

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

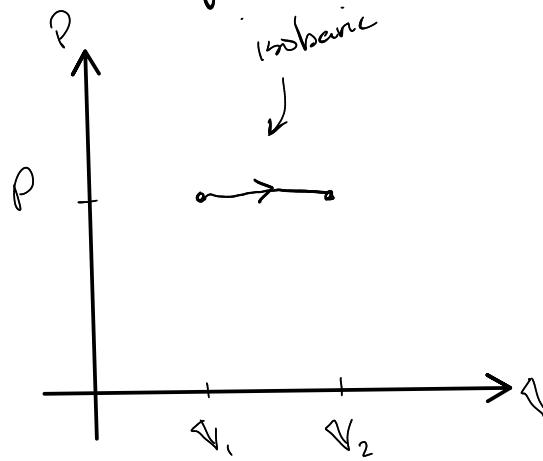
Gibbs Free Energy

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

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

$$F = U - TS$$

Enthalpy



#134

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

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

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

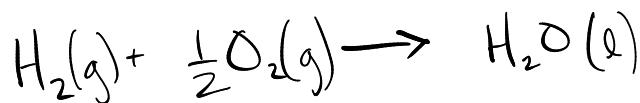
$$Q = \frac{f}{2} P(V_2 - V_1) + P(V_2 - V_1)$$

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

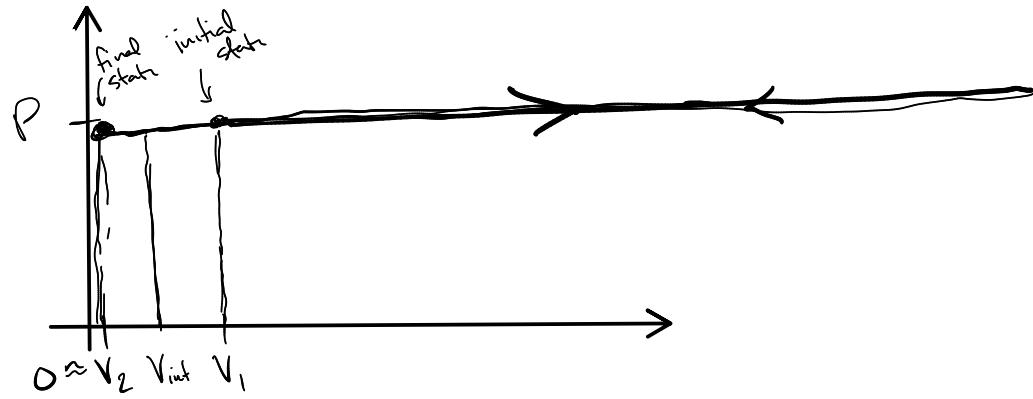
$$H \equiv U + PV$$

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

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 -

$$= \Delta P \cdot \Delta V$$

- 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

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

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

So what total work has been done?

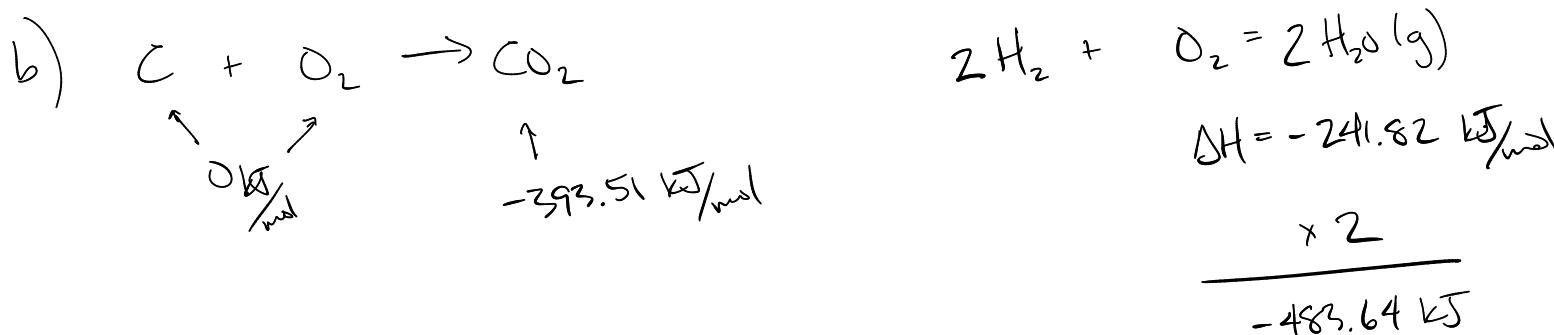
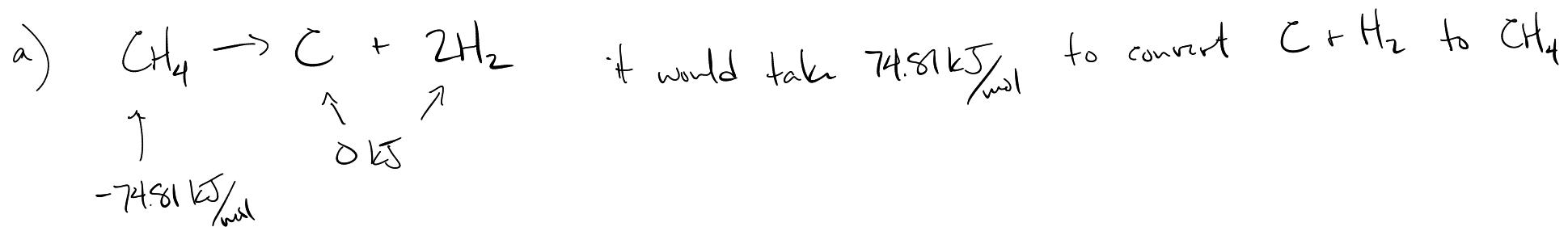
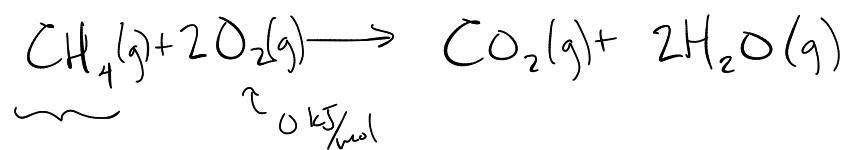
$$W = - \int_{0.0248 \text{ m}^3}^{0 \text{ m}^3} P dV = -10^5 \text{ Pa} (0 - 0.037 \text{ m}^3) \\ = 3700 \text{ J} = 3.7 \text{ kJ}$$

