

Introduction to
Differential Scanning Calorimetry

Practical Course
(English version, Sept. 2002)



Contact : Dr. R. Nicula
Physics Dept., Rostock University
e-mail : nicula@physik1.uni-rostock.de

Thermoanalytical Methods

1. Overview

2. Differential Thermal Analysis (DTA)

2.1. Introduction.

2.2. DTA Instrument.

2.3. Experimental details : potential sources of error.

2.4. Data analysis.

3. Differential Scanning Calorimetry (DSC)

3.1. Introduction

3.2. Heat-flux DSC Systems

3.2.1. Basic Components.

3.2.2. Analysis of Heat-Flow in a Heat-Flux DSC.

3.2.3. Temperature Calibration.

3.2.4. Enthalpy Calibration.

3.2.5. Baseline subtraction. Transformation Curves.

3.3. Applications of Differential Scanning Calorimetry

3.3.1. Continuous Heating/Cooling Experiments.

3.3.2. Isothermal Experiments : Kinetics of Phase Transitions.

3.4. The NETZSCH 404C Pegasus DSC/DTA/Cp Instrument

3.4.1. Basic components, technical features & specimen environment.

3.4.2. Operation Manual.

3.4.3. Data Analysis Procedures. Introduction to the Proteus software.

3.5. Experimental Module Implementation (in preparation)

Other Thermoanalytical Methods (optional)

4. Thermal-modulated DSC (TMDSC)

5. Thermogravimetric Analysis (TGA)

6. Dilatometry (DIL)

7. Related Experiments : Temperature-resolved X-ray Diffraction

List of Symbols and Abbreviations

Further Reading

Useful Links

1. Overview

Thermal analysis comprises a group of techniques in which a physical sample property is measured as a function of temperature, while the sample is subjected to a predefined heating or cooling programme.

In differential thermal analysis (DTA), the temperature difference between a sample and an inert reference material is measured, when both are subjected to identical heat treatments. The related technique of differential scanning calorimetry (DSC) relies on differences in energy required to maintain the sample and reference at an identical temperature.

Both thermogravimetry (TGA) and evolved gas analysis (EGA) are techniques which rely on samples which decompose at elevated temperatures. The former monitors changes in the mass of the specimen on heating, whereas the latter is based on the gases evolved on heating the sample. Electrical conductivity measurements can be related to changes in the defect density of materials or to study phase transitions.

Length or volume changes that occur on subjecting materials to heat treatment are detected in dilatometry (DIL). X-ray or neutron diffraction can also be used to measure dimensional changes.

2. Differential Thermal Analysis (DTA)

2.1 Introduction

The principle of the DTA technique resumes to heating (or cooling) a test sample (S) and an inert reference (R) under identical conditions while measuring the temperature difference ΔT between S and R.

The differential temperature ΔT is then plotted against time or against temperature. Chemical, physical, structural and microstructural changes in the sample S lead to the absorption (endothermic event) or evolution of heat (exothermic event) relative to R. If the response of two inert samples submitted to an applied heat-treatment programme is not identical, differential temperatures ΔT arise as well. Therefore, DTA can also be used to study thermal properties and phase changes which do not necessarily lead to a change in enthalpy.

The baseline of the DTA curve exhibits discontinuities at transition temperatures and the slope of the curve at any point will depend on the microstructural constitution at that temperature. The area under a DTA peak can be related to the enthalpy change and is not affected by the heat capacity of the sample.

2.2 DTA Instruments

The basic components of a differential thermal analysis (DTA) cell are shown in Fig.1. The sample environment consists of a ceramic (or metallic) block to ensure a uniform heat distribution, specimen crucibles and thermocouples (for the sample and reference). Metallic blocks are less likely to cause baseline drifts compared with porous ceramics, but the DTA signal is smaller, due to the higher thermal conductivity of metals.

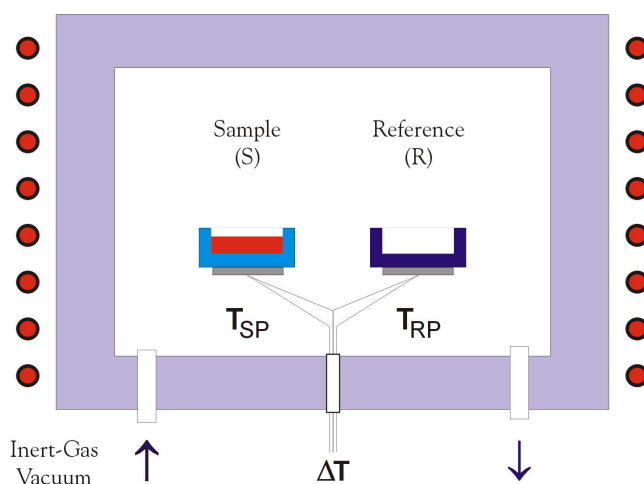


Fig. 1 Schematic illustration of a DTA cell.

