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Course 505/605 Lecture Number ______ Date 4/15/03

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Last Time: Mixing

$$\chi_{AB} = \frac{Z}{kT}\left(W_{AB} - \frac{(W_{AA} + W_{BB})}{2}\right)$$ (the exchange parameter)

Free Energy of Mixing $\left(\frac{\Delta F_{mix}}{NkT}\right)$

- Mixed State: $F(N_A, N_B)$

$$\frac{F(N_A,N_B)}{kT} = N_A \ln \frac{N_A}{N} + N_B \ln \frac{N_B}{N} + \left(\frac{ZW_{AA}}{2kT}\right) N_A + \left(\frac{ZW_{BB}}{2kT}\right) N_B + \chi_{AB} \frac{N_A N_B}{N}$$

- Unmixed State

$$\frac{F(N_A,0)}{kT} = \frac{ZN_A W_{AA}}{kT}$$

$$\frac{F(0,N_B)}{kT} = \frac{ZN_B W_{BB}}{kT}$$

$$\Delta F_{mix} = F(N_A, N_B) - F(N_A, 0) - F(0, N_B)$$

Let's calculate the free energy of mixing per molecule.

$$\boxed{\frac{\Delta F_{mix}}{NkT} = x \ln x + (1-x) \ln (1-x) + \chi_{AB}\, x(1-x)}$$

where $x = \frac{N_A}{N}$, $(1-x) = \frac{N_B}{N}$, $N = N_A + N_B$

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The expression on the previous page is valid only for regular solutions. ($A-A \approx B-B \approx A-B$).

if $\Delta F_{mix}(x, \chi_{AB}) < 0$, mixing is favored

if $\Delta F_{mix}(x, \chi_{AB}) > 0$, mixing is not favored.

These regular solutions are sometimes called "Hildebrand" solution.

<u>Example</u> Oil and Water: Do They Mix?

$$\text{Oil} + \text{Water} \rightleftharpoons \text{Oil-Water}$$

$$\frac{\Delta F_{mix}}{RT} = x \ln x + (1-x)\ln(1-x) + \chi_{AB}(1-x)x$$

where $\chi_{AB} \approx 5$ kcal/mol and x = oil mole fraction

<u>Result</u>

for small x, $\frac{\Delta F_{mix}}{RT} < 0$

for large x, " > 0

According to this "Result", mixing of these two species is favorable when there is very little oil in bulk H_2O.

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Chemical Potential

$$\mu = \left(\frac{\partial F}{\partial N}\right)_{T,V}$$

$$\frac{\mu_A}{kT} = \frac{1}{kT}\left(\frac{\partial F}{\partial N_A}\right)_{T,V} = \ln\frac{N_A}{N} + 1 - \frac{N_A}{N} - \frac{N_B}{N} + \frac{zW_{AA}}{2kT} + \chi_{AB}\frac{(N_A+N_B)N_B - N_A N_B}{(N_A+N_B)^2}$$

$$= \ln x_A + \frac{zW_{AA}}{2kT} + \chi_{AB}(1-x_A)^2$$

So: $\mu_A = \ln x_A + \mu_A^\circ$

$\mu_B = \ln x_B + \mu_B^\circ$

For "irregular" solutions (Strongly non-ideal solutions)

$x_i \longrightarrow$ "$\gamma_i x_i$" $\equiv a_i$ where activity coefficient is a_i

$\gamma_i = 1 \quad \rightarrow$ Regular Solutions

$\gamma_i \neq 1 \quad \rightarrow$ Strongly non ideal solutions.

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Chapter 16 - Partitioning Solute Between Different Solvents

Homogenous mixtures of miscible components; eg. A. and B.

$\begin{cases} \text{Solvent (present in excess)} \\ \text{Solute (present in smaller amounts)} \end{cases}$

$$\mu_B = \mu_B^\circ + kT \ln \gamma_B x_B$$

$\gamma = 1$ Regular Mixture.

Solvent Convention

$$\underset{\substack{\uparrow \\ \text{solvent}}}{B} \gg A \leftarrow \text{Solute}$$

$\gamma_B x_B = 1$

$$\boxed{\mu_B = \mu_B^\circ}$$