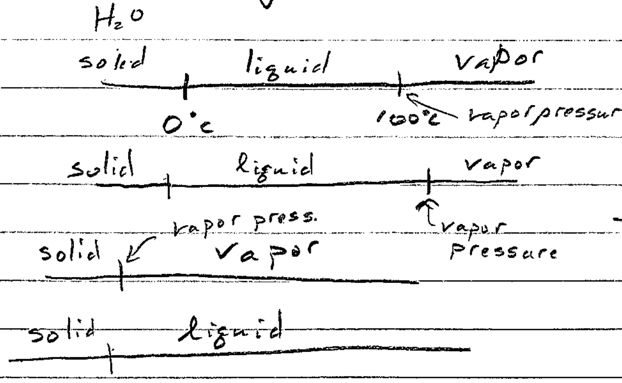
5.3 Phase Transformation of Pure Substance

Simplest picture

Raise pressure

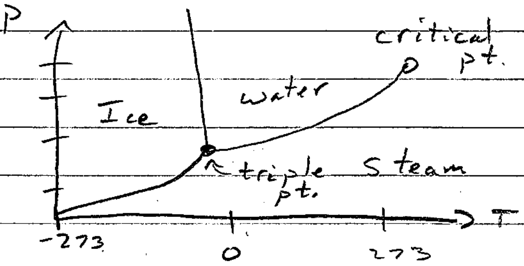
Very low pressure

very high pressure



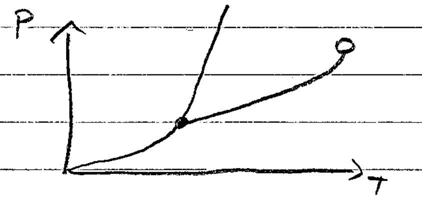
(water is peculiar raising pressure makes solid/liquid transition go to lower T)

Summarize



Triple point solid/liquid/gas coexist.
Critical pt - liquid/gas transition goes away
Vapor pressure - pressure where gas and liquid/solid coexists

More typical



All sorts of phase transitions: superfluid, superconducting lattice type changes, magnetization, ...

First order phase transition (solid-liquid, gas-liquid...) have S and V discontinuous at transition (first derivs of G)

Continuous phase transition (superconducting...) higher derivs of G discontinuous

Just because a phase of a material as smaller G than another phase does not mean material will be in that phase. Examples: super cooled water, graphite/diamond

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Graphite $\Delta H = 0$, $\Delta G = 0$, $S = 5.74 \frac{J}{K}$, $V = 5.30\ cm^3$

Diamond $\Delta H = 1.895\ kJ$, $\Delta G = 2.900\ kJ$, $S = 2.38 \frac{J}{K}$, $V = 3.42\ cm^3$

$\Rightarrow$ diamond should convert to graphite. Why doesn't?

At what pressure ΔG is same

$$\Delta G = \left(\frac{\partial G}{\partial P}\right)_{T,N} \Delta P = V \Delta P$$

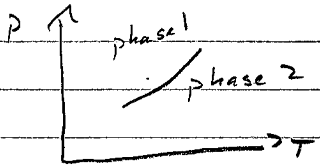
$$2.900\ kJ + 3.42 \times 10^{-6} m^3 \Delta P = 0\ kJ + 5.30 \times 10^{-6}\ cm^3 \Delta P$$

$$\Delta P = 1.54 \times 10^9\ Pa = 1.54\ GPa \cong 15\ kbar$$

5.26 Why graphite more stable? $S_{graphite} > S_{diamond}$ is a puzzle.

The slope of the line on the phase diagram can be found from the latent heat and other properties.

Clausius – Clapeyron Relation



At boundary $G_1 = G_2$ because material equally stable in form 1 or 2

$$\underset{\text{on bdry}}{dG_1 = dG_2} \Rightarrow -S_1 dT + V_1 dP + \cancelto{0}{\mu_1 dN_1} = -S_2 dT + V_2 dP + \cancelto{0}{\mu_2 dN_2}$$

$\Rightarrow$ slope of the line $\frac{dP}{dT} = \frac{S_1 - S_2}{V_1 - V_2}$

$S_1 - S_2 = \frac{L}{T}$ ← latent heat of transition $\Delta V = V_1 - V_2$ = volume change of material

$$\frac{dP}{dT} = \frac{L}{T \Delta V}$$

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$$\frac{dP}{dT} = \frac{L}{T\Delta V} \approx \frac{L}{TV} \qquad V = \frac{Nk_BT}{P}$$

$$\Rightarrow \frac{dP}{dT} = \frac{L}{Nk_BT^2}P \Rightarrow \text{ if } L \text{ is for 1 mol} \quad \frac{dP}{P} = \frac{L}{RT^2}dT$$

$$\ln P = -\frac{L}{RT}$$

$$P = (\text{const})\, e^{-L/RT}$$

only true for small changes, $L \approx$ const, go to gas, ideal gas law

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$P = P_0 e^{-L/RT}$ from Prob 5.35

From Fig 5.11 at 25 °C $L = 43.99\ \text{kJ/mol} \Rightarrow \frac{L}{R} = 5294\ k$

$0.0317\ \text{atm} = P_0\, e^{-\frac{5294k}{298k}} \Rightarrow P_0 = 1.64 \times 10^6\ \text{atm}$

a)