The samples are placed in Pyrex, silica, Ni or Pt crucibles (according to the temperature programme and purpose of the experiment). Thermocouples should not be placed in direct contact with the sample to avoid contamination and degradation, even though sensitivity may be compromised. The sample assembly is isolated against electrical interference with the wiring of the oven with an earthed metallic or Pt-coated ceramic sheath.

For heating experiments up to about 500°C, an uniform transfer of heat away from the sample may be difficult. Disc-shaped thermocouples must then be used to ensure optimum thermal contact with the bottom-side of the sample container (Al or Pt foil). The furnace should provide a stable, large enough hot-area and a fast response to the temperature-controller commands. Data acquisition and/or the real-time display is handled by a computer system or an analog device (plotter).

2.3 Experimental details : potential sources of error.

Experimental parameters such as specimen environment, chemical composition, size, surface-to-volume ratio must carefully be selected, since they might modify for example the thermal decomposition of powder materials even though their solid-state phase transitions are not affected. The packing state of powder samples is important in these thermal decomposition reactions and may lead to significant differences in thermal behaviour between otherwise identical samples. Moreover, DTA measurements on powder materials do not always correctly illustrate the thermal behaviour of bulk specimens, for which most phase transitions will also exhibit the influence of built-in strain energy.

The heat flow rate may sometimes saturate the response capability of the DTA system. It is then advisable to dilute the specimen with a thermally-inert material. For the detection of phase transition temperatures, one must also check that the peak temperature T_p does not vary with sample size. The shape of DTA peaks depends on sample weight and on the heating rate employed. Low heating rates or small sample weights lead to better resolved (sharper) DTA peaks, but the signal-to-noise ratio might however be compromised. Reducing the specimen size or the heating rate is also important in kinetic analysis (isothermal) experiments, where thermal gradients should be minimized.

2.4 Data Analysis

The heat capacity and thermal conductivity of the test specimen (S) and reference sample (R) are usually not identical. This gives rise to a certain displacement between their response in the linear regions of the DTA trace. The DTA peaks correspond to evolution or absorption of heat following physical or chemical changes in the specimen (S) under analysis.

The detection of phase transition temperatures using DTA is not very accurate. The onset of the DTA peak indicates the start of the phase transition, but temperature shifts from the true values are likely to occur depending on the location of the thermocouples with respect to the specimen, reference or to the heating block. Therefore, the temperature calibration of the DTA instrument using standard materials with known melting points is necessary.

The area (A) enclosed between the DTA peak and the baseline is related to the enthalpy change (Q) of the specimen during the phase transition. When the thermocouples are in thermal (but not in physical) contact with the specimen and reference materials, it can be shown that the peak area A is given by

$$A = \frac{Q}{g \cdot K} = \frac{m \cdot q}{g \cdot K}$$

where

- m = sample mass (weight)
- Q = enthalpy change of the specimen
- q = enthalpy change per unit mass
- g = (measured) geometrical shape factor
- K = thermal conductivity of sample

Errors in estimating the correct DTA peak areas are likely to occur for powder materials and compacted samples which retain some degree of porosity. The gas filling the pores or which eventually evolves from the specimen itself, alters the thermal conductivity of the DTA cell environment (compared to calibration experiments), leading to rather large errors in the DTA peak areas.

Enthalpy calibration : the energy scale of the DTA instrument must also be calibrated to absolute enthalpy values by measuring peak areas on standard samples over specified temperature ranges. The enthalpy calibration implies measuring at least 2 different samples for which both heating and cooling experiments must be performed. It is then possible to measure the constant pressure heat capacity (C_P) using the DTA method :

$$C_P = k \cdot \frac{T_2 - T_1}{m \cdot H}$$

where H is the heating rate employed, k is the enthalpy calibration constant and T_1 and T_2 are the differential temperatures generated during an initial 'empty' run (without sample) and during the actual DTA measurement (with sample), respectively.

Literature

Standards : DIN 51007, DIN 53765, ASTM E 474, ASTM D 3418.

3. Differential Scanning Calorimetry

3.1 Introduction

Differential scanning calorimetry (DSC) is an experimental technique for measuring the energy necessary to establish a nearly-zero temperature difference between a test substance S (and/or its reaction products) and an inert reference material R, while the two samples are subjected to an identical (heating, cooling or constant) temperature programme. Two types of DSC systems are commonly in use :

Power-compensation DSC : the specimen (T_S) and reference (T_R) temperatures are controlled independently using separate (identical) ovens. The temperature difference between the sample and reference is maintained to zero by varying the power input to the two furnaces. This energy is then a measure of the enthalpy or heat capacity changes in the test specimen S (relative to the reference R).

