Solubility calculations

ESS 312 - May 10, 2010

In class we considered a reaction at equilibrium:

$$aA + bB \rightleftharpoons cC + dD \tag{1}$$

and derived the simple relationship between the equilibrium constant and the standard-state Gibbs Free Energy difference between products and reactants:

$$ln(\frac{a_C^c . a_D^d}{a_A^a . a_B^b}) = ln(K_{eq}) = \frac{-\Delta G^0}{RT} \tag{2}$$

or equivalently:

$$K_{eq} = e^{-(\frac{\Delta G^0}{RT})} \tag{3}$$

For a dissolution reaction, this remarkable result relates the *ion activity product* (IAP) in a saturated solution to the measurable salt concentrations, and to the Gibbs Free Energy of formation ΔG_f^0 of the substances in solution.

For example, for a saturated solution of gypsum ($CaSO_4.2H_2O$), the dissolution reaction is:

$$CaSO_4.2H_2O \rightleftharpoons Ca^{2+} + SO_4^{2-} + 2\ H_2O \tag{4}$$

To calculate the equilibrium constant at 298K and 1 bar use the following data:

substance	$\mathbf{\Delta G_f^0}$ kJ/mol
$CaSO_4.2H_2O$	-1796.4
H_2O	-237.2
Ca^{2+}	-553.8
SO_4^{2-}	-742.0

Now add these up to get ΔG^0 for the reaction:

$$\Delta G^0 = -742.0 - 553.8 - 2(237.2) - (-1796.4) = 26.3\ kJ/mol \tag{5}$$

Remembering that $R = 0.008314\ kJ/(K\ mol)$:

$$K_{eq} = e^{-(\frac{\Delta G^0}{RT})} = e^{-\frac{26.3}{0.008314 \times 298.15}} = e^{-10.61} = 2.47 \times 10^{-5} = 10^{-4.61} \tag{6}$$

So ... now you know how to calculate a solubility product from tables of ΔG_f^0.