6.2
Determination of Heats of Reaction

The aim is to determine a thermodynamically well defined (temperature dependent) reaction enthalpy. If a subsequent kinetic analysis is planned, the calculation of a similarly well defined conversion-time curve is of equal importance. The interpretation assumes that both the initial and the final state of the reaction are unambiguous and well-defined. Is this not the case, the results will be, at best, semi-quantitative. Because of the limited precision of DSCs minor effects due, for example, to changes in pressure, stress or surface contributions may be neglected. The following, simplified equation is then obtained for the measured heat flow rates in a DSC:

$$\left(\frac{dQ}{dt}\right)_p = \Phi_m = C_{p,\xi}(T) \cdot \frac{dT}{dt} + \left(\frac{\partial H}{\partial \xi}\right)_{T,p} \cdot \frac{d\xi}{dt}$$

$C_{p,\xi}(T)$ is the heat capacity of the system at constant pressure and at constant extent of reaction. The partial molar reaction enthalpy $\Delta_r H = (\partial H/\partial \xi)_{T,p}$ is nearly always replaced by the average reaction enthalpy $\langle \Delta_r H \rangle$, which is independent of the instantaneous composition of the system. The Kirchhoff equation

$$\left(\frac{\partial C_{p,\xi}}{\partial \xi}\right)_{T,p} = \left(\frac{\partial \Delta_r H}{\partial T}\right)_{p,\xi} = \sum_i (\nu_i \cdot C_{p,i})$$

describes the relation between the change of the heat capacity of the reacting system and the temperature-dependent reaction enthalpy. Here the ν_i are the stoichiometric numbers and $C_{p,i}$ the partial, molar heat capacities of reactants and products.

Reactions may be carried out isothermally or non-isothermally (in scanning mode or following a special temperature program). Advantages and disadvantages of the two methods are discussed in detail in Sect 6.3.

Reactions in the Isothermal Mode

Here, the sample is heated as rapidly as possible from a temperature at which the system is inert (often room temperature) to the reaction temperature. The "drop in" technique (cf. Appendix 2) may also be used – the sample is dropped into the preheated calorimeter. The end of the reaction is indicated by a constant heat flow rate Φ_{end}. Simple extrapolation of this Φ_{end} to the start time yields the baseline of the reaction peak. As there is no heat capacity contribution to the heat flow rate in the isothermal mode, the relation between the heat produced or consumed and the average reaction enthalpy is very simple:

$$Q_m(t) = \int_0^t (\Phi_m - \Phi_{end}) \, dt = \langle \Delta_r H \rangle \int_0^\xi d\xi$$

The only uncertainty is due to possible drift in the signal. The caloric error for a typical sample mass of 10 mg and a heat production of 360 J g^{-1} is less than 1 %,

if drift during a one hour reaction is less than 10 µW. For long term reactions drift must therefore be comparable with the short time noise (cf. Sect. 7.2).

If a reaction is investigated at several temperatures (which is essential for a kinetic analysis), the temperature dependence of the reaction heat is also obtained. Alternatively, if the $C_p(T)$ functions of reactants and products are known, $\Delta_r H(T)$ may be calculated by means of the Kirchhoff equation.

The main problem with isothermal measurements results from the ill-defined behavior of the signal following the initial introduction of the sample. Even for DSCs with very short time constants this time amounts to at least 10 to 15 s. Most of this error can, however, be eliminated by subtracting the isothermal heat flow rate curve of a second run with the same (now totally reacted) sample and exactly the same conditions. Nevertheless, minor differences may remain because of the different thermal conductivities of products and reactants and because heat transfer conditions may have changed during the reaction.

In order to check the completeness of the reaction, the sample is often heated to higher temperatures. However this is only useful if side reactions or shifts of chemical equilibrium at higher temperatures can be excluded. If additional reaction has been detected, the clear assignment of a reaction heat to a definite temperature may be lost.