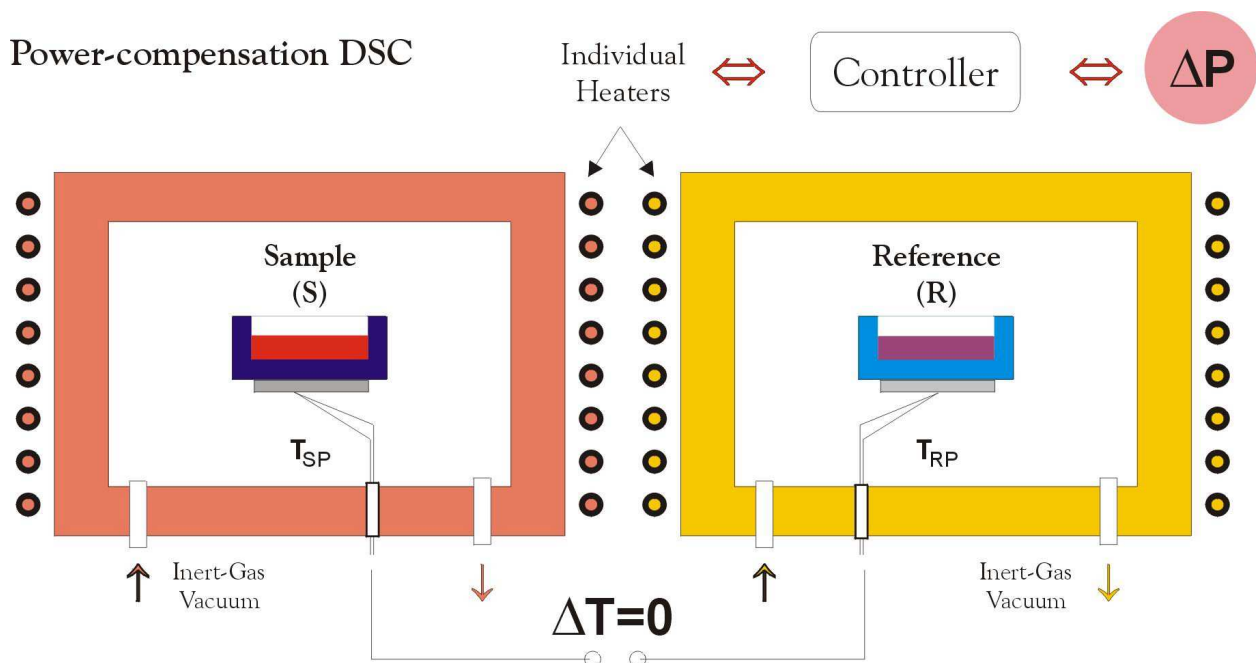


Fig. 2 Power-compensation DSC.

Heat-flux DSC : the test specimen S and reference material R (usually an empty sample pan+lid) are enclosed in the same furnace together with a metallic block with high thermal conductivity that ensures a good heat-flow path between S and R. The enthalpy or heat capacity changes in the specimen S lead to temperature differences relative to R. This results in a certain heat-flow between S and R, however small compared to those in DTA, because of the good thermal contact between S and R. The temperature difference ΔT between S and R is recorded and further related to the enthalpy change in the specimen using calibration experiments.

The heat-flux DSC system is thus a slightly-modified DTA system : the only important difference is the good heat-flow path between the specimen and reference crucibles. The DSC instrument used in the present experiment is a heat-flux type NETZSCH 404C Pegasus calorimeter. Therefore special attention will be given to this type of instruments.

3.2 Heat-Flux DSC Systems.

3.2.1 Basic Components.

The main assembly of a typical heat-flux DSC cell is enclosed in a heating block (for example Ag), which dissipates heat to the specimens (S and R) via a constantan disc attached to the Ag block. The constantan disc has two platforms on which the S (specimen) and R (reference) pans are placed. A chromel disc and connecting wire are attached to the underside of each platform: the resulting chromel-constantan thermocouples are used to determine the differential temperatures of interest. Alumel wires are also attached to the chromel discs to provide chromel-alumel junctions which measure the sample and reference temperatures separately. Another thermocouple is embedded in the Ag block and serves as temperature controller for the programmed heating/cooling cycle.

