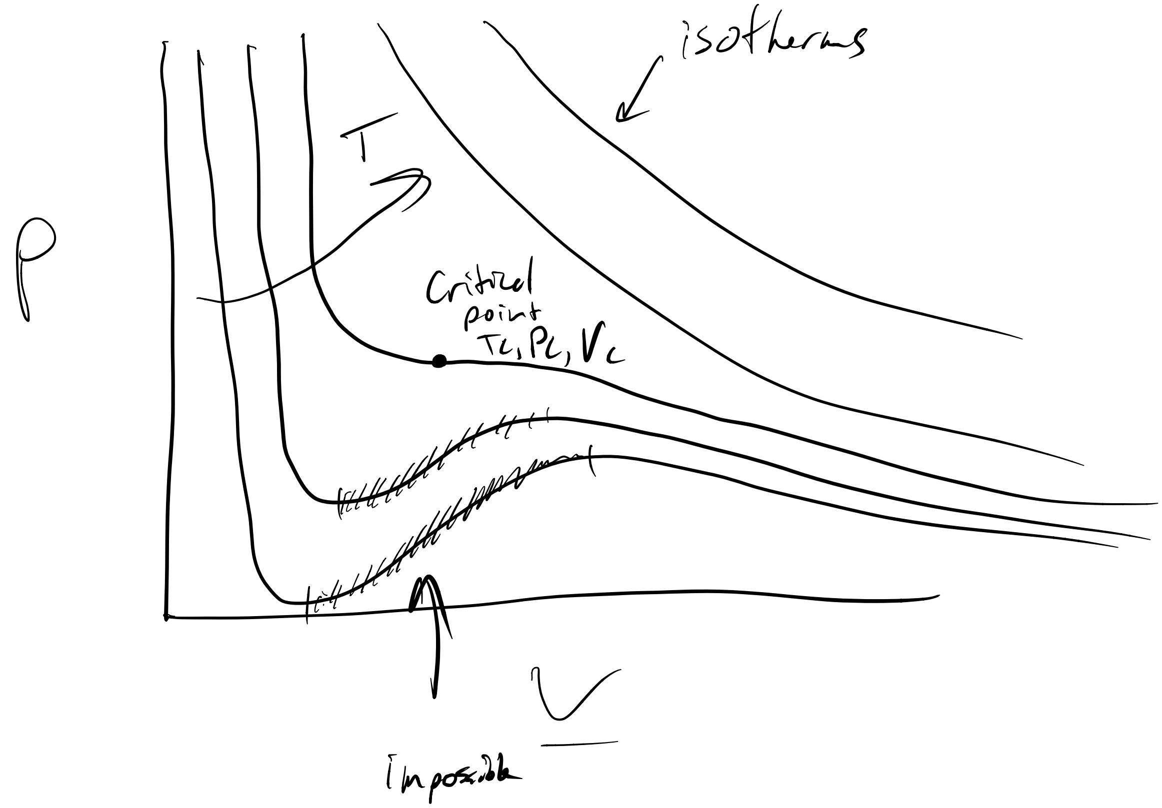
Now we will use EOS for stability & phase equilibria



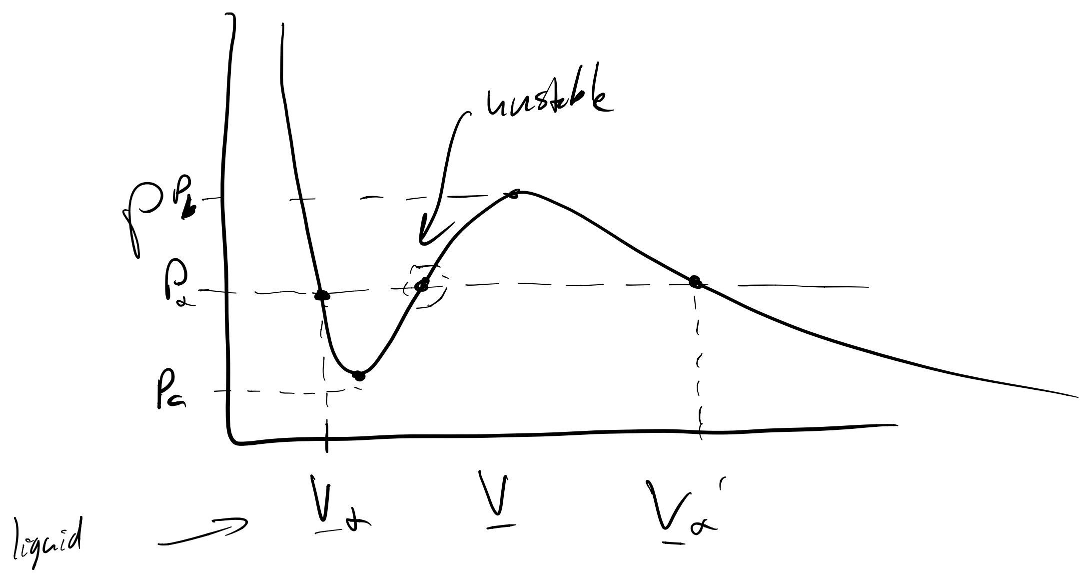
$$\left(\frac{\partial P}{\partial \underline{V}}\right)_T > 0$$

Suppose you are solving a problem puts u in impossible region

What do you do?