Reactions in the Scanning Mode

In principle the correct evaluation corresponds to that already discussed in Sect. 5.3.2. However the situation is more difficult, because it cannot be assumed that reactants and products have almost the same and temperature-independent heat capacities owing to the large temperature interval of the reaction (100 K and more). In contrast to phase transitions, which follow a zeroth order reaction law, chemical reactions do not terminate at, or shortly beyond, the reaction peak maximum. To complicate matters, the reaction products may have a glass transition within the reaction region. In addition, the glass temperature of the original reactants may shift into this temperature range. As a typical example, the curing of an epoxide resin is shown in Fig. 6.6 (Richardson, 1989). The reaction starts immediately after the glass transition of the reactants at A and is finished at B. In the following it is always assumed that the zeroline has no curvature or has been subtracted and that changes in heat transfer conditions can be neglected. Reaction enthalpies may be determined in the following ways (in the first case only the heat flow rate curve has to be measured, all other methods require C_p-measurements).

Method 1:
A linear baseline is drawn between the points A and B (Fig. 6.6). This simple and widely used procedure is only an approximation. It is better the smaller the heat capacity difference between reactants and products. The validity of this assumption can be decided very easily by comparing the original run with a rerun on the reacted material. Both curves should then fit at A and B. As can be seen from Fig. 6.7 b, this is not true for this system, even after allowance for the glass transition.

Fig. 6.6. Curing of an epox-
ide resin (according to
Richardson, 1989) and the
procedure mostly used to
determine the heat of reac-
tion. The linear baseline
between start (A) and end
(B) of the reaction ignores
all possible changes in heat
capacity
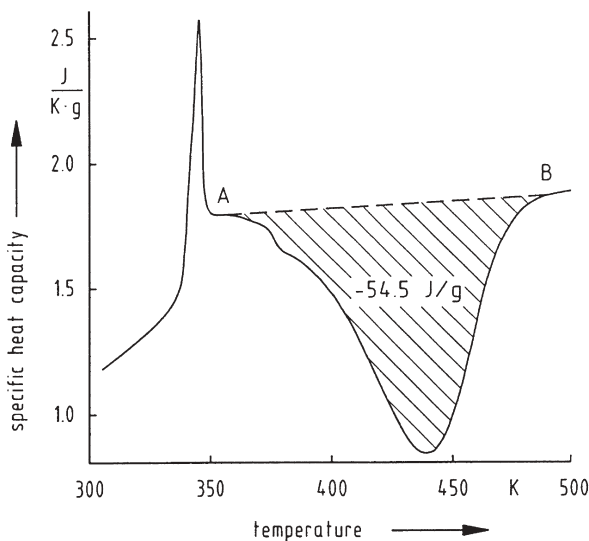
Method 2:

If the temperature dependent change of the heat capacity $C_{p,\xi}(T)$ of the reacting
system cannot be neglected, but the heat capacities of reactants and products are
known over the relevant temperature range (and there are no glass transitions),
then the baseline can be calculated by iterations similar to those of case 3 in
Sect. 5.3.2. Method 1 above gives the 0th approximation to the extent of reaction
function $\xi(T)$. The heat capacities of the products can easily be obtained from
the rerun on the fully reacted sample. If the first run of the reaction mixture can
be started at least 30 K before the reaction starts, the heat capacity of the reac-
tants may be determined from this interval. Extrapolation into the reaction tem-
perature range is generally accurate enough. Otherwise, the heat capacities of all
components of the reaction mixture must be measured separately and the C_p
function calculated using simple mixing rules.

After subtraction of the baseline constructed in this way from the measured
curve, an average heat of reaction is obtained (the term reaction enthalpy should
be avoided, the quantity has no thermodynamic significance) for the tempe-
rature range between T_1 and T_2. Improvements relative to method 1 are only
found if the heat capacity functions are known with sufficient precision (uncer-
tainties $<1\%$). Obvious improvements in the definition of the baseline should
result from the use of temperature-modulated DSC (cf. Sect 6.1.5). By this
method it is possible to get both the heat flow rate curve (which is proportional
to the actual reaction rate) from the non-reversing curve, and the heat capacity
function of the reacting mixture from the reversing curve, from the same run
(see Sect. 6.3.6)

The degree of reaction function $\alpha(T)$ can be obtained from the ratio be-
tween partial heats (up to a certain temperature) and the overall heat of the re-
action.

