Thermal Analysis

Thermal analysis refers to any technique for the study of materials which involves thermal control. Measurements are usually made with increasing temperature, but isothermal measurements or measurements made with decreasing temperatures are also possible. Table 1 shows a selection of thermal analysis techniques, illustrating the breadth of the field. In fact, any measuring technique can be made into a thermal analysis technique by adding thermal control. Simultaneous use of multiple techniques increases the power of thermal analysis, and modern instrumentation has permitted extensive growth of application. The basic theories of thermal analysis (equilibrium thermodynamics, irreversible thermodynamics and kinetics) are well developed, but have to date not been applied to actual experiments to the fullest extent possible.

1. *Thermometry*

Thermometry is by far the oldest and simplest thermal analysis technique. It always involves the measurement of temperature and usually the measurement of time. Heating and cooling curves have been used for many years to establish phase diagrams (Fig. 1). Any type of thermometer can be used for measurement. The most common for manual recording are mercury-in-glass thermometers; automatic recording and data treatment becomes possible with resistance thermometers and thermocouples.

Coupling of thermometry with other techniques such as microscopy, x-ray diffraction and spectroscopy is frequent. Melting temperatures are readily seen and easily verified by microscopic observation. Glass transitions, which cause only a change in slope in the time–temperature recording, require higher precision and are more sharply defined by observation of the disappearance of strain by polarizing microscopy. Constant transition temperature recording is frequent in the form of freezing-point determination (cryoscopy) or boiling-point determination (ebulliometry). Through two-phase equilibrium thermodynamics the changes in transition temperatures are coupled to concentration (mass and molecular mass) and heats of transition (entropies of transition). Highest accuracy is reached in the analysis of linear macromolecules (polymers). Transition temperature changes of as little as 10^{-5} K are measured for the determination of molecular masses of the order of 10^5.

Table 1
Thermal analysis techniques.

Technique[a]	Measurement (in addition to temperature)
Thermometry	time
Differential thermal analysis	temperature difference
Calorimetry	heat
Dilatometry	length or volume
Thermomechanical analysis	stress, strain
Thermogravimetry	mass
Dynamic mechanical analysis	stress, strain, time
Electrate thermal analysis	electrical discharge current
Electrical conductivity analysis	electrical resistance
Emanation thermal analysis	release of radioactive material
Evolved-gas analysis	pyrolysis with gas analysis
Thermal conductivity analysis	thermal conductivity
Thermal diffusivity analysis	thermal diffusivity
Thermoacoustimetry	sound effects
Thermofractography	thermal fractionation coupled with thin-layer chromatography
Thermoluminescence analysis	light emission
Thermomagnetic analysis	magnetic susceptibility
Thermooptical analysis	microscopy
Thermosonimetry	sound effect

[a] In addition, any other investigative technique, such as x-ray diffraction, NMR or spectroscopy, can be coupled with temperature control and become a thermal analysis technique.

2. *Differential Thermal Analysis*

In principle, differential thermal analysis (DTA) is a technique which combines the ease of measurement of heating or cooling curves with the quantitative features of calorimetry (see Sect. 3). Temperature is measured continuously as for heating or cooling curve determinations, and the differential temperature measurement permits the calculation of the heat flow difference between reference and sample, which are kept in almost identical environments (DTA furnace). Figure 2 schematically shows a DTA apparatus using thermo-

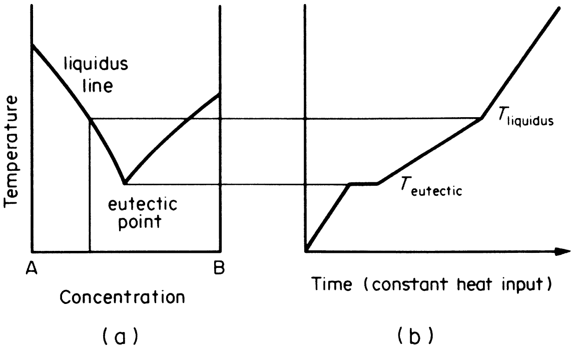

Figure 1
(a) A simple eutectic phase diagram and (b) the corresponding heating curve, with constant heat input leading to an almost linear temperature rise.

couples for measurement. The programmer supplies a linear heating rate. If during measurement the temperature gradient within the sample can be kept small, it is possible to eliminate the effect of sample heat conductivity on the sample temperature itself, and heat flows can be calculated from temperature measurements. Under such conditions the technique is frequently called differential scanning calorimetry (DSC).

DTA originated at the turn of the century when simultaneous photographic recording of two thermocouple outputs became possible. The first major applications were in the study of phase diagrams and transition temperatures, and qualitative analyses of metals, oxides, salts, ceramics, glasses, minerals and soils. By 1952, 1000 research reports on DTA were published; by 1972, the annual rate of publications exceeded 1000. This increase was brought about by the use of electronics to increase measuring accuracy and to automate data collection and treatment. At present, DTA is used in almost all fields of scientific investigation and is especially useful for the analysis of metastable systems. A modern design for use with temperatures from 100 to 1000 K is shown in Fig. 3. Typical sensitivies of 10–100 $\mu J\,s^{-1}$ have been claimed for such instruments for 1–10 mg sample size. Heating rates may range from 0.5 to 50 K min^{-1}. Heat capacity measurements as accurate as 0.5% have been reported in favorable cases. Transition temperatures may be determined to ± 0.1 K. Extreme condition DTA may span heating rates from 0.01 to 10 000 K min^{-1}, temperatures of measurement may reach above 3000 K and measurements up to pressures of 500 MPa have been achieved.

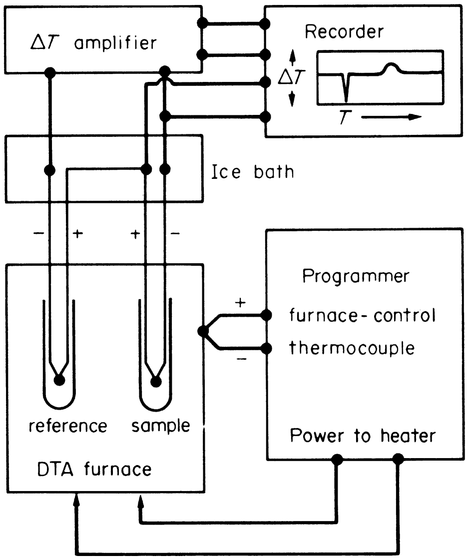

Figure 2
Schematic diagram of a DTA apparatus.

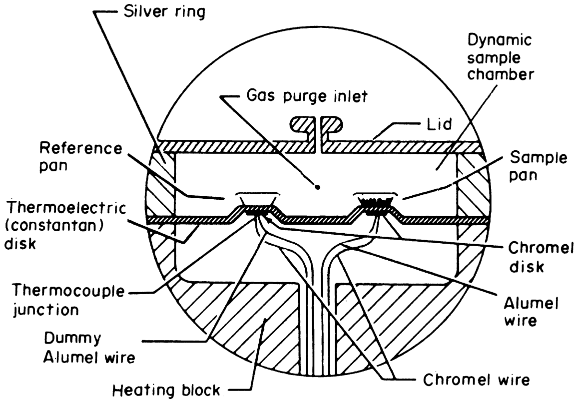

Figure 3
A typical DTA (DSC) measuring cell (courtesy of Du Pont, Analytical Instruments Division).

DTA without a temperature gradient within the sample (< 1.0 K), which can easily be interpreted quantitatively, is limited for 1 g samples to about a 1 K min^{-1} heating rate and for 1 mg samples to about 100 K min^{-1}. The heat flow into the reference (dQ_r/dt) and sample (dQ_s/dt) can be given by

