**Topic 420**

**Chemical Equilibria Solutions Simple Solutes**

A given chemical equilibrium involves association of two solutes $X(aq)$ and $Y(aq)$ to form solute $Z(aq)$.

$$2X(aq) + Y(aq) \rightleftharpoons 4Z(aq) \quad (a)$$

**Phase Rule.** The aqueous solution is prepared using two chemical substances: substance $Z$ and solvent water. Hence $C = 2$. There are 2 phases: vapour and solution so $P = 2$. Then $F = 2$. Hence at fixed temperature and in a system prepared using mole fraction $x_Z$ of substance $Z$ (an intensive composition variable), the equilibrium vapour pressure and the equilibrium amounts of $X(aq)$, $Y(aq)$ and $Z(aq)$ are unique.

At equilibrium, $2 \cdot \mu_X^{eq}(aq) + \mu_Y^{eq}(aq) = 4 \cdot \mu_Z^{eq}(aq) \quad (b)$

At fixed $T$ and $p$, assuming ambient pressure is close to the standard pressure $p^0$,

$$2 \cdot [\mu_X^{eq}(aq) + R \cdot T \cdot \ln(m_X \cdot \gamma_X / m^0)] + [\mu_Y^{eq}(aq) + R \cdot T \cdot \ln(m_Y \cdot \gamma_Y / m^0)] = 4 \cdot [\mu_Z^{eq}(aq) + R \cdot T \cdot \ln(m_Z \cdot \gamma_Z / m^0)]$$

where $\Delta G^0 = -R \cdot T \cdot \ln(K^0) = 4 \cdot \mu_Z^{eq}(aq) - 2 \cdot \mu_X^{eq}(aq) - \mu_Y^{eq}(aq) \quad (d)$

For this equilibrium at temperature $T$ and pressure $p$,

$$K^0 = \left( \frac{m_Z^{eq} \cdot \gamma_Z^{eq}}{m_X^{eq} \cdot \gamma_X^{eq} / m^0} \right)^4 \left( \frac{m_Y^{eq} \cdot \gamma_Y^{eq}}{m^0} \right)^2 \left( \frac{m_Z^{eq} \cdot \gamma_Z^{eq}}{m^0} \right)$$

If the solution is quite dilute, $\gamma_X^{eq}$, $\gamma_Y^{eq}$ and $\gamma_Z^{eq}$ are effectively unity in the real solution at equilibrium. Then

$$K^0 = \left( \frac{m_Z^{eq} / m^0} {m_X^{eq} / m^0} \right)^4 \left( \frac{m_Y^{eq} / m^0} {m_X^{eq} / m^0} \right)^2 \left( \frac{m_Z^{eq} / m^0} {m^0} \right)$$

$K^0$ is dimensionless. But the latter statement signals a common problem in this subject because chemists find it more convenient and informative to define a quantity $K_m^0$ in which the $m^0$ terms in equation (f) [or its equivalent] have been removed.

Thus, $K_m^0 = \left( \frac{m_Z^{eq}} {m_X^{eq}} \right)^4 \left( \frac{m_Y^{eq}} {m_X^{eq}} \right)^2 \left( \frac{m_Y^{eq}} {m_X^{eq}} \right)$ \quad (g)
Hence the units for $K_m^0$ signal the stoichiometry of the equilibrium whereas the dimensionless $K^0$ does not [1,2].

Footnotes

[1] As a consequence of the removal of the $m^0$ terms, $K_m^0$ quantities have units unless the equation for the chemical equilibrium is stoichiometrically balanced: e.g. n-moles of reactants form n-moles of products.

But from equation (g), $K_m^0 = \left[\text{mol kg}^{-1}\right]^4 \cdot \left[\text{mol kg}^{-1}\right]^{-2} \cdot \left[\text{mol kg}^{-1}\right]^{-1}$

or $K_m^0 = \left[\text{mol kg}^{-1}\right]$

If we write, $\Delta_r G^0 = -R \cdot T \cdot \ln(K_m^0)$

Then $\Delta_r G^0 = \left[J \text{ K}^{-1} \text{ mol}^{-1}\right] \cdot \left[K\right] \cdot \ln\left[\text{mol kg}^{-1}\right]$

There is clearly a slight problem in handling a logarithm of a composition unit. There are two approaches to this problem. The first approach ignores the problem, which is unsatisfactory practice. The second approach is to ask - what happened to the composition unit and trace the problem back through the equations.