- you have to split →
  you will be in two phases

but how much of each?



Pressure line crosses @ 3 locations

What is $\underline{V}$ for the system?

$$\underline{V} = w^v \underline{V}^v + w^L \underline{V}^L$$

dubya — vapor — Liquid

dubya w can be mass or mol fraction in phase

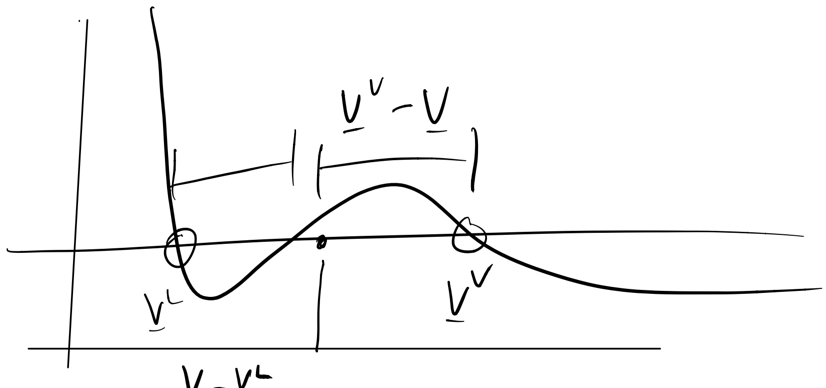
$$w^v + w^L = 1$$

$$\underline{V} = w^v \underline{V}^v + (1 - w^v) \underline{V}^L$$

$$w^v = \frac{\underline{V} - \underline{V}^L}{\underline{V}^v - \underline{V}^L}$$

$$\frac{w^v}{1 - w^v} = \frac{(\underline{V} - \underline{V}^L)}{(\underline{V}^v - \underline{V})}$$

look @ graph



specify $\underline{V}$

For 2 phase equilibrium -

$$\boxed{\begin{aligned} T^{I} &= T^{II} \\ P^{I} &= P^{II} \\ \underline{G}^{I} &= \underline{G}^{II} \end{aligned}}$$

Focus on – how do we find pressure for a system w/ two phases.

$$\underline{G}^{I} = \underline{G}^{II}$$

$$d\underline{G} = \underline{V}\,dP - \cancel{\underline{S}\,dT}$$ → we are on an isotherm

$$\rightarrow d\underline{G} = \underline{V}\,dP$$

$$\Delta \underline{G} = \int_{P_1}^{P_2} \underline{V}\,dP$$

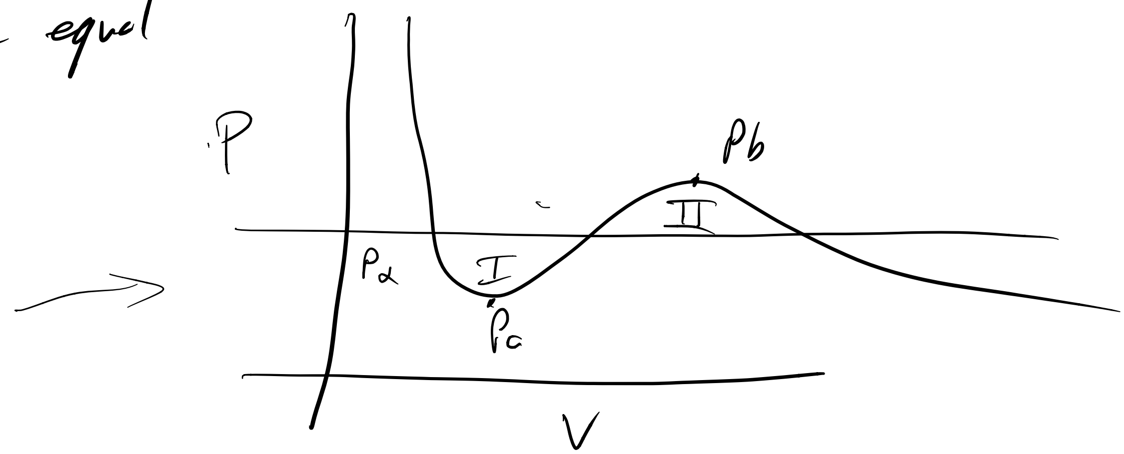
Thus, for a given EOS, we can identify conditions + equilibrium for a given T

