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Course SOS/605 Lecture Number _____ Date 4/15/03

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Last Time: Mixing

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

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

• Mixed State: $F(N_A, N_B)$

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

• Unmixed State

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

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

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

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

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

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

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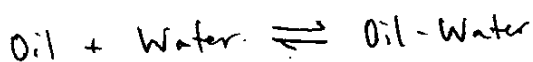
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The expression on the previous page is valid only for regular solutions ($A-A \approx B-B \approx A-B$).

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.

Example Oil and Water: Do They Mix?



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

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

Result

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

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

$$\frac{\mu_A}{kT} = \frac{1}{kT} \left(\frac{\partial F_0}{\partial N_A} \right)_{T, V} = \ln \frac{N_A}{N} + 1 - \frac{N_A}{N} - \frac{N_B}{N} + \frac{zW_{AA}}{2kT} + \chi_{AB} \frac{(N_A + N_B)N_B - N_A N_B}{(N_A + N_B)^2}$$

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

So:

$$\mu_A = \ln x_A + \mu_A^i$$

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

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

$x_i \rightarrow \gamma_i x_i \equiv a_i$ where activity coefficient is a_i

$\gamma_i = 1 \rightarrow$ Regular Solutions

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

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Chapter 16 - Partitioning Solute Between Different Solvents

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

{ Solvent (present in excess)
 Solute (present in smaller amounts)

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

$\gamma = 1$ Regular Mixture.

Solvent Convention

B \gg A \leftarrow Solute

\uparrow
solvent

$$\gamma_B X_B = 1$$

$$\mu_B = \mu_B^\circ$$