Calorimetry: Solutions: Isobaric

Classic (isobaric) calorimetric experiments often centre on the determination of the change in enthalpy $\Delta H$ for a given well-defined process. For example, the heat accompanying the mixing of known amounts of two liquids [e.g. water ($\lambda$) and ethanol ($\lambda$)] to form a binary liquid mixture yields the enthalpy of mixing, $\Delta_{\text{mix}} H$. Similarly enthalpies of solution are obtained by recording the heat accompanying the solution of a known amount of solute (e.g. urea) in a known amount of solvent; e.g. water ($\lambda$). Key equations emerge from the following analysis.

The enthalpy $H$ of a closed system is an extensive function of state which for a closed system is defined by the set of independent variables, $T$, $p$ and $\xi$ where $\xi$ represents the chemical composition.

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

Equation (b) is the complete differential of equation (a).

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

If the closed system is held at constant pressure (e.g. ambient) the differential enthalpy $dH$ equals the heat $dq$.

Thus

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

Here $\left(\frac{\partial H}{\partial T}\right)_{p,\xi}$ is the differential dependence of enthalpy $H$ on temperature at constant pressure and composition whereas $\left(\frac{\partial H}{\partial \xi}\right)_{T, p}$ is the differential dependence of enthalpy $H$ on composition at fixed temperature and pressure.