

## Chapter 5 + Section 1.6 (and) $\rightarrow$ Free Energies

Enthalpy  $\rightarrow$  energy plus the work to make room for the system under constant pressure from the environment

$$H \equiv U + PV \leftarrow \begin{array}{l} \text{total energy to create the system} \\ \text{and put it into an environment} \end{array}$$

But, the system can get its thermal energy from the surroundings, so all we really need to do is provide to the system any additional work

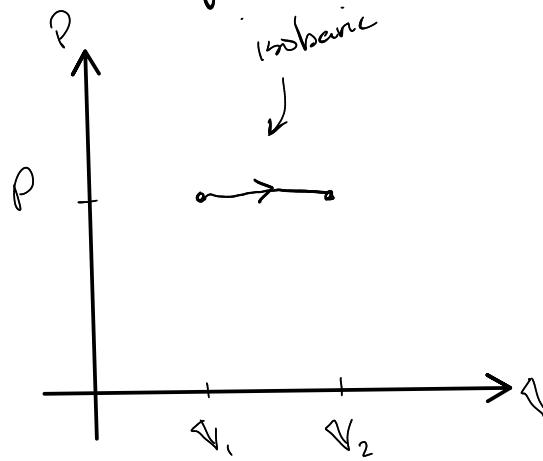
## Gibbs Free Energy

$$\begin{array}{l} G \equiv H - TS \leftarrow \begin{array}{l} \text{energy to make the system and make} \\ \text{room for the system minus the heat} \end{array} \\ G \equiv U + PV - TS \quad \text{we get to extract from surroundings.} \end{array}$$

Helmholtz Free Energy  $\rightarrow$  total energy to create the system minus the heat we can extract from the surroundings

$$F = U - TS$$

# Enthalpy



#134

$$W = -P(V_2 - V_1)$$

$$\Delta U = \frac{f}{2} N k_B \Delta T = \frac{f}{2} P \Delta V - \frac{f}{2} P(V_2 - V_1)$$

$$Q = \Delta U - W = \Delta U + P \Delta V$$

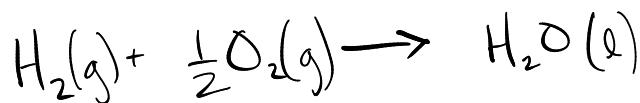
$$Q = \frac{f}{2} P(V_2 - V_1) + P(V_2 - V_1)$$

$$Q = \left(\frac{f}{2} + 1\right) P \Delta V$$

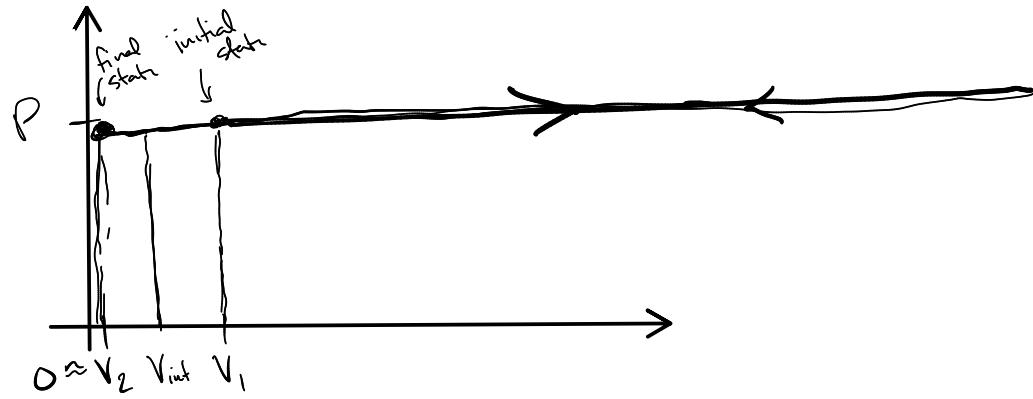
$$H \equiv U + PV$$

$$\Delta H = \Delta U + P \Delta V = Q$$

Another example, what if we cause something to happen inside the tube & we measure the heat given off at constant pressure.



$$\Delta H = -286 \text{ kJ/mol}$$



$$Nk_B \Delta T = P \Delta V$$

- or -

$$= \Delta P \cdot V$$

- but not -

$$= \underline{\underline{\Delta P \cdot \Delta V}}$$

1.4a] 1 mol  $H_2(g)$

0.5 mol  $O_2$

1.5 mol  $\rightarrow n_m$

$$PV = n \cdot RT \leftarrow 298K$$

↑      ↑      ↑  
10^5 Pa    1.5 mol    8.31

1 mL = 1 cm³

1000 L = 1 m³

$$V = \frac{nRT}{P} = \frac{1.5 \cdot 8.31 \cdot 298}{10^5} = 0.037 \text{ m}^3 = 37 \text{ L}$$

$n_m$  after the reaction?

$$V_{int} = \frac{1 \cdot 8.31 \cdot 298}{10^5} = 0.0248 \text{ m}^3$$

this condenses  
to give ~0 L  
of liquid, giving  
up heat along the way

$$V = \frac{nRT}{P} \xrightarrow{\text{constant}} V \propto n \rightarrow \frac{V_{int}}{V_i} = \frac{n_2}{n_1} = \frac{1}{1.5}$$

$$\underline{V_{int} = 0.0248 \text{ m}^3}$$

So what total work has been done?

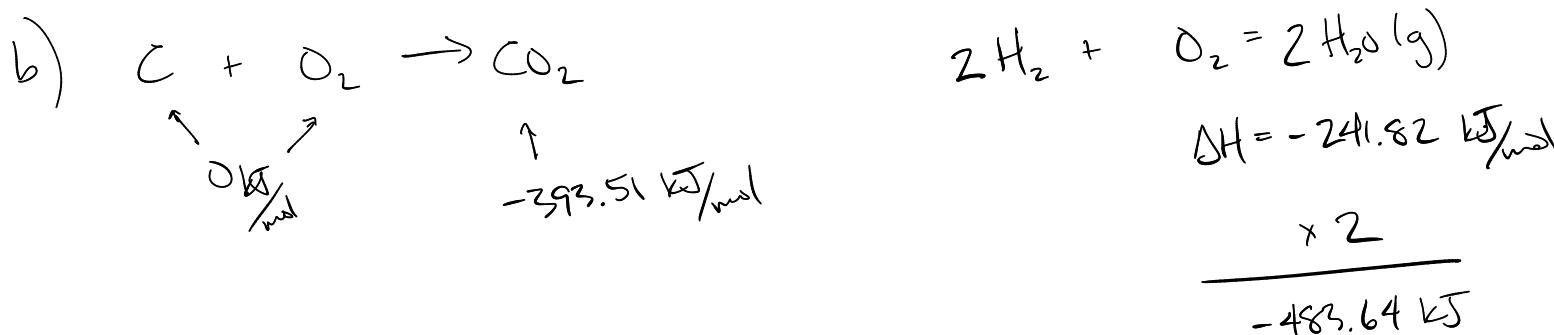
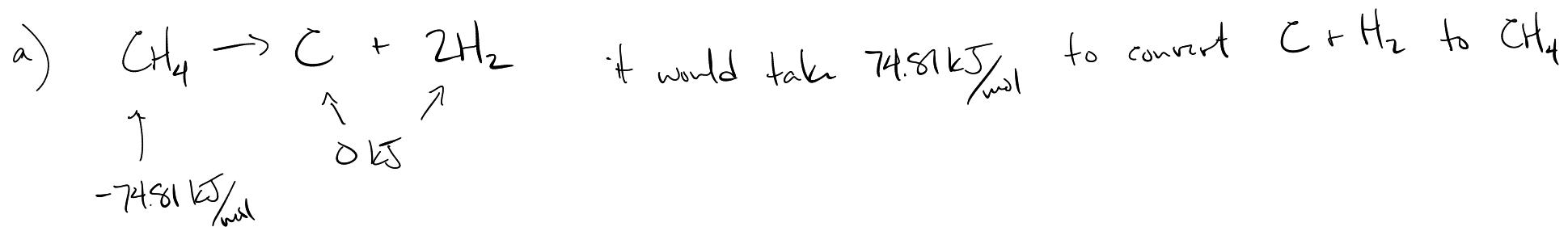
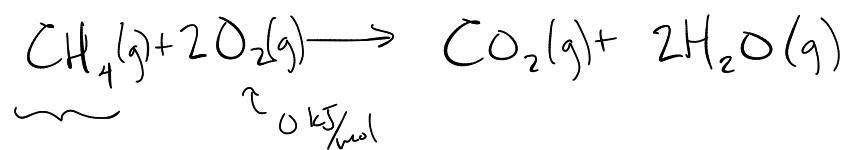
$$W = - \int_{0.0248 \text{ m}^3}^{0 \text{ m}^3} P dV = -10^5 \text{ Pa} (0 - 0.037 \text{ m}^3) \\ = 3700 \text{ J} = 3.7 \text{ kJ}$$

$$\Rightarrow \Delta H = -286 \text{ kJ} = \Delta U - W$$

$$-286 \text{ kJ} = \Delta U - 3.7 \text{ kJ}$$

$$\boxed{\Delta U = -282.3 \text{ kJ}}$$

1.50]



c)  $\Delta H_{\text{reaction}} = 74.81 - 393.51 \text{ kJ/mol} = -483.64 \text{ kJ}$

$\Delta H_{\text{reaction}} = -802.34 \text{ kJ} \rightarrow \text{heat given to the surroundings}$

d)  $802.34 \text{ kJ}$

e)  $\Delta H = U + P \Delta V$   
 $\uparrow \quad \uparrow$   
       find this

$\Delta H = U$  when final mixture is a gas

$$PV = nRT \rightarrow P\Delta V = \Delta n R \cdot T$$

$$= 0.01931 \cdot 298 \text{ K}$$

What if  $\text{H}_2\text{O}(g) \rightarrow (\ell)$   
 $\text{CH}_4 + 2\text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O}(\ell)$   
 3 mol of gas  $\rightarrow 1 \text{ mol of liquid}$

$$P\Delta V = -2 \text{ mol} \cdot 8.31 \cdot 298 \text{ K}$$

$$= -4.9 \text{ kJ}$$

$$\Delta H_{\text{reaction}} = ?$$

f) ?

also do 1.55

~~1.55~~

## Gibbs Free Energy

$$G = U + PV - TS$$

$$G = H - TS$$

$$dG = dU - TdS + pdV$$

$$dG = \pm Q + \pm W - TdS + pdV$$

- for a reversible process  
(no new entropy is created)
- $\pm Q_{\text{rev}} = TdS$

- $\pm W = -pdV + \pm W_{\text{other}}$   
 $\hookrightarrow$  electrical

$$dG = \cancel{TdS} - \cancel{pdV} + \pm W_{\text{other}} - \cancel{TdS} + \cancel{pdV}$$

$$dG = \pm W_{\text{other}}$$

not reversible

$$dG \leq \pm W_{\text{other}} \text{ at constant } T, P$$

## Thermodynamic Potentials

$$dF = dU - TdS$$

$$dF = \pm Q + \pm W - TdS$$

for a reversible process  
(no new entropy is created)

$$\pm Q_{\text{rev}} = TdS$$

$$dF = TdS + \pm W - TdS$$

$$dF = \pm W$$

$\hookrightarrow$  amount of work done  
on the system by  
you or by surroundings

otherwise, (not a reversible process)

$$dF \leq \pm W$$

How is  $\Delta G_f$  measured?

