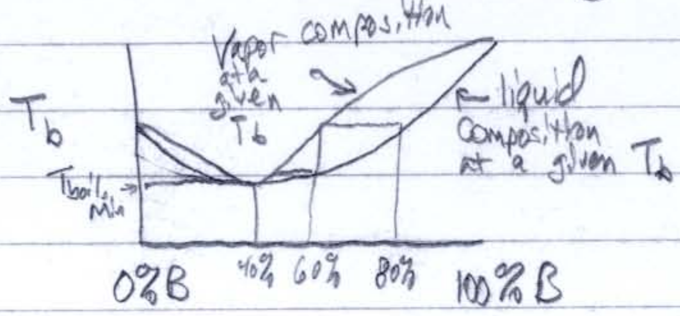
Azeotropes Revisited

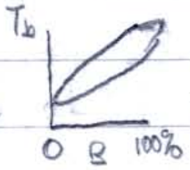
What does it mean that you get "stuck"?
eg at 40% B

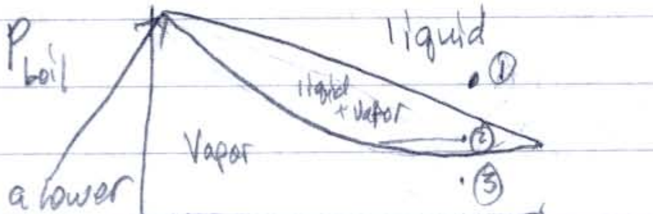


It means that at $T_{boil, min}$ the percent of B in the liquid phase equals the % B in the vapor.

So, you're "stuck", since boiling and condensing the vapor, reboiling, etc. doesn't change the % B

Lever Rule

another way to draw the  figure is:

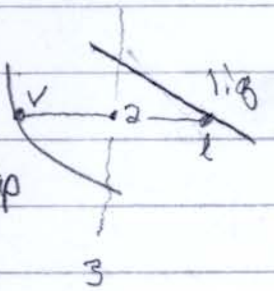


"A" has a lower boiling point, so at a given T it takes more P_{ex} to keep it just barely boiling

going from ① → ② → ③ we drop the pressure so that the 90% B, 10% A mixture will boil. If we stop at ② (before all the mixture is boiled) we see again how the vapor is enriched in A → the more volitile component

Lever Rule continued

We also see (zooming in abit): that ② is a little closer to the liquid side than the vapor side.



Can we find a rule that tells us how much is in either phase? Yes! The Lever Rule

Basically, the closer you are to the liquid side the more liquid phase there will be, but the shorter the 2-l line will be relative to v-2 line.

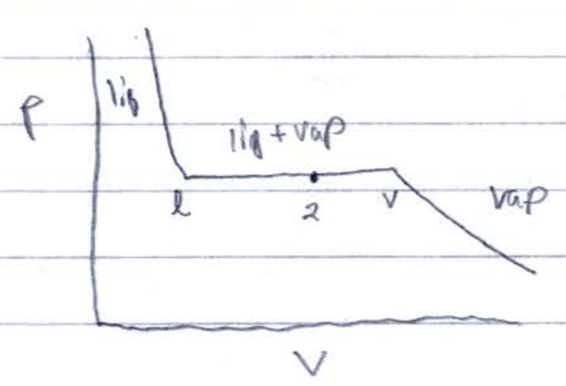
Someone thought this was like a teeter-totter, or a lever, where the shorter the distance to the Fulcrum the more force it takes to balance the force on the other side:

like distance to Fulcrum

$$X_{vap}\,(\text{v-2 dist.}) = X_{liq}\,(\text{2-l dist})$$

like force

this lever rule also works on a P-V diagram:

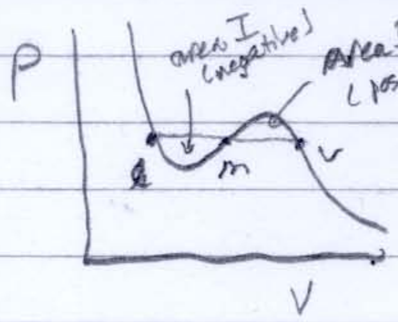


Maxwell's construction

$\Delta\mu$ for a molecule going from vapor to liquid or back is zero, since $\mu_{vap} = \mu_{liq}$. But!

$$\Delta\mu = \int_v^l d\mu$$

if we look at the van der Waals curve:



We know where to put l and v such that:

$$\int_v^l d\mu = 0$$

first let's change $d\mu$ into $\frac{-SdT}{N} + \frac{V}{N}dP$ by Gibbs-Duhem, and cancel because T is constant.

then put point M on the line connecting $l + v$. Now:

$$\int_l^m \frac{V}{N}dP + \int_m^v \frac{V}{n}dP = 0$$

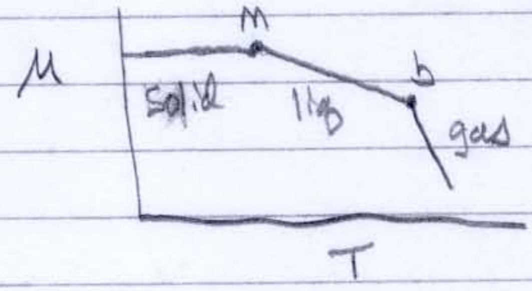
this only happens if $|\text{Area I}| = |\text{Area II}|$ since areas I + II have opposite signs.

