**Chemical Equilibria: Solutions**

The conditions for chemical equilibrium in a closed system [1,2] at fixed temperature and pressure are as follows.

(i) Minimum in Gibbs energy.

(ii) Affinity for spontaneous change, $A$ equals zero.

(iii) Rate of chemical reaction, $\frac{d\xi}{dt} = 0$.

(iv) For a chemical equilibrium involving $i$-chemical substances, the equilibrium chemical potentials of all substances in the system conform to the following condition.

$$\sum_{j=1}^{j=i} v_j \cdot \mu_j^{eq} = 0 \quad \text{(a)}$$

If all $i$-chemical substances are solutes in aqueous solution at temperature $T$ and pressure $p$, the latter being close to the standard pressure $p^0$, the equilibrium chemical potentials are related to the composition of the system [3]. Hence,

$$A^{eq} = -\left( \frac{\partial G^{eq}}{\partial \xi} \right)_{T,p} = 0 = -\sum_{j=1}^{j=i} v_j \cdot \left[ \mu_j^0(\text{aq}) + R \cdot T \cdot \ln\left( m_j \cdot \gamma_j / m^0 \right) \right]^{eq} \quad \text{(b)}$$

Hence

$$\sum_{j=1}^{j=i} v_j \cdot \mu_j^0(\text{aq}) = -\sum_{j=1}^{j=i} v_j \cdot R \cdot T \cdot \ln\left( m_j \cdot \gamma_j / m^0 \right) \quad \text{(c)}$$

The left-hand-side of equation (c) defines the standard Gibbs energy of reaction, $\Delta_r G^0$ which in turn leads to the definition of an equilibrium constant $K^0$ [1].

$$\Delta_r G^0 = -R \cdot T \cdot \ln(K^0) = \sum_{j=1}^{j=i} v_j \cdot \mu_j^0(\text{aq}) \quad \text{(d)}$$

Combination of equation (c) and equation (d) yields an equation for $K^0$ in terms of the equilibrium composition of the system [3].

$$K^0 = \left[ \prod_{j=1}^{j=i} \left( m_j \cdot \gamma_j / m^0 \right)^{v(j)} \right]^{eq} \quad \text{(e)}$$

Equation (e) is remarkable. The right hand side describes the stoichiometry of the chemical equilibrium and the composition of the closed system at defined temperature and pressure. The left-hand-side
in the form of $K^0$ defined using equation (d) is related to the ideal thermodynamic process in terms of reference chemical potentials of reactants and products. If the solutes are non-ionic and the solution is dilute then a reasonable assumption sets $\gamma_j^{eq} = 1$ for all i-solutes.

**Footnotes**

[1] From a thermodynamic standpoint, an equilibrium constant emerges from the idea of zero affinity for chemical reaction at a minimum in Gibbs energy. Accounts which treat equilibrium constants as the ratio of rate constants are unsatisfactory.

[2] The equations set out here describe the general case where substance j is one of i-simple solutes in solution. In some cases one or more of the solutes are ionic and the solvent (e.g. water) is directly involved in the chemical reaction. In each case we assume that the systems have been assayed such that the composition of the system at equilibrium is known together with the stoichiometries.

[3] In general terms for a systems at pressure p,

$$A^{eq} = -\left(\frac{\partial G}{\partial \xi}\right)^{eq}_{T,p} = 0$$

Hence for a chemical equilibrium involving i-solutes in aqueous solution the following condition holds.

$$0 = \sum_{j=1}^{i} V_j \cdot [\mu_j^{0}(aq; T; p^0) + R \cdot T \cdot \ln(m_j \cdot \gamma_j / m^0) + \int_{p^0}^{p} V_j^{\infty}(aq) \cdot dp]^{eq}$$

$$\sum_{j=1}^{i} V_j \cdot \mu_j^{0}(aq; T; p^0) = -\sum_{j=1}^{i} V_j \cdot [R \cdot T \cdot \ln(m_j \cdot \gamma_j / m^0) + \int_{p^0}^{p} V_j^{\infty}(aq) \cdot dp]^{eq}$$

where $\Delta G^0(T; p^0) = -R \cdot T \cdot \ln(K^0) = \sum_{j=1}^{i} V_j \cdot \mu_j^{0}(aq; T; p^0)$