First measure  $\Delta H \rightarrow$  heat absorbed or released for a reaction at constant pressure & no other work has been done

Then calculate  $\Delta S$  from initial + final states using heat capacity data

$$\Delta S = \int_0^T \frac{C_p}{T} dT$$

$$\Delta G = \Delta H - T\Delta S$$

So lets do an example: (5.2)



$$\begin{array}{c} \downarrow \\ \Delta H = 0 \text{ kJ} \\ S = 191.61 \text{ J/K mol} \end{array}$$

$$\begin{array}{c} \downarrow \\ \Delta H = 0 \text{ kJ} \\ S = 130.68 \text{ J/K mol} \end{array}$$

$$\begin{array}{c} \longrightarrow \\ \Delta H = -46.11 \text{ kJ} \\ S = 192.45 \text{ J/K mol} \end{array}$$

$$\Delta H = 2 \text{ mol} \cdot (-46.11 \text{ kJ/mol}) = -92.22 \text{ kJ}$$

$$\begin{aligned} \Delta S &= S_f - S_i = 2 \cdot 192.45 \text{ J/K} - 3(130.68) - 191.61 \\ &= -198.75 \text{ J/K} \end{aligned}$$

$$\Delta G = \Delta H - T\Delta S$$

watch out for kJ!

$$= -92.22 \text{ kJ} - 298(-0.19875 \text{ kJ/K})$$

from the book

$$\Delta G = -16.45 \text{ kJ/mol}$$

for this reaction

$$\Delta G = 2 \text{ mol} \cdot (-16.45 \text{ kJ/mol}) = \underline{\underline{-32.9 \text{ kJ}}}$$

$$\underline{\underline{\Delta G = -32.99 \text{ kJ}}}$$

Compare!

### Electrolysis, Fuel Cells, Batteries (another example)



↑ electrical work must be done

$\Delta H = 286 \text{ kJ}$  → heat out when we run in reverse

To run this reaction forward we need to put in 286 kJ of energy

↳ Some of this will push aside the atmosphere

$$\rho \Delta V = \Delta n RT = 1.5 \text{ mol} \cdot (8.31 \text{ J/Kmol}) (298 \text{ K}) = 3714 \text{ J}$$

↳ Trees form = 3.7 kJ

↳ So, 282 kJ will remain in the system in the form of potential energy in the chemical bonds ~ 4 kJ

Do we need to do all of this work, or can we get some help from surroundings?

What is the change in entropy?

$$S_{H_2O} = 70 \text{ J/K} \quad S_{H_2} = 131 \text{ J/K} \quad S_{O_2} = 205 \text{ J/K} \quad \leftarrow \text{from the back of the book}$$

$\underbrace{\qquad\qquad\qquad}_{\text{products}}$

$$S_{\text{prod}} = 131 \text{ J/K} + \frac{1}{2}(205 \text{ J/K}) = 233.5 \text{ J/K}$$

$$\Delta S = S_p - S_r = 233.5 \text{ J/K} - 70 \text{ J/K} = 163.5 \text{ J/K}$$

$\underbrace{\qquad\qquad\qquad}_{\text{entropy increased}}$

$$dQ \leq T dS$$

$$Q = T \Delta S = 298 \text{ K} \cdot 163.5 \text{ J/K}$$

$$Q = \underline{48.7 \text{ kJ}}$$

So of the 286 kJ that go in, 48.7 kJ can come from heat from surroundings

$$286 \text{ kJ} - 48.7 \text{ kJ} = \underline{\underline{237.3 \text{ kJ}}} \rightarrow \text{come from } \underline{\text{electrical work}}$$

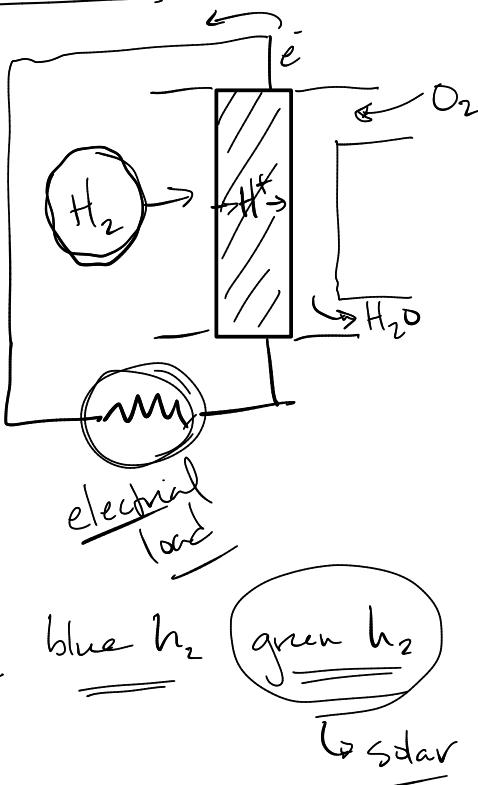
$$\Delta G = \Delta H - T \Delta S$$

$$\left| \begin{array}{l} \Delta G_{H_2O} = -228.57 \text{ kJ} \\ \Delta G_{H_2} = 0 \text{ kJ} \\ \Delta G = 0 \text{ kJ} \end{array} \right.$$

HW 5.1 + 5.5

$$\Delta G_f = \Delta G_{prod} - \Delta G_{react} = 0 - 228.57 \\ = \underline{\underline{228.57 \text{ kJ}}}$$

In reverse, we can extract 237 kJ of electrical work



- 49 kJ of waste heat goes to the environment  
→ ΔU = 282 kJ → comes from chemical reactions  
→ PΔV = 4 kJ → comes from the collapse of gas to liquid  
fuel cell
- efficiency =  $\frac{\text{get}}{\text{pay for}}$

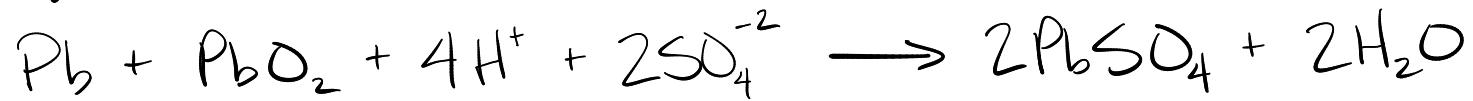
$$\frac{237 \text{ kJ}}{286 \text{ kJ}} = \underline{\underline{83\%}}$$

Compare to efficiencies  
we would have  
gotten in chapter 4

max theoretical  
engine efficiency  $\rightarrow 66\%$

max theoretical car  
engine efficiency  $\rightarrow 50\%$   
practically  $\rightarrow 20-30\%$

# Battery



start w/  $\Delta H = -316 \text{ kJ/mol}$

↑ energy out from reaction at constant pressure

what about  $\Delta G = -394 \text{ kJ/mol}$

↑ electrical energy out

$\Delta G$  is more than the  $\Delta H$ . How? Heat is coming in to the system  
from surroundings!

↳ How much?

$$394 \frac{\text{kJ}}{\text{mol}} - 316 \frac{\text{kJ}}{\text{mol}} = 78 \frac{\text{kJ}}{\text{mol}}$$

$$\Delta G = \Delta H - T\Delta S$$

$$\Delta G - \Delta H = -T\Delta S$$

$$-394 - (-316) = -298 \Delta S$$

$$\Delta S > 0$$

$$78 \frac{\text{kJ}}{\text{mol}} = T\Delta S$$

increase in entropy

means the heat  
is being absorbed ←  $\Delta S = \frac{78 \text{ kJ}}{298 \text{ K}} = 261.7 \frac{\text{J}}{\text{K}}$  ← watch  
out for units

from surroundings

Energy/charge → potential (voltage)

gibbs

$$\text{Voltage} = \frac{\Delta W_E}{q} = \frac{394 \text{ kJ}}{2e \cdot N_A \cdot 1.6 \cdot 10^{-19} \text{ C}} = 2.04 \text{ V} \quad \leftarrow \text{per "cell" in a car battery}$$

$6 \text{ "cells"} \rightarrow 12 \text{ V}$

↑  
need to know how many electrons  
are moved during the reaction

$2 e^-$

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### Thermodynamic identity

$$dU = T dS - P dV + \mu dN$$

but what about  $H, F, G$ ? How do these change when conditions change?

$$\rightarrow H = U + PV$$

$$dH = dU + \cancel{P dV} + V dp$$

$$\hookrightarrow T dS - \cancel{P dV} + \mu dN$$

$$dH = T dS + V dp + \mu dN$$

So the variables have changed from  $dU$   
we tend to use enthalpy  
when  $dp = 0$   
 $dN = 0$

$dH = T dS$  ← heat at constant pressure

what about  $F$ ?

$$\rightarrow F = U - TS$$

$$dF = dU - TdS - SdT$$

$$dF = -SdT - pdV + \mu dN$$

what about  $G$ ?  $\rightarrow$  you derive thus

We can use these identities to derive many useful statements.

