Reminder

$$\mathcal{E}(N,V,S) \xrightarrow{-TS} A(N,V,T)$$

$$\downarrow +pV \qquad\qquad \downarrow +pV$$

$$H(N,P,S) \xrightarrow{-TS} G(N,P,T)$$

These come from Legendre transforms, like

$$A(N,V,T) = \mathcal{E}(N,V,S) - S\left(\frac{\partial \mathcal{E}}{\partial S}\right)_{N,V}$$

$\nearrow$ want to get rid of S $\qquad \overset{\curvearrowleft}{T}$

Why $+pV$ for example,

@const N $\quad d\mathcal{E} = \left(\frac{\partial \mathcal{E}}{\partial V}\right)_S dV + \left(\frac{\partial \mathcal{E}}{\partial S}\right)_V dS$

but first law $\quad d\mathcal{E} = -pdV + dq = Tds$

So $\quad H(N,P,S) = \mathcal{E} - V\left(\frac{\partial \mathcal{E}}{\partial V}\right)_{S,N} = \underline{\mathcal{E} + PV}$

- Now that we know what variables Thermodynamic potentials depend on, we can derive relations between derivatives

$$G(p,T) \Rightarrow dG = \left(\frac{\partial G}{\partial p}\right)_T dp + \left(\frac{\partial G}{\partial T}\right)_p dT$$

But also know $G = \varepsilon - TS + pV$

$$\Rightarrow dG = d\varepsilon - TdS - \underline{SdT} + pdV + \underline{VdP}$$

$$= (d\varepsilon - TdS + pdV) - SdT + VdP$$

But $d\varepsilon - TdS - pdV$

$$\Rightarrow dG = -SdT + VdP$$

So $\left(\frac{\partial G}{\partial T}\right)_p = -S$ ✓

$$\left(\frac{\partial G}{\partial p}\right)_T = V$$

This is how entropy measured in experiment

Can be used to measure volume changes in reactions

Table S.1: these kinds of relationships
are useful property $\left(\frac{\partial x}{\partial y}\right)_z = 1 / \left(\frac{\partial y}{\partial x}\right)_z$

Return to $T = \left(\frac{\partial \varepsilon}{\partial S}\right)_v$

$\Rightarrow \left(\frac{\partial S}{\partial \varepsilon}\right)_v = 1/T$ amount entropy changes from

increase in ε is related to $1/T$

• Maxwell relations

Cross derivatives give surprising relationships between variables

$dG = \left(\frac{\partial G}{\partial P}\right)_T dP + \left(\frac{\partial G}{\partial T}\right)_P dT$, exact differential
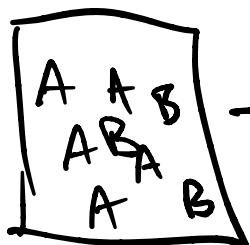
$= U dp - S dT$

so $-\left(\frac{\partial S}{\partial P}\right)_T = \left(\frac{\partial V}{\partial T}\right)_P$ ⟵ easy to measure

⟲ hard to measure

Mixtures of multiple species

So far we have not really discussed
mixtures of species

$$\boxed{\begin{array}{l} A \; A \; B \\ A \; B \; A \\ A \quad B \end{array}} \longrightarrow$$
may have $N_A + N_B = N$ molecules

or n_A, n_B moles of $A \& B$

fraction of A is $\quad \chi_A = \dfrac{n_A}{n_A + n_B} \qquad \chi_B = \dfrac{n_B}{n_A + n_B}$

st $\quad \chi_A + \chi_B = 1$

Molar quantities, divide out by number of
moles so eg

$\bar{\mathcal{E}} = \mathcal{E}/n \quad$ if one component. Can also
define terms like $\mathcal{E}_A$ st $\mathcal{E} = \mathcal{E}_A + \mathcal{E}_B$
then $\quad \bar{\mathcal{E}} = \chi_A \bar{\mathcal{E}}_A + \chi_B \bar{\mathcal{E}}_B \qquad$ and $\bar{\mathcal{E}}_A = \mathcal{E}_A / n_A$

Now - interesting to note that quantities
like $\bar{\mathcal{E}}_A$ depend on χ_A since $A-A, A-B$
and $B-B$ interactions can differ

