Reminder

\[ \chi(N, u, s) \xrightarrow{-T} A(N, u, T) \]

\[ +pV \]

\[ H(N, p, s) \xrightarrow{-T} G(N, p, T) \]

These come from Legendre transforms, like

\[ A(N, u, T) = \chi(N, u, s) - S \left( \frac{\partial \chi}{\partial s} \right)_{N, u} \]

Why +pV for example,

@ const N \[ d\chi = p \left( \frac{\partial \chi}{\partial y} \right)_s dy + \left( \frac{\partial \chi}{\partial y} \right)_V dV \]

but first law \[ d\chi = -pdV + d\theta = Tds \]

So \[ H(N, p, s) = \chi - V \left( \frac{\partial \chi}{\partial V} \right)_{s, n} = \chi + pV \]
Now that we know what variables thermodynamic potentials depend on, we can derive relations between derivatives

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

But also know \( G = E - TS + PV \)

\[ \Rightarrow dG = dE - TS - TSdT + pdV + VdP \]

\[ = (dE - TSdS + pdV) - SDT + VdP \]

\[ \Rightarrow dG = -SDT + VdP \]

So \( \frac{\partial G}{\partial T} \bigg|_p = -S \)

\( \frac{\partial G}{\partial p} \bigg|_T = V \)

This is how entropy measured in experiment can be used to measure volume changes in reactions.
Table S.1: these kinds of relationships

one useful property \( \left( \frac{\partial x}{\partial y} \right)_z = \frac{1}{\left( \frac{\partial y}{\partial x} \right)_z} \)

Return to \( T = \left( \frac{\partial E}{\partial S} \right)_V \)

\( = \left( \frac{\partial S}{\partial E} \right)_V = \frac{1}{T} \) amount entropy changes from

increase in \( E \) is related to \( \frac{1}{T} \)

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

\( = \mu dP - TS dT \)

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

hard to measure
Mixtures of multiple species

So far we have not really discussed mixtures of species

\[
\begin{array}{ccc}
A & A & B \\
A & B & A \\
A & A & B
\end{array}
\]

may have \( NA + NB = N \) molecules

or \( n_A, n_B \) moles of A & B

fraction of A is \( \chi_A = \frac{n_A}{n_A + n_B} \), \( \chi_B = \frac{n_B}{n_A + n_B} \)

\( \chi_A + \chi_B = 1 \)

Molar quantities, divide out by number of moles so eg

\( \bar{E} = \frac{E}{n} \) if one component. Can also define terms like \( \bar{E}_A \) so \( \bar{E} = \bar{E}_A + \bar{E}_B \)

then \( \bar{E} = \chi_A \bar{E}_A + \chi_B \bar{E}_B \) and \( \bar{E}_A = \frac{E_A}{n_A} \)

Now interesting to note that quantities like \( \bar{E}_A \) depend on \( \chi_A \) since A-A, A-B and B-B interactions can differ
Example of molar volumes

Let $V_A = \frac{V_A}{n_A}$ 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 $\bar{V}_{\text{ideal}} = X_A \bar{V}_A^* + X_B \bar{V}_B^*$

What happens when you add EtOH & water?

$V_{H_2O}^* \approx 18 \text{ mL/mol}$

$V_{\text{EtOH}}^* \approx 57 \frac{\text{ mL}}{\text{ mol}}$  

(1 atm room temp)

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

\[ V_{\text{H}_2\text{O}} \]  \[ V_{\text{EtOH}} \]

\[ \bar{V} \]

$\Delta V$

\[\begin{align*}
\bar{V}_A &= \frac{50}{18} = 2.8 \\
\bar{V}_B &= \frac{50}{57} = 0.88 \\
x_{\text{EtOH}} &= 0.24, \quad \Delta V \approx -0.8 \text{ mL/mol} \\
\Delta V &= \approx -2.9
\end{align*}\]

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

$\Delta \bar{V}_A$ depends on $\bar{V}_B$

To get volume, integrate along a path of fixed composition...
That was molar volumes, go back to Energies / Free Energies

Define \( \overline{G}_A = G_A/n_A = nA \) so \( G = \sum_{i=1}^{\text{species}} \mu_i n_i \)

But also, \( \overline{G}_i = \mu_i = \left( \frac{\partial G}{\partial n_i} \right)_{T, p, n_A} \)

2 potentially conflicting results

(1) \( G(P, T, n_1, n_2, ...) \Rightarrow dG = \left( \frac{\partial G}{\partial P} \right) dP + \left( \frac{\partial G}{\partial T} \right) dT + \left( \frac{\partial G}{\partial n_i} \right) d\mu_i + \left( \frac{\partial G}{\partial n_A} \right) d\mu_A \\
= -SDT + UdP + \sum \mu_i d\mu_i \)

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

Comparing, this means \( \sum n_i d\mu_i = -SDT + UdP \)

or \( \sqrt{SDT - UdP + \sum n_i d\mu_i = 0} \)

[\text{Gibbs - Duhem Relationship}]

Chemical potentials not independent

For \( dT = 0 \) and \( dP = 0 \), condition is \( \sum n_i d\mu_i = 0 \)

or divide by \( \sum n_i \Rightarrow \sum x_i d\mu_i = 0 \)

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

\( \Rightarrow \left( 1 - x_A \right) \mu_B = -x_A \mu_A \) \( \Rightarrow d\mu_B = -x_A / \left( 1 - x_A \right) d\mu_A \leq 0 \) if \( d\mu_A > 0 \)
Maxwell Relations including composition
\[ d \varepsilon = -S \, dT + V \, dp + \mu_1 \, dn_1 + \mu_2 \, dn_2 \]
\[ \Rightarrow \left( \frac{\partial S}{\partial n_1} \right)_{p,n_2,T} = \left( \frac{\partial \mu_1}{\partial T} \right)_{p,n_1,n_2} \]

Partial Pressure
\[ p_i = X_i \, p_{total} \quad \text{b/c already intensive, just define this way} \]

\[ \sum p_i = \sum X_i \, p_{total} = p_{total} \sum X_i = p_{total} \]

For ideal gas \( p_i = n_i \, RT / N \) b/c non interacting

\[ p_T = \frac{RT}{V} \sum n_i \quad \text{(Dalton's law)} \]

For non-ideal: repulsion/excluded volume increases pressure

... at larger decreases pressure
Ch 6: chemical potentials & phase transitions

Phases of matters - 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, e.g., this case

Not eq. phase: supercooled liquid/glass
diff materials properties, no discontinuity

"Metastable"