Ex:  $dF = -SdT - pdV + \mu dN$

hold  $V + N$  constant  $\rightarrow dV + dN = 0$

$$dF = -SdT$$

$$S = -\left(\frac{\partial F}{\partial T}\right)_{V,N} \quad \begin{matrix} \leftarrow \text{what does this mean?} \\ \text{entropy is the rate of change of } F \text{ w.r.t. } T \end{matrix}$$

$$P = -\left(\frac{\partial F}{\partial V}\right)_{T,N}, \quad \mu = \left(\frac{\partial F}{\partial N}\right)_{T,V}$$

What about Gibbs?

$$S = -\left(\frac{\partial G}{\partial T}\right)_{P,N}, \quad V = \underline{\underline{\left(\frac{\partial G}{\partial P}\right)_{T,N}}}, \quad \mu = \left(\frac{\partial G}{\partial N}\right)_{T,P}$$

How does the Gibb Free Energy change w/ pressure

volume of  
1 mol

Use reference data  $\rightarrow$  1 mol of C (graphite)  $\Rightarrow 5.3 \cdot 10^{-6} \text{ m}^3$

$$\Delta G_E = 0 \text{ kJ} \leftarrow \text{most stable form}$$

Gibbs will increase by  $5.3 \cdot 10^{-6} \text{ J}$  for each additional Pa of pressure above atmospheric pressure

Ex: 1 mol of  $\text{H}_2\text{O(l)}$  at  $25^\circ\text{C}$  ( $298\text{K}$ )

Gibbs at  $30^\circ\text{C}$ ? ( $303\text{K}$ ) -

$G_{\text{H}_2\text{O}} = -237.13 \text{ kJ}$  at  $298\text{K}$  and 1 atm

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

$$S_{\text{H}_2\text{O}} = 69.91 \text{ J/K}$$

$$\Delta G = S \cdot \Delta T$$

$$= 69.91 \cdot 5 \text{ K} = 349.55 \text{ J}$$

units warming!



new  
Gibbs

$$+ \underline{-237.13 \text{ kJ}} \quad \underline{-236.78 \text{ kJ}}$$

5.14 → Monday

Now do 5.12 then come back to 5.14.

Thermodynamic identity

$$dU = \underbrace{T dS}_{\text{constant } P} - \underbrace{P dV}_{\text{constant } S} + \mu dN$$

$$dU = \underbrace{\left(\frac{\partial U}{\partial S}\right)_{\bar{V}} dS}_{\text{constant } N} + \underbrace{\left(\frac{\partial U}{\partial V}\right)_{\bar{S}} dV}_{\text{constant } N} + \underbrace{\frac{\partial U}{\partial N} dN}_{\text{constant } S, V}$$

$$f(x, y)$$

$$\left(\frac{\partial f}{\partial x}\right)_y$$

$$\left(\frac{\partial f}{\partial y}\right)_x$$

$$\frac{\partial^2 f}{\partial x \partial y}$$

$$\frac{\partial U}{\partial S} = T$$

$$\frac{\partial U}{\partial V} = -P$$

$$\frac{\partial}{\partial V} \left( \frac{\partial U}{\partial S} \right) = \left( \frac{\partial T}{\partial V} \right)_S$$

$$\frac{\partial}{\partial S} \left( \frac{\partial U}{\partial V} \right) = - \left( \frac{\partial P}{\partial S} \right)_V$$

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

$$dS(U, V, N) = \underbrace{\left(\frac{\partial S}{\partial U}\right)_{V,N} dU}_{\frac{1}{T}} + \underbrace{\left(\frac{\partial S}{\partial V}\right)_{U,N} dV}_{\frac{P}{T}} + \underbrace{\left(\frac{\partial S}{\partial N}\right)_{U,V} dN}_{-\frac{\mu}{T}}$$

$$T dS = dU + P dV - \mu dN$$

Now do for Gibbs

$$dG = dU + \cancel{pdV} - TdS \quad | \quad dN = 0$$

$$\frac{\partial}{\partial S} \left( \frac{\partial G}{\partial V} \right) = \frac{\partial}{\partial V} \left( \frac{\partial G}{\partial S} \right)$$

$$dG = \frac{\partial G}{\partial U} dU + \cancel{\frac{\partial G}{\partial V} dV} + \cancel{\frac{\partial G}{\partial S} dS}$$

$$\left( \frac{\partial p}{\partial S} \right)_V = - \left( \frac{\partial T}{\partial V} \right)_S$$

Now for Helmholtz + Enthalpy then back to 5.14...

answers

$$\left| \begin{array}{l} \left( \frac{\partial T}{\partial p} \right)_S = \left( \frac{\partial \nabla}{\partial S} \right)_p \\ \left( \frac{\partial S}{\partial V} \right)_T = \left( \frac{\partial p}{\partial T} \right)_V \\ \left( \frac{\partial S}{\partial p} \right)_T = - \left( \frac{\partial V}{\partial T} \right)_p \end{array} \right.$$

## 5.2 | Free Energy as a Force toward Equilibrium

$$dS_{\text{total}} = dS + \underbrace{dS_R}_{}$$

rewrite in  
terms of system's  
variables

$$dS_R = \frac{1}{T} dU_R + \cancel{\frac{P}{T} dV_R} + \cancel{\frac{\mu}{T} dN_R}$$

$$dV_e = 0$$

$$dN = 0$$

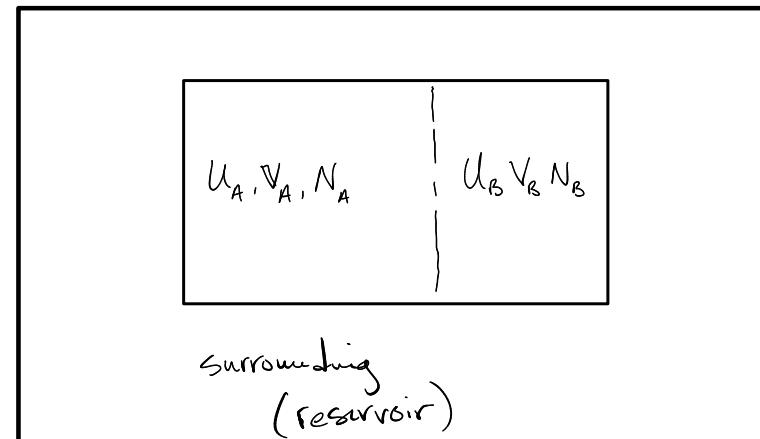
$$dU = -dU_R \leftarrow \text{energy is conserved}$$

$$dS_{\text{total}} = dS_I - \frac{1}{T} dU$$

$$= \frac{1}{T} (T dS - dU)$$

$$= -\frac{1}{T} (dU - T dS)$$

Helmholtz!  $\delta F$



$$dS_{\text{total}} = -\frac{\delta F}{T}$$

↑                      ↓  
increase            decrease  
this                that

So, the system will minimize  
its Helmholtz free energy

Conditioning       $dT = 0$   
 $dV = 0$   
 $dN = 0$

What about keeping Pressure, temperature and number constant and letting  $\Delta$  change?

$$dS_{\text{total}} = dS + dS_{\text{res}}$$

$$\hookrightarrow dS_{\text{res}} = \frac{1}{T} dU + \frac{P}{T} dV - \frac{\mu}{T} dN$$

$$dS_{\text{res}} = -dS$$

$$dS_{\text{total}} = dS - \frac{1}{T} dU - \frac{P}{T} dV$$

$$= -\frac{1}{T} (dU - TdS + PdV)$$

$\Delta$  Gibbs free energy

conditions:

$$dT = 0$$

$$dP = 0$$

$$dN = 0$$

$$dS_{\text{total}} = -\frac{dG}{T}$$

system will spontaneously minimize Gibbs

At constant energy & volume,  $S$  tends to increase

At constant temperature & volume,  $F$  tends to decrease.

At constant temperature & pressure,  $G$  tends to decrease

Is this intuitive from their definitions?

$$G = U + PV - TS$$

↓      ↓      ↑

Derive chemical potential for an ideal gas, as a function of pressure

$$\mu = \frac{G}{N} \leftarrow \text{find this}$$

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

$$\frac{\partial \mu}{\partial P} = \frac{1}{N} \frac{\partial G}{\partial P}$$

$$\left( \frac{\partial G}{\partial P} \right)_{TN} = V$$

$$\frac{\partial \mu}{\partial P} = \frac{1}{N} V$$

$$\text{ideal gas} \rightarrow \frac{V}{N} = \frac{k_B T}{P}$$

$$\frac{\partial \mu}{\partial P} \xrightarrow{=} \frac{k_B T}{P}$$

$$\int d\mu = \int \frac{k_B T}{P} dP \Rightarrow \mu(T, P) - \mu^\circ(T) = \underbrace{k_B T \ln P - k_B T \ln P^\circ}_{\text{another reference}}$$

$$\Delta \mu = k_B T \ln \frac{P}{P^\circ}$$

$$\mu(T, P) = k_B T \ln \left( \frac{P}{P^\circ} \right) + \mu^\circ(T)$$

We already have an expression for  $\mu(T, P)$  from chapter 3.5 notes

$$\mu = -k_B T \ln \left[ \frac{N}{V} \left( \frac{2\pi m k_B T}{h^2} \right)^{3/2} \right] \quad (\text{problem 5.22})$$

$$\mu = -k_B T \ln \left( \frac{N}{V} \right) - \frac{3}{2} k_B T \ln \left( \frac{2\pi m k_B T}{h^2} \right)$$

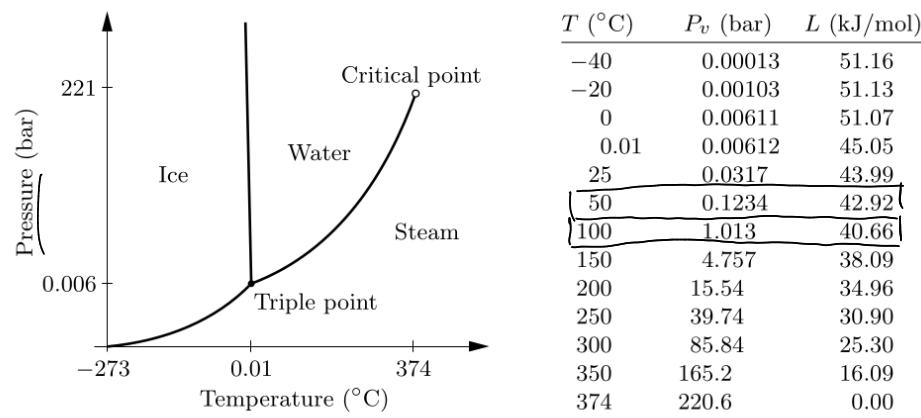
$\uparrow$   
 $\frac{k_B T}{P}$

$$\mu = -k_B T \ln \left( \frac{k_B T}{P} \right) - \frac{3}{2} k_B T \ln \left( \frac{2\pi m k_B T}{h^2} \right)$$

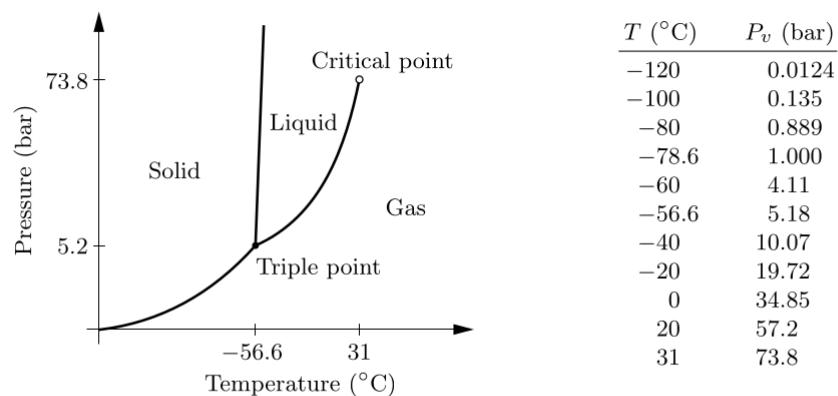
$$\mu = k_B T \ln \left( \frac{P}{k_B T} \right) - \frac{3}{2} k_B T \ln \left( \frac{2\pi m k_B T}{h^2} \right)$$

