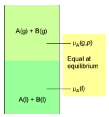
# 59-240 Lecture 16 Simple Mixtures

## Chemical Potentials of Liquids

### Basics




$$\mu_A = \mu_A^* + RT \ln \left( \frac{p_A}{p_A^*} \right)$$

$$p_A = x_A p_A^*$$

### Raoult's Law

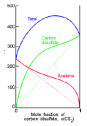
ideal solutions obey exactly; **solvent's** point of view

$$\mu_A = \mu_A^* + RT \ln x_A$$

Molecular interpretation

#### Ideal dilute solutions

Only obey law when solute is very dilute

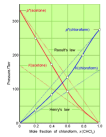


CS2/acetone

### Henry's Law

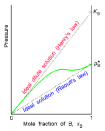
$$p_B = x_B K_B$$

ideal solutions obey exactly; **solutes's** point of view



chloroform/acetone example

#### validity of laws



comparison of laws

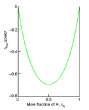
$O_2$ solubility example

#### using Henry's law

## Thermodynamics of Mixing

$$\Delta_{mix} G = n_A RT \ln \left( \frac{p_A}{p} \right) + n_B RT \ln \left( \frac{p_B}{p} \right)$$

$$\Delta_{mix} G = nRT \left( x_A \ln x_A + x_B \ln x_B \right)$$



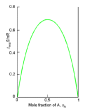
$\Delta G$ at most negative for a 50:50 mixture; gases mix spontaneously

$$G_i = (3.0 \text{ mol}) \left\{ \mu_{H_2}^* + RT \ln 3p \right\} + (1.0 \text{ mol}) \left\{ \mu_{N_2}^* + RT \ln p \right\}$$

$$G_f = (3.0 \text{ mol}) \left\{ \mu_{H_2}^* + RT \ln \tfrac{3}{2}p \right\} + (1.0 \text{ mol}) \left\{ \mu_{N_2}^* + RT \ln \tfrac{1}{2}p \right\}$$

H2/N2 example

$$\Delta_{mix} S = -\left( \frac{\partial \Delta_{mix} G}{\partial T} \right)_{p,n_A,n_B} = -nR \left( x_A \ln x_A + x_B \ln x_B \right)$$



$\Delta S$ for mixing at most positive for a 50:50 mixture

## Simple Mixtures

non-reacting subtances

binary systems

energetics of mixing

## Partial Molar Volume

water/ethanol example

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

partial mol. vol.

$$dV = \left( \frac{\partial V}{\partial n_A} \right)_{p,T,n_B} dn_A + \left( \frac{\partial V}{\partial n_B} \right)_{p,T,n_A} dn_B = V_A dn_A + V_B dn_B$$

$$V = n_A V_A + n_B V_B$$

## Partial Molar Gibbs Energies

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

Total Gibbs energy: $G = n_A \mu_A + n_B \mu_B$

FET: depends on composition as well:

$$dG = Vdp - SdT + \mu_A dn_A + \mu_B dn_B + \ldots$$

**non-expansion work** can occur just by **mixing** two substances together!

Gibbs-Duhem equation

$$d\mu_B = -\frac{n_A}{n_B} d\mu_A$$

Self-test 5.1/7.1 (question like this on final)