Example of molar volumes

Let $\bar{V}_A = V_A/n_A$ for a system
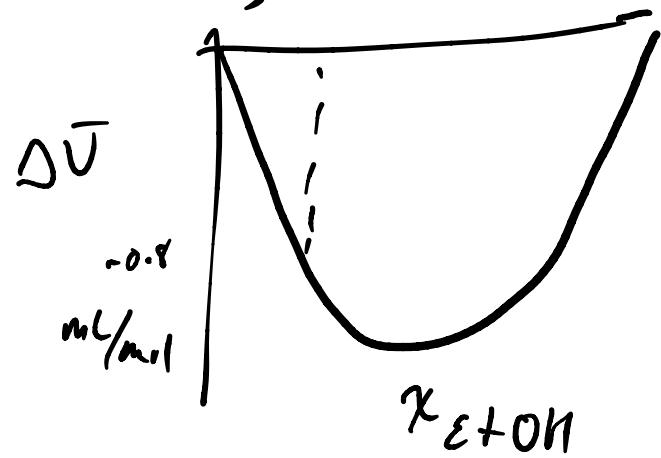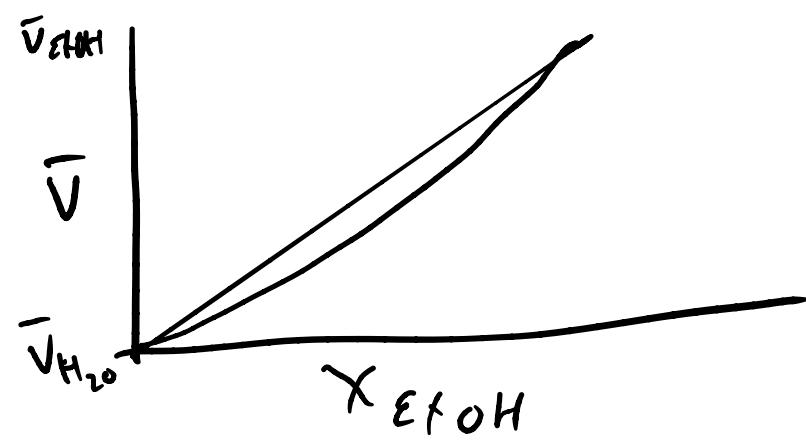
and $\bar{V}_A^*$ be the volume of A per mole
in a solution with only A $(X_A = 1)$

Then for a mixture $\bar{V}_{ideal} = X_A \bar{V}_A^* + X_B \bar{V}_B^*$
what happens when you add EtOH & water?

$V_{H_2O}^* \approx 18\,mL/mol$ $V_{EtOH}^* \approx 57\frac{mL}{mol}$ ($\begin{smallmatrix}1\,atm\\room\,temp\end{smallmatrix}$)

Add $50\,mL + 50\,mL$ get $97\,mL$, non-ideal!

$n_A = \frac{50}{18} = 2.8$ $n_B = \frac{50}{57} = 0.88$

$X_{EtOH} = 0.24$, $\Delta\bar{V} \approx -0.8\,mL/mol$
                       $\Delta V\,tot \approx -2.9$

Since $V(n_A, n_B) \Rightarrow dV = \left(\frac{\partial V}{\partial n_A}\right)dn_A + \left(\frac{\partial V}{\partial n_B}\right)dn_B$

$\curvearrowright \bar{V}_A \longleftrightarrow \curvearrowright \bar{V}_B$
depends on state

To get volume, integrate along a path of fixed composition...

That was molar volumes, go back to
Energies / Free Energies

Define $\overline{G}_A = G_A/n_A = \mu_A$ st $G = \sum_{i=1}^{n_{species}} \mu_i n_i$

But also, $\overline{G}_i = \mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{T,P,n_j \neq i}$

2 potentially conflicting results

① $G(P,T,n_1,n_2,..) \Rightarrow dG = \left(\frac{\partial G}{\partial P}\right)dP + \left(\frac{\partial G}{\partial T}\right)dT$

$$+ \left(\frac{\partial G}{\partial n_1}\right)dn_1 + \left(\frac{\partial G}{\partial n_2}\right)dn_2 +...$$