$\underbrace{\text{only a function of } T = \mu^\circ(T)}$  (monatomic ideal gas)

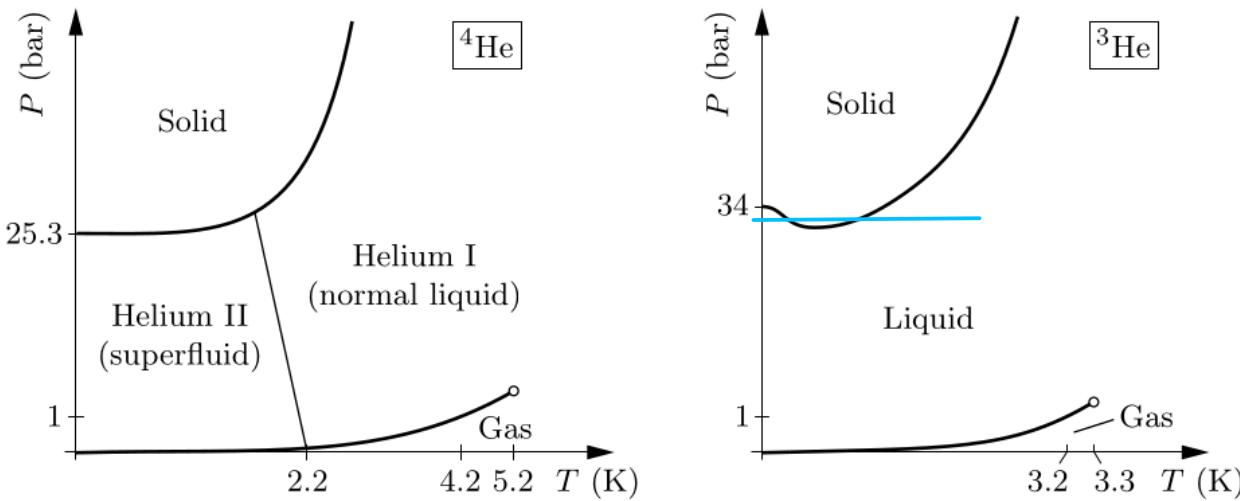
does this  
mean the  
 $P^\circ$  is  $k_B T$ ?



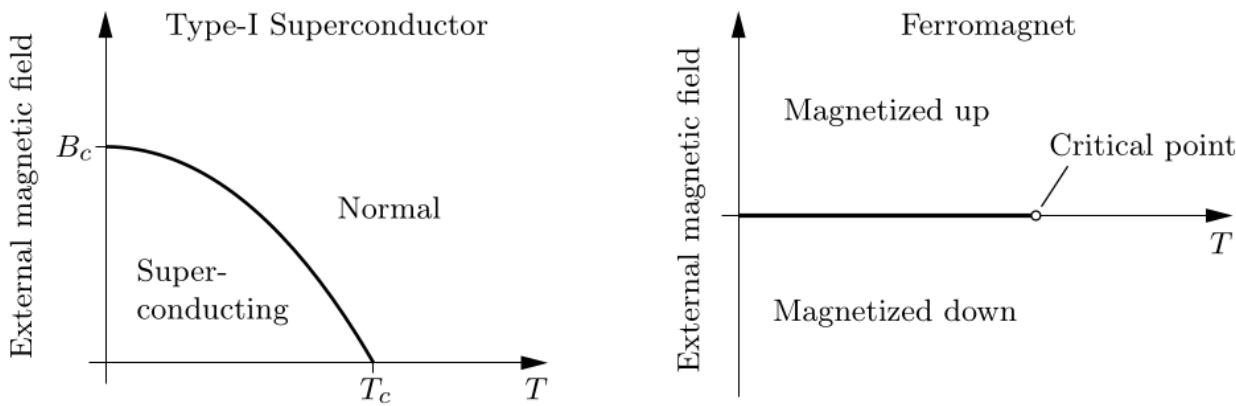
**Figure 5.11.** Phase diagram for  $\text{H}_2\text{O}$  (not to scale). The table gives the vapor pressure and molar latent heat for the solid-gas transformation (first three entries) and the liquid-gas transformation (remaining entries). Data from Keenan et al. (1978) and Lide (1994).



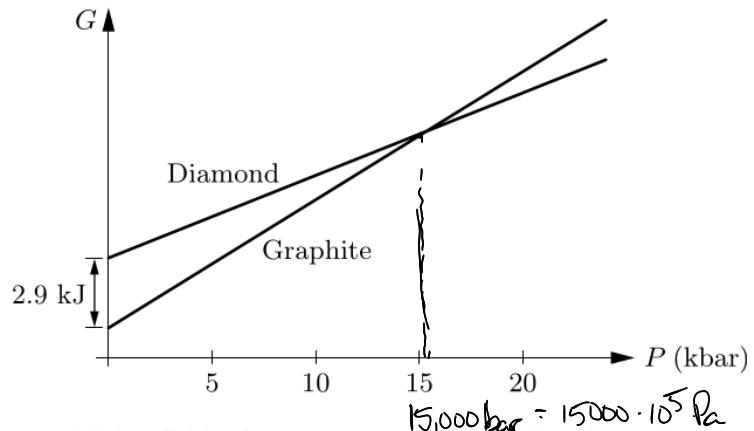
**Figure 5.12.** Phase diagram for carbon dioxide (not to scale). The table gives the vapor pressure along the solid-gas and liquid-gas equilibrium curves. Data from Lide (1994) and Reynolds (1979).



**Figure 5.13.** Phase diagrams of  $^4\text{He}$  (left) and  $^3\text{He}$  (right). Neither diagram is to scale, but qualitative relations between the diagrams are shown correctly. Not shown are the three different solid phases (crystal structures) of each isotope, or the superfluid phases of  $^3\text{He}$  below 3 mK.



**Figure 5.14.** Left: Phase diagram for a typical type-I superconductor. For lead,  $T_c = 7.2$  K and  $B_c = 0.08$  T. Right: Phase diagram for a ferromagnet, assuming that the applied field and magnetization are always along a given axis.



**Figure 5.15.** Molar Gibbs free energies of diamond and graphite as functions of pressure, at room temperature. These straight-line graphs are extrapolated from low pressures, neglecting the changes in volume as pressure increases.

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

$$V_{\text{graphite}} = 5.31 \cdot 10^{-6} \text{ m}^3 \quad | \text{STP}$$

$$V_{\text{diamond}} = 3.42 \cdot 10^{-6} \text{ m}^3$$

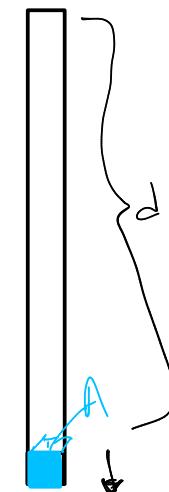
Temperature dependence follows entropy

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

$$S_{\text{graphite}} = 5.74 \text{ J/K}$$

$$S_{\text{diamond}} = 2.38 \text{ J/K}$$

As the temperature increases, Gibbs goes down, but it goes down more quickly for graphite



$$\begin{aligned} \text{Pressure} &= \frac{Mg}{A} \\ &= \text{frack} \cdot V \cdot g \\ &= \text{frack} \cdot \frac{A \cdot d \cdot g}{A} \\ &= \text{frack} \cdot A \cdot d \cdot g \end{aligned}$$

$$\rho_{\text{H}_2\text{O}} = 1 \text{ g/mL}$$

$$= 1000 \text{ kg/m}^3$$

$$\text{frack} = 3000 \text{ kg/m}^3$$

$$P = \text{frack} \cdot g \cdot d$$

$$d = \frac{P}{\rho \cdot g}$$

So what is the shape of the phase boundary line?

On the phase boundary line

$$G_e = G_g$$

so, if we increase the  $p + T$  a little bit but we stay on the phase boundary line, then,

$$dG_e = dG_g$$

$$dG = -SdT + VdP + \cancel{\mu dN}$$

$$-S_e dT + V_e dP = -S_g dT + V_g dP$$

$$\frac{dP}{dT} = \frac{S_g - S_e}{V_g - V_e} = \frac{\Delta S}{\Delta V}$$

$$\Delta S = \frac{Q}{T} = \frac{L}{T}$$

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

Clausius-Clapeyron relation  
(applies to any phase boundary)

$$d = \frac{1.5 \cdot 10^9 \text{ Pa}}{3 \cdot 10^3 \cdot 10 \frac{\text{N}}{\text{kg}}}$$

$$d = 0.5 \cdot 10^5 \text{ m}$$

$$d = 5 \cdot 10^4 \text{ m}$$

$$d = 50 \cdot 10^3 \text{ m}$$

$$\underline{d = 50 \text{ km}}$$

So lets apply this to diamond/graphite

$$\Delta V = 1.9 \cdot 10^{-6} \text{ m}^3$$

$$\Delta S = 3.4 \text{ J/K}$$

$$\frac{\Delta P}{\Delta T} = \frac{3.4 \text{ J/K}}{1.9 \cdot 10^{-6} \text{ m}^3} = 1.8 \cdot 10^6 \text{ Pa/K} = 18 \text{ bar/K}$$

We found 15 kbar at 298K to be the phase change b/t graphite + diamond, but what about 100°C higher temperatures?

$$100^\circ\text{C} = \Delta T = 100 \text{ K}$$

$$\frac{\Delta P}{\Delta T} = 1.8 \cdot 10^6 \text{ Pa/K}$$

$$\Delta P = 1.8 \cdot 10^6 \text{ Pa/K} \cdot \Delta T = 1.8 \cdot 10^6 \text{ Pa} \cdot 100 \text{ K} = 1.8 \cdot 10^8 \text{ Pa} = 1.8 \cdot 10^3 = 1800 \text{ bar} = \underline{\underline{1.8 \text{ kbar}}}$$

Problems: 5.32, 35, 36, 37

| So more pressure  
| is necessary to  
| make diamond  
| become the more  
| stable form.

| more depth is  
| required  
100 - 200 km

# Van der Waals Model - equation of state

$$\left( P + \frac{aN^2}{V^2} \right) (V - Nb) = Nk_B T$$

}  
 - Nb correction since  
 the gas cannot be  
 compressed to zero volume  
 b represents the volume  
 of a molecule

