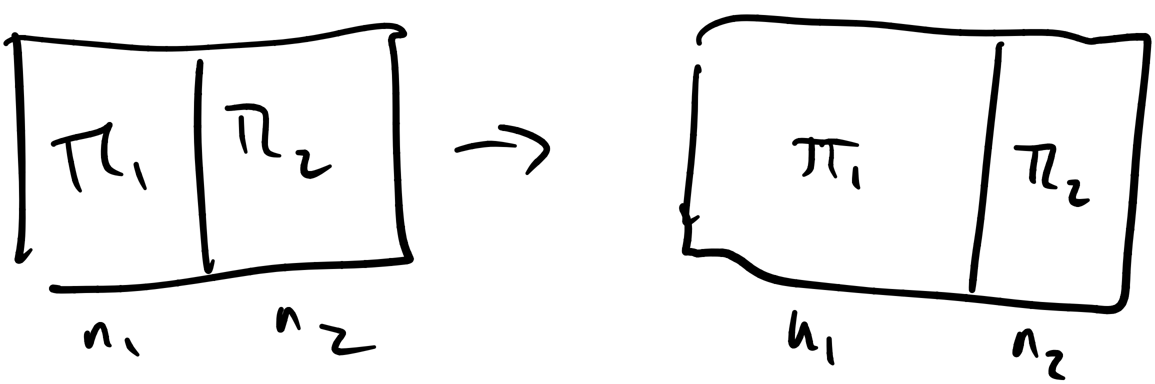
Chemical potentials of mixtures

Previously showed how chemical potentials (partial molar Gibbs Free Energies) govern phase equilibria

Now we will look more at how these depend on concentration of mulltiple components (mixtures & reactions)

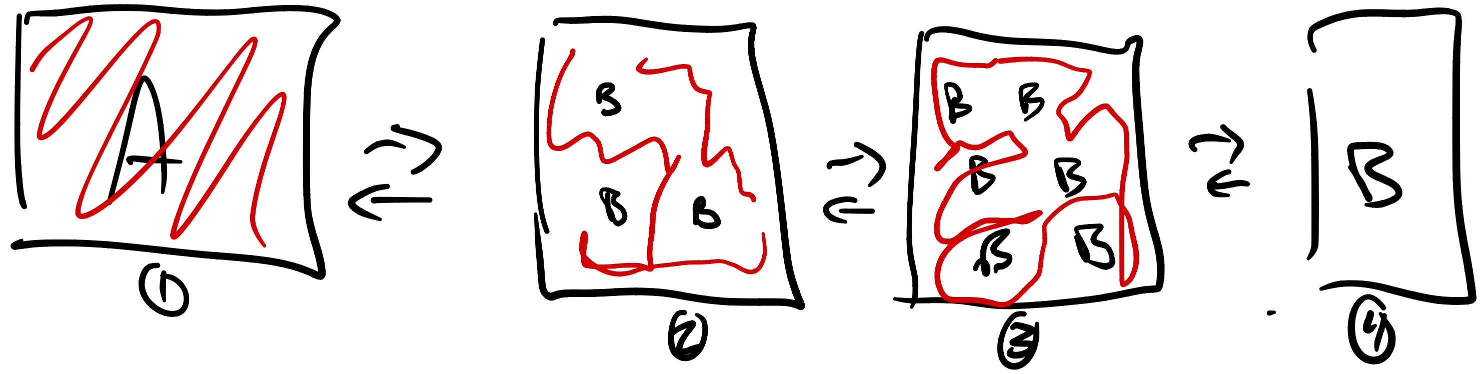
Difference between phases & reactions



$$G = n_1\mu_1 + n_2\mu_2 + (\text{interface})$$
$$\approx n_1\mu_1^* + n_2\mu_2^* \quad \text{for all } n_1, n_2$$

where μ_i^* is chem pot of pure material

$A \rightleftharpoons B$



$G = n_1\mu_1 + n_2\mu_2$ but

$\mu_1 \neq \mu_1^*$ $\mu_2 \neq \mu_2^*$ except at 1 & 4 respectively

2 contributions to non ideality:

$\mu_i = \bar{H}_i - T\bar{S}_i$

↖ energy changes due to interactions and change in structure

S changes b/c minimized in pure states

Need to compute these contributions relative to some known value

Concentration scales (see also, worksheet)

Reference concentrations can be measured different ways and different ones are useful for different situations

All concentration scales are <u>intensive</u> (doubling system keeps same)

Species normalized scales:

- mole fraction $x_i = n_i / \sum n_i = n_i / N_T$

- molality: moles of i over kg solvent

$$m_i = n_i / 1000 n_s \cdot w_s = x_i / 1000 w_s x_s$$

w_s = molecular weight solvent (eg water = 18 g/mol)

note: $\sum m_i = \frac{1}{1000 w_s x_s}$

Volume normalized

- Molarity $M_i = [i] = \frac{n_i}{V_T} = \frac{n_i}{\sum n_i \bar{V}_i} = \frac{x_i}{\sum x_i \bar{V}_i}$

$$\sum M_i = n_T / V_T = [\text{everything}]$$

- Partial density

$$\rho_i = \frac{n_i w_i}{V_T} = \frac{x_i w_i}{\sum x_i \bar{V}_i}$$

$$\sum \rho_i = \rho_{\text{everything}} = \frac{\text{mass total}}{\text{volume total}}$$

[Do water on worksheet]

- Partial pressure (for gas)

$$P_T = \sum P_i \Rightarrow P_i = P_T - \sum_{i \neq j} P_j$$

$$\text{ideal gas} = \frac{RT n_i}{V} = RT M_i$$

Return to concentration dep of μ:

Previously, G-D relation:

$$\sum n_i \, d\mu_i = V dp - S dT$$

since $V = \sum n_i \bar{V}_i$ & $S = \sum n_i \bar{S}_i$

↳ n equations $d\mu_i = \bar{V}_i \, dp - \bar{S}_i \, dT$

$p = \sum p_i \Rightarrow dp = \sum dp_i$

for const T & $p_{j \neq i}$

$$d\mu_i = \bar{V}_i \, dp_i$$

consider ideal gas $\bar{V} = RT/p$

$$\Rightarrow \int_{\mu_i^\circ} d\mu_i = \int_{p_i^\circ} \frac{RT}{p} dp$$

$$\Rightarrow \mu_i = \mu_i^\circ - RT \ln(p_i/p_i^\circ)$$

What is ref? for gas choose $p_i = 1 atm$

& $\mu_i = \mu_i @ 1 atm$

Can choose other standard states

$X_i^* = 1$ already discussed (high con mixtures)

$[i]^\circ = 1$ molar (low conc mixtures)

Note, it is possible to have

$P_A = P_B = P_C = \ldots = 1\text{atm}$

& $[A] = [B] = [C] \ldots = 1$ molar (to some limit)

but not $X_A^* = X_B^* = 1$

also $\mu_A^\circ \neq \mu_B^\circ$ in general

Chemical potentials for liquid mixtures

Liquid & vapor are in eq

$$\mu_i^{liq} = \mu_i^{gas} = \mu_i^\circ + RT \ln (P_i / p_i^\circ)$$

assuming gasses behave ideally

This p_i° is a property of the liquid

called the vapor pressure

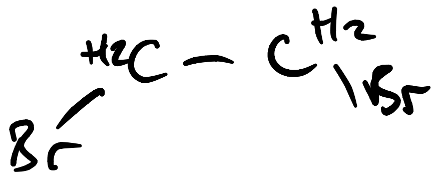
But how does this help us determine μ_i as a function of species concentrations?

Raoult's Law (ideal solution approximation)

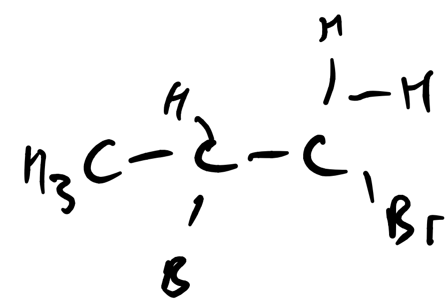
$$p_i = \chi_i p_i^*$$

This doesn't mean A & B don't interact, it means AA, AB, BB interactions all very similar

Eg:



Ethelene dibromide
(dibromo ethane)



propylyne dibromide