$$dQ_r/dt = K(T_b - T_r) \tag{1}$$

$$dQ_s/dt = K(T_b - T_s) \tag{2}$$

where the thermal conductivity K is dependent on the geometry and material of the cell, but is independent of the sample. For simplicity, the cell arrangement is assumed to be such that sample and reference have the same K. T_b is the DTA furnace or heating block temperature and T_r, and T_s are the reference and sample temperatures, respectively. Equations (1) and (2) are simple representations of Newton's law of cooling. The heat flow equation can be derived from Eqns. (1) and (2) by making T_b increase linearly with the heating rate q (i.e., $T_b = T_0 + qt$) and assuming that all sample heat flow is used to increase the sample temperature (i.e., $Q_s = C_p(T_s - T_0)$), with C_p representing the (constant) sample heat capacity:

$$dQ_s/dt = K[qt - (Q_s/C_p)] \tag{3}$$

The solutions of the heat flow equation in terms of total heat flow up to time t or temperature T are (initial conditions $t = 0$, $T_b = T_s = T_0 = 0$, $Q = 0$):

$$Q_s = qC_pt - (qC_p^2/K)[1 - \exp(-Kt/C_p)] \tag{4}$$

$$T_s = qt - (qC_p/K)[1 - \exp(-Kt/C_p)] \tag{5}$$

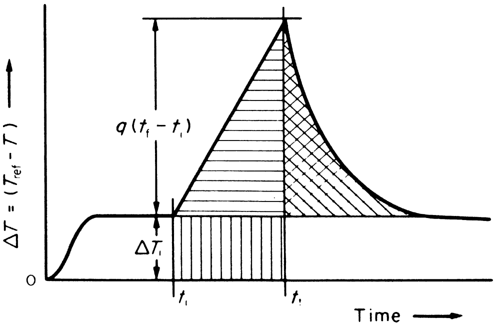

Figure 4
A typical DTA trace showing first the approach to steady state ΔT_{i}, then melting (between times t_{i} and t_{r}), and finally the renewed approach to steady state.

Under steady-state conditions ($Kt \gg C_{\mathrm{p}}$) the temperature difference between sample (T_{s}) and block ($T_{\mathrm{b}} = qt$) is thus directly proportional to the heat capacity and permits calculation of enthalpy changes (DSC). The exponential term represents the approach to steady state. Figure 4 illustrates the approach to steady state starting from $\Delta T = qt - T_{\mathrm{s}} = 0$. Figure 4 also shows the change in ΔT during a sharp transition in the sample such as is found, for example, in melting. During the transition (from t_{i} to t_{f}) the sample temperature remains constant, so that ΔT increases with a slope equal to the heating rate q. When melting is complete, a renewed approach to steady state, described by Eqn. (5), occurs. The vertically and horizontally shaded areas are proportional to the total heat of fusion. The crosshatched area A is expressed by

$$A = \int_{t_{\mathrm{f}}}^{t_{\infty}} q(t_{\mathrm{f}} - t_{\mathrm{i}}) \exp[-K(t - t_{\mathrm{f}})/C_{\mathrm{p}}]\,\mathrm{d}t \qquad (6)$$

This is easily integrated to

$$A = q(t_{\mathrm{f}} - t_{\mathrm{i}})C_{\mathrm{p}}/K \qquad (7)$$

which in turn is seen to be equal to the vertically shaded area. This simple calculation leads to the commonly applied "baseline method" for the evaluation of the heats of transitions or reactions. The area above the baseline is proportional to the heat of transition; the baseline is proportional to the heat capacity, but does not have to be evaluated. In cases where the baseline (heat capacity) is not the same before and after the transition, a small correction may be necessary.