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

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

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

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 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 ΔG_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 ΔS 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)



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

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

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

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

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

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

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?

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

products

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

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

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

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

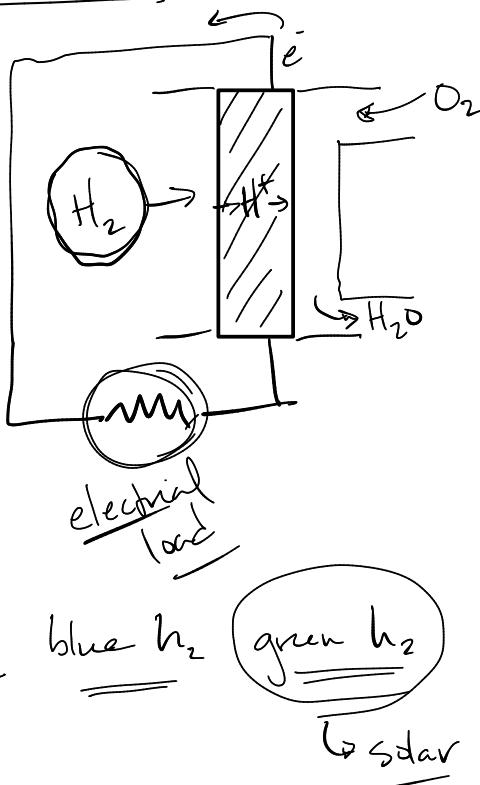
$$\Delta G = \Delta H - T \Delta S$$

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

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 = $\frac{\text{get}}{\text{pay for}}$

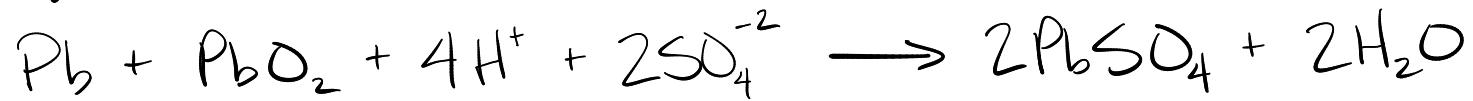
$$\frac{237 \text{ kJ}}{286 \text{ kJ}} = \underline{\underline{83\%}}$$

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

ΔG is more than the ΔH . 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

$2 e^-$

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°C (298K)