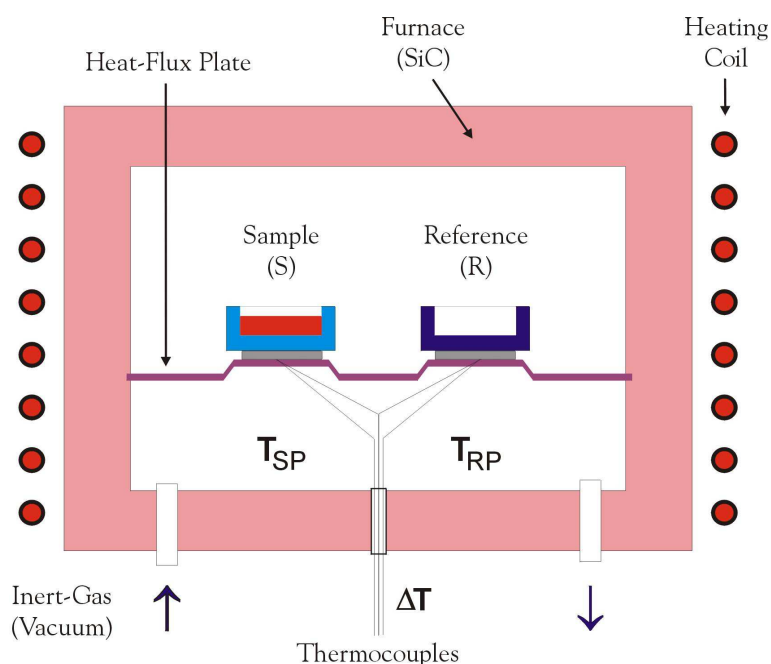


Fig. 3 Main components of a typical heat-flux DSC cell.

In heat-flux DSC instruments, the difference in energy required to maintain both S and R at the same temperature is a measure of the energy changes in the test specimen S (relative to the inert reference R). The thermocouples are usually not embedded in neither S or R materials. The temperature difference ΔT that develops between S and R is proportional to the heat-flow between the two. In order to detect such small temperature differences, it is essential to ensure that both S and R are exposed to the same temperature programme.

The measurements are usually performed under vacuum or inert-gas flow : the flow rate (typically around 40 ml/min.) is maintained constant throughout the experiment.

3.2.2 Analysis of Heat-Flow in Heat-Flux DSC.

The assembly of thermal resistances of the heat-flux DSC system changes with temperature. Nevertheless, DSC instruments may be used in the so-called 'calibrated' mode : the amplification of the DSC signal is then also automatically varied with temperature to maintain a constant calorimetric sensitivity with temperature.

Temperature shifts may occur between the samples (S and R) and thermocouples, since these are not in direct physical contact with the samples. The measured temperature difference ΔT_{exp} is not equal to $(T_S - T_R)$ where T_S and T_R are the sample and reference temperatures, respectively. The temperature difference of interest $(T_S - T_R)$ may however be deduced by considering the heat-flow paths in the DSC system (Fig.4).

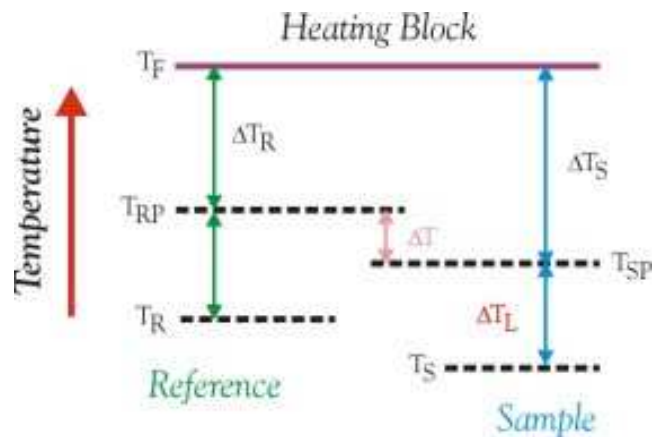


Fig. 4 Thermal-resistance diagram for a typical heat-flux DSC system.

Greer and Baxter notation :

T_{SP} , T_{RP} = temperature of the sample (SP) and reference (RP) platforms as measured by the thermocouples. T_{SP} is plotted as the abscissa of the measured DSC curve.

T_F = temperature of the heating block (furnace).

R_D = thermal resistance between the furnace wall and the SP or RP platforms [$C \cdot \text{min}/J$].

R_S , R_R = thermal resistance between the SP (or reference RP) platform and the sample S (or reference R).

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

H = external (imposed) heating rate.

ΔT_R = temperature difference of the reference platform RP relative to the furnace.

ΔT_S = temperature difference of the sample platform SP relative to the furnace.

ΔT_L = temperature difference of the sample S relative to the sample thermocouple.

Then the following equations hold:

$$\Delta T_R = H \cdot R_D C_R \quad (1)$$

$$\Delta T_S = H \cdot R_D C_S \quad (2)$$

$$\Delta T = H \cdot R_D (C_S - C_R) \quad (3)$$

$$\Delta T_L = H \cdot R_S C_S \quad (4)$$

$$\Delta T_S = \Delta T_R + \Delta T \quad (5)$$

$$\Delta T_L = R_S / R_D \Delta T_S \quad (6)$$

The temperature shift (ΔT_L) occurs because the thermocouple is not in physical contact with the sample. If a certain phase transition temperature T_x does not vary with the

external heating rate H , equation (4) indicates that the plot of the apparent T_x vs. H (with all other parameters fixed), extrapolates to the true transition temperature value T_{x0} of T_x at $H=0$. Therefore, the apparent T_x is the true value T_{x0} plus the temperature difference. Note that the plot of apparent T_x versus C_S also extrapolates to T_{x0} at $C_S = 0$, when H and R_S are constant.