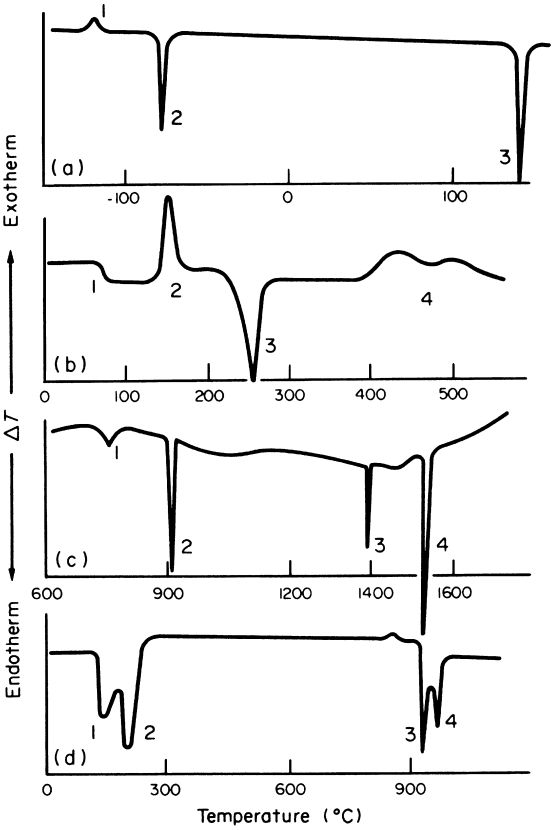

Figure 5
Qualitative analysis by DTA. Four DTA curves of pure substances. (a) Amyl alcohol (2 μl sample in air at atmospheric pressure, heating rate 10 K min^{-1}. Transitions: 1, some crystallization at −119 °C; 2, melting at −79 °C; 3, boiling at 139 °C). (b) Poly(ethylene terephthalate) (10 mg sample in nitrogen at atmospheric pressure, heating rate 20 K min^{-1}. Transitions: 1, glass transition at about 75 °C, characteristic of noncrystalline materials; 2, crystallization at 145 °C; 3, melting at 253 °C; 4, exothermic decomposition above 360 °C). (c) Iron (~ 30 mg sample in helium at atmospheric pressure, heating rate 20 K min^{-1}. Transitions: 1, α- to β-iron transition at 757 °C; 2, β- to γ-iron transition at 910 °C; 3, γ- to δ-iron transition at 1389 °C; 4, melting at 1533 °C). (d) Barium chloride (~ 10 mg sample in air at atmospheric pressure, heating rate 20 K min^{-1}. Transitions: 1 and 2, loss of water in two stages at 130 and 187 °C, respectively; 3, orthorhombic-to-cubic transition at 923 °C; 4, melting at 950 °C).

Figure 5 gives some examples of typical DTA traces for the indentification of materials (fingerprinting). The traces can also be used for quantitative evaluation of temperatures and heats of transition as well as kinetic parameters. A typical example of an analysis of a more complicated phase diagram is shown in Fig. 6. The bottom half of Fig. 6 represents the phase diagram

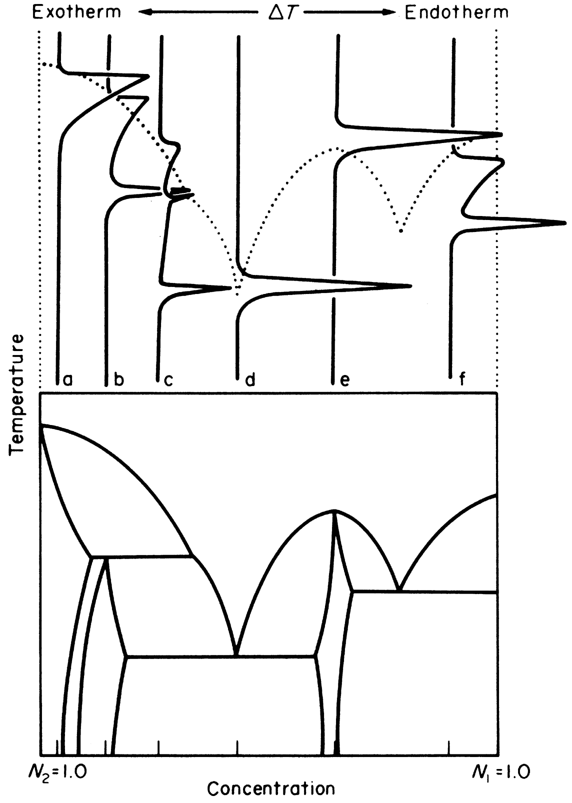

Figure 6
Hypothetical phase diagram of reasonable complication (eutectic points, compound formation, partial solid-state solubility and a peritectic point). The curves a–f drawn above the phase diagram illustrate typical heating curves that could be obtained with a differential scanning calorimeter.