→ attractive intermolecular forces

↳ lower potential energy

}  
 ↳ proportional to the number of  
 nearest neighbors  
 ↳ proportional to the density  
 ↳ proportional to the number of atoms

$$U_{vdw} = -a \cdot \overset{\downarrow}{N} \cdot \overset{\downarrow}{\frac{N}{V}}$$

$$U_{vdw} = -\frac{aN^2}{V}$$

$$P_{ideal} V_{ideal} = Nk_B T$$

$$\rightarrow V = V_{ideal} + Nb$$

$$V_{ideal} = V - Nb$$

$$P = P_{ideal} + P_{vdw}$$

$$P_{ideal} = P - P_{vdw}$$

$$dU = T dS^\circ - P dV + \mu dN^\circ$$

$$dU = -P dV$$

$$P = - \left( \frac{dU}{dV} \right)_{SN}$$

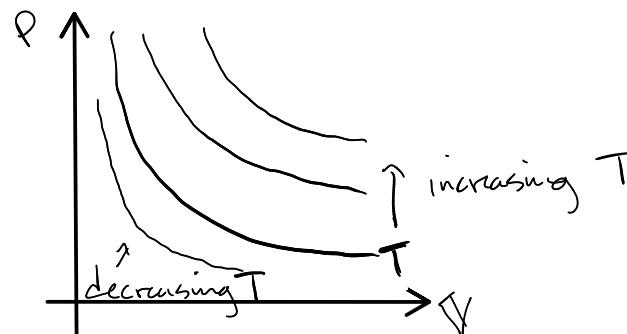
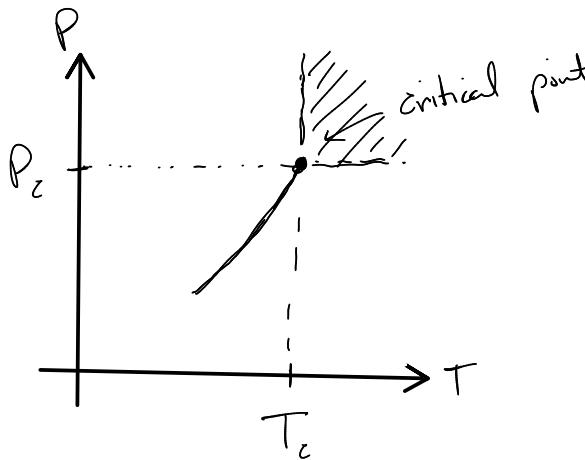
$b \sim$  volume of a molecule

$$(4\text{ \AA})^3 = 6 \cdot 10^{-29} \text{ m}^3$$

$a$  more variable, but  $N_2 \sim 4 \cdot 10^{29} \text{ J m}^{-3}$

Plot in reduced units.

$$\left. \frac{P}{P_c}, \frac{V}{V_c}, \frac{T}{T_c} \right\} \stackrel{\text{HW}}{=}$$

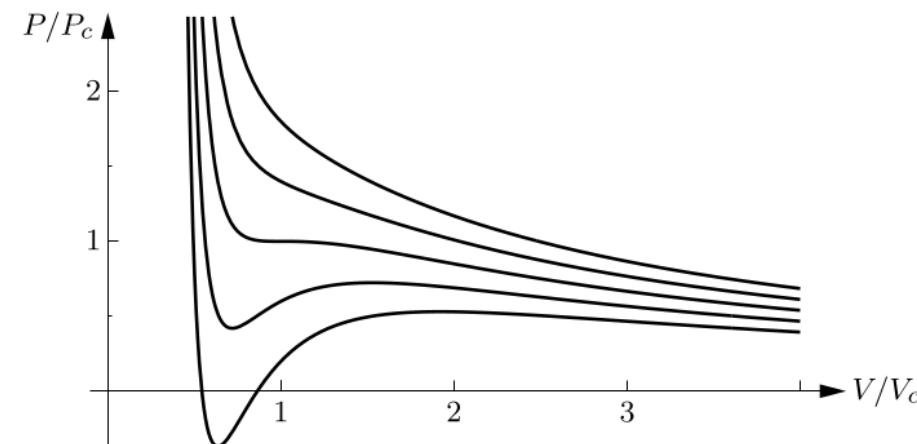


$$P = -\left(\frac{d}{dV}\left(\frac{-aN^2}{V}\right)\right)$$

$$P = aN^2 \left( \frac{1/V}{dV} \right)$$

$$P = -\frac{aN^2}{V^2} \rightarrow P_{\text{ideal}} = P - P_{\text{vdw}}$$

$$P_{\text{ideal}} = P + \underbrace{\frac{aN^2}{V}}$$



**Figure 5.20.** Isotherms (lines of constant temperature) for a van der Waals fluid. From bottom to top, the lines are for 0.8, 0.9, 1.0, 1.1, and 1.2 times  $T_c$ , the temperature at the critical point. The axes are labeled in units of the pressure and volume at the critical point; in these units the minimum volume ( $Nb$ ) is  $1/3$ .

Calculate the Gibbs for van der Waals fluid

$$dG = -SdT + \nabla dp + \mu dN$$

$$dT = 0$$

$$dN = 0$$

$$dG = \nabla dp$$

$$\nabla = \left( \frac{dG}{dp} \right)_{NT} = \left( \frac{dG}{d\nabla} \right) \left( \frac{d\nabla}{dp} \right)$$

$$\left( p + \frac{aN^2}{\nabla^2} \right) (\nabla - Nb) = Nk_B T$$

$$\left( \frac{dG}{d\nabla} \right)_{NT} = \nabla \cdot \left( \frac{dp}{d\nabla} \right)_{NT}$$

do this!

solve for  $p$   $\rightarrow p = \frac{Nk_B T}{\nabla - Nb} - \frac{aN^2}{\nabla^2}$

$$\begin{aligned} & aN^2 \nabla^{-2} \\ & 2aN^2 \nabla^{-3} \end{aligned}$$

$$\frac{dp}{d\nabla} = -\frac{Nk_B T}{(\nabla - Nb)^2} + \frac{2aN^2}{\nabla^3}$$

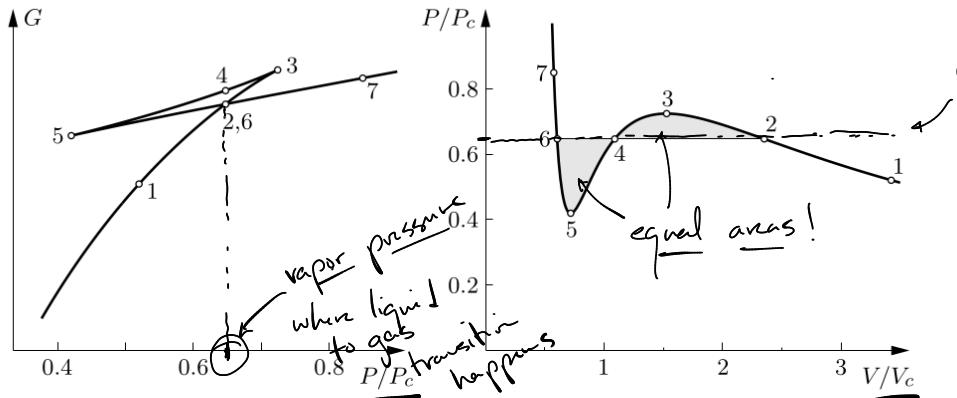
$$\left( \frac{dG}{d\nabla} \right)_{NT} = -\frac{Nk_B T \nabla}{(\nabla - Nb)^2} + \frac{2aN^2}{\nabla^2}$$

$$G = -Nk_B T \ln(\nabla - Nb) + \frac{(Nk_B T)(Nb)}{\nabla - Nb} - \frac{2aN^2}{\nabla} + C$$

rewrite

\* See the bottom of  
this file after problem  
5.51 for how this  
change of variables works!

$$\frac{G_1}{Nk_B T_c} = -\frac{T}{T_c} \ln \left( \frac{3V}{V_c} - 1 \right) + \frac{T/T_c}{\frac{3V}{V_c} - 1} - \frac{9}{4V/V_c}$$



**Figure 5.21.** Gibbs free energy as a function of pressure for a van der Waals fluid at  $T = 0.9T_c$ . The corresponding isotherm is shown at right. States in the range 2-3-4-5-6 are unstable.

increasing the pressure will cause this gas to go from 2  $\rightarrow$  6 directly.