T	P
273k	0.006 atm
283k	0.012 atm
293k	0.023 atm
303k	0.042 atm

b)

$$0.9 \times 0.042 = 0.038 = P_0\, e^{-\frac{L}{RT}}$$

$$e^{-L/RT} = 2.32 \times 10^{-8}$$

$$-\frac{L}{RT} = -17.6 \Rightarrow T = 301k = 28°C$$

$$0.4 \times 0.042 = 0.0168 = P_0\, e^{-L/RT}$$

$$e^{-L/RT} = 1.02 \times 10^{-8}$$

$$-L/RT = -18.4 \Rightarrow T = 288k = 15°C$$

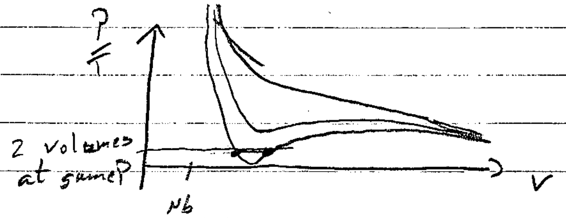
The van der Waals model

Equation of state $\left(P + \frac{aN^2}{V^2}\right)(V - Nb) = Nk_BT$

$$\Rightarrow P = \frac{Nk_BT}{V - Nb} - \frac{aN^2}{V^2}$$

This simple equation of state gives a phase transition!!

Typical size $b \approx 10^{-28} m^3$ $\quad a \approx 10^{-21} J \; 10^{-28} m^3$

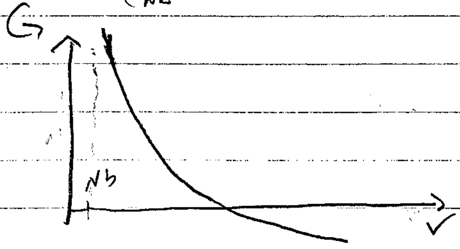


To find how system behaves when in contact with environment need to know G

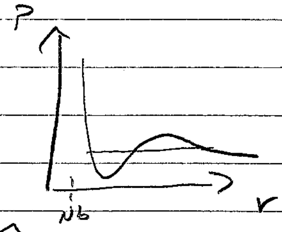
$$dG = -S\,dT + V\,dP + \mu\,dN$$

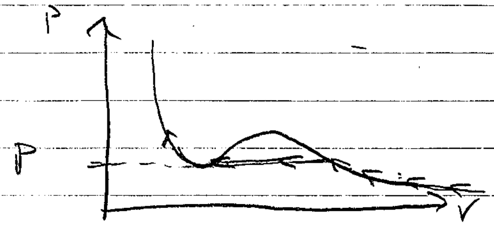
$$\Rightarrow \left(\frac{\partial G}{\partial V}\right)_{N,T} = V\left(\frac{\partial P}{\partial V}\right)_{N,T} = -V\frac{Nk_BT}{(V-Nb)^2} + \frac{2aN^2}{V^2}$$
$$= -\frac{Nk_BT}{V-Nb} + \frac{N^2bk_BT}{(V-Nb)^2} + \frac{2aN^2}{V^2}$$

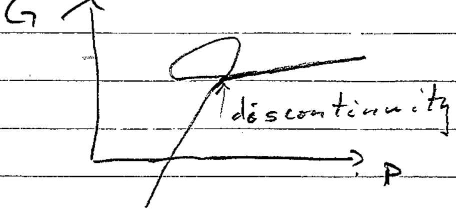
$$\Rightarrow G = -Nk_BT\ln(V-Nb) + \frac{Nk_BT\,Nb}{(V-Nb)} - \frac{2aN^2}{V} + \underbrace{C(N,T)}_{\text{doesn't depend on } V}$$
$$-Nk_BT\left[\ln\left(\frac{V}{Nb}-1\right) - \frac{1}{\frac{V}{Nb}-1}\right] - \frac{2aN^2}{V} + \tilde{C}(N,T)$$
$$= \frac{+Nk_BT}{\left(\frac{V}{Nb}-1\right)}\left[1 - \left(\frac{V}{Nb}-1\right)\ln\left(\frac{V}{Nb}-1\right)\right] - \frac{2aN^2}{V} + \tilde{C}(N,T)$$

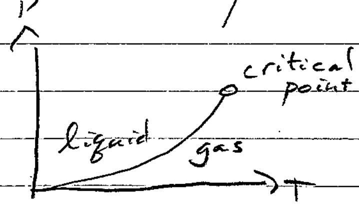


For Case









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To have phase transition must have $\frac{dP}{dV} = 0$

$$\Rightarrow \quad -\frac{Nk_BT}{(V-Nb)^2} + \frac{2aN^2}{V^3} = 0 \quad \Rightarrow \quad 2aN^2(V-Nb)^2 = Nk_BT\,V^3$$

Must also have $\frac{d^2P}{dV^2} = \frac{2Nk_BT}{(V-Nb)^3} - \frac{6aN^2}{V^4} = 0 \Rightarrow (V-Nb)^3\,6aN^2 = 2Nk_BT\,V^4$

ratio of eqs $\quad 2V = 3(V-Nb) \Rightarrow \boxed{V_c = 3Nb}$

$$Nk_BT = 2aN^2(V-Nb)^2/V^3 = 2aN^2\frac{4}{27Nb} = \frac{8aN}{27b} \Rightarrow \boxed{k_BT_c = \frac{8a}{27b}}$$

$$P_c = \frac{Nk_BT}{V-Nb} - \frac{aN^2}{V^2} = \frac{4}{27}\frac{a}{b^2} - \frac{1}{9}\frac{a}{b^2} = \boxed{\frac{1}{27}\frac{a}{b^2}}$$