for two eutectic systems, with some limited solubility in the crystalline state, compound formation and a peritectic point. The top half of Fig. 6 shows the DTA traces corresponding to the concentrations a to f. An analysis of metastable crystals of polyoxymethylene is illustrated by Fig. 7. On using low heating rates (e.g., 5 °C min^{-1}), the metastable crystals melt (first endotherm), recrystallize (exotherm), melt again (second endotherm), recrystallize again partially and have a final melting endotherm. All melting crystals are of the same crystal structure and differ only in crystal size and perfection. At faster heating rates the recrystallization is increasingly suppressed and the only metastable crystal present in the original crystal is revealed.

3. *Calorimetry*

Calorimetry was first developed in the eighteenth century. Since there is no direct heat meter, measurements of heat must rely on secondary effects such as temperature rises, changes of state, or chemical, electrical or mechanical heat–energy conversions. The major difficulty of calorimetry is the fact that there is no perfect insulator for heat. Therefore, loss calculations to correct for imperfect containment of the heat to be measured are basic to all calorimetry. Isothermal or nearly isothermal calorimeters permit the best handling of the heat loss problem. A typical example of an isothermal calorimeter is shown in Fig. 8. The isothermal environment is created by a water–ice mixture. The sample to be investigated is dropped from a constant-temperature reservoir, or a reaction or other change of state is induced after the equilibrium temperature is achieved. A change in the heat content of the sample is detected by the volume change due to the melting or crystallization of the ice in the inner calorimeter container. The volume change is measured by detection of the change in mercury mass inside the calorimeter.

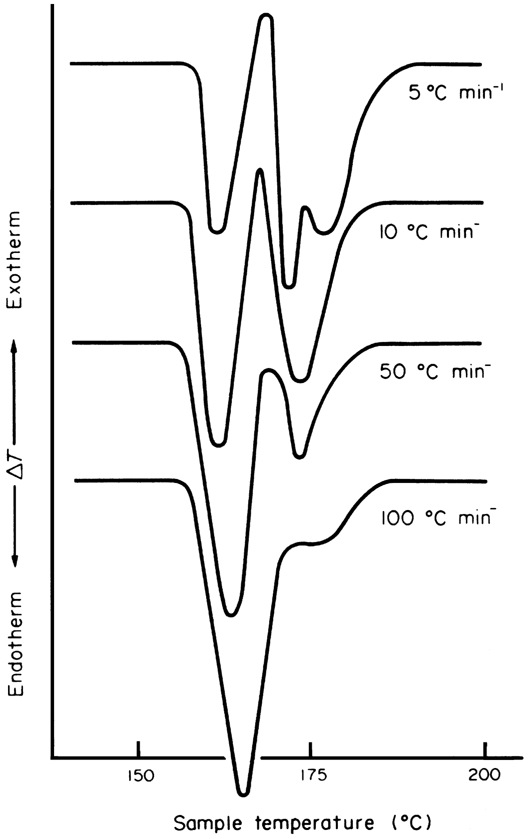

Figure 7
Typical set of melting curves of polyoxymethylene taken at the indicated heating rates, for sample masses between 10 and 1 mg. The samples represent solution-grown stacks of thin, lamellar crystals.

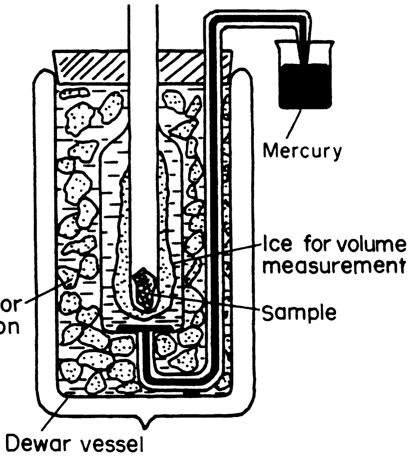

Figure 8
Bunsen ice calorimeter.

Closely related to isothermal calorimeters are aneroid and liquid calorimeters, in which a small temperature rise in a solid (metal block) or liquid (water) reservoir is measured precisely (± 0.001 K) to determine the change in heat content of the unknown. Bomb calorimeters are well known, being commonly used to measure heats of combustion to a precision of up to $\pm 0.01\%$.