Method 3:

Many of the above problems and difficulties can be avoided by integration of the C_p curves (Richardson, 1989; 1992b; Flynn, 1993). The specific reaction enthalpy $\Delta_r h(T_1)$ at the starting temperature T_1 (e.g., 350 K) may be determined in a thermodynamically correct way even if a glass transition occurs within the temperature range of the reaction. From Fig. 6.7 it follows that

$$\Delta_r h(T_1) = h_l(P, 350\ K) - h_l(R, 350\ K)$$

The reaction enthalpy at temperature T_1 ($\Delta_r h(T_1)$) is obtained as difference between the areas X and Y. The baseline is not necessary in this case, because only differences are needed:

$$\Delta_r h(T_1) = X - Y = (h_l(P, 490\ K) - h_l(R, 350\ K)) - (h_l(P, 490\ K) - h_l(P, 350\ K))$$

The enthalpy subscript l represents the liquid state of the reactants R and the liquid-like or rubbery state of the products P. The difference $h_l(P, 490\ K) - h_l(R, 350\ K)$ corresponds to the experimental quantity, the area X, defined by the lines at $T_1, T_2, c_p = 0$ and the reaction curve. The horizontal hatched area Y follows from the rerun on the reacted sample.

$$Y = h_l(P, 490\ K) - h_l(P, 350\ K) = \int_{350\ K}^{490\ K} c_{p,l}(P)\ dT$$

If the glass transition of the products is above T_1, as is the case in Fig. 6.7, $C_{p,l}$ must be extrapolated as shown. Without this extrapolation another result would be obtained:

$$\Delta_r h'(T_1) = h_g(P, 350\ K) - h_l(R, 350\ K)$$

The procedure can also be extended to the determination of reaction enthalpies at any temperature T between T_1 and T_2 (Richardson, 1992b; cf. also Sect. 5.3.2). At first a possible glass transition is disregarded. One obtains:

$$\Delta_r h(T) = h(P, T) - h(R, T)$$
$$= (h(P, T_2) - h(R, T_1)) - (h(P, T_2) - h(P, T)) - (h(R, T) - h(R, T_1))$$

or:

$$\Delta_r h(T) = X - \int_T^{T_2} c_p(P)\ dT - \int_{T_1}^T c_p(R)\ dT = X - Z$$

This procedure is schematically shown in Fig. 6.8. The areas X and Z are hatched horizontally and vertically respectively. A simple rearrangement of the last equation gives:

$$\Delta_r h(T) = X - \int_{T_1}^{T_2} c_p(P)\ dT + \int_{T_1}^T (c_p(P) - c_p(R))\ dT$$