Phase transitions

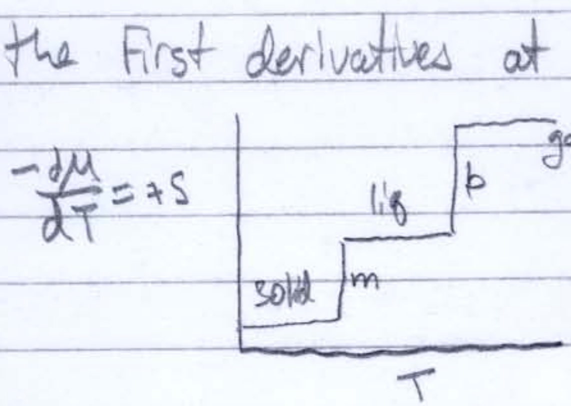
First order phase transitions are what we've looked at so far, (melting, boiling, etc.)

They're characterized by a discontinuity in the first derivative of μ

We saw how μ changes with phase:



the First derivatives at m + b are discontinuous

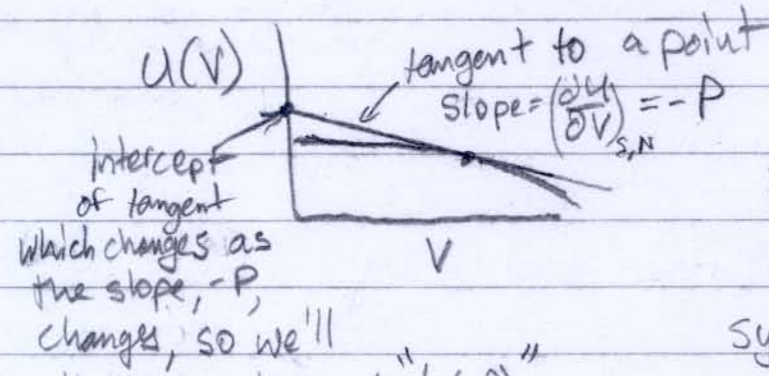


Other transitions are discontinuous for higher derivatives of μ.

These are called 2^{nd} order phase transitions or simply "continuous" (as opposed to 1^{rst} order ones which are called "discontinuous")

Legendre Transforms

Pretend that the internal energy, U, is only a function of V (for an adiabatic, closed system this is true), then we graph:



(note how the internal energy drops as the volume increases, system is doing work on the surroundings)

Question: can we reconstruct $U(V)$ from a knowledge of $\frac{dU}{dV}$?
Answer: No, since the same set of slopes fits any $f(V) = U(V) + C$

So, we need to use the set of intercepts, $b(-P)$, to specify $U(V)$, given a knowledge of dU/dV:

$$U(V) = V\underbrace{\left(\frac{dU}{dV}\right)}_{\text{slope}} + b(-P) \quad \leftarrow \text{like } y = mx + b$$

$$b(-P) = U(V) - V\left(\frac{dU}{dV}\right) \quad \leftarrow \text{rearrange}$$

rename this function "H" for enthalpy

$$\underbrace{H(P) = U(V) + VP}_{\text{this is the legendre transform from } U \text{ to } H\text{, i.e. how we define } H} \quad \leftarrow \text{b/c } \frac{dU}{dV} = -P$$

H can be thought of as a function that depends on the slope of U in the V dimension related to the intercept

7.12

The bottom line in Legendre transforms is that, by replacing V with $\frac{dU}{dV}$, some information about $U(V)$ is lost. Recovering that information involves taking $\underbrace{\frac{dU}{dV}}_{\text{slope}}$ times $\underbrace{V}_{\text{variable}}$ and adding in a new $\underbrace{\text{function}}_{\text{intercept}}$.

The new function is interesting in its own right, since it depends on dU/dV and not on V. In this case $dU/dV = -P$ so the new function depends on P.

Now we write:

$$U = TS - PV + \sum_i \mu_i N_i$$
$$H = TS + \sum_i \mu_i N_i$$
$$F = -PV + \sum_i \mu_i N_i$$
$$G = \sum_i \mu_i N_i$$

So, if G only depends on μ_i and N_i why does:

$$dG = -S\,dT + V\,dP + \sum_i \mu_i\,dN_i \;? \quad ①$$

Answer: $dG = \sum_i \mu_i\,dN_i + \sum_i N_i\,d\mu_i$ ② but by Gibbs-Duhem:

$$\sum_i N_i\,d\mu_i = -S\,dT + V\,dP \quad ③$$

Substituting ② into ③ gives ① ✓