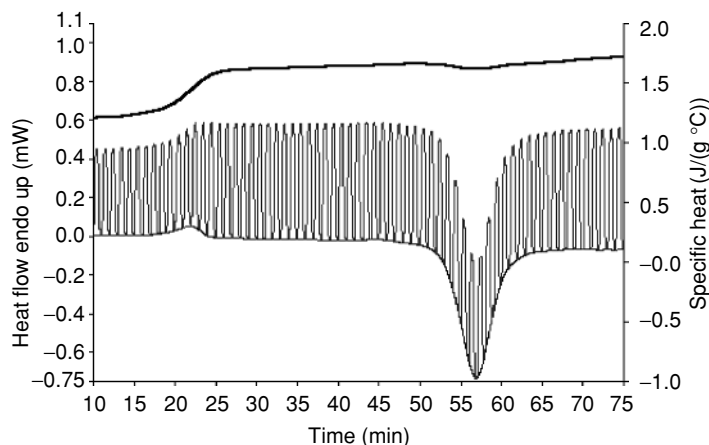


**Figure 1.23** A diagram of the temperature profile used in step-based methods and the heat flow signal that results. Heat capacity is calculated either from peak height as in the classical method, or peak area of the heat flow trace. The kinetic response is obtained from the isothermal portion.

section [18] and the above equations do not apply directly. As Figure 1.23 shows, the ‘non-reversing’ signal can more correctly be labelled the ‘slow’ component, and is the power offset at the end of the isotherm, whilst the reversing trace is calculated from the amount of heat required to raise the sample temperature by a given amount – a conventional heat capacity measurement. This can be achieved using either amplitude of heat flow, or the area under the curve. In order to achieve a reasonable (if only approximate) separation into reversing or rapid and non-reversing or slow signals it is important that the isotherm length is chosen correctly. If it is too short, then an artificially high signal can appear in the non-reversing trace. In general, the isothermal period should be long enough for the system to reach stability, typically 30–60 s. Moreover, if the slow signal varies with time or the isothermal profile changes with temperature, as has been shown for the rapid transitions between polymorphic forms such as in tripalmitin or chocolate, then there will be unavoidable sources of error. Additionally, if the amplitude of the step is too large, the peaks will be widened due to averaging so reducing resolution. To a first approximation, the slope of the step is unimportant in determining the heat capacity; at least in this form of analysis.

One example of information obtained from step-based methods is shown in Figure 1.24. The heat capacity of the material is obtained, separated from the crystallisation and relaxation phenomena which appear in the kinetic trace, leading to a clearer measurement of the glass transition. This is typical of the type of information available from modulated methods in general.

There is also a step-based equivalent technique founded on linear-response theory. This has been presented by Schick and co-workers [19] and is formally equivalent to the real and imaginary heat capacities generated by modulation at a single frequency. In principle, it is therefore possible to apply a Fourier transform to step-scan type data and break down the overall response into heat flow responses to a series of sinusoidal temperature modulations.



**Figure 1.24** Step-scan trace of PET shown as a function of time. The step increase in  $C_p$  identifies the glass transition, whilst a slight reduction also occurs as the sample recrystallises. The IsoK curve matches the lower envelope of the heat flow data. Quantitative data of these types require a baseline subtraction in accord with the requirements of the  $C_p$  method. Qualitative data showing the events can be obtained if this is not performed.

In this case, the slope of the initial step is important as this contains the high-frequency information. Any phase differences observed between stimulus and response and not caused by the DSC instrument itself will invalidate the simple reversing/non-reversing methods, but are coped with in linear-response theory.

