

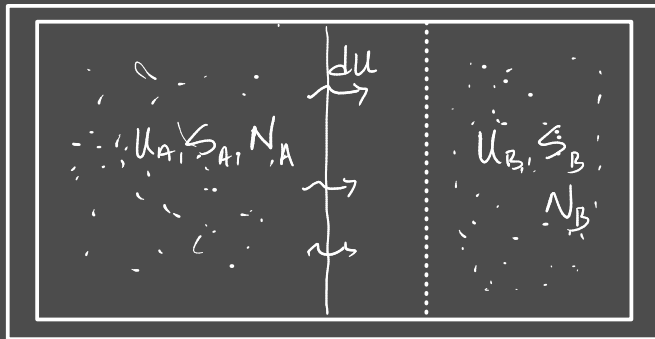
Chapter 5 - Free energy and chemical thermodynamics

↳ available

Goal: Apply laws of thermodynamics to non-cyclic processes like chemical reactions, phase changes, and other transformations.

Previously:

$$\rightarrow dU = TdS - pdV + \mu dN$$



total U was fixed
total V was fixed
total N was fixed

What if T is fixed but not U ?

What if p is fixed but not V ?

Constant T + Constant p processes

(u)
Enthalpy - energy plus the work to make room for a system under constant pressure from the surroundings

$$H \equiv U + pV$$

Helmholtz Free Energy \rightarrow total energy to create a system
minus the heat you can extract
from the surroundings at constant T .

$$F \equiv U - TS$$

\hookrightarrow all work done on the system
by us and the surroundings.

Gibbs Free Energy

$$G \equiv U - TS + pV$$

$$G = H - TS$$

$U, H, F, G \rightarrow$ thermodynamic potentials

What about changes in $F + G$?

$$dF = dU - TdS$$

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

for a reversible process

$$\pm Q_{\text{rev}} = T \cdot dS$$

$$dF = \cancel{TdS} + \pm W - \cancel{TdS}$$

$$dF = \pm W$$

↳ amount of work done on the system

otherwise,

$$dF \leq \pm W$$

$$dG = dU - TdS + p dV$$

$$= \pm Q + \pm W - \cancel{TdS} + \cancel{p dV}$$

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

$$\pm W = \cancel{-p dV} + \pm W_{\text{other}}$$

↳ electrical, etc.

$$dG = \pm W_{\text{other}} \quad \text{at constant } T, p$$

ΔG is very useful, how is it measured.

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

↓
Then calculate ΔS from initial and final states.

$$S_{\text{react}} = \int_0^{T_f} \frac{C_p}{T} dT \quad \swarrow \text{react}$$

$$S_{\text{prod}} = \int_0^{T_f} \frac{C_p}{T} dT \quad \swarrow \text{product}$$

$$\Delta S = S_{\text{prod}} - S_{\text{react}}$$

Then $\underline{\Delta G} = \Delta H - T \cdot \Delta S$

Problem 5.2

Calculate ΔG , from ΔH & S .

$$T = 298 \text{ K}$$

$$p = 1 \text{ bar} = 10^5 \text{ Pa} \approx 1 \text{ atm} = 1.013 \cdot 10^5 \text{ Pa}$$



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

$$\begin{aligned} \Delta H &= 0 \text{ kJ} \\ S &= 191.61 \text{ J/Kmol} \end{aligned}$$

$$\begin{aligned} \Delta H &= 0 \text{ kJ} \\ S &= 130.68 \text{ J/Kmol} \end{aligned}$$

$$\begin{aligned} \Delta H &= -46.11 \text{ kJ/mol} \\ S &= 192.45 \text{ J/Kmol} \end{aligned}$$

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

$$\Delta S = S_{\text{prod}} - S_{\text{react}} = 2 \text{ mol} \cdot 192.45 \text{ J/Kmol} - 191.61 \text{ J/Kmol} - 3 \text{ mol} \cdot 130.68 \text{ J/Kmol}$$

$$\Delta S = -198.75 \text{ J/K}$$

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

$$= \underline{-92.22 \text{ kJ}} - (298 \text{ K})(\underline{-198.75 \text{ J/K}})$$