Greer procedure: is based on equation (6) and involves the evaluation of $R_S=R_D$. (ΔT_R) is measured for a particular reference (usually an empty pan and lid). An 'empty' heating run is first performed with an empty pan on both the sample and reference platforms. This provides a baseline, from which measurements of ΔT can be carried out. A second run is then performed, with 2 pans on the sample platform and one on the reference platform. The difference between the first and second DSC curves is a measure of (ΔT_R) as a function of temperature.

This results directly equations (1) and (3) : for the first 'empty' run, $C_S=C_R$ and therefore $\Delta T = 0$ (eqn.3), while for the second run $C_S=2C_R$, so that $\Delta T=\Delta T_R$ (eqn.1). By repeating this procedure for different heating rates, ΔT_R can be obtained as a function of heating rate H . To obtain the sample-to-thermocouple temperature difference (ΔT_L) we use the fact that :

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

A series of test measurements is conducted for different heating rates H with a standard sample with known transition temperature T_x (which does not depend on H) mounted in the sample pan and an empty pan mounted on the reference platform. These measurements will provide $\Delta T(H)$. Since $\Delta T_R(H)$ was previously obtained, the above equation will give $\Delta T_S(H)$. The gradient g_1 of the ΔT_S vs. H plot equals $R_D C_S$ (eqn.2).

Another set of experiments (see eqn.4) finally gives a plot of the apparent transition temperature $T_x(H)$ and its extrapolation at $H=0$ yields the true transition temperature T_{x0} . The dependence T_L vs. H can now be plotted, and its gradient $g_2 = R_S C_S$ (eqn.4) can be obtained. Then :

$$\frac{g_1}{g_2} = \frac{R_D}{R_S}$$

and the temperature shift ΔT_L may be calculated (R_S/R_D and ΔT_R known) using equation (6) for any given reference R and at any heating rate H or C_S .

3.2.3 Temperature Calibration

The measured temperature values are related to the emf generated at the thermocouples located under the sample. The emf is converted to temperature units using standard calibration charts, however several effects cause the thermocouple to age and shift calibration. It is therefore recommended to calibrate the temperature axis using substances with precisely known melting points. Most DSC instruments allow calibration over limited temperature ranges. In calibrating the temperature scale to true temperature values, one must also consider the thermal shift (ΔT_L). Nevertheless, the temperature shift effect can in principle be avoided by using very low heating rates during the calibration measurement.

3.2.4 Enthalpy Calibration

The energy calibration is carried out by measuring changes in specific heat or in enthalpy of standard specimens for which these quantities are known. The heat balance equation for the heat-flux DSC system can be shown to be as follows (eqn.7) :

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

dH'/dt refers to the heat evolution of an exothermic transition; the first term on the right side is the area under the DSC peak, after the baseline correction. The second term refers to the actual baseline (this is used in specific heat determinations). The last term takes into account the fact that the evolved heat partially will be consumed by the specimen to heat itself. It does not affect the DSC peak area, but may distort the peak shape.

When $dH'/dt = 0$, the second term of equation 7 can be used to determine specific heat. The method involves a comparison of the thermal shift (difference) between sample and reference. The system is first calibrated with a sapphire specimen, so that

$$C_{sapphire} = \frac{E \cdot q \cdot Y}{H \cdot m}$$

where

m = mass of the specimen

E = calibration constant

$C_{sapphire}$ = specific heat capacity of sapphire

qY = axis range (Js/mm)

H = heating rate

and Y = difference in Y-axis deflection between sample (or sapphire) and 'empty' runs (blank curves) at the temperature of interest.

Enthalpy changes can be determined by measuring the areas under peaks on the DSC curve ΔT vs. time. A relationship of the form indicated in equation (1) applies when the instrument is in calibrated mode.

3.2.5 Baseline subtraction. Transformation Curves.

Both DSC and DTA experiments are commonly performed either isothermally or with the temperature changing at a constant rate. In isothermal experiments, the DSC signal is plotted against time at for each constant temperature. In dynamic experiments, the DSC signal is plotted against either time or temperature.

The *height* of the DSC signal commonly refers to the signal above the baseline. For DTA measurements, the height of the curve at any time t is a measure of the temperature difference ΔT between the specimen and the reference. For power compensated DSC, the height of the curve at some particular time t is a measure of the heat evolving from the sample per unit time (dH'/dt). The same applies for heat-flux DSC measurements, after suitable calibration.

With x = the volume fraction of the transformation, H' = the enthalpy change, and t = elapsed time, measured from the onset point of the transition (i.e. where the DSC/DTA signal departs from the baseline) one may assume that :

$$\Delta T \sim dx/dt$$

The proportionality constant is obtained from the condition that the DSC/DTA peak area corresponds to $x = 1$ (transformation completed) or more generally, $x = \text{const.}$ (if for some reason the transition is not completed).

