

Ideal Mixtures

$$\text{gas: } P_A + P_B = P$$

entropy of mixing

$$\Delta x_{\text{mix}} = 0 \quad \Delta U_{\text{mix}} = 0 \quad \Delta H_{\text{mix}} = 0$$

$$\Delta S_{\text{mix}} = \Delta S_A + \Delta S_B + \Delta S'$$

↓

$$\Delta S_{\text{mix}} = -R x_A \ln(P_A/P) - R x_B \ln(P_B/P) + 0$$

↓

$$\Delta S_{\text{mix}} = -R (x_A \ln x_A + x_B \ln x_B)$$

general: $\Delta S_{\text{mix}} = -R \sum_i n_i \ln x_i$

Non-Ideal Liquid Ad Soln Solutions

Partial Molar Properties

$$H = \sum_i n_i \bar{h}_i(T, n_i)$$

$$dH = \sum_i \left(\frac{\partial H}{\partial n_i} \right)_{T, P, n_j} dn_i$$

$$\Rightarrow dH = \sum_i \bar{h}_i dn_i$$

change in enthalpy of solution with change in n_i

$$dH = \sum_i n_i d\bar{h}_i + \sum_i \bar{h}_i dn_i \Rightarrow \sum_i (n_i d\bar{h}_i) = 0$$

Binary: $h = x_A \bar{h}_A + x_B \bar{h}_B \Rightarrow x_A d\bar{h}_A + x_B d\bar{h}_B = 0$

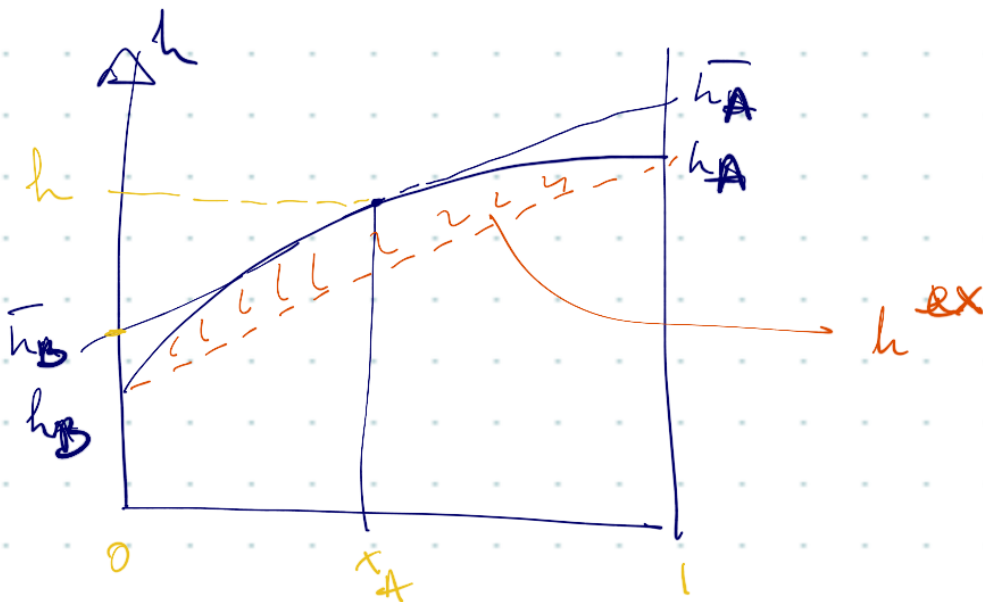
$$dh = \bar{h}_A dx_A + \bar{h}_B dx_B$$

$$x_A dh_A + x_B d\bar{h}_B = 0 \Rightarrow$$

$$\bar{h}_B - h_B = - \int_0^{x_A} \frac{x_A}{1-x_A} \frac{d\bar{h}_A}{dx_A} dx_A$$

\Downarrow

if $\bar{h}_A(x_A, T)$ is known $\Rightarrow \bar{h}_B(x_B)$ is known



$$h = \bar{h}_A x_A + \bar{h}_B x_B \quad \Leftrightarrow$$

$$dh = \bar{h}_A dx_A + \bar{h}_B dx_B$$

$$\bar{h}_A = h + x_B \frac{dh}{dx_A}$$

$$\bar{h}_B = h + x_A \frac{dh}{dx_B}$$

partial molar properties (\bar{h}_A, \bar{h}_B)
can't be measured directly \Rightarrow
this relationship is important.

Excess properties

$$h = x_A h_A + x_B h_B + \underbrace{h^{ex}}_{\text{solution nonideality}}$$

$$\Rightarrow h^{ex} = x_A (\bar{h}_A - h_A) + x_B (\bar{h}_B - h_B)$$

$$x_A d\bar{h}_A + x_B d\bar{h}_B = 0 \Rightarrow$$

$$\bar{h}_A - h = (1 - x_A)^2 \frac{d}{dx_A} \left(\frac{h^{ex}}{1 - x_A} \right)$$

important, because experimentally we can measure h^{ex} and h , but not \bar{h}_A .

