

Midterm 2 Review

MT2.1

Here's an outline of our review session:

10 Key Concepts - Plus an explanation of the Thermodynamic Triangle

- ① Maxwell Relations
- ② Chemical potential, activity, fugacity, Affinity
- ③ ΔG_{mix} (and how it affects ΔG_{rxn})
- ④ G vs. ξ graphs, minimization, Laplace equation
- ⑤ Equilibrium constants and Le Chatelier's principle
- ⑥ Calculating final concentrations from K_{eq}
- ⑦ μ vs. T graphs for solid, liq. + gas, order of transition
- ⑧ Phase diagrams, phase changes
- ⑨ Distillation and azeotropes
- ⑩ α and κ

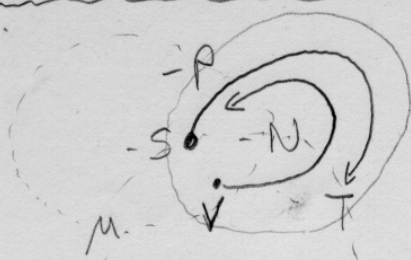
10 Key Derivations - Plus the ones from last test

- ① Gibbs-Helmholtz eq.
- ② $\Delta G_{rxn}^{\circ} = nRT \ln K^{\circ}$
- ③ $\Delta G_{mix} = nRT \sum_i x_i \ln x_i$
- ④ $K^{\circ} = K_x \left(\frac{P_{TOT}}{P^{\circ}} \right)^{\Delta \nu} = K_c \left(\frac{C^{\circ} RT}{P^{\circ}} \right)^{\Delta \nu}$ and $\left(\frac{\partial \ln K_x}{\partial P} \right)_T = -\frac{\Delta \nu}{RT}$
- ⑤ Van't Hoff eq.
- ⑥ Clapeyron eq. and liq. or sol. integral form
- ⑦ Clausius-Clapeyron eq.
- ⑧ Gibbs phase rule
- ⑨ Maxwell construct
- ⑩ Lever rule

3 levels:

- memorize - fastest:
- obtain from octahedron/triangle - next fastest
- derive - slowest

Maxwell Relations. → how can we obtain them quickly?



← look at this circle.
if we start at S and
move clockwise we get:

$$\left(\frac{\partial S}{\partial P}\right)_T$$

which is related to what we get
when we start at V and go counter clockwise:

$$\left(\frac{\partial V}{\partial T}\right)_P$$

but since the first two variables in each
expression are of different types (extensive vs intensive)
we need a negative sign: *

$$\left(\frac{\partial S}{\partial P}\right)_T = - \left(\frac{\partial V}{\partial T}\right)_P$$

Using the same circle we can get lots of relations:

$$\left(\frac{\partial P}{\partial T}\right)_V = \left(\frac{\partial S}{\partial V}\right)_T, \left(\frac{\partial T}{\partial V}\right)_S = - \left(\frac{\partial P}{\partial S}\right)_V, \left(\frac{\partial V}{\partial S}\right)_P = \left(\frac{\partial T}{\partial P}\right)_S$$

And there are 2 other circles, so 12 relations total.

The most useful 2 are: $\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$ and
since they tell us how entropy changes.

(*another way to get the negative sign is to just
use the negative signs on P, S + N as a guide;
if the negative signs cancel, the Maxwell relation
won't have a negative sign)

Chemical potential, activity, fugacity, affinity MT2.3

When a system is open (or changing composition) we need to consider energy entering and exiting as matter, in addition to coming and going as heat or work.

Just like heat and work are borrowing + lending energies built from an intensive force (P or T) and an extensive flow (V or S), borrowing or lending matter or chemical energy has a force, μ_i , and a flow, N_i .

So we have $U = TS - PV + \sum \mu_i N_i$ and $dU = TdS - PdV + \sum \mu_i dN_i$

Just as pressure causes volume changes, μ , the chemical potential, causes chemical changes: the number of moles of substance i (N_i) to change.

Affinity helps us know how substances will change. By adding the chemical potentials of each substance in a reaction like so:

$$A \equiv \mu_1 + \mu_2 - 2\mu_3 \quad (\text{for the reaction } 1 + 2 \rightleftharpoons 3)$$

We obtain the affinity. If it is positive the reaction goes right.

$\Delta G_{\text{rxn}} = -A$, but affinity is more able to do non-equilibrium things.