$= -SdT + VdP + \sum_i \mu_i dn_i$

② $G = \sum \mu_i n_i \Rightarrow dG = \sum_i (\mu_i dn_i + n_i d\mu_i)$

Comparing, this means $\sum n_i d\mu_i = -SdT + VdP$

or $\boxed{SdT - VdP + \sum_i n_i d\mu_i = 0}$

[Gibbs - Duhem Relationship]

Chemical potentials not independent

For $dT=0$ $dp=0$, condition is $\sum n_i d\mu_i = 0$

or divide by $\sum n_i \Rightarrow \sum_i x_i d\mu_i = 0$

$x_A d\mu_A + x_B d\mu_B = 0$ for 2 species

$\quad\quad\quad \overset{\frown}{} (1-x_A)$

$\Rightarrow d\mu_B = -x_A/(1-x_A) d\mu_A < 0$ if $d\mu_A > 0$

Maxwell Relations including composition

$$dG = -S \, dT + V \, dp + \mu_1 \, dn_1 + \mu_2 \, dn_2$$

$$\Rightarrow -\left(\frac{\partial S}{\partial n_1}\right)_{P, n_2, T} = \left(\frac{\partial \mu_1}{\partial T}\right)_{P, n_1, n_2}$$

etc

Partial Pressures

$$p_i \equiv x_i P_{total} \qquad \text{b/c already intensive, just define this way}$$

$$\sum p_i = \sum x_i P_{total} = P_{total} \sum x_i = P_{total}$$

For ideal gas $\qquad p_i = n_i RT / V \quad$ b/c non interacting

$$P_T = \frac{RT}{V} \sum n_i \qquad \text{(Dalton's law)}$$

For non-ideal: repulsion / excluded volume increases pressure
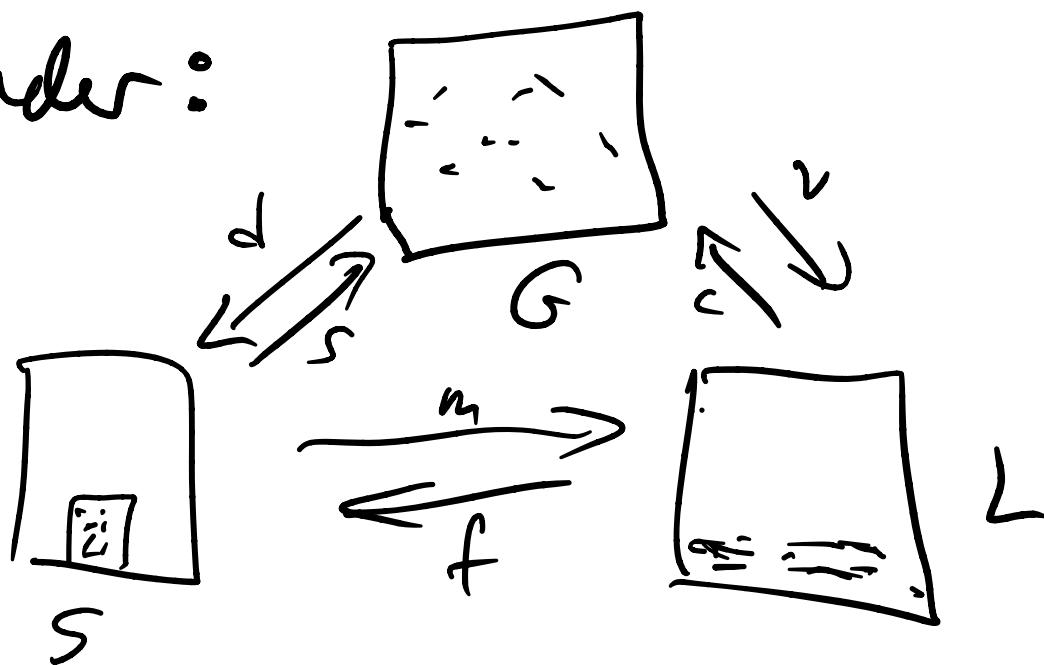
$\qquad$: attraction decreases pressure

Ch 6: chemical potentials & phase transitions

Phases of matter — solid, liquid, gas are simple examples. Each differs in bulk properties

Density, compressibility, heat capacity etc

Reminder:

Other phase types:

Carbon: diamond, graphite, C60

★ kinetics can be very slow, eg this case

Not eq phase: supercooled liquid/glass

diff materials properties, no discontinuities

"Metastable"