+ 59.23 kJ

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

the energy
out of the
system

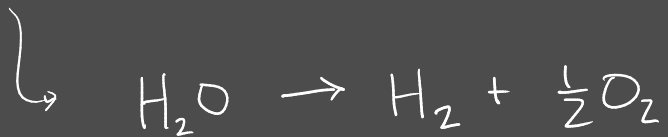
Compare to: ΔG_{NH_3}

$$\rightarrow -16.45 \text{ kJ/mol} \times 2 \text{ mol} =$$

$$\boxed{-32.9 \text{ kJ}}$$

back tabulated
value

Electrolysis, Fuel Cells, Batteries



How much electrical work?

$$\Delta H = \underline{286 \text{ kJ}} \rightarrow \begin{array}{l} \text{heat out to run} \\ \text{in reverse} \end{array}$$

\rightarrow to push atmosphere away

$$p\Delta V = \underline{\Delta n \cdot R \cdot T} = 1.5 \text{ mol} (8.31 \text{ J/Kmol}) (300 \text{ K})$$
$$= \underline{\underline{3.7 \text{ kJ}}} \sim 4 \text{ kJ}$$

\rightarrow 282 kJ will remain in the system in the form of potential energy

\rightarrow do we need to do all of this work?
heat from the environment?

What is the change in entropy for this system?

$$S_{H_2O} = 70 \text{ J/K} \quad S_{H_2} = 131 \text{ J/K} \quad S_{O_2} = 205 \text{ J/K}$$

$$\underbrace{\hspace{10em}}_{\text{products}} \quad \begin{array}{c} \downarrow H_2 \\ \downarrow \frac{1}{2} O_2 \end{array}$$
$$S_{\text{prod}} = 131 \text{ J/K} + \frac{1}{2} \cdot 205 \text{ J/K} = 233.5 \text{ J/K}$$

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

entropy increase
so the most heat that
can enter the system
will be

$$\Delta Q \leq T \Delta S$$

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

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

So of the 286 kJ that go in, 48.7 kJ come from heat from surroundings.
 $286 \text{ kJ} - 48.7 \text{ kJ} = \underline{237.3 \text{ kJ}} \rightarrow$ come from electrical work
matches ΔG from the book

In reverse, we can extract 237 kJ of electrical work!

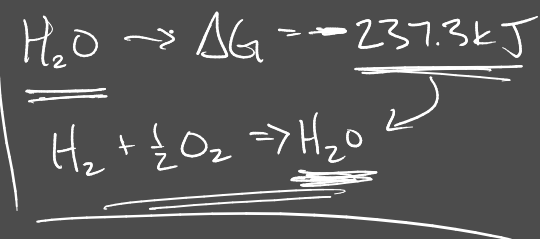
→ 49 kJ of waste heat to surrounding.

→ $\Delta H = 282 \text{ kJ}$ → from chemical reaction

→ $P\Delta V = 4 \text{ kJ}$ → from collapse of gas to liquid

→ Fuel Cell

$$\text{efficiency} = \frac{\text{what we get}}{\text{what we pay for}} = \frac{273 \text{ kJ}}{286 \text{ kJ}} = \underline{\underline{83\%}}$$



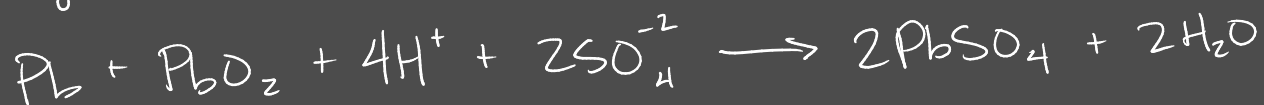
Compare to chapter 4

→ prob. 4.2 → 66%

↳ car (theoretical)
~50%

(practical)
20-30%

Battery



Start w/ ΔH → heat to accomplish this reaction

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

↑ energy out from this
reaction at constant pressure

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

↑ electrical energy out

more than ΔH !

How? Heat coming into the system from the surroundings

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

$$78 \text{ kJ/mol} = T \underbrace{\Delta S}_{\text{increase!}}$$

$$\Delta S = \frac{78 \text{ kJ/mol}}{298 \text{ K}} = 261.7 \text{ J/K}$$

increase in entropy
means the system can
absorb heat from
the surroundings

What about the energy/charge = voltage

↳ $2e^-$ are given up at the - electrode

↳ $2e^-$ are taken up at the + electrode

$$\text{voltage} = \frac{W_e}{q} = \frac{394 \text{ kJ}}{\underbrace{2e^- \cdot N_A \cdot 1.6 \cdot 10^{-19} \text{ C/e}}_{\substack{\text{2 mol of} \\ e^-}}} = \underline{\underline{2.04 \text{ V}}}$$

