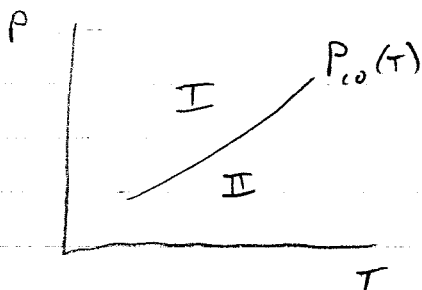


Lecture 7

Phase transitions

Last time, developed Clausius-Clapeyron relation



$$\left(\frac{\partial P}{\partial T}\right)_{\text{coex}} = \frac{\Delta H}{T\Delta V} = \frac{L}{T\Delta V}$$

ΔH = enthalpy of transition
= heat that must be added
to system to drive
all particles from I to II
= $H_{\text{II}} - H_{\text{I}}$

$\Delta V = V_{\text{II}} - V_{\text{I}}$ = difference in volume for
all particles in state II
vs state I (at this P & T)

Here N
= total #
of particles
= $N_{\text{I}} + N_{\text{II}}$

$L \equiv \frac{\Delta H}{N}$ = latent heat
= enthalpy/particle needed to drive transition
(typ $\sim 10^5 \text{ J/mol}$ or $\sim 10^4 \text{ eV/molecule}$)

$v = \frac{\Delta V}{N}$ = difference in volume/particle between phases
↳ "specific volume"

This is for PVT system

More generally,

$$\left(\frac{\partial Y}{\partial T}\right)_{\text{co}} = - \frac{\Delta H}{T\Delta X}$$

But if II is a gas, I = solid or liquid
can go further...

First, expect $V_{II} \gg V_I$

$$\text{so } \Delta V \approx V_{II} \quad \Delta v \approx v_{II}$$

Also, if gas is close to ideal, $v_{II} \approx \frac{NkT}{P}$

$$\text{So } \left(\frac{\partial P}{\partial T} \right)_{co} = \frac{PL}{kT^2} \quad v_{II} \approx \frac{kT}{P}$$

Integrate:

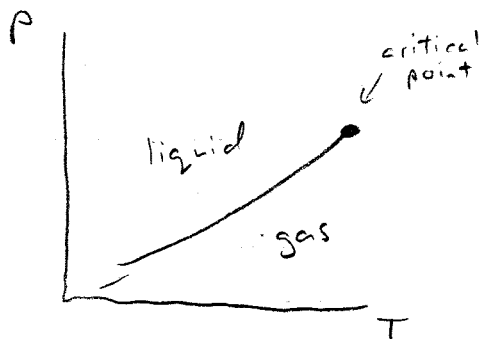
$$\frac{dP}{P} = \frac{L}{k} \frac{dT}{T^2}$$

$$\ln P = -\frac{L}{k} \frac{1}{T} + \text{const}$$

$$P_{coex}(T) = P_0 e^{-L/kT}$$

Gives vapor pressure of phase I
- exp dependence on T

Breaks down near critical point:



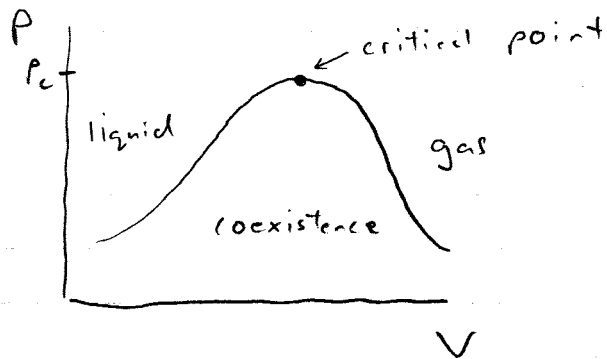
L depends on T
 $\rightarrow 0$ as $T \rightarrow T_c$

Also $\Delta V \rightarrow 0$ too

So can say a fair bit about P/T relation

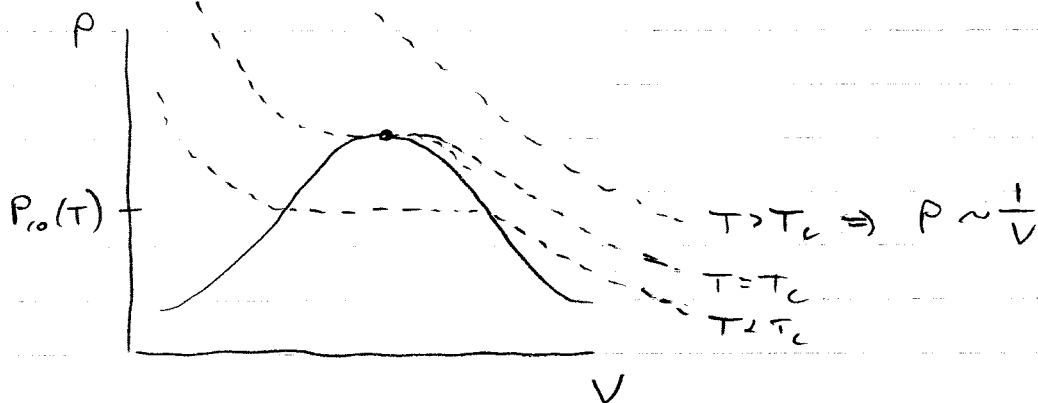
But can use other variables too!