## 1.7 DSC design

### 1.7.1 Power compensation DSC

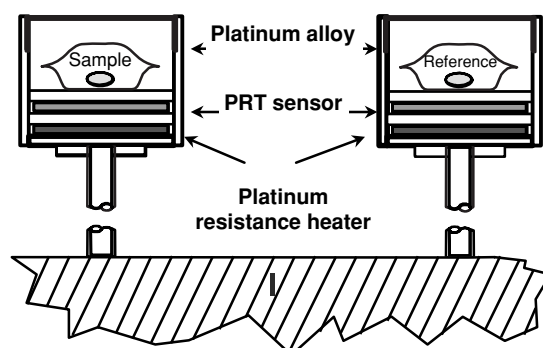
Power compensation DSC has at its heart two small identical furnaces, one for the sample and one for the reference (normally an empty pan), the reference being the right-hand furnace; Figure 1.25. These are both heated at a pre-programmed heating (or cooling) rate and power compensations are applied to either furnace as required to maintain this rate. In the resulting DSC trace the difference in energy flowing into the sample furnace is compared to the inert reference and plotted as a function of temperature or time. This design measures flow of energy directly in mW or J/s.

The fundamental equation of DSC is

$$\text{DSC signal (W/g)} = \text{Heat Capacity (J/(K g))} \times \text{Scanning Rate (K/s)}$$

$$dH/dt = dH/dT \times dT/dt$$

Therefore the raw heat flow signal can be viewed as a form of heat capacity. In practice, it reflects the changes occurring in heat capacity, and the absolute value is obtained when the



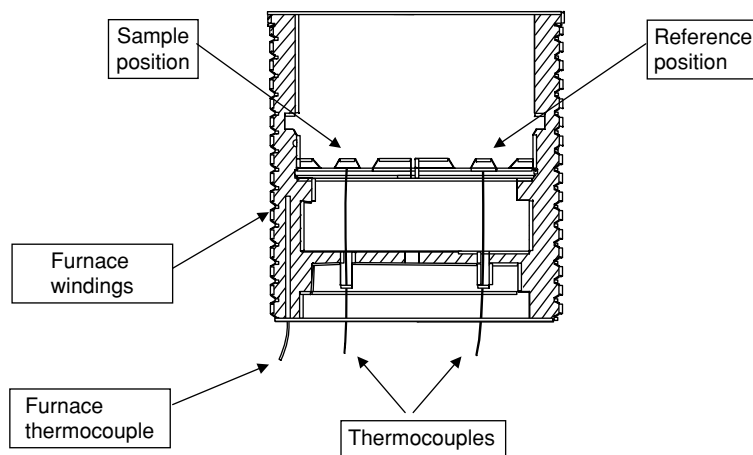
**Figure 1.25** Diagram of a power compensation DSC. In this system, both the sample and reference furnaces are heated at a programmed heating/cooling rate. In order to maintain this rate when transitions occur in the sample, a power compensation circuit increases or reduces power to either furnace as required in order to maintain the heating rate. The power compensation circuit therefore reflects the energy changes occurring in the sample and is presented on the screen as a function of temperature or time. This technique measures energy changes directly.

method used takes into account the contribution of the empty pans and reference together with the scan rate.

The small furnaces of this system can be heated or cooled at very low rates to very high rates and are ideal for a range of different techniques, particularly fast scan DSC. Power-compensated DSC also permits true isothermal operation, since under constant temperature conditions both the sample and furnace are held isothermally. The temperature range of use is from liquid nitrogen temperatures to around 730°C.

### 1.7.2 Heat flux DSC

Heat flux DSC is of a single furnace design with a temperature sensor (or multiple sensors) for each of the sample and reference pans located within the same furnace; see Figure 1.26. Sample and reference pans are placed in their required positions and the furnace heated at the pre-programmed heating (or cooling) rate. When transitions in the sample are encountered a temperature difference is created between sample and reference. On continued heating beyond the transition this difference in temperature decreases as the system reaches equilibrium in accordance with the time constant  $\tau$  (see Glossary) of the system. It is the difference in temperature or  $\Delta t$  signal that is the basic parameter measured. Modern analysers are carefully calibrated so that the  $\Delta t$  signal is converted to a heat flow equivalent and this is displayed as a function of temperature or time. The reason a difference in temperature is created is easily understood if melting is considered. When melting of a single crystal occurs the resulting mixture of solid and liquid remains at the melting point until melting is complete, so the temperature of the sample will fall behind that of the reference. Typical heat flux DSC analysers can be used from liquid nitrogen temperatures to a maximum of around 700°C similar to power compensation DSC, though modern