Another type of calorimeter is the adiabatic calorimeter, in which an attempt is made to minimize the heat loss by raising or lowering the temperature of the surroundings to match the sample temperature (Fig. 9). Adiabatic calorimeters are commonly built for operation from 10K to about 700K, and may reach a precision of $\pm 0.01\%$ in heat capacity determinations for large sample masses (100–500g). Special instrumentation is available for very low temperatures.

In compensating calorimeters, the effect of a chemical reaction is compensated by heating or cooling. The best-known compensating calorimeters are those that make use of the Peltier effect (Tian–Calvet calorimeters) and stirred-liquid calorimeters; their construction is usually adapted to the specific application.

A bridge to DTA is achieved with scanning calorimeters, which can operate on the adiabatic or the differential calorimeter principle. DSC has seen the largest development recently because of ease of handling and computer coupling. Heat capacity accuracies have reached $\pm 0.1\%$ for sample masses as small as 10mg. Temperature ranges from 100 to 1000K and heating rates between 1 and 20K min^{-1} are common.

The goal of most calorimetry is the establishment of the thermodynamic functions of systems of interest. Heats of transition and heat capacities lead to enthalpy data at various temperatures. Using the thermodynamic relationships for equilibrium,

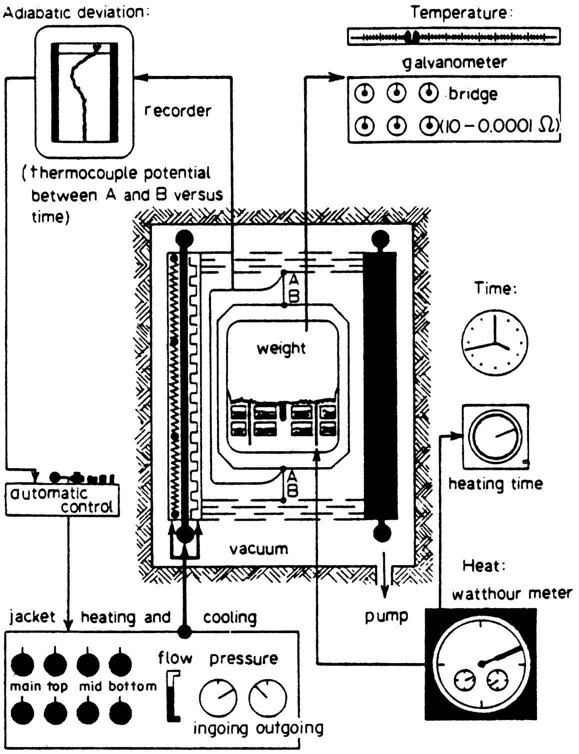

Figure 9
Example of a typical adiabatic calorimeter.

$$H = H_0 + \int_0^T C_p \,\mathrm{d}T \tag{8}$$

$$S = S_0 + \int_0^T (C_p/T)\,\mathrm{d}t \tag{9}$$

$$G = H - TS \tag{10}$$

$$T_t = \Delta H_t / \Delta S_t \tag{11}$$

allows complete thermal analysis whenever heat capacities C_p and transition enthalpies ΔH_t and temperatures T_t are given. Standard functions are widely tabulated and the theory of heat capacities is well developed.

4. *Dilatometry and Thermomechanical Analysis*

Dilatometry deals with the determination of length or volume as a function of temperature. Thermomechanical analysis (TMA) is the term applied to dilatometry carried out under tension or load. Historically, dilatometry and TMA date back to ancient metrology. Obvious length measurements are made