Gibbs at 30°C ? (303K) -

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

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

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

$$f(x,y)$$

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

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

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

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

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

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

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

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

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

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

Now do for Gibbs

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

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

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

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

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

5.2 | Free Energy as a Force toward Equilibrium

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

rewrite in
terms of system's
variables

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

$$dV_e = 0$$

$$dN = 0$$

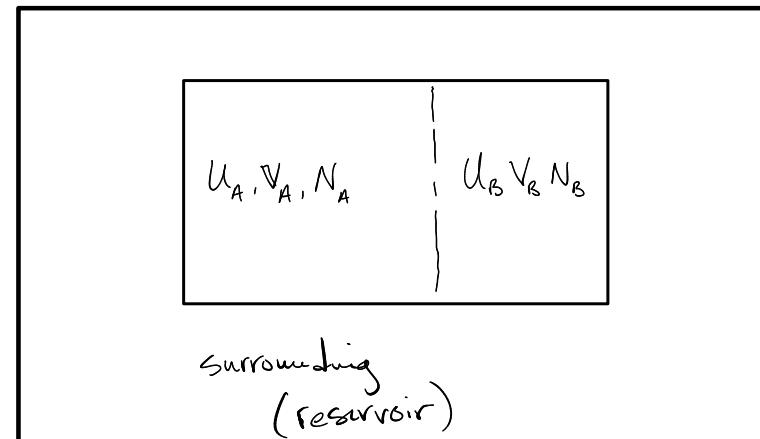
$$dU = -dU_R \leftarrow \text{energy is conserved}$$

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

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

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

Helmholtz! δF



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

↑ ↓
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 Δ change?

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

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

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

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

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

Δ 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° is $k_B T$?

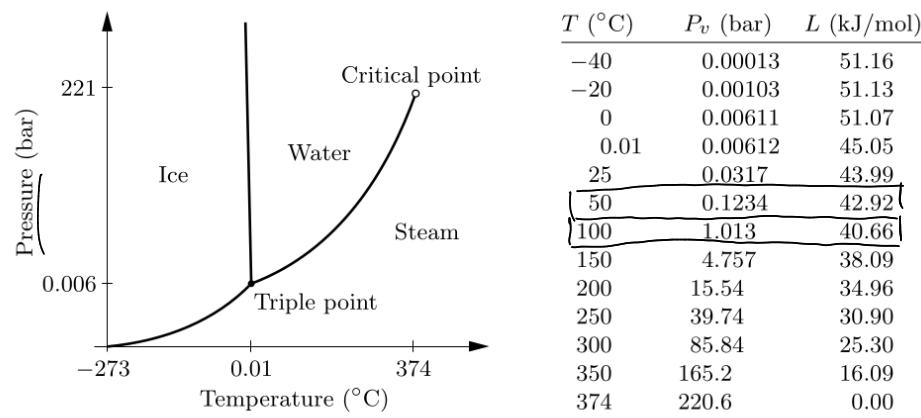


Figure 5.11. Phase diagram for H_2O (not to scale). The table gives the vapor pressure and molar latent heat for the solid-gas transformation (first three entries) and the liquid-gas transformation (remaining entries). Data from Keenan et al. (1978) and Lide (1994).

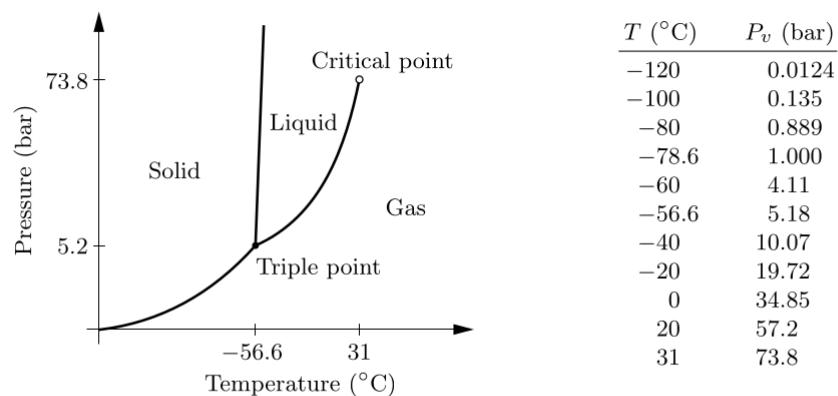


Figure 5.12. Phase diagram for carbon dioxide (not to scale). The table gives the vapor pressure along the solid-gas and liquid-gas equilibrium curves. Data from Lide (1994) and Reynolds (1979).

