Flory-Huggins Equation for Mixing:

When an ideal gas mixes the change in free energy is just the change in entropy since there is no interaction between the molecules. The statistical description of entropy can be used to calculate the change in entropy by the change in the number of possible states in the system. Before mixing the two molecule types are homogenous so there is only one distinguishable state. After mixing there are Ω possible states,

$$\Omega = \frac{N!}{N_1! N_2!}$$

using the Boltzman expression for entropy we have,

$$\Delta S = k \ln \Omega = k\left(\ln N! - \ln N_1! - \ln N_2!\right)$$

Sterling's approximation can be used to simplify this expression, $\ln N! = N \ln N - N$, so

$$\Delta S = k\left(N \ln N - N_1 \ln N_1 - N_2 \ln N_2 + N - N_1 - N_2\right)$$

$$= k\left(N \ln N - N_1 \ln N_1 - N_2 \ln N_2\right) = k\left(-N_1 \ln N_1 + N_1 \ln N - N_2 \ln N_2 + N_2 \ln N\right)$$

$$= k\left(N_1 \ln \frac{N_1}{N} - N_2 \ln \frac{N_2}{N}\right) = -k\left(N_1 \ln x_1 + N_2 \ln x_2\right)$$

where x_1 is the mole fraction of component 1.

For an ideal gas system with no enthalpic interaction this is the free energy for mixing, $\Delta G = -T\Delta S$. We can consier a probability $p(x_1)$ associated with the probability of one configuration of this ideal gas mixture occurring which can be obtained using the Boltzman relationship,

$$p(x_1) = \exp\left(\frac{-\Delta G}{kT}\right) = \exp\left(\frac{kT\left(\ln x_1^{N_1} + \ln x_2^{N_2}\right)}{kT}\right)$$

$$= x_1^{N_1} x_2^{N_2}$$

so that the probability of finding one site with a molecule of type 1, x_1, is raised to the number of such sites, N_1 and similarly with the probability of finding a site with a molecule of type 2. The two molecules are indistinguishable other than some minor difference such as color, that is they occupy the same volume and have no interaction.

This probability changes when one of the molecules is a polymer since the two molecules do not occupy the same volume. Then the probability of finding one polymer chain is the number of solvent like units in the chain (monomers) times the mole fraction of polymer, x_2. The mole fraction times the number of units is the volume fraction, ϕ_2. Then for molecules of different size we must replace the mole fraction with the volume fraction. This probability is still raised to the N2 power since there are still N_2 cases to consider, so the probability, $p(\phi_1)$ becomes,

$$p(\phi_1) = \phi_1^{N_1} \phi_2^{N_2}$$

and the associated entropy of mixing ΔS becomes,

$$\Delta S = k\left(N_1 \ln \phi_1 + N_2 \ln \phi_2\right)$$

This equation works for both the original ideal gas as well as for the polymer or other macromolecular system since the volume fraction and mole fractions are the same for an ideal gas. In considering the probability of finding a polymer chain as only that of the volume fraction we ignore the internal conformations of the chain (the isolated chain conformational free energy considered previously).

We considered previously the average enthalpy of interaction per lattice site (solvent or monomer),

$$\chi = \frac{z\overline{\Delta\varepsilon}}{kT}$$

and this same chi-parameter can be used to describe the enthalpic contribution to the free energy of mixing for a system containing N molecules. We consider N_1 solvent molecules that have a probability of interacting with a polymer mer unit of ϕ_2. The free energy expression becomes,

$$\Delta G = -T\Delta S + \Delta H = -kT\left(N_1 \ln\phi_1 + N_2 \ln\phi_2 + \chi N_1\phi_2\right)$$

If we consider the free energy per lattice site, per kT unit of energy we obtain,

$$\frac{\Delta G}{NkT} = -\left(n_1 \ln\phi_1 + n_2 \ln\phi_2\right) + \chi n_1\phi_2$$

For a polymer blend this becomes, (Polymer Blends By Lloyd M. Robeson)

2.1.3 Flory-Huggins Theory

The most relevant theory for modeling the free energy of binary polymer mixtures is the Flory-Huggins theory, initially employed for solvent-solvent and polymer-solvent mixtures. This theory was independently derived by Flory [4, 5] and Huggins [6, 7]. The key equation (combined from discussions earlier in this chapter on entropy and enthalpy of mixing) is:

$$\Delta G_m = kTV\left[\frac{\phi_1}{V_1}\ln\phi_1 + \frac{\phi_2}{V_2}\ln\phi_2\right] + \phi_1\phi_2\chi_{12}\, kTV/v_r \quad \text{(molecular basis)} \qquad (2.20a)$$

$$\Delta G_m = RTV\left[\frac{\phi_1}{v_1}\ln\phi_1 + \frac{\phi_2}{v_2}\ln\phi_2\right] + \phi_1\phi_2\chi_{12}\, RTV/v_r \quad \text{(molar basis)} \qquad (2.20b)$$

where V = total volume, R = gas constant, ϕ_i = volume fraction of component i, V_i = molecular volume, v_i = molar volume of polymer chain i, v_r = molecular or molar volume of a specific segment (depending on whether Eq. 2.20a or 2.20b is employed), χ_{12} = Flory-Huggins interaction parameter and k is the Boltzmann's constant. v_r is often calculated as the square root of the product of the individual segmental unit molecular or molar volumes of the polymeric components ($v_r = \sqrt{v_1 v_2}$). χ_{12}' is further simplified to χ_{12} (binary interaction parameter), defined as $\chi_{12}' = \chi_{12}/v_r$ and often as a binary interaction density parameter, B, defined as $B = \chi_{12}'RT$. As the use of χ_{12} and χ_{12}' is often interchanged in the literature, some confusion may exist. The following discussion will employ the molar basis (Eq. 2.20b). From Eq. 2.12, it is apparent that the term in Eq. 2.20b: