Reminder:

Concentration of solute in solution can be characterized by vapor pressure, the pressure where $\mu^{gas} = \mu^{liq}$,

Assuming ideal gas

$$\mu_\alpha^{liq} = \mu^\circ_\alpha + RT \ln\left(P_\alpha^{vap} / P_\alpha^\circ\right)$$

where P^α_{vap} is the partial pressure of molecule α, where P_α° is the reference pressure, usually 1atm

Raoult's law says that we can guess (true in close to $X_\alpha = 1$ limit)

$$P_\alpha^{vap} = P_\alpha^* X_\alpha$$

, where P_α^* is the vapor pressure of the pure component

Plugging in to the above

For Raoult's Law:

$$\mu_i^{liq} = \mu_i^{gas} = \mu_i^{\circ} + RT\ln\left(\frac{p_i^* x_i}{p_i^{\circ}}\right)$$

$$= \underbrace{\mu_i^{\circ} + RT\ln\left(p_i^*/p_i^{\circ}\right)}_{\mu_i^*} + RT\ln(x_i)$$

New standard state for pure component i

$$\mu_i^{liq} = \mu_i^* + RT\ln(x_i)$$

switches from $p_i = 1$ standard state to $x_i = 1$ std state

Changing reference does not change the chemical potential though! One value for a particular mixture

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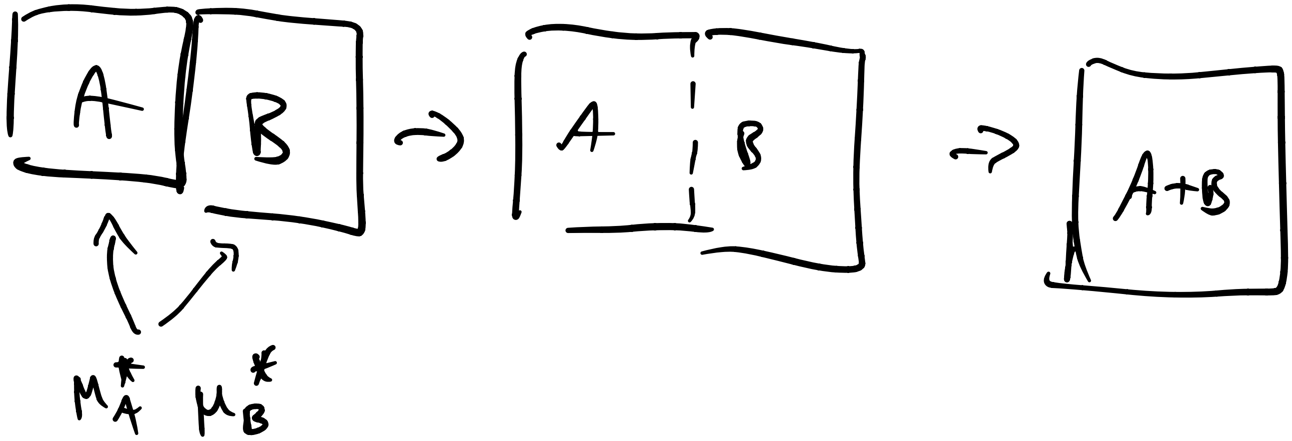
Does it mix? Gibbs free energy controls spontaneous reaction

$$\Delta G_{mix} = \Delta G_{mixed} - \Delta G_{unmixed}$$

$$= (n_A\mu_A + n_B\mu_B)_{mixed} - (n_A\mu_A + n_B\mu_B)_{unmix}$$



For ideal mixture

$$G_{mixed} = n_A(\mu_A^* + RT\ln X_A) + n_B(\mu_B^* + RT\ln X_B)$$

$$\Delta G_{mix} = n_A RT \ln X_A + n_B RT \ln X_B$$

$$\Rightarrow \Delta\bar{G}_{mix} = RT\left(X_A \ln X_A + X_B \ln X_B\right)$$

$$\Delta\bar{S}_{mix} = \left(-\partial\bar{G}/\partial T\right)_P = -R(\quad)$$

Entropy maximized at $X_A = X_B = 0.5$

Since $\Delta\bar{G} = \Delta\bar{H} - T\Delta\bar{S}$

and $\Delta\bar{G} = T\Delta\bar{S}$, $\Delta H_{mix}^{ideal} = 0$!

as expected

But what about non ideal mixtures?

Close to $\chi = 1$ and $\chi = 0$, should probably behave like an ideal mixture.

