Part 3

Thermodynamics of Mixing Liquids

Partial Molar Quantities

The partial molar volume of component J in a mixture is the volume change in the mixture when 1 mole of J is added to a large volume of the mixture.

$$V_J = \left(\frac{\partial V}{\partial n_J}\right)_{p,T,n'}$$

The total volume of a mixture $V = \sum_J n_J V_J$ (*e.g.*, for a binary mixture $n_A V_A + n_B V_B$).

The partial molar Gibbs energy of component J in a mixture is the chemical potential of J.

$$\mu_J = \left(\frac{\partial G}{\partial n_J}\right)_{p,T,n'}$$

The total Gibbs energy of a mixture $G = \sum_J n_J \mu_J$ (*e.g.*, for a binary mixture $n_A \mu_A + n_B \mu_B$).

The fundamental equation of chemical thermodynamics s: $\mathrm{d}G = V\mathrm{d}p - S\mathrm{d}T + \mu_A \mathrm{d}n_A + \mu_B \mathrm{d}n_B + \ldots$

The chemical potential in terms of each of the internal energy U , the enthalpy H and the Helmholtz energy is;

$$\mu_J = \left(\frac{\partial U}{\partial n_J}\right)_{S,V,n'} \quad \mu_J = \left(\frac{\partial H}{\partial n_J}\right)_{p,S,n'} \quad \mu_J = \left(\frac{\partial A}{\partial n_J}\right)_{V,T,n'}$$

The *Gibbs-Duhem equation* is:

$$\sum_J n_J d\mu_J = 0$$

The Chemical Potential of Liquids

Raoult's law is: $p_A = x_A p_A^*$

An ideal solution is one that obeys Raoult's law at all compositions of the mixture

The chemical potential of component A of an ideal solution is : $\mu_A = \mu_A^* + RT \ln x_A$

Henry's law is: $p_B = x_B K_B$

An *ideal-dilute solution* is one for which the solute obeys Henry's law and the solvent obeys Raoult's Law.

Liquid Mixtures

The Gibbs energy of mixing two ideal liquids A and B is: $\Delta_{mix}G = nRT(x_A \ln x_A + x_B \ln x_B)$

The corresponding entropy of mixing is: $\Delta_{mix}S = -nR(x_A \ln x_A + x_B \ln x_B)$

The corresponding enthalpy of mixing is: $\Delta_{mix}H = \Delta_{mix}G + T\Delta_{mix}S = 0$

An *excess function* (X^E) is the difference between the observed (real) function of mixing and the ideal function *(e.g.,* $S^E = \Delta_{mix}S^{real} - \Delta_{mix}S^{\mathrm{ideal}}$)

A *regular solution* is one for which $H^E \neq 0$, but $S^E = 0$.

Colligative Properties

A colligative property is a property that depends only on the number of solute particles present (not their identity).

Elevation of the boiling point: $\Delta T = K_b b$

Depression of the freezing point: $\Delta T = K_f b$

Activities

Solvent activity: $a_A = p_A/p_A^*$

Solvent activity and chemical potential: $\mu_A = \mu_A^* + RT \ln a_A$

Raoults law basis of activity and activity coefficient: $\gamma_J = a_J/x_J$

Solute activity of an ideal-dilute solution: $\mu_B = \mu_B^\ominus + RT \ln a_B$

Henry's law basis and activity coefficient: $\gamma_J = a_J/x_J$

Solute activity of an ideal-dilute solution in terms of molalities: $\mu_B = \mu_B^\ominus + RT \ln b_B$ (note $\mu_B^\ominus$ has different numerical values when using a_B and b_B, but it is still nevertheless still a standard)