Topic 2660

Solubility Products

A given closed system at temperature T and pressure p (which is close to ambient) contains an aqueous solution of a sparingly soluble salt MX; e.g. AgCl. The system also contains solid salt MX. When a soluble salt (e.g. KNO3) is added the solubility of salt MX increases. This remarkable observation is readily accounted for. The equilibrium involving the sparingly soluble salt is represented as follows.

\[ \text{MX}^{(s)} \leftrightarrow \text{M}^\text{aq}^+ \text{X}^- \text{(aq)} \]

We represent the salt MX by the symbol \( j \). At equilibrium,

\[ \mu_j^* (s) = \mu_j^{eq} (aq) \]  \hspace{1cm} (a)

In terms of the solubility \( S_j \) of the salt MX, a 1:1 salt,

\[ \mu_j^* (s) = \mu_j^{0} (aq) + 2 \cdot R \cdot T \cdot \ln(S_j \cdot \gamma_z / m^0) \]  \hspace{1cm} (b)

By definition \( \Delta_{sp} G^0 = -R \cdot T \cdot \ln K_S = \mu_j^0 (aq) - \mu_j^* (s) \)  \hspace{1cm} (c)

\( K_S \) is the solubility product, a characteristic property of salt MX (at defined T and p).

\[ K_S = [S_j \cdot \gamma_z / m^0]^2 \]  \hspace{1cm} (d)

Or,

\[ \ln(S_j / m^0) = (1/2) \cdot \ln(K_S) - \ln(\gamma_z) \]  \hspace{1cm} (e)

According to the DHLL,

\[ \ln(\gamma_z) = -S \gamma \cdot (I / m^0)^{1/2} \]  \hspace{1cm} (f)

\( I \) is the ionic strength of the solution which can be changed by adding a soluble salt. From equations (e) and (f),

\[ \ln(S_j / m^0) = (1/2) \cdot \ln(K_S) + S \gamma \cdot (I / m^0)^{1/2} \]  \hspace{1cm} (g)

The key point to note is the positive sign in equation (g) showing that the theory accounts for the observed salting-in of the sparingly soluble salt. Further a plot of \( \ln(S_j / m^0) \) against \( (I / m^0)^{1/2} \) is linear yielding an estimate for \( K_S \) from the intercept.