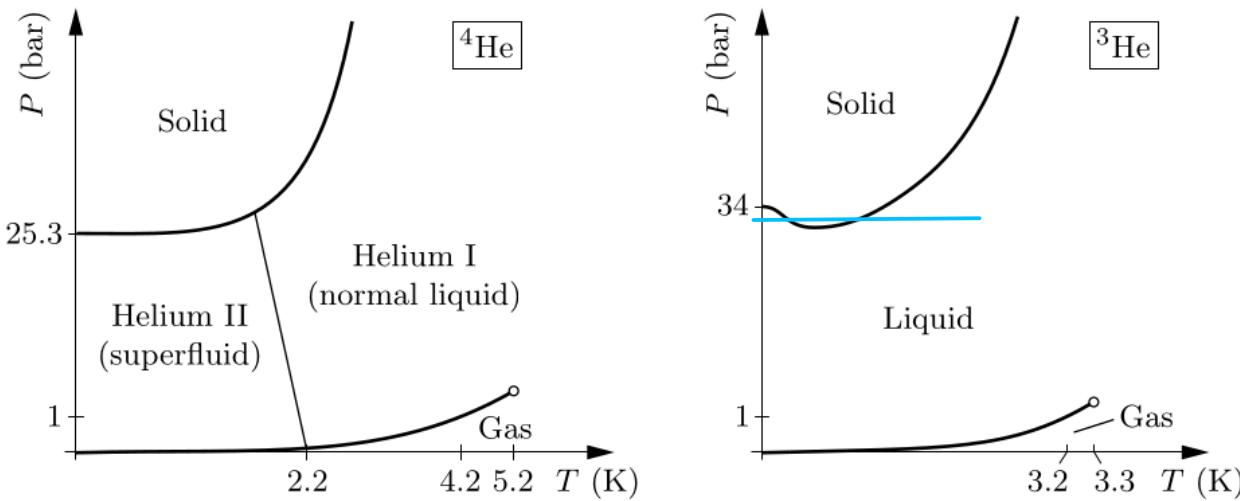


Figure 5.13. Phase diagrams of ^4He (left) and ^3He (right). Neither diagram is to scale, but qualitative relations between the diagrams are shown correctly. Not shown are the three different solid phases (crystal structures) of each isotope, or the superfluid phases of ^3He below 3 mK.

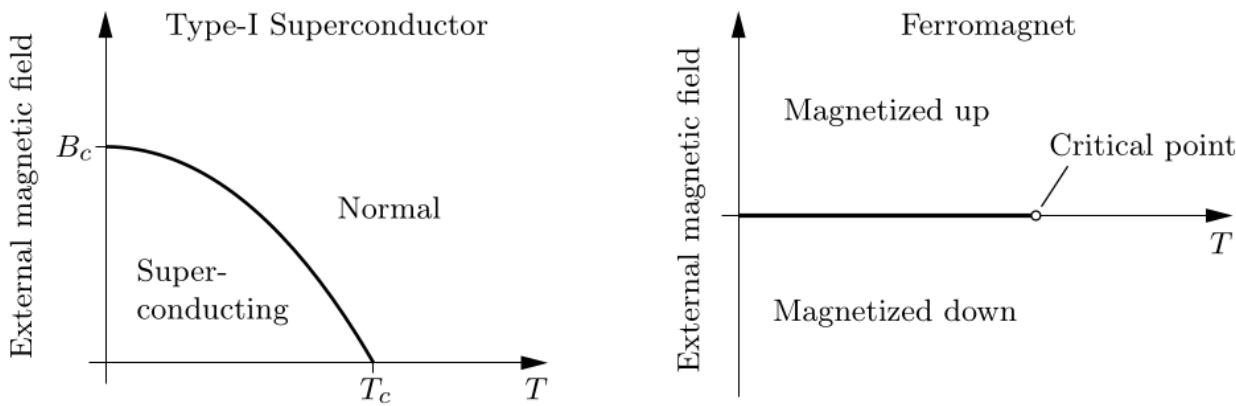


Figure 5.14. Left: Phase diagram for a typical type-I superconductor. For lead, $T_c = 7.2$ K and $B_c = 0.08$ T. Right: Phase diagram for a ferromagnet, assuming that the applied field and magnetization are always along a given axis.

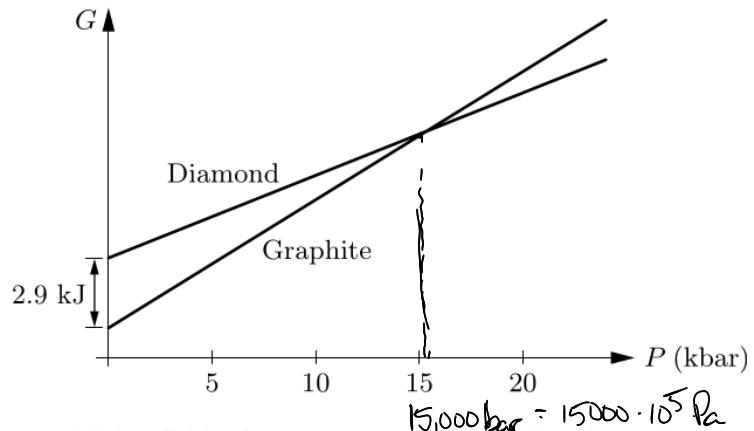


Figure 5.15. Molar Gibbs free energies of diamond and graphite as functions of pressure, at room temperature. These straight-line graphs are extrapolated from low pressures, neglecting the changes in volume as pressure increases.