Imagine 0.001% EtOH in water, vapor pressure of H_2O will be very close to that for pure water, also for 99.999% vapor pressure of EtOH very close to pure EtOH

That is the Raoult's law limit for the solvent

$$p_i \approx p_i^* \chi_i \quad (\chi_i \approx 1)$$

For "solute", Henry's law:

$$p_i \approx K_i^H \chi_i$$

, solutes don't interact just the vapor pressure of isolated molecules

If both true "ideally dilute solutions"

In reality for this case, $K_i^H \gg p_i^*$

so water & ethanol better solvents for themselves than eachother

Chemical potential for ideally dilute solution is given by

$$\mu^{liq} = \mu_i^\bullet + RT\ln\left(\frac{k_i^H x_i}{p_i^\bullet}\right)$$

$$= \underbrace{\mu_i^\bullet + RT\ln\left(k_i^H/p_i^\bullet\right)}_{\mu_i^\otimes} + RT\ln(x_i)$$

$\mu_i^\otimes$ ← chemical pressure at infinite dilution $(x_i \to 0)$

Can get ΔG mixing from simple lattice model - will have read for HW!

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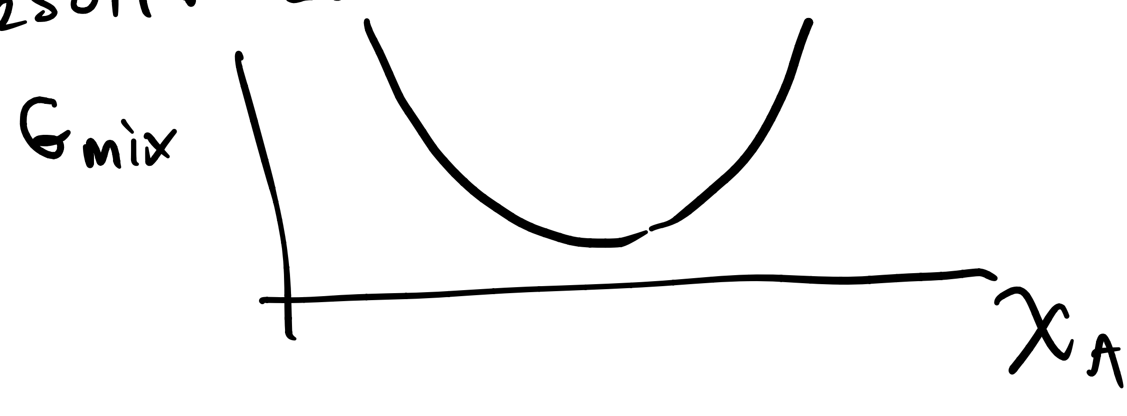
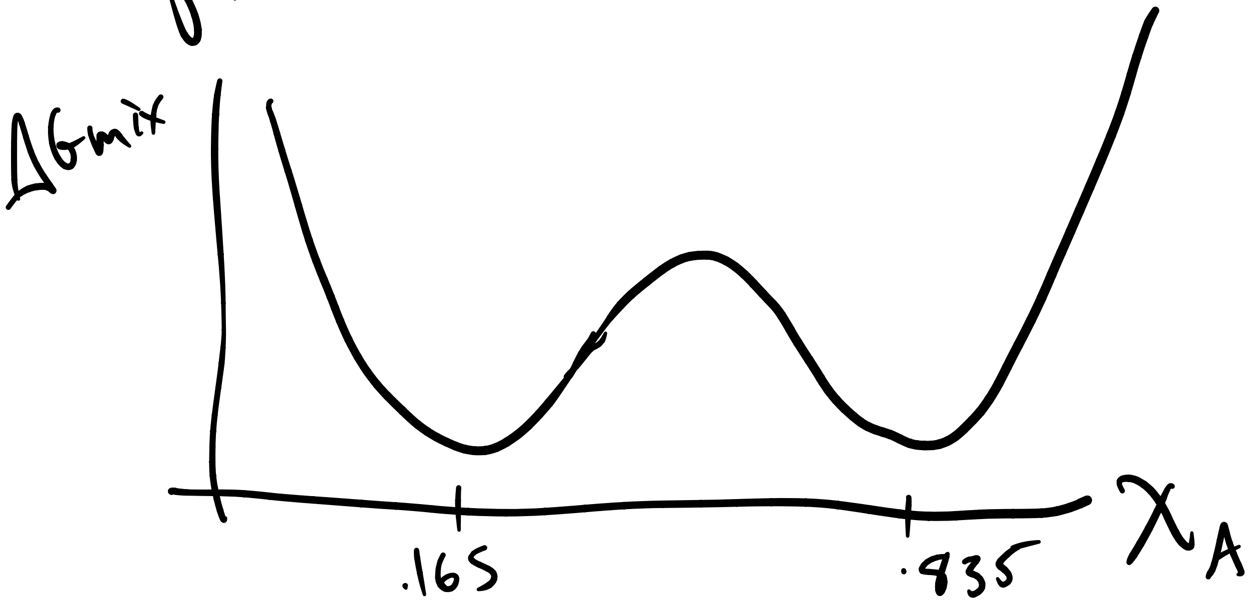
Result: Low interaction