voltage of reaction

Thermodynamic Identity

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

$\underbrace{\quad\quad\quad}_{\text{variables}}$

$$\frac{1}{T} = \left(\frac{\partial S}{\partial U} \right)_{V, N}$$

Enthalpy

• $H = U + pV$

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

$$\uparrow T dS - \cancel{p dV} + \mu dN$$

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

Ex. $d_p = 0$

$$dN = 0$$

for reversible
isobaric process
 $\pm Q = dH$

$$dH = T dS$$

Helmholtz Free Energy

$$F = U - TS$$

$$dF = dU - T dS - S dT$$

$$\rightarrow dF = -S dT - p dV + \mu dN$$

T, V, N

Ex. $dT = 0$ isothermal process

$$dN = 0$$

$$dF = -p dV$$

↳ reversible

$$\pm W = -p dV$$

$$dF = \pm W$$

Gibbs Free Energy

$$\rightarrow dG = -SdT + Vdp + \mu dN$$

$T, p, N \rightarrow$ very natural variables
for experiments

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

- hold $V + N$ constant

$$dV = 0$$

$$dN = 0$$

$$dF = -SdT$$

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

← entropy is the
rate of change of
 F w.r.t. T .

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

Similarly for Gibbs

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

$$1 \text{ mol of C} \Rightarrow 5.3 \cdot 10^{-6} \text{ m}^3$$

(graphite)

$$G = 0 \text{ kJ} \leftarrow \text{most stable elemental form of C}$$

Gibbs increases by $5.3 \cdot 10^{-6} \text{ J}$ per Pa of pressure above atmospheric pressure

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

Gibbs at 30°C (303 K)

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

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

$$S = \left(\frac{\partial G}{\partial T} \right)_{P,N} \Rightarrow \Delta G = S \cdot \Delta T = 69.91 \text{ J/K} \cdot 5 \text{ K} = 349.55 \text{ J}$$
$$\begin{array}{r} + (-237.13 \text{ kJ}) \\ \hline -236.78 \text{ kJ} \end{array}$$

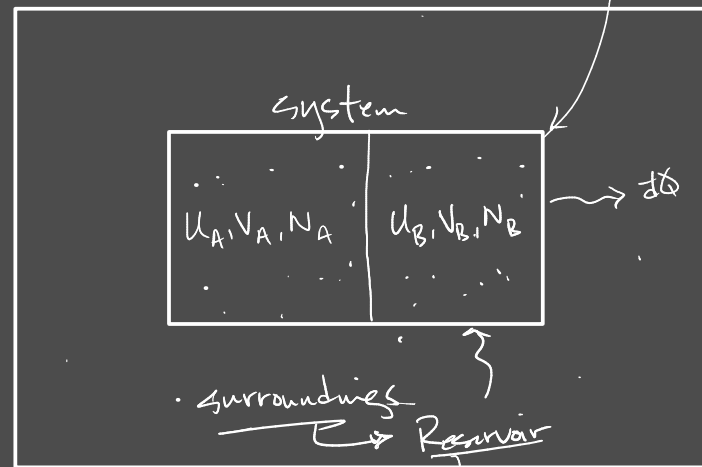
5.2 Free Energy as a force toward equilibrium

isolated system



constant volume

system entropy increase



surroundings
Reservoir

constant T

total entropy increase

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

express in
system variables

$$dS_R = \frac{1}{T} dU_R + \frac{P}{T} dV_R - \frac{\mu}{T} dN$$

$$dU = -dU_R$$

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

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

Helmholtz Free Energy
 dF

increase

this

$$\rightarrow dS_{\text{total}} = -\frac{dF}{T}$$

decrease
that

system will minimize
its Helmholtz Free Energy

limiting conditions
$dT=0$
$dV=0$
$dN=0$

what about keeping pressure, temperature, number constant?