Chemical Potential = Partial Molar free energy, \bar{g}_i
 μ_i

$$dG = \sum \left(\frac{\partial G}{\partial n_i} \right)_{T, P, n_j} dn_i$$

$$\mu_i \equiv \bar{g}_i = \left(\frac{\partial G}{\partial n_i} \right)_{T, P, n_j}$$

$$g = \sum_i x_i \mu_i$$

$$dg = \sum \mu_i dx_i$$

$$\sum x_i d\mu_i = 0$$

Gibbs-Duhem Eqn.

Activity

$$\mu_i \equiv g_i + RT \ln a_i$$

chosen
because
measurable:

$$a_i = \frac{P_{i, \text{in solution}}}{P_i, \text{pure substance}}$$

Activity Coefficient

$$\gamma \equiv a_i / x_i = \frac{P_{\text{soln}}}{P_i \cdot x_i}$$

pure substance: $\gamma = 1$

ideal solution: $\gamma = 1$

$$\gamma(T, x_i)$$

Raoult's law: dilute B in solvent A $\Rightarrow \gamma_A \rightarrow 1$

A-A interactions dominate

$$\lim_{x_B \rightarrow 0} \gamma_B = \gamma_B^H$$

Henry's law

A-B interactions dominate for B

↓ we can show that

$$\sum x_i d \ln \gamma_i = 0$$

$$x_A d \ln \gamma_A + x_B d \ln \gamma_B = 0$$

$$\ln \gamma_B = - \int_{\ln \gamma_{A0}}^{\ln \gamma_A} \frac{x_A}{x_B} d \ln \gamma_A$$

$$\Rightarrow \ln \gamma_B = - \int_0^{x_A} \frac{x_A'}{(1-x_A')} \frac{d \ln \gamma_A}{dx_A'} dx_A'$$

We can compute γ_B from γ_A

Excess Free Energy

ideal & nonideal sol'n

entropy of mixing

$$g = x_A g_A + x_B g_B + \underbrace{g^{ex}} + \underbrace{\Delta g_{mix}}$$

solution nonlinearity

$$g = h - Ts$$

$$\Delta g_{mix} = \cancel{\Delta h_{mix}} - T \Delta S_{mix} \Rightarrow \Delta g_{mix} = -T \Delta S_{mix}$$

$$\Delta S_{mix} = R \ln W_{mix}$$

W_{mix} = # different arrangements of atoms on the lattice.

we can show

$$\Delta S_{mix} = -R (x_A \ln x_A + x_B \ln x_B)$$

$$\rightarrow \boxed{g = x_A g_A + x_B g_B + g^{ex} + RT(x_A \ln x_A + x_B \ln x_B)}$$

(*)

Regular Solutions

$$g^{ex} = h^{ex} - T \Delta s^{ex} \rightarrow 0$$

no tendency for molecules to form CLUSTERS

→ "regular solution"

$$h^{ex} = \sum x_A x_B$$

interaction energy of the A-B pair

lim $x_A \rightarrow 0$

$h^{ex} = 0$
 $h \rightarrow h_B$

regular solutions preserve randomness of mixing

constituents of similar sizes & no H-bonding or "coordination" bonds

Activity Coefficients

$$\mu_A = g + x_B \frac{dg}{dx_A} \rightarrow RT \ln \gamma_A = h^{ex} + x_B \frac{h^{ex}}{dx_A}$$

$$\rightarrow \boxed{RT \ln \gamma_A = \sum x_B^2} \Rightarrow \ln \gamma_A = f\left(\frac{1}{T}\right)$$

Chemical Potentials in Gas Mixtures

Phase equilibrium: $\mu_i = g_i(p_i)$ $\textcircled{\ast}$

\uparrow in solution \uparrow in gas-phase pressure-dep.

Common pressure reference: $g_i^\circ(T, p=1 \text{ atm})$

$$\left. \left(\frac{dg_i}{dp_i} \right)_T = v_i \right\} \Rightarrow \frac{dg_i}{dp_i} = \frac{RT}{p_i}$$

ideal gas

$$\Rightarrow \int_{g_i^\circ}^{g_i} dg_i = \int_{1 \text{ atm}}^{p_i} \frac{RT}{p_i} dp_i \Rightarrow$$

$$\textcircled{\ast} \Rightarrow \mu_i = g_i^\circ + RT \ln p_i$$

standard state of the pure gas

measurement of pressure gives us chem. potential in the condensed phase, assuming ideal gases