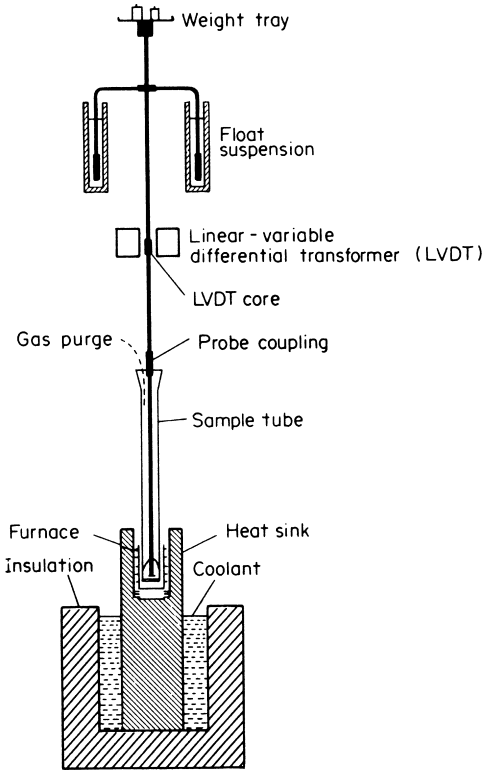

Figure 10
TMA apparatus (courtesy of Mettler Instrument Company).

through side-by-side comparison with a standard; obvious volume measurement is through comparison with the content of a standard vessel. The highest precision in length measurement is achieved by interferometry, which allows, for example, the maintenance of the standard meter to a precision within 1 part in 10^8. Volume determination with pycnometers, volumetric flasks, cylinders, burettes and pipettes is difficult to push beyond 0.01%.

A schematic drawing of a typical TMA apparatus is shown in Fig. 10. The length measurement is performed via a linear-variable differential transformer (LVDT). A change in the position of the core, which floats frictionlessly within the transformer coil, results in a linear change in output voltage. A force is applied to the sample by balancing flotation and weight. Measurement is possible in the compression, tension and bending modes. Typical heating rates range from 0.1 to $40\,\mathrm{K\,min^{-1}}$. Temperature ranges from 100 to 1000 K are common, but high-temperature TMA to 2500 K is available. Sample sizes are usually of the gram and centimeter magnitudes.

A typical TMA of a drawn fiber, such as a polyester (poly(ethylene terephthalate)), is shown schematically in Fig. 11. Below the glass-transition temperature T_g the TMA curve shows normal, almost linear expansion. At T_g, the fiber shrinks owing to relaxation of the only partially crystallized molecules. This trend is reversed as some low-temperature crystallization stabilizes the fiber. Close to the melting temperature T_m the fiber expands limitlessly owing to flow. Details of manufacturing and performance variables can thus be quickly evaluated by TMA. Expansivities, shrinkage, glass and melting transitions are most easily measurable by TMA.

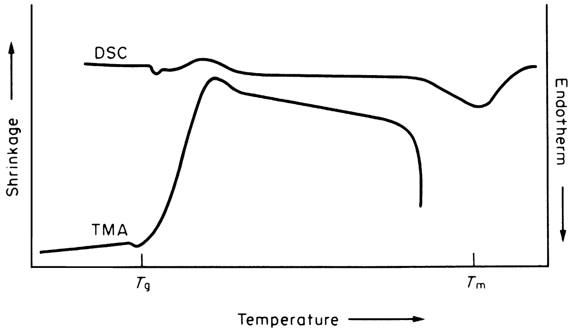

Figure 11
TMA of a drawn polyester fiber.

Two extensions of TMA are pressure–volume–temperature determinations and dynamic mechanical analysis. The former lead to the equilibrium functions of state and are available for many substances up to the gigapascal range, revealing many high-pressure and high-temperature crystal forms. The latter involves time-dependent stress–strain determination at various temperatures and is basic to the analysis of mechanical properties (elasticity and viscoelasticity).

5. *Thermogravimetry*

Thermogravimetry was developed around 1900 and basically involves the mass determination of a sample under controlled isothermal or linearly varying temperature in a given atmosphere. A plot of mass as a function of time or temperature is the result of a thermogravimetric experiment. A block diagram of a typical thermogravimetric apparatus is shown in Fig. 12. Continuous mass recording and compensation is possible by electromagnetic weight compensation. Sensitivities are usually several micrograms. Total sample masses may range from milligrams to grams. Temperature ranges are usually from room temperature to as high as 2700 K.

