7.7: Solubility

The maximum solubility of a solute can be determined using the same methods we have used to describe colligative properties. The chemical potential of the solute in a liquid solution can be expressed

$$\mu_B(solution) = \mu_B^o(liquid) + RT\ln\chi_B$$

If this chemical potential is lower than that of a pure solid solute, the solute will dissolve into the liquid solvent (in order to achieve a lower chemical potential!) So the point of saturation is reached when the chemical potential of the solute in the solution is equal to that of the pure solid solute.

$$\mu_B^o(solid) = \mu_B^o(liquid) + RT\ln\chi_B$$

Since the mole fraction at saturation is of interest, we can solve for $\ln(\chi_B)$.

$$\ln\chi_B = \frac{\mu_B^o(solid) = \mu_B^o(liquid)}{RT}$$

The difference in the chemical potentials is the molar Gibbs function for the phase change of fusion. So this can be rewritten

$$\ln\chi_B = \frac{-\Delta G^o_{fus}}{RT}$$

It would be convenient if the solubility could be expressed in terms of the enthalpy of fusion for the solute rather than the Gibbs function change. Fortunately, the Gibbs-Helmholtz equation gives us a means of making this change. Noting that

$$\left(\frac{\partial\left(\frac{\Delta G}{T}\right)}{\partial T}\right)_p = \frac{\Delta H}{T^2}$$

Differentiation of the above expression for $\ln(\chi_B)$ with respect to T at constant p yields

$$\left(\frac{\partial\ln\chi_B}{\partial T}\right)_p = \frac{1}{R}\frac{\Delta H_{fus}}{T^2}$$

Separating the variables puts this into an integrable form that can be used to see how solubility will vary with temperature:

$$\int_0^{\ln\chi_B} d\ln\chi_B = \frac{1}{R}\int_{T_f}^{T}\frac{\Delta H_{fus}dT}{T^2}$$

So if the enthalpy of fusion is constant over the temperature range of T_f to the temperature of interest,

$$\ln\chi_B = \frac{\Delta H_{fus}}{R}\left(\frac{1}{T_f} - \frac{1}{T}\right)$$

And χ_B will give the mole fraction of the solute in a saturated solution at the temperature T. The value depends on both the enthalpy of fusion, and the normal melting point of the solute.