1.50, 1.55

5.12, 5.14

5.32, 35, 36, 37

Problems: 5.48, 5.51

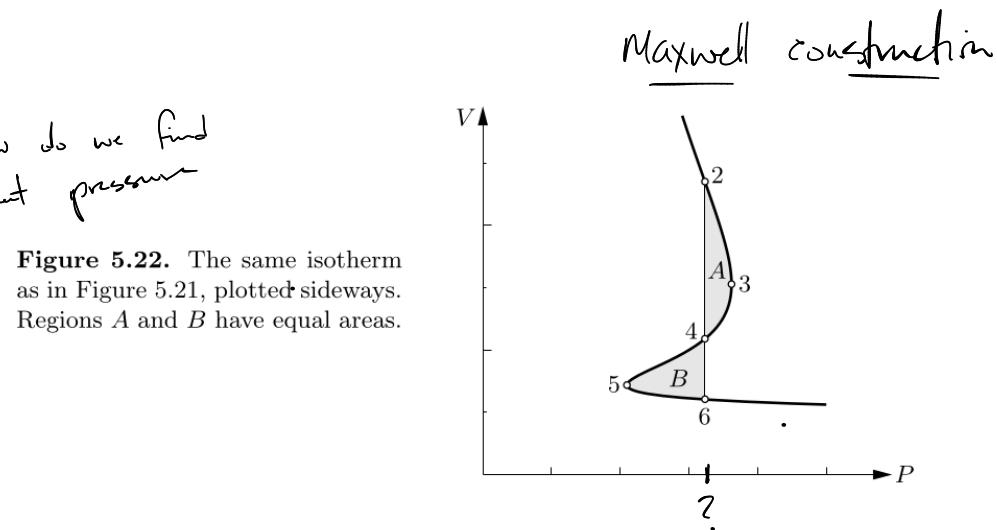
+ 5.52

$$\int dG = 0$$

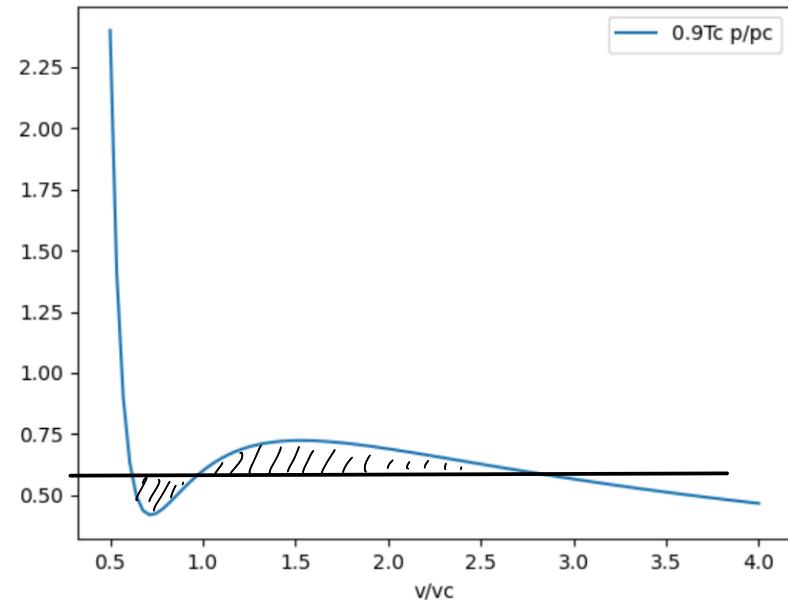
loop

$$\int \underbrace{\left( \frac{\partial G}{\partial P} \right)_T}_{V} dP = 0$$

$$\int V dP = 0$$



**Figure 5.22.** The same isotherm as in Figure 5.21, plotted sideways. Regions A and B have equal areas.





5.32

$$\rho_{ice} = 917 \text{ kg/m}^3$$

a) Clapeyron - Clapeyron

$$\frac{\Delta P}{\Delta T} = \frac{L}{T \Delta V}$$

slope of the graph to the right  $\rightarrow$

this can only be negative if the  $\Delta V$  is negative.

So for 0°C ice at standard pressure means that the volume decreases as the temperature rises.

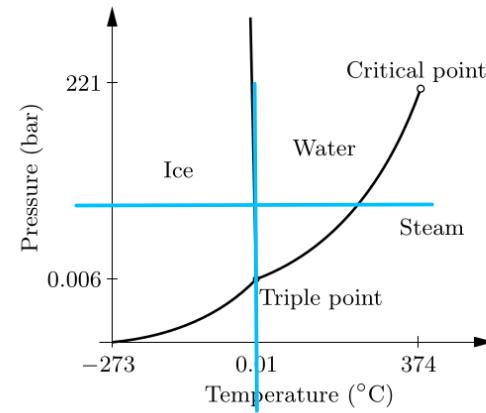
Perhaps a better way to think about this is as the pressure increases, the temperature necessarily decreases, which is counterintuitive because water is special. As it freezes, it forms bonds that cause the structure to occupy a larger form than it does as a liquid. Most things do this but their crystalline structure is simpler and more compact.

c)  $P = \rho g d$  ← hydrostatic pressure so we are treating a glacier like a fluid!

$$d = \frac{P}{\rho g} = \frac{7.62 \cdot 10^8 \text{ Pa}}{917 \text{ kg/m}^3 \cdot 9.8} = 84,800 \text{ m}$$

52 miles!

so that is not why glaciers move



T (°C)	P <sub>v</sub> (bar)	L (kJ/mol)
-40	0.00013	51.16
-20	0.00103	51.13
0	0.00611	51.07
0.01	0.00612	45.05
25	0.0317	43.99
50	0.1234	42.92
100	1.013	40.66
150	4.757	38.09
200	15.54	34.96
250	39.74	30.90
300	85.84	25.30
350	165.2	16.09
374	220.6	0.00

Figure 5.11. Phase diagram for H<sub>2</sub>O (not to scale). The table gives the vapor pressure and molar latent heat for the solid-gas transformation (first three entries) and the liquid-gas transformation (remaining entries). Data from Keenan et al. (1978) and Lide (1994).

b)  $\frac{\Delta P}{\Delta T} = \frac{L}{T \Delta V}$  ← 333 kJ/kg  
1 mole of H<sub>2</sub>O at 298 K  
↑ ↑ 273 K  
-1 K

$$\frac{\Delta P}{\Delta T} = \frac{3.33 \cdot 10^5 \text{ J/kg}}{273 \text{ K} \cdot (1.8 \cdot 10^{-5} - 1.96 \cdot 10^{-5}) \text{ m}^3}$$

$$\frac{\Delta P}{\Delta T} = -7.62 \cdot 10^8 \text{ Pa/K}$$

$$\Delta P = 7.62 \cdot 10^8 \text{ Pa}$$

$\Delta T = -1 \text{ K}$

$\therefore \Delta P = 7.62 \cdot 10^8 \text{ Pa}$

7620 atm!

$$V = \frac{M}{\rho} = \frac{0.018 \text{ kg}}{917 \text{ kg/m}^3} = 1.96 \cdot 10^{-5} \text{ m}^3$$

$\therefore \text{The } V \text{ is larger for ice}$

$\rho_{water} = 1000 \text{ kg/m}^3$

$\therefore V = \frac{M}{\rho} = \frac{0.018 \text{ kg}}{1000 \text{ kg/m}^3} = 1.8 \cdot 10^{-5} \text{ m}^3$

d)  $m = 70 \text{ kg}$   
 $A_{skirt} \approx 5 \text{ cm}^2 ? \text{ idk}$   
 $P = \frac{mg}{A} = \frac{70 \text{ kg} \cdot 9.8}{5 \cdot 10^{-4} \text{ m}} = 13.7 \cdot 10^5 \text{ Pa}$   
 $13.7 \text{ atm}$

compare!  
Not it!

5.35

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

Assumptions

- $L$  is constant
- $\Delta V = \overbrace{V_{\text{gas}} - V_{\text{liquid}}}$   
very small  
compared to  
 $V_{\text{gas}}$

So, trying to solve directly

$$\frac{dP}{dT} = \frac{L}{V_{\text{gas}}} \cdot \frac{1}{T}$$

in that spot

$$dP = \frac{L}{V_{\text{gas}}} \cdot \frac{1}{T} dT$$

$$P = \frac{L}{V_{\text{gas}}} \int \frac{1}{T} dT$$

$\ln(T) + \text{constant}$

$$P = \frac{L}{V_{\text{gas}}} \ln T + C$$

that does not work

so for a second round,  $V_{\text{gas}}$  is not a constant  
so we should put in the ideal gas law  
and then solve

$$V_{\text{gas}} = \frac{Nk_B T}{P} \rightarrow dP = \frac{L}{Nk_B} \cdot P \cdot \frac{1}{T^2} dT$$

integrate

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

$$\ln P = \frac{L}{Nk_B} \cdot (-1) \cdot \frac{1}{T} + \text{constant}$$

$$P = (\text{constant}) \cdot e^{-\frac{L}{Nk_B T}}$$

$\frac{Nk_B}{A} = R$

for one mole

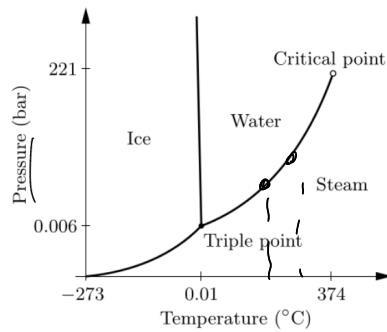
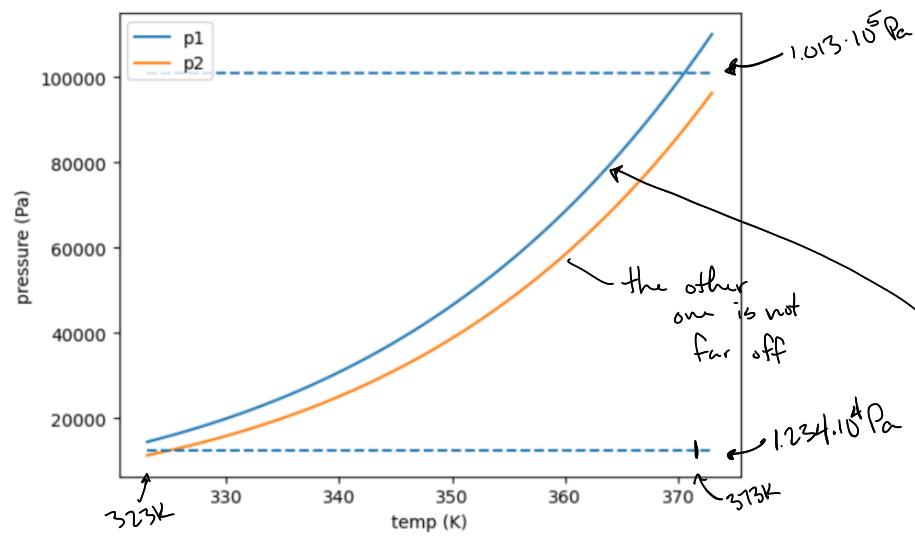
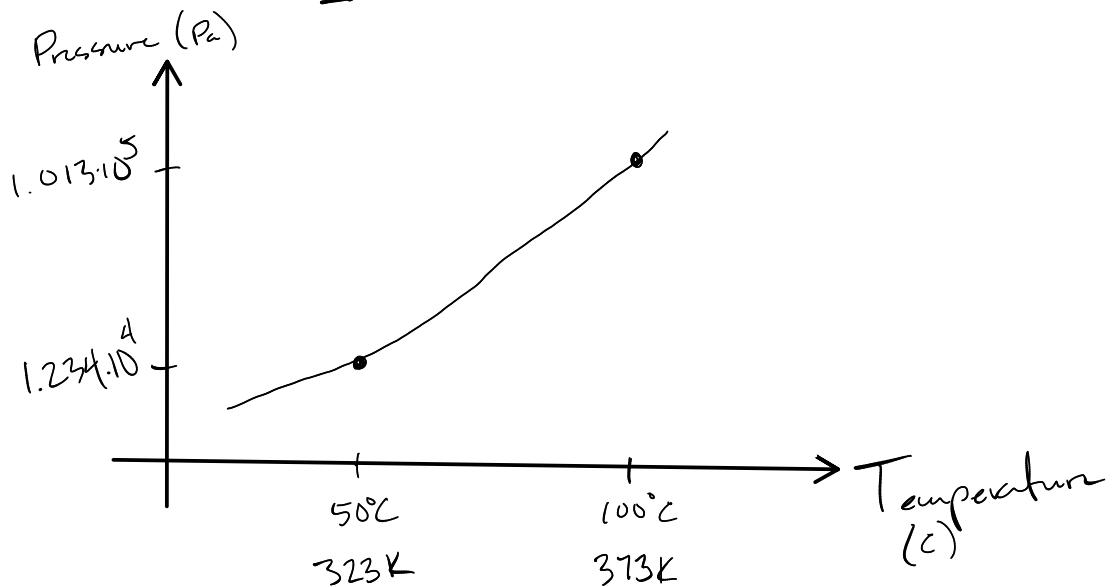
$$P = (\text{constant}) \cdot e^{-\frac{L}{RT}}$$