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

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

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

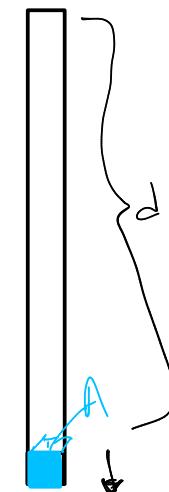
Temperature dependence follows entropy

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

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

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

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



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

$$\begin{aligned} \rho_{\text{H}_2\text{O}} &= 1 \text{ g/mL} \\ &= 1000 \text{ kg/m}^3 \end{aligned}$$

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

$$\begin{aligned} P &= \text{frack} \cdot g \cdot d \\ d &= \frac{P}{\rho \cdot g} \end{aligned}$$

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,

$$dG_e = dG_g$$

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

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

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

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

Latent Heat
(Enthalpy)

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

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

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

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

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

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

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

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

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

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

$$dU = -P dV$$

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

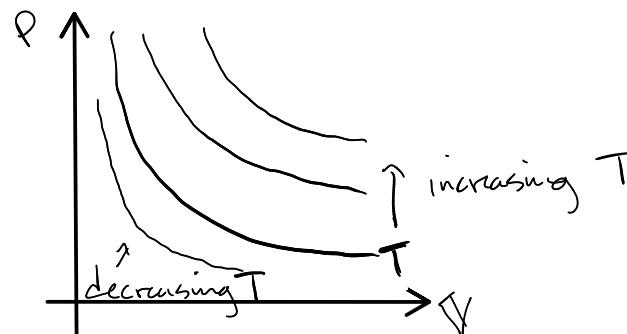
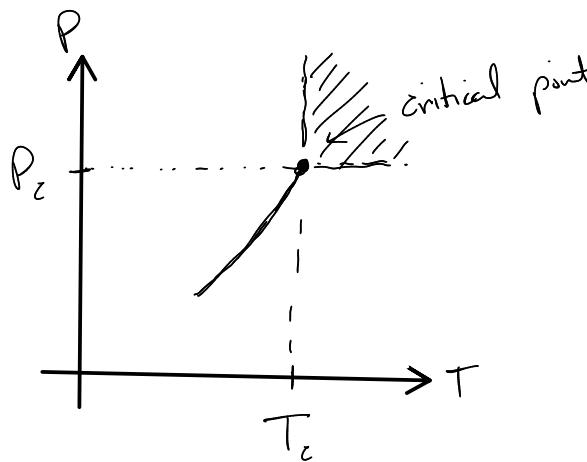
$b \sim$ volume of a molecule

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

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

Plot in reduced units.

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



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

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

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

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

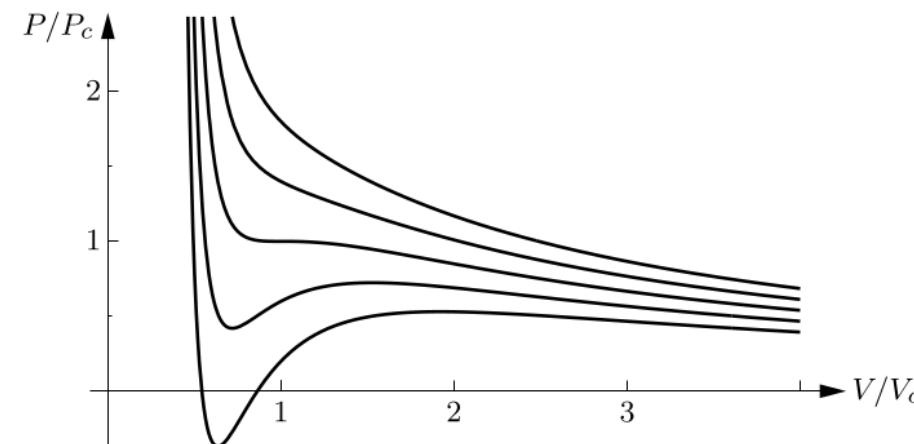


Figure 5.20. Isotherms (lines of constant temperature) for a van der Waals fluid. From bottom to top, the lines are for 0.8, 0.9, 1.0, 1.1, and 1.2 times T_c , the temperature at the critical point. The axes are labeled in units of the pressure and volume at the critical point; in these units the minimum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

Calculate the Gibbs free energy 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