The evaluation of the DSC peak areas is based on the assumption that a reliable baseline is obtained experimentally. The quantitative estimation of the baseline is more difficult for broader DSC peaks. Even without a phase transition, the DSC instrument measures the effect of the heat capacity of the sample, which usually changes with temperature. This change is nearly linear, however a non-linear behaviour (curvature) becomes noticeable over wider temperature ranges.

The simplest approximation to the baseline is a straight line connecting the start and finish of the transformation, valid for sharp enough DSC peaks. Nevertheless, the most reliable way of calculating the baseline is the iterative technique proposed by Scott and Ramachandrarao : the transformed fractions are first calculated using a linear baseline between the initial and final points of the reaction. The baselines before and after the transition are then extrapolated under the DSC peak to give two separate baselines (the heat capacity of the initial specimen and reaction product are usually different). A new baseline at any t is then chosen to be at a position between the extrapolated baselines. The exact position of this new baseline depends on the amount of reaction product at any time t (calculated using a kind of lever rule). The new baseline can further be used as the starting point of another iteration. The iteration process can be repeated to the desired accuracy. In practice, one iteration seems good enough for most purposes.

As previously mentioned, the peak shape may exhibit some distortion, due to the fact that some of the evolved heat may actually serve to heat the sample itself. In dynamic (continuous heating) experiments, the magnitude of this self-heating effect can be shown to be proportional to the heat capacity of the sample and to the rate of change of the differential temperature with time.

Autocatalysis and recalescence : DSC/DTA experiments are either adiabatic (no heat exchange) or isothermal (constant temperature). In practice, experiments are performed somewhere between the ideal isothermal and adiabatic conditions. Whenever the rate of heat evolution is larger than the calorimeter's capacity to maintain isothermal conditions, the specimen temperature rises until a steady state is reached. This adiabatic rise in temperature will affect the rate of the transition (reaction), which further stimulates the exothermal event (evolution of heat). This effect is known as *autocatalysis*. *Recalescence* describes the case where the release of heat reduces the transformation rate.

3.3 Applications of Differential Scanning Calorimetry

3.3.1 Dynamic DSC/DTA Experiments

In **dynamic** DSC/DTA experiments, the specimen is continuously heated (or cooled) with a steady heating/cooling rate (H). Fig. 6 illustrates a typical DSC scan (heat-flow vs. temperature or time), showing the phase transitions of a well-known polymer (PEEK, polyetheretherketone) upon a first heating cycle. The small endothermic peak around

140°C corresponds to the glass-transition and may be taken as proof for the initial glassy-state of the specimen. Upon further heating, crystallization occurs exothermally (heat released from the specimen) at 169°C, followed by melting of the sample (indicated by the endothermic – heat absorption - event at 339°C).

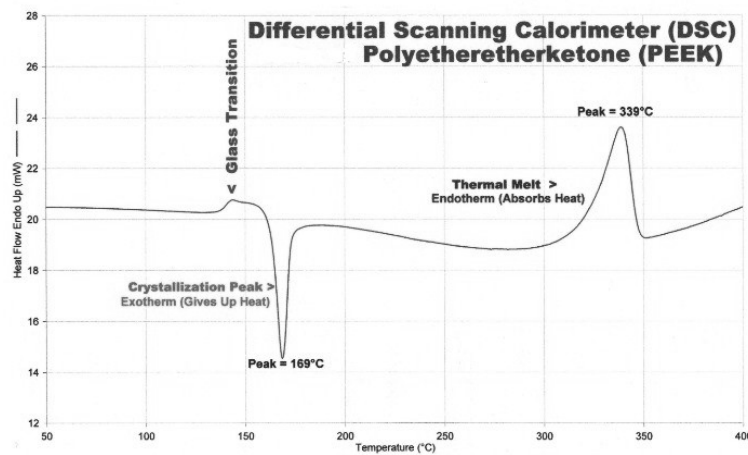


Fig. 6 Typical DSC scan : continuous heating of PEEK.

Differential Scanning Calorimetry (DSC) therefore measures the amount of energy absorbed (**endothermal** event) or released (**exothermal** event) by a specimen either during continuous heating/cooling (**dynamic** or **non-isothermal**) experiments or during **isothermal** experiments (specimen maintained at a constant temperature).