✓ ✓

5.36

$$P = A \cdot e^{-\frac{L}{RT}}$$

Latent Heat



T (°C)	P <sub>v</sub> (bar)	L (kJ/mol)
-40	0.00013	51.16
-20	0.00103	51.13
0	0.00611	51.07
0.01	0.00612	45.05
25	0.0317	43.99
50	0.1234	42.92
100	1.013	40.66
150	4.757	38.09
200	15.54	34.96
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300	85.84	25.30
350	165.2	16.09
374	220.6	0.00

Figure 5.11. Phase diagram for H<sub>2</sub>O (not to scale). The table gives the vapor pressure and molar latent heat for the solid-gas transformation (first three entries) and the liquid-gas transformation (remaining entries). Data from Keenan et al. (1978) and Lide (1994).

$$e^{-\frac{42920}{8.31 \cdot 373} \leftarrow 50^\circ C}$$

$$e^{1.13 \cdot 10^{-7}}$$

$$1.234 \cdot 10^4 \text{ Pa} = A_1 \cdot 1.13 \cdot 10^{-7}$$

$$A_1 = 9.94 \cdot 10^{10} \text{ Pa}$$

$$1.013 \cdot 10^5 \text{ Pa} = A_2 \cdot 2.01 \cdot 10^{-6}$$

$$A_2 = 5.48 \cdot 10^{10} \text{ Pa}$$

*almost the same number! but each was a different L*

I'll use this one  $\rightarrow P(T) = 5.48 \cdot 10^{10} e^{\frac{-40660}{8.31 \cdot T}}$

from problem 1.16, part (d) we need to find the pressure at these locations:  
 From that problem we had  $P(z) = P(0) \cdot e^{-\frac{Mgz}{RT}}$

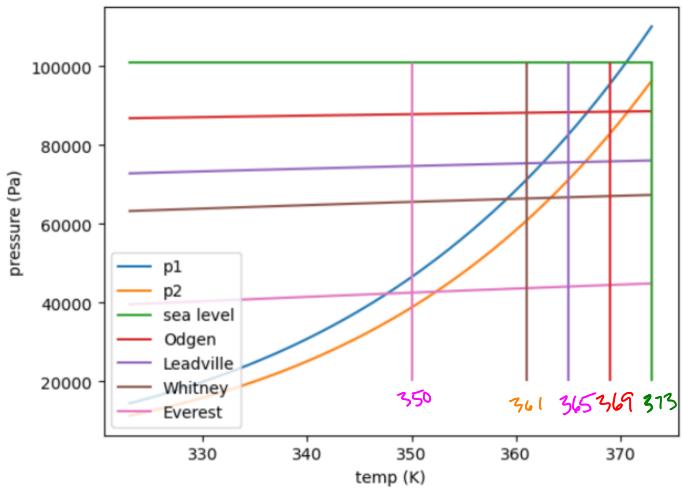
sea level  $\rightarrow 0 \text{ m} \rightarrow 373 \rightarrow 100^\circ\text{C} \leftarrow \text{not surprising}$

Odgen, UT  $\rightarrow 1430 \text{ m} \rightarrow 369 \text{ K} \rightarrow 96^\circ\text{C} \rightarrow 205^\circ\text{F}$

Leadville, CO  $\rightarrow 3090 \text{ m} \rightarrow 365 \text{ K} \rightarrow 92^\circ\text{C} \rightarrow 197.6^\circ\text{F}$

Mt Whitney  $\rightarrow 4420 \text{ m} \rightarrow 361 \text{ K} \rightarrow 88^\circ\text{C} \rightarrow 190^\circ\text{F}$

Mt Everest  $\rightarrow 8850 \text{ m} \rightarrow 358 \text{ K} \rightarrow 77^\circ\text{C} \rightarrow 170^\circ\text{F}$



$$P(z) = P(0) \cdot e^{-\frac{Mgz}{RT}} = P(0) \cdot e^{-\frac{Mgz}{RT}}$$

↑ altitude      ↑ 1 atm or  $1.01 \cdot 10^5 \text{ Pa}$

where  $m$  is the mass per mole of air. That will be  $29 \text{ g/mol} = 0.029 \text{ kg/mol}$

An easier way than estimating from the plot is plugging in the pressure.

$$T = \frac{L}{R \ln(P/P_0)} \quad \text{when } P \text{ is the pressure at each height}$$

What if we plugged in that function for  $P(z)$  above into the above function for  $T$ ?

$$T = \frac{L}{R \ln\left(e^{-\frac{Mgz}{RT}}\right)} = \frac{L}{R\left(-\frac{Mgz}{RT}\right)}$$

$$T = \frac{LT}{-Mgz}$$

$L = -\frac{L}{Mgz}$  whoops I guess that doesn't work  
nevermind

5.37

calcium aragonite at 298K

we have info from 5.28 so I should do  
that one first

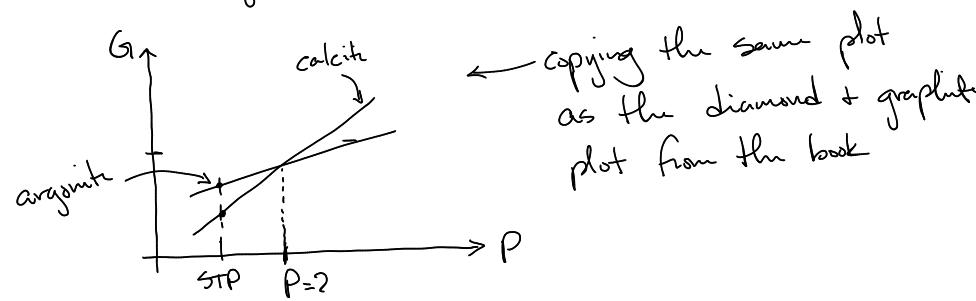
5.28 | calcite vs. aragonite

a) which is stable at STP

$$\begin{array}{ll} \text{calcite} & \text{aragonite} \\ \Delta G_f = -1128.8 \text{ kJ} & \Delta G_f = -1127.8 \text{ kJ} \end{array}$$

Similarly to what we said in class, the lower value is more stable  
so in this case w/ this data, calcite is more stable

b) calculate the pressure at which the other one is stable  
so when does aragonite become stable?



$$\left(\frac{\partial G}{\partial P}\right)_T = V \quad \text{so}$$

$$\nabla_{\text{aragonite}} = 34.15 \text{ cm}^3 \cdot \frac{(1 \text{ m})^3}{(100 \text{ cm})^3} = 34.15 \cdot 10^{-6} \text{ m}^3$$

$$\nabla_{\text{calcite}} = 36.93 \text{ cm}^3$$

Slope of calcite is  
higher so at some  
point they will meet.

point slope form for a line

$$y - y_0 = m(x - x_0)$$

$$\rightarrow G - G_0 = \frac{\partial G}{\partial P} (P - P_0)$$

for calcite:

$$G_c + 1.1288 \cdot 10^6 = 36.93 \cdot 10^{-6} (P - 10^5)$$

for aragonite:

$$G_a + 1.1278 \cdot 10^6 = 34.15 \cdot 10^{-6} (P - 10^5)$$

$$\begin{aligned} \text{so... } G_a &= G_c \rightarrow \text{then solve for } P \\ 34.15 \cdot 10^{-6} (P - 10^5) - 1.1278 \cdot 10^6 + 1.1288 \cdot 10^6 &= 36.93 \cdot 10^{-6} (P - 10^5) \\ (34.15 \cdot 10^{-6} - 36.93 \cdot 10^{-6}) P &= 36.93 \cdot 10^{-6} (-10^5) \\ &\quad + 34.15 \cdot 10^{-6} (10^5) \end{aligned}$$

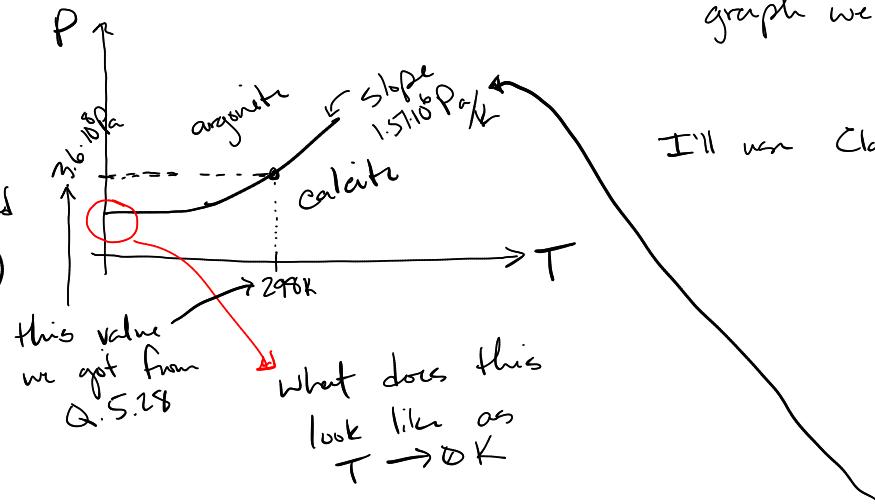
$$\begin{aligned} P &= \frac{-3.693 + 3.415 - 1 \cdot 10^3}{(34.15 - 36.93) \cdot 10^{-6}} \\ P &= \frac{-10^3 \cdot 10^6}{-2.78} = 3.60 \cdot 10^5 \text{ Pa} \end{aligned}$$

OK so now I'm ready to go back to 5.37 ↗

This Q is asking about the phase boundary, so I'll be looking at P vs T, since that is the kind of graph we have been

(as pressure increases)

we go from calcite to aragonite. this is what we learned by doing Q 5.28)



$$\frac{dP}{dT} = \frac{\Delta S}{\Delta V}$$

this should be getting closer to zero, as the temperature nears 0K.

so the slope should level out.