Major applications of thermogravimetry involve stability analysis of materials in different atmospheres or vacuum. A typical example is shown in Fig. 13. The

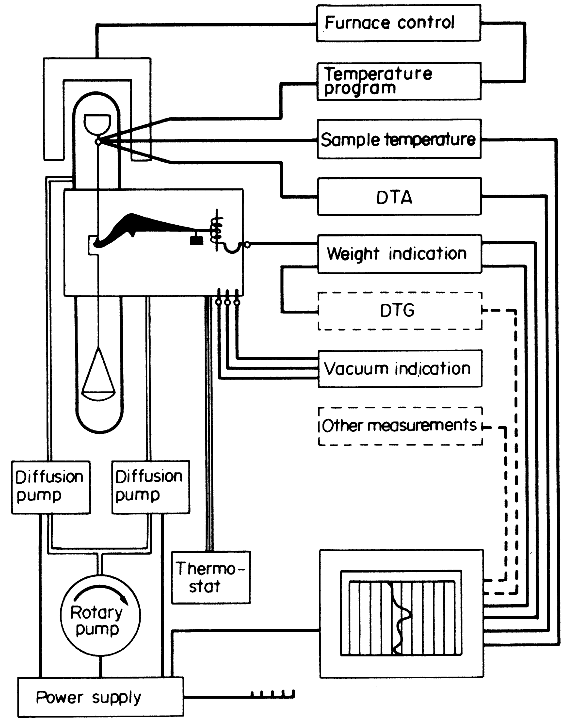

Figure 12
Schematic diagram of a thermogravimetry apparatus with differential thermogravimetry (DTG) facility (courtesy of Mettler Instrument Company).

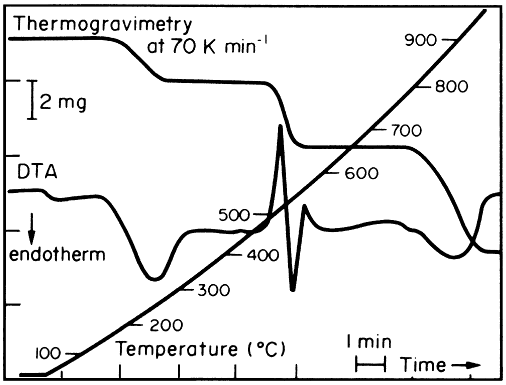

Figure 13
Thermogravimetric analysis of calcium oxalate with the corresponding DTA curve.

analyzed $CaC_2O_4 . H_2O$ is seen to decompose in three stages:

$$CaC_2O_4 . H_2O \rightarrow CaC_2O_4 + H_2O \qquad (12)$$

$$CaC_2O_4 \rightarrow CaCO_3 + CO \qquad (13)$$

$$CaCO_3 \rightarrow CaO + CO_2 \qquad (14)$$

Figure 13 also shows a DTA curve which reveals that the first and third reactions are endothermic, whereas the second reaction is complex, involving at least one exothermic and one endothermic stage.

The quantitative data analysis of the nonisothermal reactions is usually attempted using standard reaction kinetics:

$$d[A]/dt = k[A]^n \qquad (15)$$

where [A] is the reactant concentration, k is the specific rate constant and n is the order of the reaction. The temperature dependence of k is incorporated in Eqn. (15) using the Arrhenius equation:

$$dk/dT = A\exp(-E_a/RT) \qquad (16)$$

where E_a is the activation energy. Frequently, however, Eqn. (15) is an oversimplification; more complicated and multiple reaction paths often make a simple analysis impossible. Other difficulties involve the precise sample-temperature measurement, which must usually be done by positioning a thermocouple close to, but outside of, the weighing pan. Since most of the reactions to be studied involve gas evolution, the rate of diffusion of these out of the sample may influence the position of the equilibrium, so that packing density and sample size become of importance. An interesting application of thermogravimetry is the lifetime prediction of materials such as polymers. The stability of the materials is determined in a short-time experiment at elevated temperature and the results are extrapolated using Eqns. (15) and (16) to use temperatures.

See also: Thermal Analysis: Further Developments

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