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

$$\bullet dS_R = \frac{1}{T} dU_R + \frac{P}{T} dV - \frac{\mu}{T} dN$$

$$\bullet dU = -dU_R$$

$$\bullet dV = -dV_R$$

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

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

Gibbs Free Energy
 $\rightarrow dG$

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

limiting conditions
 $dT=0$
 $dP=0$
 $dN=0$

system's Gibbs will
minimize spontaneously

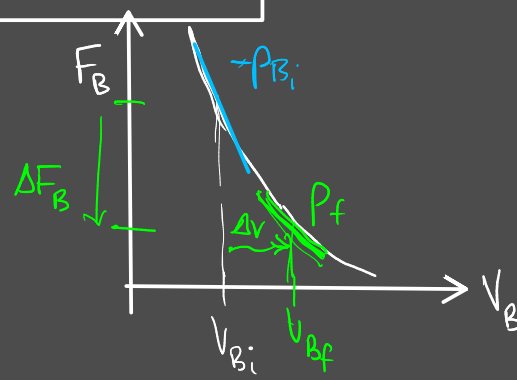
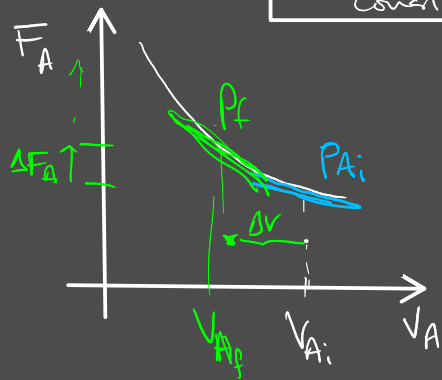
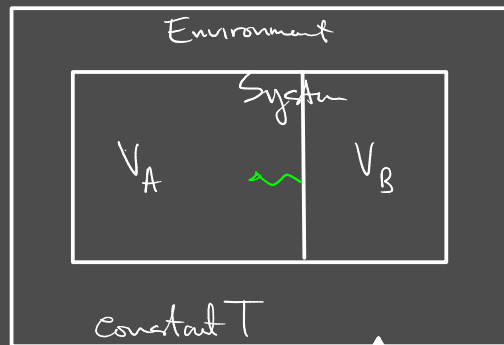
- * At constant energy and volume, S tends to increase
- * At constant temperature and volume, F tends to decrease
- * At constant temperature and pressure, G tends to decrease

$$F = U - TS$$

$$G = U + PV - TS$$

#5.19

$$\left(\frac{\partial F}{\partial V} \right)_T = -P$$



Gibbs Free Energy + Chemical Potential

$$dG = -SdT + Vdp + \mu dN$$

$$\begin{array}{l} \downarrow dT = 0 \\ \downarrow dp = 0 \end{array}$$

$$dG = \mu dN$$

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

$$\Rightarrow G = \mu N$$

↳ is μ constant
w/ N .

each new particle
adds more space
so the density does
not change.

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

is μ constant
w/ N here?

No! density increases
to keep constant volume.

How can we use this?

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

$$\mu = \frac{G}{N}$$

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

↑
constant N

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

$$\frac{\partial \mu}{\partial p} = \frac{V}{N} \leftarrow \text{ideal gas law: } \frac{V}{N} = \frac{k_B T}{p}$$

$$\frac{\partial \mu}{\partial p} = \frac{k_B T}{p} \Rightarrow \Delta \mu = \int_{p_i}^{p_f} \frac{k_B T}{p} dp$$

$$\mu(T, p) - \mu(T, p^0) = k_B T \ln\left(\frac{p}{p^0}\right)$$

$$\rightarrow \mu(T, p) = k_B T \ln\left(\frac{p}{p^0}\right) + \underbrace{\mu(T, p^0)}$$

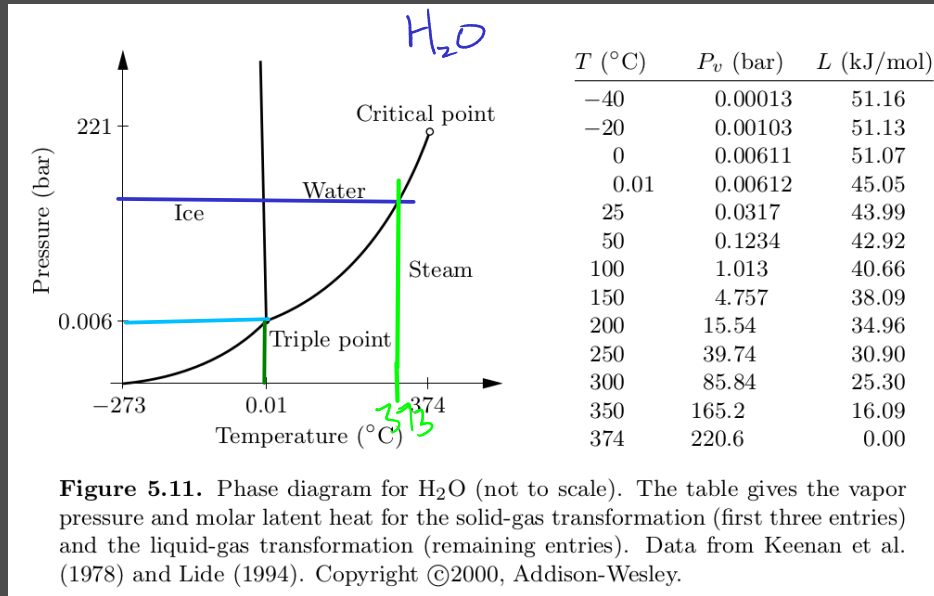
$\mu^0 \rightarrow$ chemical potential
at atmospheric pressure