Diagram in P - V plane:



For given $P < P_c$, could have liquid at low V ,
gas at high V
or mixture in between

Add isotherms



For $T > T_c$, approximately ideal gas

$T < T_c$, move from liquid to gas at const P, T
 $\Rightarrow V$ no longer determined by P & T !

So how is V determined?

To go further, need eqn of state

Ideal gas has no phase transition
Consider van der Waals gas

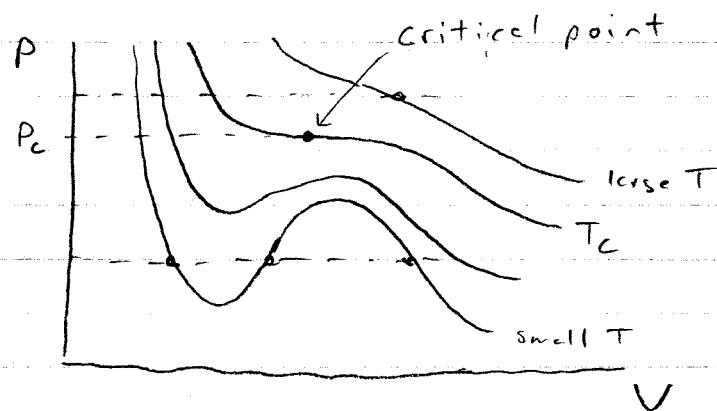
In terms of specific volume, $(P + \frac{a}{v^2})(v-b) = kT$

$$\text{or } Pv^3 - (Pb + kT)v^2 + av - ba = 0$$

cubic eqn in v : expect 3 roots
for given P, T

But often only one is real

Plot P vs V , various T



For $T < T_c$ and $P < P_c$, see 3 possible V 's
for each (P, T)

Above P_c or T_c , only one solution

See that at critical point, $(\frac{\partial P}{\partial V})_T = 0 = (\frac{\partial^2 P}{\partial V^2})_T$

Use this to find T_c, P_c

$$P = \frac{kT}{v-b} - \frac{a}{v^2}$$

$$\left(\frac{\partial P}{\partial v}\right)_T = -\frac{kT}{(v-b)^2} + \frac{2a}{v^3} = 0 \Rightarrow \frac{v^3}{(v-b)^2} = \frac{2a}{kT}$$

$$\left(\frac{\partial^2 P}{\partial v^2}\right)_T = \frac{2kT}{(v-b)^3} - \frac{6a}{v^4} = 0 \Rightarrow \frac{v^4}{(v-b)^3} = \frac{3a}{kT}$$

Divide: $\frac{v}{v-b} = \frac{3}{2}$

$$2v = 3v - 3b \Rightarrow \boxed{v_c = 3b}$$

$$kT_c = 2a \cdot \frac{(v-b)^2}{v^3} = 2a \cdot \frac{(2b)^2}{(3b)^3}$$

$$\boxed{kT_c = \frac{8}{27} \frac{a}{b}}$$

and
$$P_c = \frac{kT_c}{v_c-b} - \frac{a}{v_c^2} = \left(\frac{8}{27} \frac{a}{b}\right) \frac{1}{2b} - \frac{a}{9b^2}$$

$$= \frac{a}{b^2} \left(\frac{4}{27} - \frac{3}{27}\right)$$

$$\boxed{P_c = \frac{1}{27} \frac{a}{b^2}}$$

Can rewrite eqn of state in terms of $\bar{P} = \frac{P}{P_c}$, etc

Get
$$\left(\bar{P} + \frac{3}{\bar{v}^2}\right)(3\bar{v} - 1) = 8\bar{T}$$

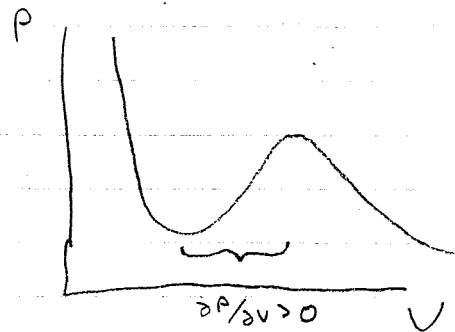
\Rightarrow a & b drop out!

