At temperature $T$ and pressure $p$, the enthalpy of a closed system having composition $\xi$ can be defined by equation (a).[1]

$$H = H[T, p, \xi] \quad (a)$$

The general differential of equation (a) takes the following form.

$$dH = \left(\frac{\partial H}{\partial T}\right)_{p, \xi} \cdot dT + \left(\frac{\partial H}{\partial p}\right)_{T, \xi} \cdot dp + \left(\frac{\partial H}{\partial \xi}\right)_{T, p} \cdot d\xi \quad (b)$$

If the pressure is constant at, for example, ambient pressure, $dH$ equals the differential heat $dq$ passing between system and surroundings. In the application considered here, the temperature is held constant.

The following equation describes heat $dq$ in terms of changes in composition at constant pressure and constant temperature.

Thus

$$dq = \left(\frac{\partial H}{\partial \xi}\right)_{T, p} \cdot d\xi \quad (c)$$

Moreover $d\xi$ is the extent of chemical reaction in the time period $dt$.

Then

$$\left(\frac{dq}{dt}\right) = \left(\frac{\partial H}{\partial \xi}\right)_{T, p} \cdot \left(\frac{d\xi}{dt}\right) \quad (d)$$

If the chemical reaction in the sample cell involves a single chemical reaction, $(\partial H/\partial \xi)_{T, p}$ is the enthalpy of reaction $\Delta H$.

Therefore,

$$\left(\frac{dq}{dt}\right) = \Delta H \cdot \left(\frac{d\xi}{dt}\right) \quad (e)$$

In Heat Flow Calorimetry [2,3], a small closed reaction vessel is in contact with a heat sink so that the reaction vessel is held at constant temperature. The flow of heat between sample cell and heat sink is monitored such that the recorded quantity is the thermal power, the rate of heat production $(dq/dt)$ as a result of chemical reaction. The property $(dq/dt)$ is recorded as a function of time; also as the amount of reactants decreases, limit $(t \to \infty)(dq/dt)$ is zero. Nevertheless because $(d\xi/dt)$ is a function of time, $(dq/dt)$ effectively monitors the progress of chemical reaction. Intuitively it is apparent that for an exothermic reaction $(dq/dt)$ at time zero is also zero, rises rapidly and then decreases to zero as all reactants are consumed.
The Law of Mass Action relates \( (d\xi/dt) \) to the composition of the system at time \( t \). Because \( (d\xi/dt) \) depends on time, \( (dq/dt) \) also depends on time, approaching zero as reactants are consumed.

For example, in the case of a simple chemical reaction of the form \( X \rightarrow Y \) where at \( t = 0 \) the amount of chemical substance \( X \) is \( n_X^0 \), the amounts of \( X \) and \( Y \) at time \( t \) are \( (n_X^0 - \xi) \) and \( \xi \) moles respectively. If the volume of the sample cell is \( V \),

\[
(1/V) \cdot d\xi/dt = (1/V) \cdot k \cdot (n_X^0 - \xi) \quad (f)
\]

Or,

\[
d\xi/dt = k \cdot V \cdot [c_X^0 - (\xi/V)] \quad (g)
\]

Or,

\[
d\xi/dt = k \cdot V \cdot c_X^0 \cdot \exp(-k \cdot t) \quad (h)
\]

Hence using equation (e) and for a dilute solution,

\[
dq/dt = \Delta H^\circ \cdot k \cdot V \cdot c_X^0 \cdot \exp(-k \cdot t) \quad (i)
\]

The integral of equation (i) between \( t = 0 \) and \( t \) yields the amount of heat passing between system and heat sink.[3,4]

\[
\int_0^t dq = \Delta H^\circ \cdot k \cdot V \cdot c_X^0 \cdot [1 - \exp(-k \cdot t)] \quad (j)
\]

Hence the measured dependence of \( (dq/dt) \) is compared with that calculated using equations (i) and (j). The analysis is readily extended to second order reactions. [4,5]

The technique of heat flow calorimetry has been applied across a wide range of subjects (e.g. screening of catalysts [6] and characterising complex reactions[7]) and subject to different analytical approaches.

**Footnotes**