Process / Transition	Exothermal	Endothermal
Solid-solid transition	♣	♣
Crystallization	♣	
Melting		♣
Vaporization		♣
Sublimation		♣
Adsorption	♣	
Desorption		♣
Drying (solvent removal)		♣
Decomposition	♣	♣
Solid-state reaction	♣	♣
Solid-liquid reaction	♣	♣
Solid-gas reaction	♣	♣
Polymerization	♣	
Catalytic reactions	♣	

3.3.2 Isothermal Experiments : Kinetics of Phase Transitions

The DSC/DTA technique has also been employed to investigate the crystallization of glassy materials. Most results have been analysed using the **Johnson-Mehl-Avrami (JMA)** equations. The general form of the JMA equation is:

$$x(t) = 1 - \exp(-kt^n)$$

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

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

Activation energy : the term k is temperature dependent since it is a function of the nucleation and growth rates of the transformation product; for most solid-state transformations both these processes can be expected to be thermally activated. We assume a transformation with random nucleation, constant nucleation and growth rates and isotropic growth. The JMA equation then becomes:

$$x(t) = 1 - \exp\left(-\frac{\gamma^3 N \cdot t^4}{3}\right)$$

where γ is the growth rate and N is the nucleation rate per unit volume. It follows that :

$$k = \frac{\gamma^3 N}{3} = C_1 \cdot \left[C_2 \cdot \exp\left(-\frac{G_\gamma}{RT}\right) \right]^3 \cdot \left[C_3 \cdot \exp\left(-\frac{G_N}{RT}\right) \right] = C_4 \cdot \exp\left(-\frac{3G_\gamma + G_N}{RT}\right)$$

where G_γ and G_N are the activation free energies for growth and nucleation, respectively (both are assumed to be temperature-independent; R is the gas constant). A further assumption is that growth and nucleation events are single-activated processes. The activation energies may be combined into a unique *effective* activation energy given by G_{eff} , which is the final activation energy result. G_{eff} cannot be isolated using this kind of analysis since x depends on more than just the growth rate.

For isothermal transformation experiments, G_{eff} can be obtained plotting the time taken to achieve a fixed amount of transformation (i.e. t_x) versus $1/T$, a plot based on equation below (in turn derived from the previous equation above) :

$$t_x = C_5 \cdot \exp\left(\frac{G_{eff}}{nRT}\right)$$

It is difficult to determine the effective activation energy G_{eff} from non-isothermal experiments. For any thermally-activated process, the DTA/DSC peaks will shift with heating rate; **Kissinger** derived a relationship between the peak shift and the effective activation energy when assuming a homogeneous transformation:

$$\frac{dx}{dt} = C_6 \cdot (1-x)^m \cdot \exp\left(-\frac{G_{eff}}{RT}\right)$$

where m is the order of the reaction. Kissinger showed that :

$$\frac{d(\ln\{\frac{H}{T_p^2}\})}{d(\frac{1}{T_p})} = -\frac{G_{eff}}{R}$$

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

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

Marseglia has suggested that the activation energy G_{eff} for anisothermal experiments can be deduced from a plot of $\ln\{H/T_p^2\}$ versus $1/T_p$. The difference between Marseglia and Henderson arises because the former takes account of the variation of k with time, whereas the latter does not. However, the manner in which the dependence of k on time is taken into account is not rigorous:

$$dk/dt = dk/dT \cdot dT/dt = dk/dT \cdot H$$

The variation in growth rate with time is obviously not fully accounted for.

Phase Transitions

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

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

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

$$\ln(P) = L/RT' + C$$

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

Greater care is needed when studying solid-solid transitions where the enthalpy changes are much smaller than those associated with vaporisation. Stored energy in

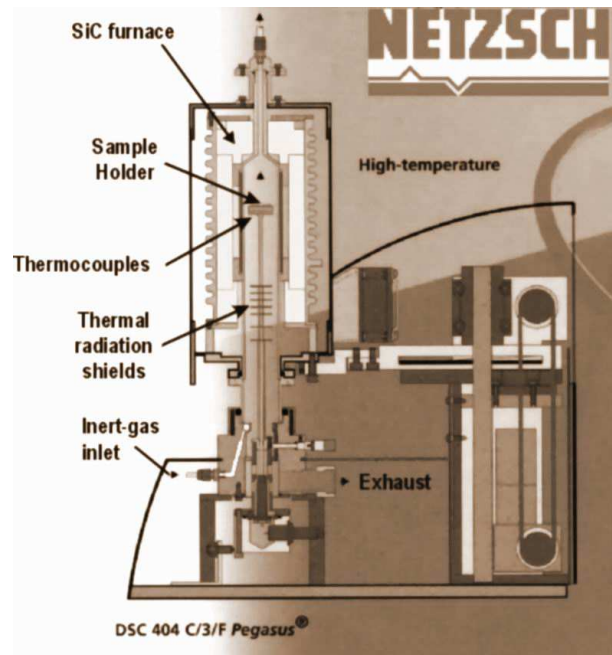
the form of elastic strains and defects can contribute to the energy balance, so that the physical state of the initial solid, and the final state of the product, become important. This stored energy reduces the observed enthalpy change.

