

## Mixtures

**Raoult's law:** states that the partial vapour pressure,  $p_A$ , in a liquid mixture,  $A$ , is proportional to its mole fraction,  $x_A$ , and its vapour pressure when pure,  $p_A^*$ :  $p_A = x_A p_A^*$ .

**Henry's law:** states that the vapour pressure,  $p_B$ , of a volatile solute,  $B$ , is proportional to its mole fraction,  $x_B$ , in a solution:  $p_B = x_B K_B$ . Here  $K_B$  is Henry's law constant.

**Chemical potential of a solvent:**

$$\mu_A = \mu_A^* + RT \ln x_A$$

where  $\mu_A^*$  = chemical potential of pure  $A$  and  $x_A$  is the mole fraction.

**Properties of mixtures:** suppose an amount  $n_A$  of substance  $A$  is mixed with  $n_B$  of substance  $B$ . The total volume of the mixture is

$$V = n_A V_{m,A} + n_B V_{m,B}$$

where  $V_{m,A}$  = partial molar volume of  $A$  and  $V_{m,B}$  = partial molar volume of  $B$ . More generally,  $V = \sum_i n_i V_{m,i}$ , where  $V_{m,i}$  is the partial molar volume of the  $i$ th substance.

**Total Gibbs energy for the mixture** is  $G = n_A G_A + n_B G_B$  where  $G_A$  and  $G_B$  are the **partial molar Gibbs energies** of substances  $A$  and  $B$  respectively. The partial molar Gibbs energies are also denoted  $\mu_A$  and  $\mu_B$  so that  $G = n_A \mu_A + n_B \mu_B$ . More generally, with mixtures of several substances  $G = \sum_i n_i \mu_i$ .

## Reaction Thermodynamics

**Standard state:** The standard state of a substance is the pure substance at a pressure of 1 bar. The standard state value is denoted by the superscript symbol  $\ominus$ , as in  $G^\ominus$ .

**Reaction Gibbs energy:**  $\Delta_r G = \frac{\Delta G}{\Delta \xi}$  is the slope of the graph of Gibbs energy against the progress of the reaction. Here,  $\Delta \xi = \Delta n_J / \nu_J$  for all species J in the reaction. Reaction Gibbs energy at any composition of the reaction mixture can be written

$$\Delta_r G = \Delta_r G^\ominus + RT \ln Q \quad \text{where } Q = \prod_J a_J^{\nu_J}$$

where  $a_J$  is the activity of species J and  $\nu_J$  is its stoichiometric number.

At equilibrium  $Q = K$ ,  $\Delta_r G = 0$  and  $-\Delta_r G^\ominus = RT \ln K$  where

$$K = \prod_J (a_J^{\nu_J})_{\text{equilibrium}}$$

**van't Hoff equation:**  $\frac{d}{dT} \ln K = \frac{\Delta_r H^\ominus}{RT^2}$ .

$$\ln \left( \frac{K_2}{K_1} \right) = -\frac{\Delta_r H^\ominus}{R} \left[ \frac{1}{T_2} - \frac{1}{T_1} \right]$$