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

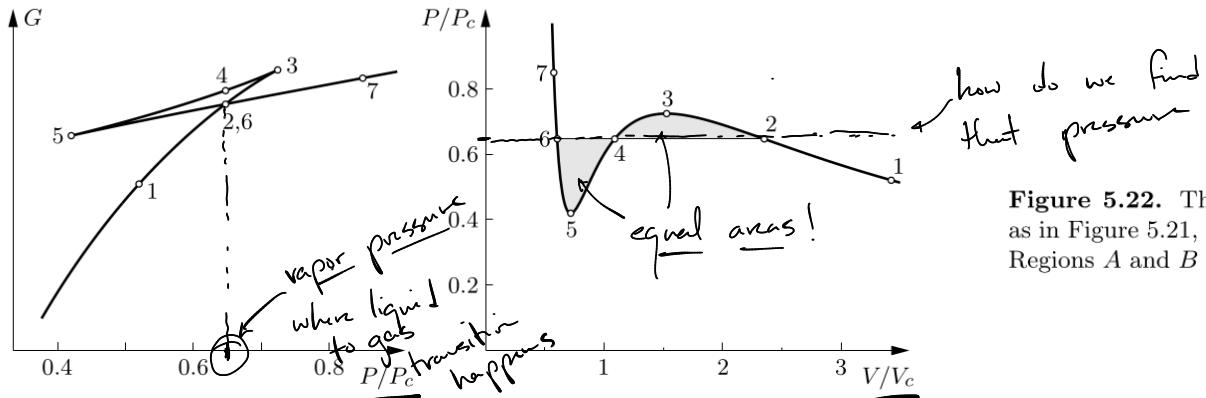


Figure 5.21. Gibbs free energy as a function of pressure for a van der Waals fluid at $T = 0.9T_c$. The corresponding isotherm is shown at right. States in the range 2-3-4-5-6 are unstable.

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

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

$$\int V dP = 0$$

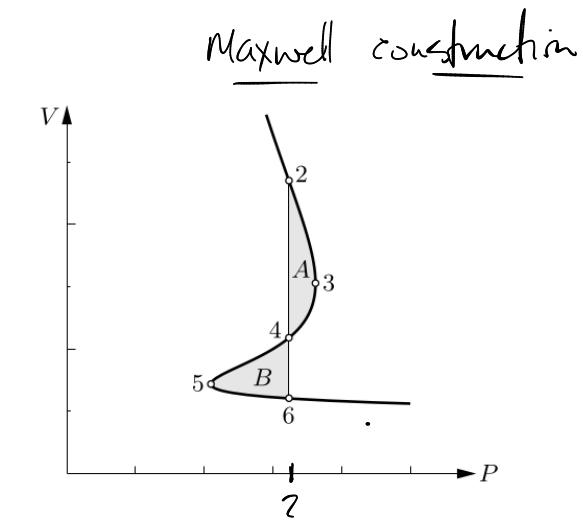
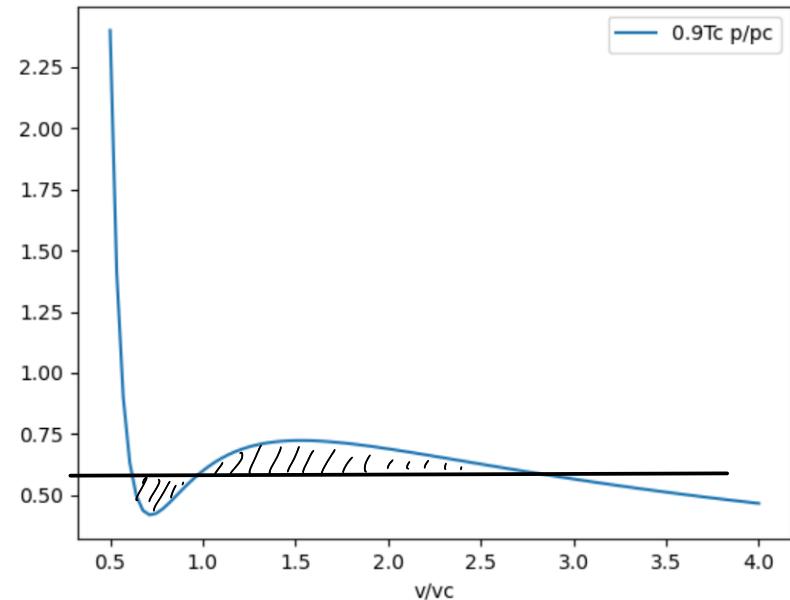


Figure 5.22. The same isotherm as in Figure 5.21, plotted sideways. Regions A and B have equal areas.



5.32

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

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 ΔV is negative.

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

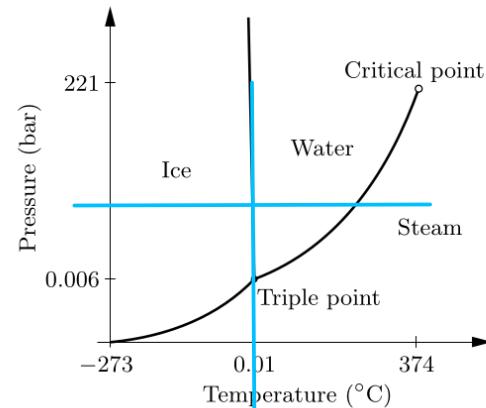
Perhaps a better way to think about this is as the pressure increases, the temperature necessarily decreases, which is counterintuitive because water is special. As it freezes, it forms bonds that cause the structure to occupy a larger form than it does as a liquid. Most things do this but their crystalline 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 _v (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 H₂O (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 H₂O at 298 K
↑ ↑
273 K
-1 K
 ∇ of 1 mole of ice?