3.4 The NETZSCH 404C Pegasus DSC Instrument

3.4.1 Basic components, technical features & specimen environment

The experiments will be performed using a NETZSCH 404C DSC instrument with the following components :

- measuring unit : including the high-temperature SiC oven, sample & reference holders, vacuum and/or inert gas connections
- specimen crucibles : corundum Al_2O_3 ($T_{\text{max}} : 1650^\circ\text{C}$, 0.085 cm^3).
- thermocouples: type S (Pt_{10%}Rh-Pt).
- NETZSCH TASC/414 T-controller
- furnace power supply
- computer system running the Proteus data acquisition and analysis software (Windows NT).



TECHNICAL FEATURES:

Sample environment : O (oxidizing), R (reducing), I (inert), V (vacuum). The DSC unit presently operates under vacuum conditions better than 0.0001 mbar, in air or under an inert-gas flow. Allowed gases : nitrogen, argon, helium and oxygen (please note that special rules apply for other gases or gas-mixtures).

Temperature range: [30°C (RT) ÷ 1650°C]

The accessible temperature range depends also on the **thermocouples** used, namely :

- Type E : (-120° ... 700°C), Chromel-Constantan.
- Type K : (RT ... 800°C), Chromel-Alumel.
- Type S : (RT ... 1650°C), Pt10%Rh-Pt.
- Type B : (150° ... 1650°C), Pt30%Rh-Pt6%Rh.

(...)

3.4.2 Operation Instructions

The instrument operation instructions are provided below as a stepwise check-list :

1. SWITCH-ON [**60 min. before measurement**] the components in the following order :

- TASC 414/4 Controller
- DSC (measuring unit)
- PC (start the Proteus software, data-acquisition module)
- Thermostat (if available)

2. Verify/Check purge gas supply / Vacuum :

• **Allowed** environment (gases) :

Air

N₂

Ar (Argon)

O₂ (Oxygen)

• Vacuum ($\leq 10^{-4}$ mbar) : measurements under vacuum are also possible, whenever oxidation or the formation of unwanted secondary phases must be avoided.

3. Move furnace into PARK position.

4. Place 2 empty crucibles (with lid) onto the sample carrier.

5. Move furnace a few mm above the sample carrier head & check if sample carrier is centered with respect to the furnace opening; adjust if necessary (use the front screws; maintain the factory position if possible).

6. Move furnace into the MEASUREMENT position.

7. Adjust expt. conditions (gas, vacuum) :

8. Start the Proteus software package (measurement program).

9. Start the **Correction** procedure :

- File / New
- Test parameters / Measurement Type : Correction (Sample Mass = 0)
- Open Temperature Recalibration
- Open Sensitivity
- Set Temperature Program {link}
- Define Filename (*.bdc).

10. Adjustment window :

- set threshold values
- if necessary, switch the initial conditions ON
- START the **Correction** measurement

11. Sample preparation.

12. **After** the furnace did cool down, open the furnace.

13. Remove the empty sample-crucible (i.e. in the front of the operator).

14. Weigh the sample using a balance.

15. Fill-in the sample & Insert the sample crucible into the holder.

16. Move the furnace into the MEASUREMENT position.

17. Adjust measuring conditions (gas or vacuum; see Step.10).

18. Start the **Sample+Correction** measurement :

- Open previously measured correction file (see Step.9)
- Sample Mass = X [mg] (see Step.15)
- Test Parameters / Measurement Type : Sample + Correction
- Open Temperature Recalibration (confirm presetting)
- Open Sensitivity (confirm presetting)
- Accept temperature program
- Define filename (*.ddc)
- Adjustment window (see Step.10)
- Start **Sample+Correction** measurement.

(...)

References

1. M. I. Pope and M.J. Judd: "Differential Thermal Analysis", London, Heyden, Academic Press 1977.
2. J. Sestak, V. Satava and W.W. Wendlandt: *Thermochimica Acta*, 7, 333 (1973).
3. V. Konryushin and L.N. Larikov: *J. Mat. Sci.*, 13, 1 (1978).
4. A. L. Greer: *Thermochimica Acta*, 42, 193 (1980).
5. R. A. Baxter: 'Thermal Analysis', 1, 65 (1969) - eds. R.F. Sswenker and P.D. Garn, Academic Press.
6. H. K. Yuen, C.J. Yosef: *Thermochimica Acta*, 33, 281 (1979).
7. L. M. Clareborough, M. E. Hargreaves, D. Mitchell and G. West: *Proc. Roy. Soc.*, A215, 507 (1952). Description of the original DSC concept and measurement of the stored energy of deformation.
8. M. G. Scott and P. Ramachandrarao: *Mat. Sci. & Eng.* 29, 137 (1977).
9. M. G. Scott: *J. Mat. Sci.*, 13, 291 (1978). Kinetics of glass crystallisation. *Anal. Chem.*, 29, 1702 (1957). Deals with the kinetics of non-isothermal homogeneous transformations.