$$= \Delta_r h(T_1) + \int_{T_1}^T (c_p(P) - c_p(R))\ dT$$

Fig. 6.7 a, b. The thermodynamically correct determination of the specific heat of reaction (according to Richardson, 1989); for details see text. **a** 1st run curve, **b** 1st and 2nd run curves Hatched areas extended to $c_p = 0$; Δh (350 K) = $X - Y = h_{products}$ (350 K) $-$ $h_{reactants}$ (350 K) = $- 44.7$ J g^{-1}
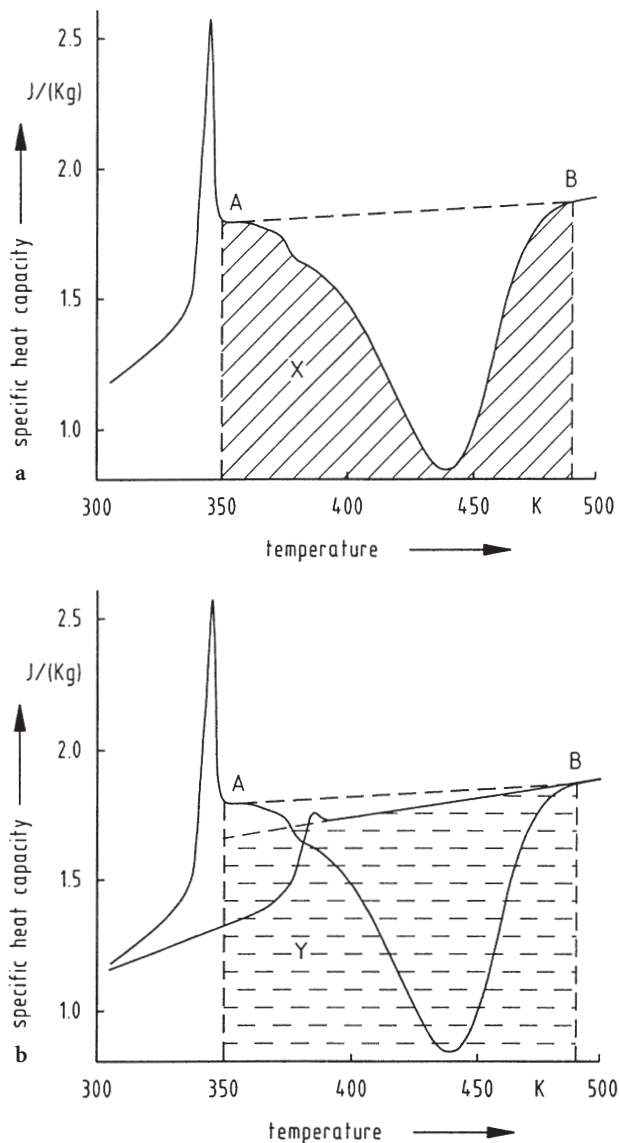
It is clear from Fig. 6.8 that this procedure is a direct application of the Kirchhoff equation. An enthalpy-temperature diagram (Fig. 6.9) is especially clear and instructive. Here, for the sake of simplicity, temperature independent heat capacities are assumed. The enthalpies are then linear functions of the temperature. The diagram also recognizes that both reactants and products may be in the glassy [curves H_g(R) and H_g(P)] or liquid [curves H_l(R) and H_l(P)] state. A reaction usually proceeds at a measurable rate only when the reactants are in the liquid state [above glass transition T_g(R)]. Further, the glass transition of the

Fig. 6.8. The thermodynamically correct determination of a reaction enthalpy (according to Richardson, 1992b); for details see text
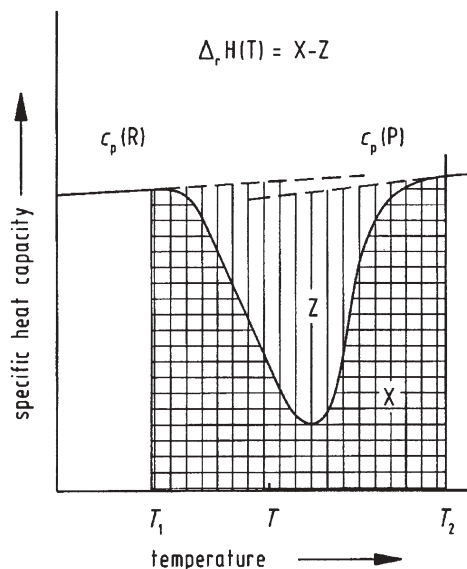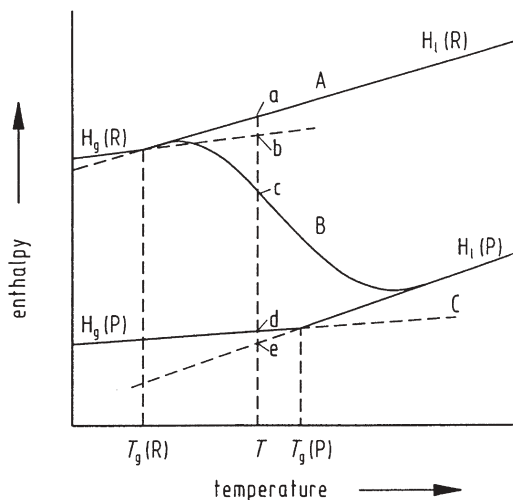
$\Delta_r H(T) = X - Z$