Chemical potential depends on pressure: $\mu_i(P_2) = \mu_i(P_1) + \int_{P_1}^{P_2} \bar{V} dP$

For an ideal gas the integral yields: $RT \ln\left(\frac{P_2}{P_1}\right)$

but for real gases we use the activity instead of pressure:

$$\mu_i(P_2) = \mu_i(P_1) + RT \ln a_i \quad \text{when } P_1 = P^\circ = 1 \text{ bar}$$

Real chemical potentials differ from ideal gas chemical potentials by a factor, $RT \ln\left(\frac{f}{P}\right)$, where f is the fugacity:

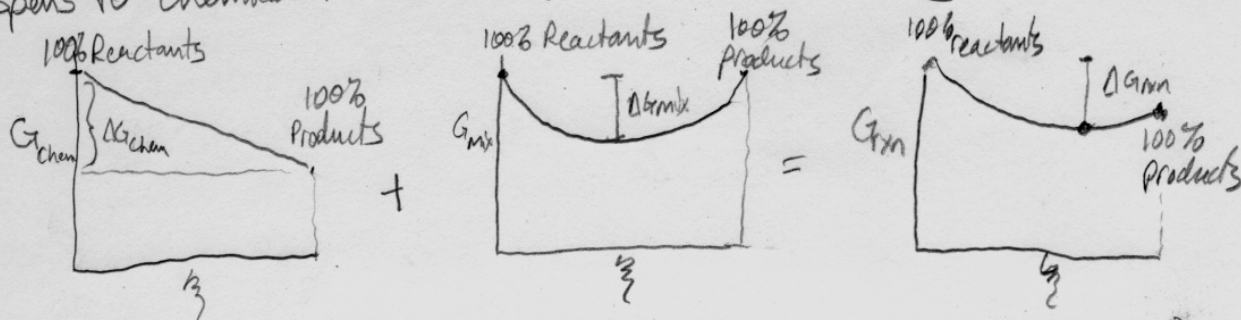
$$\mu_{\text{real}}(P) = \mu_{\text{ideal}}(P) + RT \ln\left(\frac{f}{P}\right)$$

ΔG_{mix} and ΔG_{rxn} , G vs ξ graphs, etc

MT2.4

ΔG_{mix} is related to ΔS_{mix} : $\Delta G_{mix} = T\Delta S_{mix}$

We've already derived ΔS_{mix} , so this is to remind us what happens to chemical reactions when there is mixing:



These graphs illustrate how G is minimized vs ξ (ΔG too!).
If the "reaction" occurs at constant volume ΔF is minimized vs ξ .

For example a drop of water keeps the same volume in its "reaction" to become spherical* (not a chemical reaction, per se)

Also a column of water rising up a capillary keep the same volume in its "reaction" to go higher, here ξ is h and:

$$\left(\frac{\partial(\Delta F)}{\partial h}\right)_{V,T} = 0$$

$$\text{Since } \Delta F = \underbrace{\frac{1}{2}\pi g g r^2 h^2}_{\text{weight } \downarrow} - \underbrace{2\pi r h \gamma \cos\theta}_{\text{capillary force } \uparrow}$$

$$\left(\frac{\partial \Delta F}{\partial h}\right)_{V,T} = \pi g g r^2 h - 2\pi r \gamma \cos\theta$$

$$\text{or } h = 2\gamma \cos\theta / g r$$

(* the equation relating the pressure difference inside + outside the drop is the Laplace equation: $\Delta p = \frac{2\gamma}{r}$)

Equilibrium constants

MT2.5

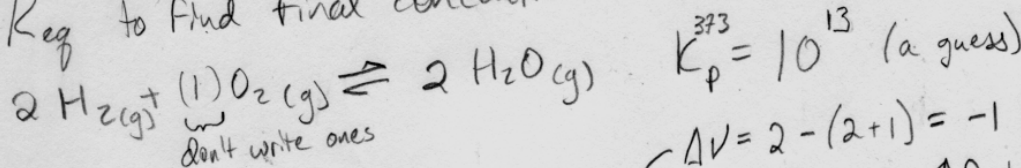
There are 3 equilibrium constants K^0 , K_x and K_c (generally "K_{eq}")
 (K_p) K^0 is the one that works in $\Delta G_{rxn}^0 = -RT \ln K^0$ and is pressure-based

$$K_x = K^0 \left(\frac{P_{TOT}}{P^0} \right)^{-\Delta V} \quad \text{where } \Delta V = \sum (\text{product coeff.}) - (\text{reactant coeff.})$$

$$K_c = K^0 \left(\frac{C^0 RT}{P^0} \right)^{-\Delta V} \quad \text{where } C^0 = \frac{N}{V} \text{ at standard conditions}$$

$$\Delta G_{rxn}^0 = -RT \ln K_c \text{ if no gases are involved or if } \Delta V = 0$$

To use K_{eq} to find final concentrations start with chemical equation:



Starting pressures:

0.01 bar, 0.1 bar

0.001 bar

$\Delta V = 2 - (2+1) = -1$
 Le Chatelier says $\uparrow P$ shifts K_{eq} $\uparrow$
 based on H₂, the limiting reagent

during reaction:

0.01(1-ξ) $\frac{0.1(\xi)}{2} + 0.1$ 0.01(ξ) + 0.001

$$K_p = \frac{(0.01\xi + 0.001)^2}{(0.01 - 0.01\xi)^2 (0.1 - 0.1\xi)} = 10^{10} \approx \frac{(0.01)^2 \xi^2}{[(0.01)^2 - 2(0.01)^2 \xi + \xi^2] (0.1 - 0.1\xi)}$$

$$10^{-13} = \frac{0.1}{\xi^2} - \frac{0.1}{\xi} - \frac{0.2}{\xi} + 0.2 + \frac{0.1}{(0.01)^2} - \frac{0.1}{(0.01)^2} \xi$$

$$= 0.1x^2 - 0.3x + 1000.2 - 1000 \frac{1}{x} \quad x \approx 1 \text{ so last term dominates}$$

$$\xi \approx 1 - 10^{-6} \quad \text{plugging back in:}$$

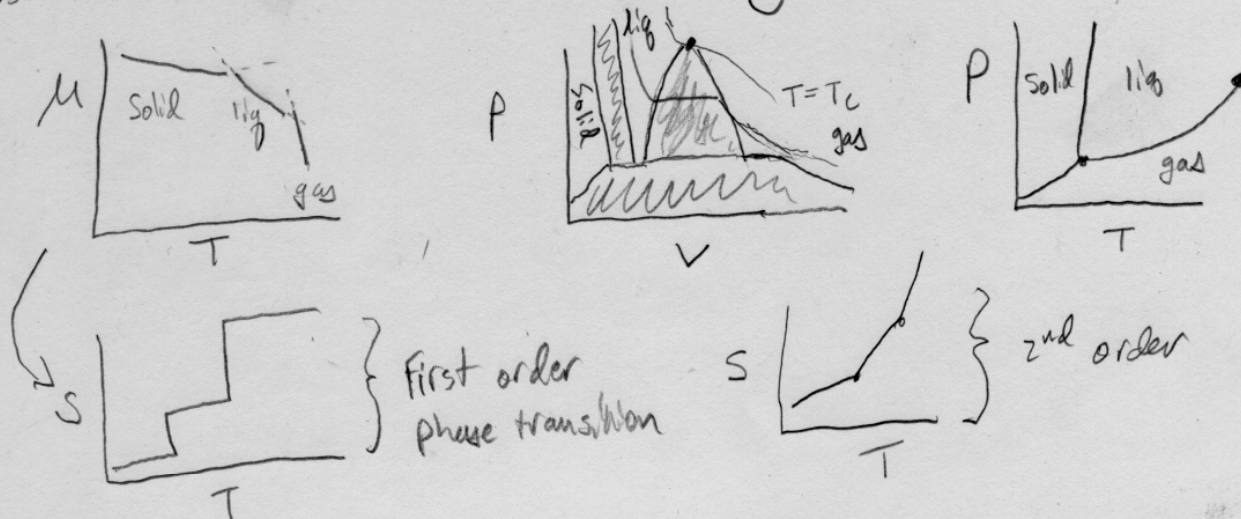
$$\text{H}_2 = 10^{-8} \text{ bar} \quad \text{O}_2 = 0.095 \text{ bar} \quad \text{H}_2\text{O} = 0.01 \text{ bar}$$

$$\text{Check } K_p = \frac{(10^{-8})^2 (0.095)}{(10^{-8})^2 (0.1)} \approx \frac{10^{+17}}{10^{+4}} = 10^{13} \checkmark$$

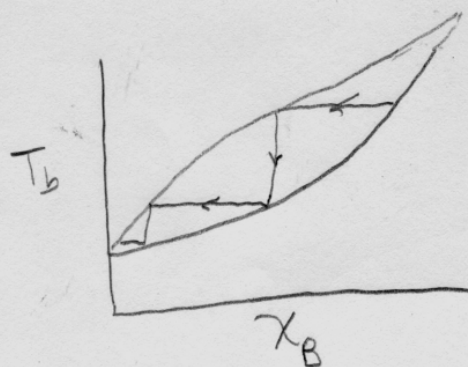
Phase changes

MT2.6

Most of this we've been over recently. The key graphs are!



For distillation:
(A is more volatile)



α and κ_T : Coeff. of thermal (or volume) expansion
and " of isothermal compressibility

$$\alpha \equiv \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P$$

$$\kappa_T \equiv -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T$$

these derivatives show up in lots of places so they get special names + symbols.