All van der Waals gases are equivalent in reduced units

True to good approximation for most real gases

Now, for $T < T_c$ have

Have region where $\frac{\partial P}{\partial V} > 0$



⇒ Unstable:

Suppose small element of fluid dV increased in size

Then P in that element would increase

→ cause size to increase further

Expansion runs away

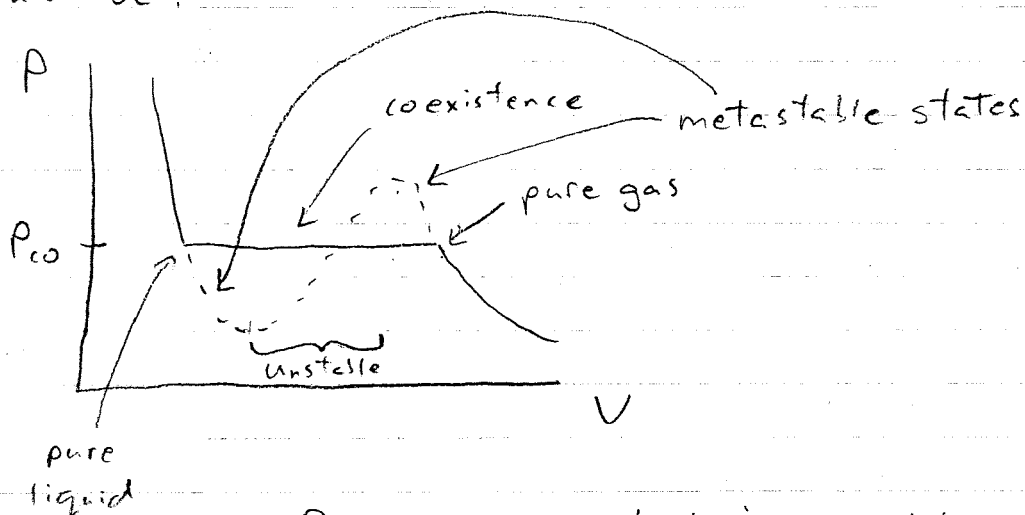
→ form bubble in liquid

Similarly if dV decreases, P goes down

→ form droplet in vapor

So curve as drawn isn't really right

Should be:



P remains constant in coexistence region

But how do we know where to draw line?

Use method called Maxwell construction

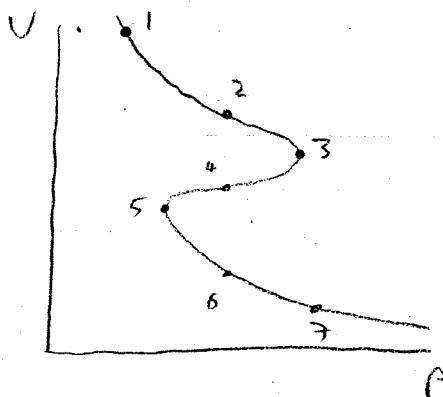
Know that in equilibrium, G is minimized

$$dG = -SdT + VdP$$

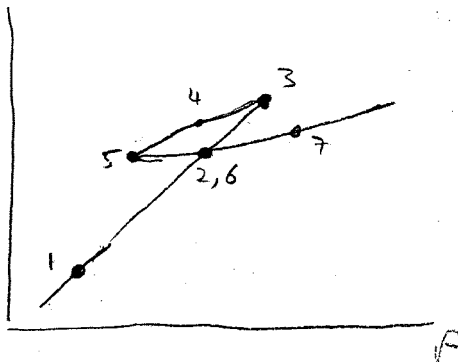
On isotherm, $dT=0$, so

$$G = \int_{\text{fixed } T} V dP$$

Draw $V(P)$:



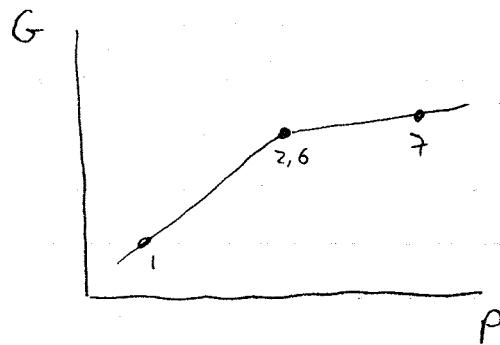
$\int V dP$ G



Between 2 & 6, G is multivalued

But want smallest possible value

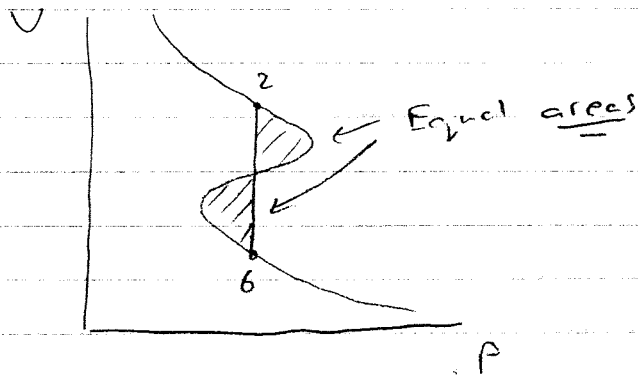
So observe



Location of 2 & 6 determined by $G(2) = G(6)$

$$G(6) - G(2) = \int_{P_2}^{P_6} V dP = 0$$

= area enclosed



Can't solve analytically, but can integrate numerically to locate transition points

Summary: For given T , find onset of transition by locating points in liquid & gas states where $G(P, V_g) = G(P, V_l)$

Can locate points by equalizing area enclosed by coexistence line & eqn of state