**Figure 1.26** Diagram of a heat flux DSC. In this system, both the sample and reference experience the same heat flux, but as energy demands differ, the heating or cooling effect will differ resulting in a difference in temperature between sample and reference. This difference in temperature is converted to an energy equivalent by the analyser giving the familiar DSC signal in mW. (This figure was produced by Anantech in Holland.)

high-temperature DTA analysers normally offer a calibrated DTA (heat flow) signal giving a measurement derived from the heat flux to significantly higher temperatures.

### 1.7.3 Differential thermal analysis DTA

This design principle is similar to heat flux DSC, except that the  $\Delta t$  signal remains as a microvolt signal and is not converted to a heat flow equivalent. This was the original instrument approach used before quantitative energy measurements were established using DSC. Often instruments capable of heating to around 1500°C or higher use this principle and are referred to as DTA analysers. The furnace design is usually quite different to that of lower temperature systems, though modern equipment may offer a choice of heat flow or microvolt signals.

### 1.7.4 Differential photocalorimetry DPC

Reactions not only occur as a function of temperature but may also be initiated by irradiation, specifically ultraviolet (UV) light for materials that are photosensitive. UV systems have therefore been attached to DSC analysers to provide DPC systems. This can be done fairly crudely by shining a light on a material using fibre optics, but formal accessories are available from a number of manufacturers. Isothermal control of these systems is important, and the light source should not adversely affect the calorimetry. Applications are found in curable materials in the composites and manufacturing industries, dentistry and dental materials together with films, coatings and printing inks. The wavelength chosen and the intensity of



the light are significant factors, which together with the temperature of reaction and length of exposure can be used to define a method. The effects of temperature, light intensity, and wavelength can be investigated on different materials and additives, and the kinetics of reaction investigated using isothermal kinetics models.

The effect of infrared light can also be investigated in a similar manner [20]. These authors also highlight the ability to measure a simultaneous non-contact TMA signal from a sample placed in the DSC cell.

### 1.7.5 High-pressure cells

Many manufacturers provide pressure cells as an accessory to the DSC. These normally work to fairly modest pressures of around 50–100 bar and are designed with a view to the suppression of volatiles in OIT tests involving oils and greases. A high-pressure cell capable of working to much higher pressures has been constructed by Höhne and co-workers and can be operated at pressures from 0.1 to 500 MPa over a temperature range from 20 to 300°C [21] and is potentially capable of being added to some commercial analysers.

## Appendix: standard DSC methods

### ISO Standards

11357-1:1997 Plastics – Differential Scanning Calorimetry (DSC)

#### Part 1: General Principles

11357-2:1999 Plastics – Differential Scanning Calorimetry (DSC)

#### Part 2: Determination of Glass Transition Temperature

11357-3:1999 Plastics – Differential Scanning Calorimetry (DSC)

#### Part 3: Determination of Temperature and Enthalpy of Melting and Crystallisation

11357-4:2005 Plastics – Differential Scanning Calorimetry (DSC)

#### Part 4: Determination of Specific Heat Capacity

11357-5:1999 Plastics – Differential Scanning Calorimetry (DSC)

#### Part 5: Determination of Characteristic Reaction Curve Temperatures and Times Enthalpy of Reaction and Degree of Conversion

11357-6:2002 Plastics – Differential Scanning Calorimetry (DSC)

#### Part 6: Determination of Oxidative Induction Time

11357-7:2002 Plastics – Differential Scanning Calorimetry (DSC)

#### Part 7: Determination of Crystallisation kinetics

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