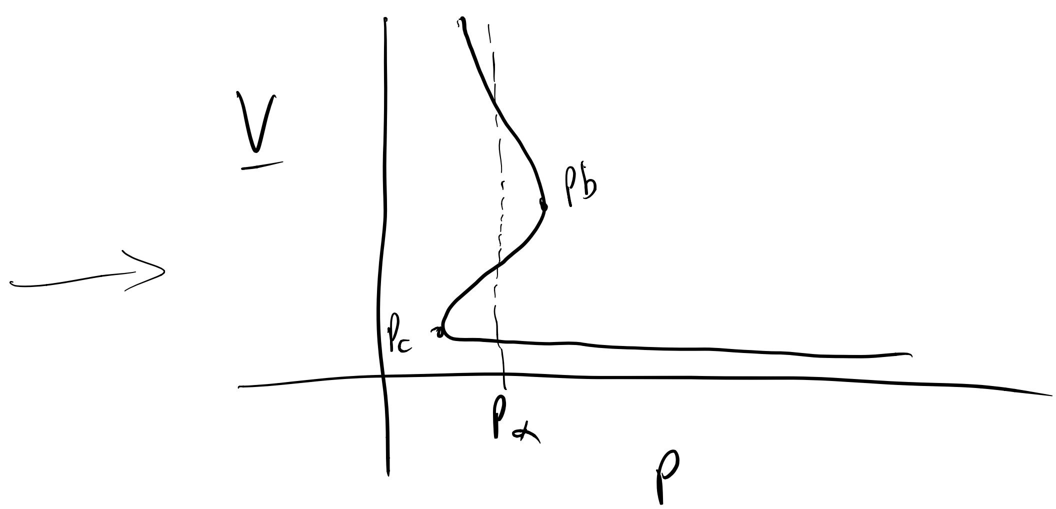
Method I

$P_\alpha \in [P_a, P_b]$ and iterate P_α until $\underline{G}^{V} - \underline{G}^{L} = 0$

$$\underline{G}^V - \underline{G}^L = 0 = \int_{P_\alpha}^{P_a} \underline{V}\,dP + \int_{P_a}^{P_b} \underline{V}\,dP + \int_{P_b}^{P_\alpha} \underline{V}\,dP$$

Graphically, the area of region I, II must be equal





Rules to construct your own P-V diagram:

1) Use the stability criterion $\left(\frac{\partial P}{\partial V}\right)_T < 0$

2) Require $T_I = T_{II}$ and $P_I = P_{II}$

$\Rightarrow$ draw a straight line across to guess a coexistence line.

3) move the line until $\underline{G}^{I} = \underline{G}^{II}$

Conceptually — this is the process

In practice we need a few modifications to make it actually work.

In practice, the thing that makes it easier to calculate is called

Fugacity

What is the Fugacity?

Fug: ancient extinct language root word for "to flee"

Like <u>fugative</u> — a person fleeing or running away from the law

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fugacity — the fleeing tendency of a particle

heat → fleeing tendency for both particles + fugitives

For coexisting phases, the following must be true.

$$\underline{G}^L(T,P) = \underline{G}^V(T,P)$$

$$d\underline{G} = -\underline{S}dT + \underline{V}dP$$

for equilibrium, $T_I = T_{II}$

@ constant T, $dT = 0$

$$\boxed{\underline{G}(T, P_2) - \underline{G}(T, P_1) = \int_{P_1}^{P_2} \underline{V}\, dP}$$

If the fluid were ideal, then

$$\underline{G}^{IG}(T, P_2) - \underline{G}^{IG}(T, P_1) =$$

$$\int_{P_1}^{P_2} \left(\frac{RT}{P}\right) dP$$

Subtact ideal situation from real.

and recall behaviour for materials @ $P_1 = 0$ is ideal.

$$\underline{G}_{real}(T, P=0) - \underline{G}^{IG}(T, P=0) = 0$$

subtract ideal from real and use $P=0$ for reference state.

$$\boxed{\underline{G}(T, P_2) - \underline{G}^{IG}(T, P_2) = \int_0^{P_2} \left(\underline{V} - \frac{RT}{P}\right) dP}$$

This is already a more convenient way of calculating $\underline{G}(T, P_2)$, but we can do better.

— transform it into an even more convenient form —

$$\boxed{f = P\exp\left[\frac{1}{RT}\left(\underline{G}(T, P) - \underline{G}^{IG}(T, P)\right)\right]}$$

FUGACITY

What are units of fugacity?

Pressure

$$f = P\exp\left[\frac{1}{RT}\int_0^P \left(\underline{V} - \frac{RT}{P}\right) dP\right]$$

sub in your favorite

<u>EOS</u>

related quantity

$$\phi = \frac{f}{P}$$ fugacity coefficient.

$$\text{as } \left.\begin{array}{l} P \to 0 \\ f \to P \end{array}\right\} \to \phi \to 1$$

present criterion for equilibrium $\Rightarrow$

$$\underline{G}^{I} = \underline{G}^{II}$$

using definition of fugacity -

$$\cancel{\underline{G}^{IG}(T,P)} + RT\ln\left(\frac{f^{I}(T,P)}{P}\right) =$$

$$\cancel{G^{IG}} + RT\ln\left(\frac{f^{II}(T,P)}{P}\right)$$

$$\ln\left(\frac{f^{I}(T,P)}{P}\right) = \ln\left(\frac{f^{II}(T,P)}{P}\right)$$

$$\boxed{\begin{gathered} f^{I}(T,P) = f^{II}(T,P) \\ \phi^{I} = \phi^{II} \end{gathered}}$$

conditions for phase equilibrium

→ allows for easier calculation of equilibrium