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

$$\frac{\Delta P}{\Delta T} = \frac{3.33 \cdot 10^5 \text{ J/kg}}{273 \text{ K} \cdot (1.8 \cdot 10^{-5} - 1.96 \cdot 10^{-5}) \text{ m}^3} = M = 18 \text{ g/mole}$$

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

∇ is larger for ice
 $\rho_{\text{water}} = 1000 \text{ kg/m}^3$
 $\nabla = 0.018 \text{ kg} = 1.8 \cdot 10^{-5} \text{ m}^{-3}$
 1000 kg/m^3

d) $m = 70 \text{ kg}$
 $A_{\text{skate}} \approx 5 \text{ cm}^2$? 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 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_{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_{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

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

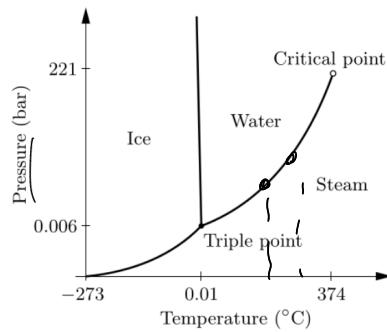
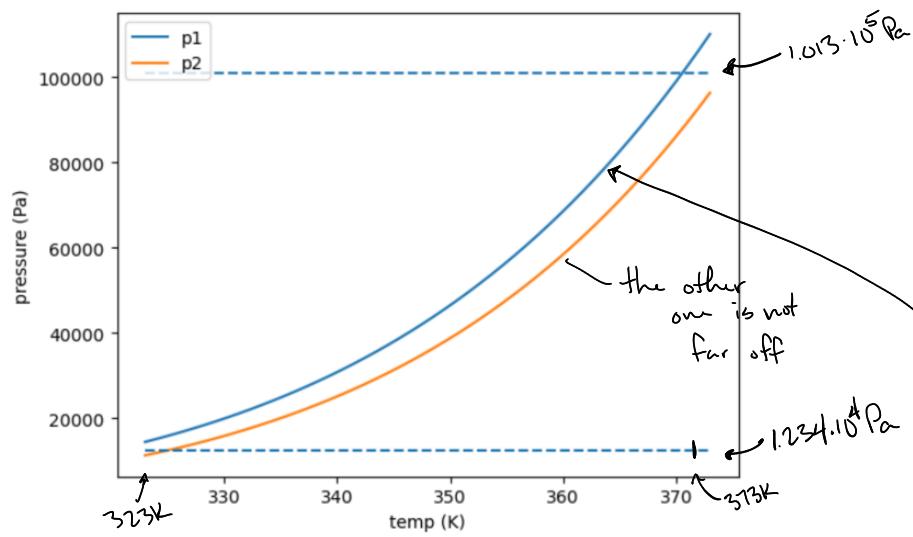
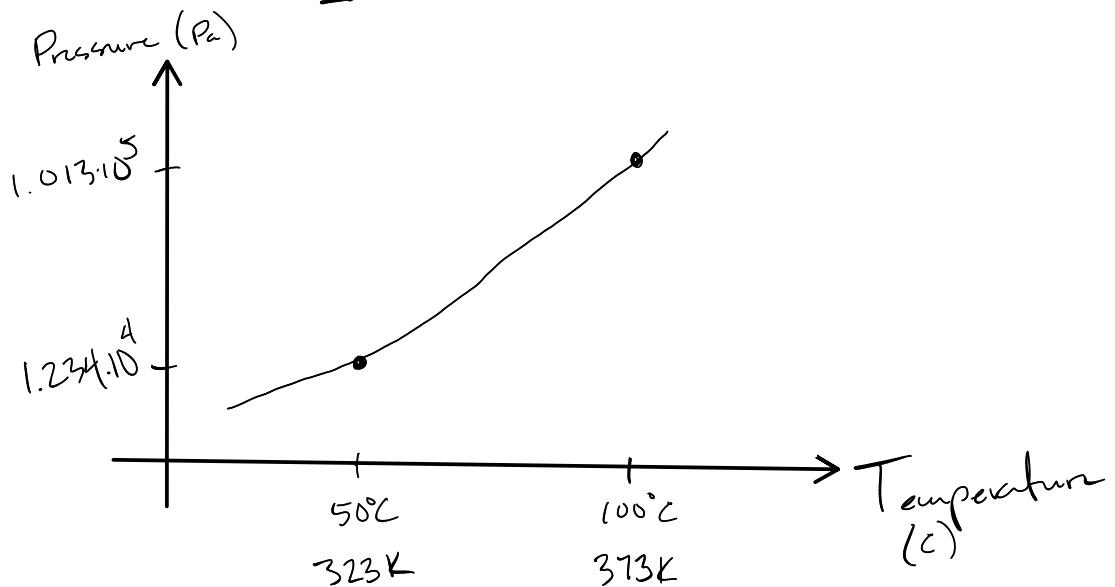
✓ ✓