High interaction:



If equal mixed - split into 2 parts, an A rich phase & a B rich phase

Can do a lot more w/ this model, but have to move on to Chemical Reactions

Since reactions are usually studied in molar not mole fraction, can switch reference again:

$$\chi_i = \frac{n_i}{n_T} \approx n_i / n_s \Rightarrow n_i \approx \chi_i n_s$$

and $V = \sum n_j \bar{V}_j \approx n_s \bar{V}_s^*$

so $[i] = n_i / V = \frac{\chi_i n_s}{n_s \bar{V}_s^*} = \frac{\chi_i}{\bar{V}_s^*}$

$\chi_i \approx \bar{V}_s^* [i]$

so $\mu_i^{liq} = \mu_i^{\chi} + RT \ln [\bar{V}_s^* [i]]$

dilute limit

$= \mu_i^* + RT \ln [\bar{V}_s^*] + RT \ln [i] / \text{1 molar}$

$= \underbrace{\mu_i^* - RT \ln [S]}_{\mu_i^\circ} + RT \ln [i]$

molarity solvent, ≈ 55.5 mol/liter

so $\mu_i^{liq} = \mu_i^\circ + RT \ln [i]$

Chemical Reactions

$$aA + bB \rightleftharpoons gG + hH$$

$$\sum \nu_i I = 0$$

species

reaction numbers $a, b, -g, -h$

This constraint means reaction can be described by a single progress variable, number of mols reacted "η"

$$\Delta G_{rxn} = \eta_{rxn}\left(-a\bar{G}_a - b\bar{G}_b + g\bar{G}_g + h\bar{G}_h\right)$$

etc $\Delta G_{rxn} = \eta_{rxn} \sum \nu_i \mu_i$

or $\Delta \bar{G}_{rxn} = \sum \nu_i \mu_i$

so subbing $\mu_i = \mu_i^\circ + RT \ln [i]$

$$\overline{\Delta G}_{rxn} = \sum \nu_i \mu_i^\circ + RT \ln \underbrace{\prod [i]^{\nu_i}}_{Q}$$

eg $Q = \dfrac{[G]^g [H]^h}{[A]^a [B]^b}$

and $\sum \nu_i \mu_i^\circ \equiv \underbrace{\overline{\Delta G}^\circ}_{\text{constant}}$ (all at std state)

@ Eq $\overline{\Delta G}_{rxn} = 0$

$$\Rightarrow \boxed{\overline{\Delta G}^\circ = -RT \ln K_{eq}}$$

Where K_{eq} is $\prod [i]_{eq}^{\nu_i}$

Since K_{eq} can be measured, gives some access to μ°

$G(n_1, \ldots, n_N)$

$$\Rightarrow \quad dG = \sum \underbrace{\left(\frac{\partial G}{\partial n_i}\right)}_{\mu_i} dn_i$$

$dn_i = \nu_i \, d\xi$ ← reaction coordinate

so $dG = \sum \mu_i \nu_i \, d\xi$

$$\Rightarrow \quad \left(\partial G / \partial \xi\right) = \sum \mu_i \nu_i = \overline{\Delta G}_{rxn}$$

shows G is a reaction potential, minimized at Eq

Dependence on temp

$$\Delta \bar{G}^\circ = \Delta \bar{H}^\circ - T \Delta S^\circ$$

so $-RT \ln K = \Delta H^\circ - T \Delta S^\circ$

$$\ln K = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT}$$

"Van't Hoff equation"

plot $\ln K$ vs $1/T$, intercept ΔS, slope $-\Delta H$ ⇐ deviation means T dependent

Dependence on Pressure

$$d\bar{G} = -\bar{S}\,dT + \bar{V}\,dp$$

@ const T

$$d\Delta\bar{G} = \Delta\bar{V}\,dp \quad \text{or}$$

$$\Delta\bar{V}^{\circ} = \left(\partial \Delta G^{\circ} / \partial p\right)_T$$ @ standard conditions

To first order (ΔV° constant)

$$\Delta G^{\circ}(p) = \Delta G^{\circ}(p^{ref}) + (p - p^{ref})\,\Delta\bar{V}^{\circ}$$

if $\Delta V^{\circ} > 0$ (product have larger volume)

then increasing pressure increases ΔG° (bad) so pushes back towards reactants (Le Chatelier)