Compare to

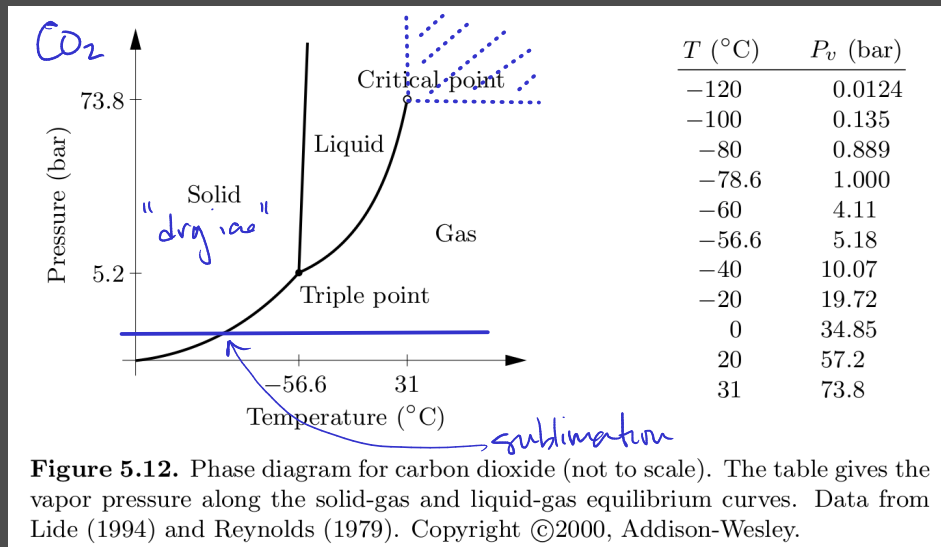
$$\mu = -T \left(\frac{\partial S}{\partial N}\right)_{U,V} = -k_B T \ln \left[\frac{V}{N} \left(\frac{2\pi m k_B T}{h^2} \right)^{3/2} \right] \leftarrow \text{What is } \underline{\mu^0}?$$

