Reminder:
Concentration of solute in solution can be characterized by vapor pressure, the pressure where \( \mu_X = \mu_{X^*} \).

Assuming ideal gas
\[
\mu_{X^*} = \mu_X + RT \ln \left( \frac{P_X}{P_*} \right)
\]
where \( P_X \) is the partial pressure of molecule \( X \), where \( P_* \) is the reference pressure, usually 1 atm.

Raoult's law says that we can guess (true in close to \( X^* = 1 \) limit)
\[
P_X = P_{X^*} X^* \]
where \( P_{X^*} \) is the vapor pressure of the pure component

Plugging in to the above
For Raoult's Law:

\[ \mu_{i}^{\text{liq}} = \mu_{i}^{\text{gas}} = \mu_{i}^{\ast} + RT \ln \left( \frac{P_{i}^{\ast} X_{i}}{P_{i}} \right) \]

\[ = \mu_{i}^{\ast} + RT \ln \left( \frac{P_{i}^{\ast}}{P_{i}} \right) + RT \ln (X_{i}) \]

New standard state for pure component:

\[ \mu_{i}^{\text{liq}} = \mu_{i}^{\ast} + RT \ln (X_{i}) \]

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

\[ \Delta G_{\text{mix}} = \Delta G_{\text{mixed}} - \Delta G_{\text{unmixed}} \]

\[ = (n_{A} \mu_{A} + n_{B} \mu_{B})_{\text{mixed}} - (n_{A} \mu_{A} + n_{B} \mu_{B})_{\text{unmixed}} \]
For ideal mixture

\[ G_{\text{mix}} = n_A (M_A^* + RT \ln X_A) + n_B (M_B^* + RT \ln X_B) \]

\[ \Delta G_{\text{mix}} = n_A RT \ln X_A + n_B RT \ln X_B \]

\[ \Rightarrow \Delta G_{\text{mix}} = RT \left( X_A \ln X_A + X_B \ln X_B \right) \]

\[ \Delta S_{\text{mix}} = \left( -\frac{\Delta G}{\partial T} \right)_P = -RT \]

Entropy maximized at \( X_A = X_B = 0.5 \)

Since \( \Delta G = \Delta H - T \Delta S \)

and \( \Delta S = \Delta H / \Delta T \), \( \Delta H_{\text{mix}} \) ideal \( = 0 \)!

as expected
But what about non-ideal mixtures?

Close to \( x=1 \) and \( x=0 \), should probably behave like an ideal mixture.

Imagine 0.001\% EtOH in water, vapor pressure of EtOH 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

\[ p_i \approx p_i^f x_i \quad (x_i \approx 1) \]

For “solute”, Henry’s law:

\[ p_i \approx k_i^H x_i \quad \text{solute don’t interact just the vapor pressure of isolated molecules} \]

If both true “ideally dilute solutions”

In reality for this case, \( k_i^H \gg p_i^f \)

so water & ethanol better solvents for themselves than each other.
Chemical potential for ideally dilute solution is given by

$$\mu^{\text{ii}} = \mu^i + RT \ln \left( \frac{K_i}{P_i} \right)$$

$$= \mu_i + RT \ln \left( \frac{K_i^H}{P_i} \right) + RT \ln (X_i)$$

$$\mu_i \propto \text{chemical pressure at infinite dilution} \quad (X_i \to 0)$$

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

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Result: Low interaction

$G_{\text{mix}}$ vs $X_A$
High interaction:

$$\Delta \text{mix}$$

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:
\[ \chi_i = \frac{n_i}{n_T} \sim \frac{n_i}{n_s} \Rightarrow n_i \approx \chi_i n_s \]

and \[ V = \sum n_j \bar{V}_j \sim n_s \bar{V}_s \]

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

so \[ \mu_i^{\text{liq}} = \mu_i^0 + RT \ln \left( \frac{\bar{V}_s^*}{[i]} \right) \]

\[ \text{in dilute limit} \]

\[ = \mu_i^* + RT \ln \left( \frac{\bar{V}_s^*}{[i]} \right) + RT \ln [i] \]

\[ = \mu_i^* - RT \ln [55.5] + RT \ln [i] \]

\[ \mu_i^0 \quad \text{molarity solvent, } \]

so \[ \mu_i^{\text{liq}} = \mu_i^0 + RT \ln [i] \]
Chemical Reactions

\[ aA + bB \rightarrow gG + hH \]

\[ \Sigma v_i I = 0 \]

\[ \text{species} \]

\[ \text{reaction numbers} \quad a, b, g, h \]

This constraint means reaction can be described by a single progress variable, number of mols reacted "\( \gamma \)"

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

etc \[ \Delta G_{rxn} = \gamma \sum \bar{G}_i \gamma_i \mu_i \]

or \[ \Delta G_{rxn} = \sum \gamma_i \mu_i \]
so subbing \( \mu_i = \mu_i^0 + RT \ln \Pi \)

\[ \Delta G_{\text{rxn}} = \sum v_i \mu_i^0 + RT \ln \Pi [i] \]

eq \( Q = \frac{[C6] [CH3]_v}{[CA] [B]_v} \)

and \( \Sigma v_i \mu_i^0 = \overline{\Delta G} \) \( \text{ (all at std state) constant} \)

\[ \text{Eq } \Delta G_{\text{rxn}} = 0 \]

\[ \overline{\Delta G} = -RT \ln K_{\text{eq}} \]

where \( K_{\text{eq}} \) is \( \Pi [i] \) \( \text{eq} \)

Since \( K_{\text{eq}} \) can be measured, gives some access to \( \mu_i^0 \).
\[ G(n_1, \ldots, n_m) \]
\[ \Rightarrow \quad \Delta G = \sum \left( \frac{\partial G}{\partial n_i} \right) \mu_i \]
\[ \mu_i = n_i \rho_{di} \]
\[ \text{reaction coordinate} \]

so \( \Delta G = \sum \mu_i \rho_{di} \)

\[ \Rightarrow \quad (\Delta G/n_e) = \sum \mu_i n_i = \Delta G_{\text{rxn}} \]

\[ \text{shows } G \text{ is a reaction potential, minimized at Eq} \]

Dependence on Temp

\[ \Delta G^\circ = \Delta H^\circ - T \Delta S^\circ \]

so \( -RT \ln k = \Delta H^\circ - T \Delta S^\circ \)

\[ \ln k = \frac{\Delta S^\circ}{R} - \frac{\Delta H^0}{RT} \]

"Van't Hoff equation"

plot \( \ln k \) vs \( \frac{1}{T} \), intercept \(-\Delta S\)
slope \(-\Delta H\) \( \text{deviation from } \text{ men's } T \text{ dependent} \)
Dependence on Pressure

\[ d \bar{G} = -SdT + \bar{V}dp \]

@ constant \( T \)

\[ d \Delta \bar{G} = \Delta \bar{V}dp \] or

\[ \Delta \bar{V}^0 = \left( \frac{\partial \Delta \bar{G}^0}{\partial p} \right)_T \] @ standard conditions

To first order (\( \Delta V^0 \) constant)

\[ \Delta \bar{G}^0(p) = \Delta \bar{G}^0(p^\text{ref}) + (p - p^\text{ref}) \Delta \bar{V}^0 \]

if \( \Delta V^0 > 0 \) (product has larger volume)

then increasing pressure increases \( \Delta \bar{G}^0 \) (bad) so pushes back towards reactants (Le Chatelier)