I'll use Clapeyron to do this

$$\frac{dP}{dT} = \frac{\Delta S}{\Delta V} \quad \text{from one phase to another}$$

=  $\frac{88.7 - 92.9}{(34.15 - 36.93)} \cdot 10^6$  Pa/K

from the back of the book  
Change units from  $\text{cm}^3$  to  $\text{m}^3$

↑ aragonite      ↓ calcite

$$\frac{dP}{dT} = 1.51 \cdot 10^6 \text{ Pa/K}$$

5.48

$$\left(P + \frac{aN^2}{V^2}\right)(V - Nb) = Nk_B T$$

solve for P  $\rightarrow P = \frac{Nk_B T}{V - Nb} - \frac{aN^2}{V^2}$   $\nwarrow$  1<sup>st</sup> + 2<sup>nd</sup> derivative are zero

$$\frac{dP}{dV} = (-1) \frac{Nk_B T}{(V - Nb)^2} - (-2) \frac{aN^2}{V^3} = -\frac{Nk_B T}{(V - Nb)^2} + \frac{2aN^2}{V^3} \quad \text{when } P = P_c + V = V_c + T = T_c$$

$$\frac{d^2P}{dV^2} = (-2) \left(-\frac{Nk_B T}{(V - Nb)^3}\right) + (-3) \cdot \frac{2aN^2}{V^4} = \frac{2Nk_B T}{(V - Nb)^3} - \frac{6aN^2}{V^4}$$

| then these equations are equal to zero

First we have two equations; solve for  $T_c$ , then plug in to solve for  $V_c$ , then  
reconstruct to find  $T_c$

$$\textcircled{1} \quad -\frac{Nk_B T_c}{(V_c - Nb)^2} + \frac{2aN^2}{V_c^3} = 0$$

$$\textcircled{2} \quad \frac{2Nk_B T_c}{(V_c - Nb)^3} - \frac{6aN^2}{V_c^4} = 0$$

$$(V_c - Nb)^2 \frac{2aN^2}{V_c^3} = Nk_B T_c$$

$$\frac{2N}{(V_c - Nb)^3} \cancel{(V_c - Nb)^2} \frac{2aN^2}{V_c^3} = \frac{\cancel{6aN^2}}{V_c^4}$$

$$(3Nb - Nb)^2 \frac{2aN}{(3Nb)^3} = k_B T_c$$

$$\frac{2}{V_c - Nb} = \frac{3}{V_c}$$

$$2V_c = 3V_c - 3Nb$$

$$\boxed{V_c = 3Nb} \quad \checkmark$$

$$\frac{(2Nb)^2 \cdot 2aN}{(3Nb)^3} = k_B T_c$$

then both of these go back into the original van der Waals formula

$$\frac{4N^2 b^2 \cdot 2aN}{27N^3 b^3} =$$

$$\boxed{\frac{8a}{27b} = k_B T_c}$$

$$P_c = \frac{Nk_B T_c}{V_c - Nb} - \frac{aN^2}{V_c^2}$$

$$P_c = \frac{N}{3Nb - Nb} \cdot \left(\frac{8a}{27b}\right) - \frac{aN^2}{(3Nb)^2}$$

$$P_c = \frac{4 \frac{8a}{27b}}{2b \cdot 27b} - \frac{a}{9b^2} \left(\frac{3}{3}\right)$$

to get a common denominator

$$P_c = \frac{4a - 3a}{27b^2}$$

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

5.51 Rewrite van der Waals, in terms of the critical temperatures

$$P = \frac{Nk_B T}{V - Nb} - \frac{aN^2}{V^2}$$

So rather than  $T$  in the equation, I want to write  $\frac{T}{T_c}$  and so on w/ the other quantities, then I want to simplify. I actually start w/  $\frac{V}{V_c}$ . That would be equal to  $\frac{V}{3Nb}$ . So ↴

$$P = \frac{Nk_B T}{\frac{V}{V_c} \cdot 3Nb - Nb} + \frac{aN^2}{\left(\frac{V}{V_c} \cdot 3Nb\right)^2}$$

$\frac{3Nb}{V_c}$

$$P = \frac{Nk_B T}{\frac{V}{V_c} \cdot 3Nb - Nb} + \frac{aN^2}{\left(\frac{V}{V_c} \cdot 3Nb\right)^2}$$

$$= \frac{k_B T}{\left(\frac{3V}{V_c} - 1\right) \cdot b} + \frac{a}{\left(\frac{V}{V_c}\right)^2 \cdot 9b^2}$$

Next, we will substitute for

$$k_B T \cdot k_B T_c = \frac{8a}{27b} \text{ so}$$

multiply & divide by that  
in the numerator of the first term

$$= \frac{k_B T}{\left(\frac{3V}{V_c} - 1\right) b} \cdot \frac{8a}{27b} \cdot \frac{27b}{8a} + \frac{a}{\left(\frac{V}{V_c}\right)^2 \cdot 9b^2}$$

$= \frac{1}{k_B T_c}$

$$= \frac{k_B T}{\left(\frac{3V}{V_c} - 1\right) b} \cdot \frac{8a}{27b} \cdot \frac{1}{k_B T_c} + \frac{a}{\left(\frac{V}{V_c}\right)^2 \cdot 9b^2}$$

$$P = \frac{T/T_c}{\frac{3V}{V_c} - 1} \cdot \frac{8a}{27b^2} + \frac{a}{\left(\frac{V}{V_c}\right)^2 \cdot 9b^2}$$

OK. Now we want to see  $P_c = \frac{a}{27b^2}$

if I multiply here

$$P = \frac{T/T_c}{\frac{3V}{V_c} - 1} \cdot \frac{8a}{27b^2} + \frac{a}{\left(\frac{V}{V_c}\right)^2 \cdot 9b^2} \left( \frac{3}{3} \right)$$

$$P = \frac{8T/T_c}{\frac{3V}{V_c} - 1} \cdot \frac{a}{27b^2} + \frac{1}{\left(\frac{V}{V_c}\right)^2} \cdot \frac{a}{27b^2}$$

$= P_c$

so  
divide both  
sides by  $P_c$

$$\boxed{\frac{P}{P_c} = \frac{8T/T_c}{\frac{3V}{V_c} - 1} + \frac{1}{\left(\frac{V}{V_c}\right)^2}}$$

and now  $a + b$  have disappeared!

But now! I want to write the Gibbs Free Energy in terms of these reduced variables. To do this. Use the transformations, that we derived in problem 5.48.

$$V_c = 3Nb, T_c = \frac{8a}{27b}, \text{ and } P_c = \frac{a}{27b^2}$$

So, from the notes we had

$$G = -Nk_B T \ln(V - Nb) + \frac{Nk_B T (Nb)}{V - Nb} - \frac{2aN^2}{V} + C(T)$$

↑ an interaction constant which is a function of  $T$ , but which we may ignore

First I'm going to divide both sides by  $Nk_B T_c$ .

$$\frac{G}{Nk_B T_c} = -\frac{T}{T_c} \ln(V - Nb) + \frac{T/T_c (Nb)}{V - Nb} - \frac{2aN^2}{V N k_B T_c}$$

Next, I know that  $V_c = 3Nb$ , so I will substitute  $Nb = \frac{V_c}{3}$ , and then do some algebra

$$\frac{G}{Nk_B T_c} = -\frac{T}{T_c} \ln\left(V - \frac{V_c}{3}\right) + \frac{T/T_c \cdot \frac{V_c}{3}}{V - \frac{V_c}{3}} - \frac{2aN}{V k_B T_c} \begin{pmatrix} V \\ b \\ b \end{pmatrix}$$

RECALL:

$$\frac{8a}{27b} = k_B T_c$$

$$\frac{G}{Nk_B T_c} = -\frac{T}{T_c} \ln\left(\frac{3}{V_c} \cdot \frac{V_c}{3} \left(V - \frac{V_c}{3}\right)\right) + \frac{T/T_c}{\left(V - \frac{V_c}{3}\right) \left(\frac{3}{V_c}\right)} - \frac{2 \left( \frac{a}{V_c k_B T_c \cdot b} \right)}{3}$$

so,  $\frac{a}{k_B T_c b} = \frac{27}{8}$   
and apply here

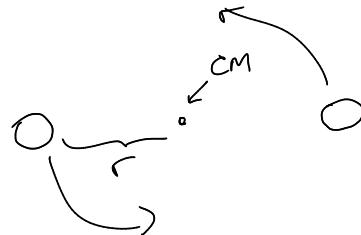
$$\frac{G}{Nk_B T_c} = -\frac{1}{T_c} \underbrace{\ln\left(\frac{V_c}{3} \cdot \left(\frac{3V}{V_c} - 1\right)\right)}_{= \ln \frac{V_c}{3} + \ln\left(\frac{3V}{V_c} - 1\right)} + \frac{T/T_c}{\frac{3V}{V_c} - 1} - \frac{2}{3V} \cdot \frac{2T}{84}^q$$

this is  
a constant  
so I will  
lump it in w/  
the C(T) that  
we will ignore

$$\frac{G}{Nk_B T_c} = -\frac{1}{T_c} \ln\left(\frac{3V}{V_c} - 1\right) + \frac{T/T_c}{\frac{3V}{V_c} - 1} - \frac{9}{4V} + \text{some constant stuff we can ignore}$$

5.52] check my pdf of this problem done in Jupyter, posted in Canvas.

1.55



$$U_g = -2K$$

$$\langle K \rangle = \frac{3}{2} k_B T$$

$$K = \frac{3}{2} N k_B T$$

$$U_g = -2K \Rightarrow K = \frac{U_g}{-2}$$

$$U_g = -3N k_B T$$

$$\begin{aligned} \uparrow \text{Total Energy} &= K + U_g = K - 2K \\ &= \frac{3}{2} N k_B T - \frac{6}{2} N k_B T \end{aligned}$$

the only way to add energy is for the total kinetic to decrease, which increases the total potential by more.

$$\text{Total Energy} = -\frac{3}{2} N k_B T$$

$$d) -k \frac{GM^2}{R}$$

$$F = \frac{G m_1 m_2}{r^2}$$

$$G = \left[ \frac{\text{distance}^2}{\text{mass}^2} \cdot \text{force} \right]$$

$$\left[ \frac{\text{distance}^2}{\text{mass}^2} \cdot \text{force} \right] \cdot \frac{[\text{mass}]^2}{\text{distance}}$$

$$[\text{force} \cdot \text{distance}] = [\text{energy}] ?$$

$$e) -\frac{3}{2} N k_B T = -\frac{U_g}{2} + U_g$$

$$-3N k_B T = U_g = \frac{GM^2}{R}$$

goofy  
↓  
 $N = 10^{51}$

$$T = \frac{GM^2}{R} \cdot \frac{1}{3N k_B}$$

$$\sim T = 9.1 \cdot 10^6 \text{ K} \sim$$

5.14

$$\left(\frac{\partial p}{\partial S}\right)_V = - \left(\frac{\partial T}{\partial V}\right)_S \quad a)$$

$$\left(\frac{\partial T}{\partial p}\right)_S = \left(\frac{\partial V}{\partial S}\right)_p$$

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V$$

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

Maxwell relations