Phase Transformations of Pure Substances

↳ discontinuous change in properties or state for a small change in variable



supercritical fluid



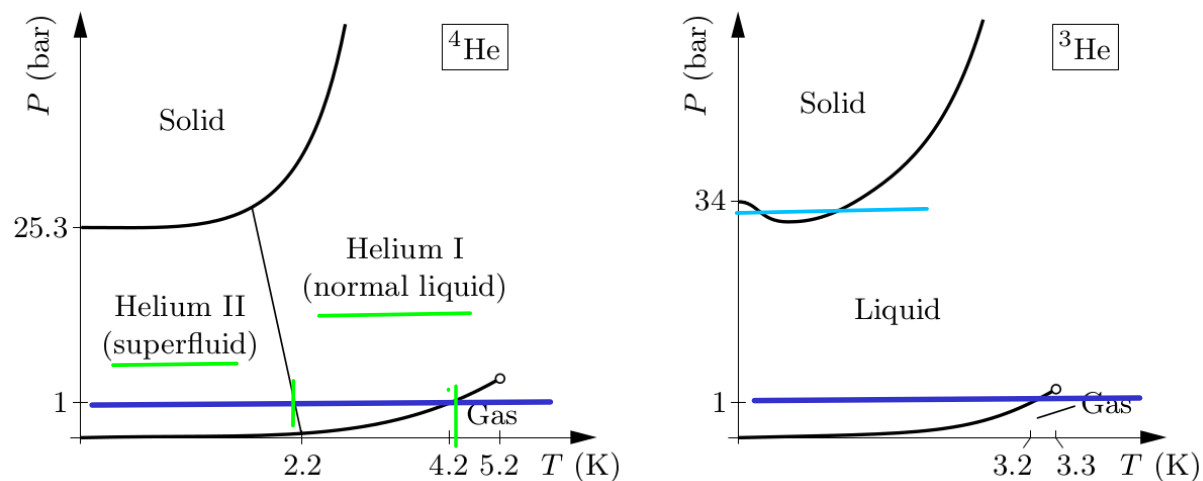


Figure 5.13. Phase diagrams of ^4He (left) and ^3He (right). Neither diagram is to scale, but qualitative relations between the diagrams are shown correctly. Not shown are the three different solid phases (crystal structures) of each isotope, or the superfluid phases of ^3He below 3 mK. Copyright ©2000, Addison-Wesley.

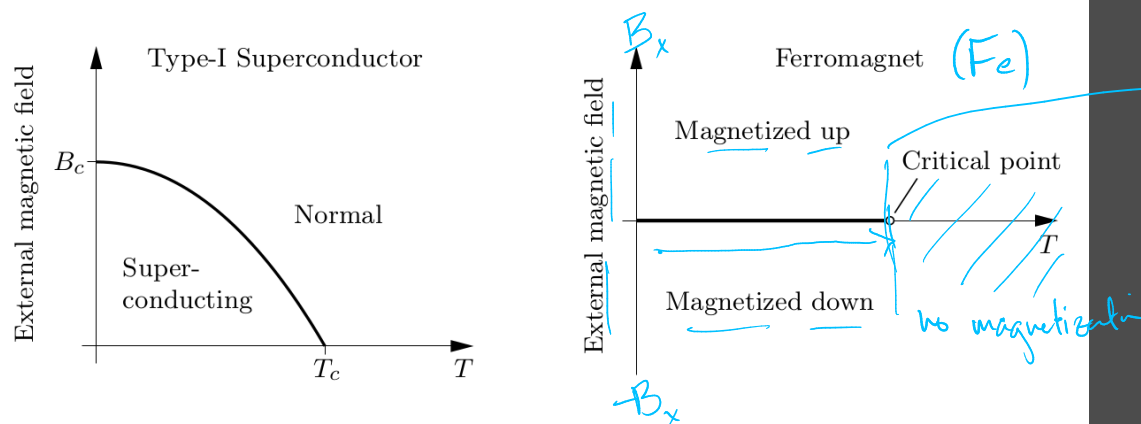


Figure 5.14. Left: Phase diagram for a typical type-I superconductor. For lead, $T_c = 7.2$ K and $B_c = 0.08$ T. Right: Phase diagram for a ferromagnet, assuming that the applied field and magnetization are always along a given axis. Copyright ©2000, Addison-Wesley.

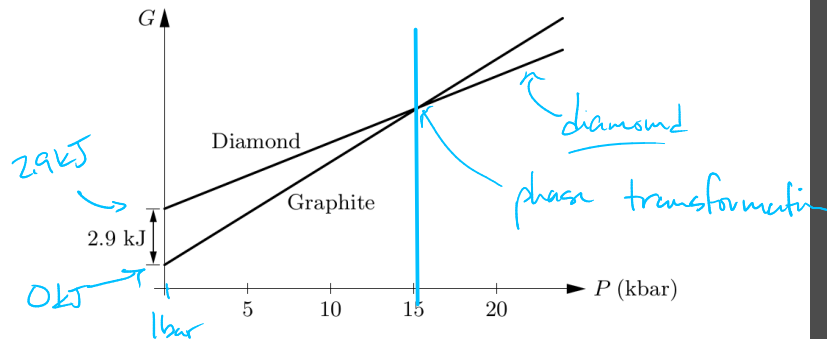


Figure 5.15. Molar Gibbs free energies of diamond and graphite as functions of pressure, at room temperature. These straight-line graphs are extrapolated from low pressures, neglecting the changes in volume as pressure increases. Copyright ©2000, Addison-Wesley.

$$\left(\frac{\partial G}{\partial P}\right)_{T,N} = V \leftarrow \text{does not change much w/ pressure}$$

$$\begin{cases} V_{\text{graphite}} = 5.3 \cdot 10^{-6} \text{ m}^3 \\ V_{\text{diamond}} = 3.42 \cdot 10^{-6} \text{ m}^3 \end{cases}$$

What about T dependence?