5.36

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

Latent Heat

\equiv



T (°C)	P _v (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 H₂O (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).

$$e^{-\frac{42920}{831.3}} \leftarrow 50^\circ C$$

$$e^{-\frac{40660}{831.373}} \leftarrow 100^\circ C$$

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

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

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

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

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

almost the same number!
but each was a different L

I'll use this one $\rightarrow P(T) = 5.48 \cdot 10^{10} e^{-\frac{40660}{831 \cdot T}}$

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

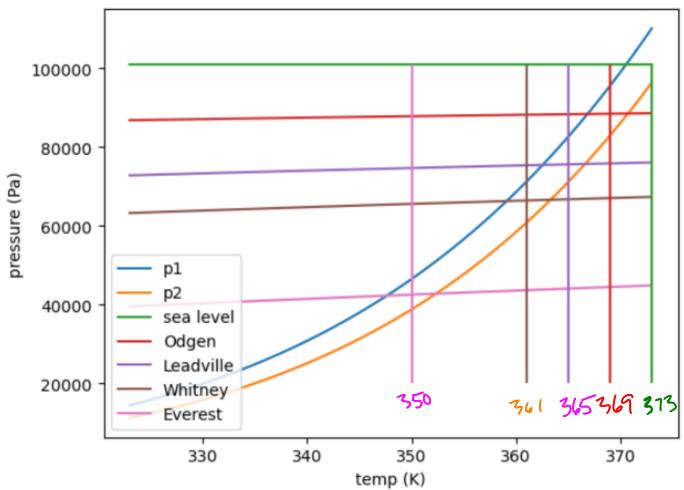
sea level $\rightarrow 0 \text{ m} \rightarrow 373 \rightarrow 100^\circ\text{C} \leftarrow \text{not surprising}$

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

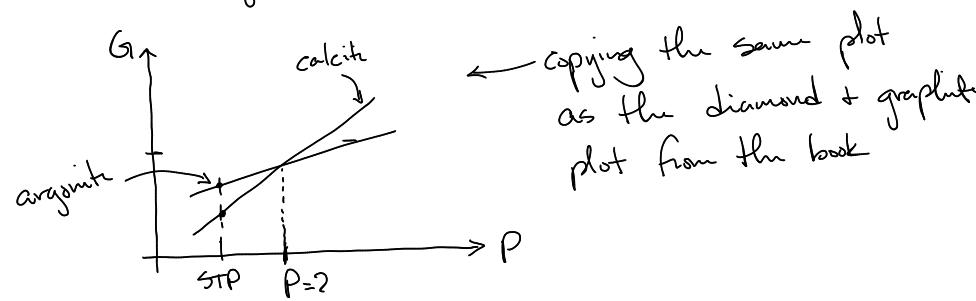
5.28 | calcite vs. aragonite

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?



$$\left(\frac{dG}{dP}\right)_T = V \quad \text{so}$$

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

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

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

point slope form for a line

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

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

for calcite:

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

for aragonite:

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

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

-1

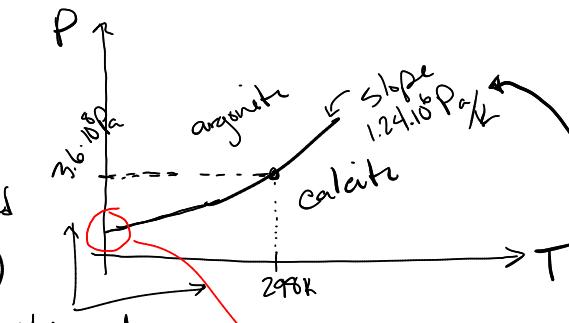
$$\begin{aligned} P &= \frac{-3.693 + 3.415 - 1 \cdot 10^3}{(34.15 - 36.93) \cdot 10^{-6}} \\ P &= \frac{-10^3 \cdot 10^6}{-2.78} = 3.60 \cdot 10^5 \text{ Pa} \end{aligned}$$

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)



this value
we got from
Q.5.28

what does this
look like as
the T goes to
OK? OR as it
gets higher?

I'll use Clapeyron to do this

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

$$= \frac{88.7 - 92.2}{(34.15 - 36.93) \cdot 10^{-6}}$$

→ Change units
from cm^3 to m^3

↑
aragonite
calcite

$$\frac{dP}{dT} = 1.24 \cdot 10^6 \text{ Pa/K}$$