Fig. 6.9. The determination of reaction enthalpies from an enthalpy-temperature diagram (according to Flynn 1993); A: integral of $C_p(T)$ for the reactants, B: integral of $C_p(T)$ for the reaction mixture, C: integral of $C_p(T)$ for the products

products $[T_g(P)]$ is very often somewhere between T_1 and T_2. A formal (Flynn, 1993) and thermodynamically correct procedure yields four different reaction enthalpies and four different α values at each temperature (see Fig. 6.9):

glassy reactants	$\rightarrow$	glassy products	$\Delta_r H = bd,$	$\xi = bc/bd$
glassy reactants	$\rightarrow$	liquid (rubbery) products	$\Delta_r H = be,$	$\xi = bc/be$
liquid reactants	$\rightarrow$	glassy products	$\Delta_r H = ad,$	$\xi = ac/ad$
liquid reactants	$\rightarrow$	liquid (rubbery) products	$\Delta_r H = ae,$	$\xi = ac/ae$

Only the final case has any meaning for kinetic studies.

In exceptional cases, e.g., when there is a possibility of side or decomposition reactions, the heating run should be stopped at a temperature at which such disturbing reactions don't contribute to the heat flow rate. The reaction should then be completed isothermally at this temperature. Baselines are needed for both the scanning and isothermal parts of the reaction (Richardson, 1989). However, it may be more convenient to carry out the reaction totally in the isothermal mode.

6.3
Kinetic Investigations

6.3.1
Introduction and Definitions

Every chemical reaction is associated with a certain heat of reaction. From this it follows that the heat flow rate is proportional to the rate of reaction. The assignment of the time dependent heat flow rates to defined reactions leads to kinetic data. Every quantitative kinetic analysis starts with the determination of a continuous sequence of concentration-time data. DSC methods are widely used to solve kinetic problems because of the simple and fast sample preparation and the wide range of experimental conditions – much information is produced in a short time. The technique, by contrast with many other methods, immediately gives a series of "reaction rates" as function of the extent of reaction ξ, dependent on time and temperature. The aim of kinetic investigations is then to find quantitatively this functional relation. The methodology is quite general and it is immaterial whether the reactions investigated come from inorganic, organic or macromolecular chemistry. Continuing advances in instrumentation and data treatment facilitate refined calculations.

The framework of the kinetic description of reactions was originally developed in physical chemistry for reactions in homogeneous phases. A generalized reaction with the educts A, B, … and the products C, D, … is described by the following stoichiometric equation:

$$aA + bB + \ldots \rightarrow cC + dD + \ldots$$
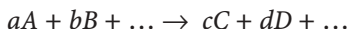
According to the definition ($n_i = n_{i,0} + v_i \cdot \xi$), ξ can be related to the consumption of an educt ($v_i < 0$) or to the formation of a product ($v_i > 0$). The rate of reaction is then quite generally given by:

$$r = \frac{1}{V} \cdot \frac{\mathrm{d}\xi}{\mathrm{d}t}$$

Considering a reaction in homogeneous phase and at constant volume, the rate law for the overall or the elementary reaction may then be formulated as usual:

$$r = \frac{1}{V} \cdot \frac{\mathrm{d}\xi}{\mathrm{d}t} = \frac{1}{v_i} \cdot \frac{\mathrm{d}c_i}{\mathrm{d}t} = f(c_A, c_B, \ldots T, p, \ldots)$$