Course 565/665 Lecture Number ____ Date 4/14/03

Lecturer Dr. Silvia Cavagnero Note Taker Eric Fulmer

Last Time

$$W = \frac{N!}{N_A!\,N_B!} \qquad N = N_A + N_B$$

$$\Delta S_{mixing} = k\left(N_A \ln N + N_B \ln N - N_A \ln N_A - N_B \ln N_B\right)$$

Define Mole fractions: $x_A = \frac{N_A}{N}$ $x_B = \frac{N_B}{N}$

$$\Delta S_{mixing} = k\left(N_A \ln \frac{N}{N_A} + N_B \ln \frac{N}{N_B}\right)$$

$$= -k\left(N_A \ln x_A + N_B \ln x_B\right)$$

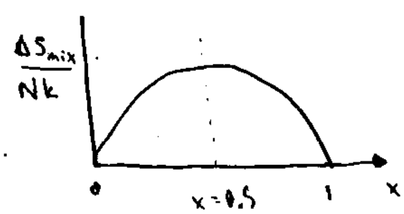
Define $x_A \equiv x$ $\quad x = \frac{N_A}{N}$

$x_B \equiv 1 - x$

$$\frac{\Delta S_{mixing}}{Nk} = -\left(\frac{N_A}{N} \ln x + \frac{N_B}{N} \ln(1-x)\right)$$

$$= -x \ln x - (1-x)\ln(1-x)$$

$$\boxed{\frac{\Delta S_{mix}}{Nk} = -x \ln x - (1-x)\ln(1-x)}$$



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<u>Example</u> H_2O/Ethanol 15% / 85% mole

<u>Tip</u>: If given V% or weight %, convert it to mole %.

$$\text{density } (\rho) = \frac{\text{mass}}{\text{volume}} \quad ; \quad n = \frac{\text{mass}}{MW}$$

$$V\% \xrightarrow{\rho} \text{mass}\% \xrightarrow{n} \text{mole}\% \xrightarrow{/100} x$$

$$\Delta S_{mix} = \underbrace{Nk}_{R} \left(-0.15 \ln 0.15 - 0.85 \ln 0.85 \right) = 0.83 \text{ cal/mol K}$$

$$\Delta S_{mixing} > 0 \quad \text{[Entropically Favored]}$$

<u>Ideal Solutions</u> (no interactions: A-A, A-B, B-B)

$$\Delta G_{mix} = \cancel{\Delta H_{mix}}^{\,0} - T\Delta S_{mix} \qquad \text{constant } P, T$$

$$\Delta F_{mix} = \cancel{\Delta U_{mix}}^{\,0} - T\Delta S_{mix} \qquad \text{constant } V, T$$

With no interactions, the energy or enthalpy (which accounts for the interactions) must be zero. Multiplicity will always increase with mixing, making $T\Delta S_{mix}$ always positive. Thus, mixing of Ideal Solutions is always favored. ($\Delta G_{mix}, \Delta F_{mix} < 0$) and is thus entropically driven.

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Not-so-ideal (Nonideal) Solutions

- Interaction energies are not zero.
- W_{ij} ≡ interaction internal energy

  m_{ij} ≡ # of ij bonds ; Z ≡ # of lattice sides per lattice unit.


← 6 for a cube.

For the mixed system:

$$U = m_{AA} W_{AA} + m_{AB} W_{AB} + m_{BB} W_{BB}$$

$$Z N_A = 2 m_{AA} + \text{[redacted]} m_{AB}$$

$$Z N_B = 2 m_{BB} + \text{[redacted]} m_{AB}$$

$$m_{AA} = \frac{Z N_A - \text{[redacted]} m_{AB}}{2} \qquad m_{BB} = \frac{Z N_B - \text{[redacted]} m_{AB}}{2}$$

$$U = \frac{(Z N_A - \text{[redacted]} m_{AB})}{2} W_{AA} + m_{AB} W_{AB} + \frac{(Z N_B - \text{[redacted]} m_{AB})}{2} W_{BB}$$

$$= \frac{Z W_{AA}}{2} N_A + \frac{Z W_{BB}}{2} N_B + \left[W_{AB} - \frac{(W_{AA} + W_{BB})}{2} \right] m_{AB}$$

Mean Field Approximation

"p" of A surrounded by B = "p" of B surrounded by A

$$p_B = \frac{N_B}{N} - (1-x)$$

[redacted] $$\frac{ZN_B}{N} = Z(1-x)$$

$$m_{AB} = \frac{ZN_AN_B}{N} = ZNx(1-x)$$

$$Nx = \frac{N_A}{N} = N_A$$

$$U = \left(\frac{ZW_{AA}}{2}\right)N_A + \left(\frac{ZW_{BB}}{2}\right)N_B + Z\left(W_{AB} - \frac{(W_{AA}+W_{BB})}{2}\right) \times \frac{N_AN_B}{N}$$

$$= \frac{ZW_{AA}}{2}N_A + \frac{Z\ W_{BB}}{2}N_B + kT\,\chi_{AB}\,\frac{N_AN_B}{N}$$

where $$\chi_{AB} \equiv \frac{Z}{kT}\left(W_{AB} - \frac{(W_{AA}+W_{BB})}{2}\right)$$

or the "Exchange Parameter"

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① Ideal Solutions

No Interactions: $\chi_{AB} = 0$

② Nonideal, but interactions are approximately equal

$(W_{AA} \simeq W_{AB} \simeq W_{BB})$

$\chi_{AB} = 0$

③ Nonideal, but like interactions are stronger than unlike

$(W_{AA}, W_{BB} < W_{AB})$

$\chi_{AB} > 0$

④ Nonideal, unlike stronger $(W_{AB} < W_{AA}, W_{BB})$

$\chi_{AB} < 0$

Determine ΔF_{mix}

$F = U - TS$

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

$$F(N_A, 0) = F(N_A, N_B) - F(N_A, 0) \ldots$$