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

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

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

as T is raised, Gibbs goes down, graphite will decrease more quickly

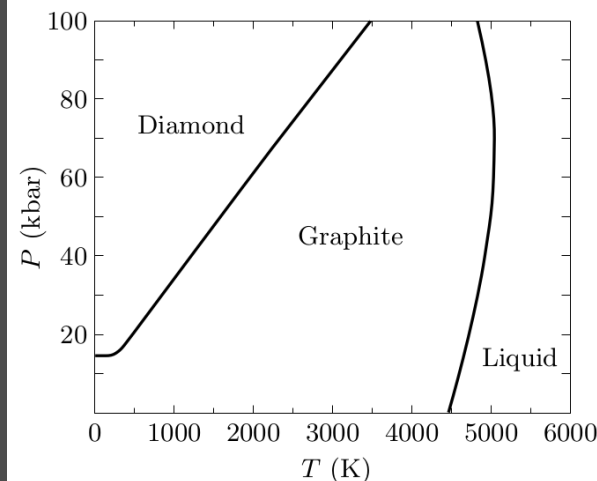


Figure 5.17. The experimental phase diagram of carbon. The stability region of the gas phase is not visible on this scale; the graphite-liquid-gas triple point is at the bottom of the graphite-liquid phase boundary, at 110 bars pressure. From David A. Young, *Phase Diagrams of the Elements* (University of California Press, Berkeley, 1991). Copyright ©2000, Addison-Wesley.

At what depth on earth would 15 kbar?

$$\begin{cases} \rho_{\text{H}_2\text{O}} = 1000 \text{ kg/m}^3 \\ \rho_{\text{rock}} = 3000 \text{ kg/m}^3 \end{cases}$$

$$15 \text{ kbar} = 1.5 \cdot 10^4 \text{ bar} = 1.5 \cdot 10^4 \cdot 10^5 \text{ Pa} = 3000 \frac{\text{kg}}{\text{m}^3} \cdot 10 \frac{\text{N}}{\text{kg}} \cdot h$$

$$h = \frac{1.5 \cdot 10^9 \text{ Pa}}{3 \cdot 10^4 \text{ N/m}^3}$$

$$h = 0.5 \cdot 10^5 \text{ m} = 50 \cdot 10^3 \text{ m}$$

$$\boxed{h = 50 \text{ km}}$$



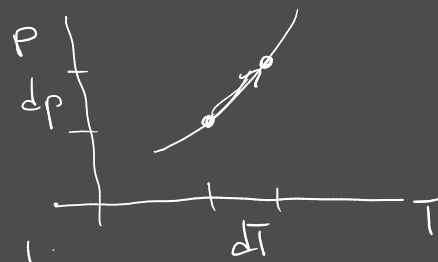
$$P = \frac{mg}{A}$$

$$p = \frac{\rho \cdot V \cdot g}{A}$$

$$p = \frac{\rho \cdot A \cdot h \cdot g}{A}$$

$$p = \rho h g$$

So what about the shape of the phase boundary line?



on the line $\rightarrow G_l = G_g$

increase p and T so we are still on boundary line

$$dG_l = dG_g$$
$$dG = -SdT + Vdp + \cancel{\mu dN}$$

$$-S_l dT + V_l dp = -S_g dT + V_g dp$$

$$S_g dT - S_l dT = V_g dp - V_l dp$$

$$\frac{S_g - S_l}{V_g - V_l} = \left[\frac{dp}{dT} = \frac{\Delta S}{\Delta V} \right]$$

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

Latent Heat
(Enthalpy)

$$\left[\frac{dp}{dT} = \frac{L}{T \Delta V} \right]$$

Clausius-Clapeyron relation
(any phase)

So go back to diamond/graphite:

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

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

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

graphite becomes stable 15 kbar at 298 K

What about 100 K higher temp?

$$\Delta P = 18 \frac{\text{bar}}{\text{K}} \cdot 100 \text{ K} = 1800 \text{ bar} = \underline{\underline{1.8 \text{ kbar}}}$$

more depth

100 km - 200 km

Lab conditions

1800 K

60 kbar

van der Waals Model \rightarrow liquid-gas model \rightarrow above the critical temperature

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

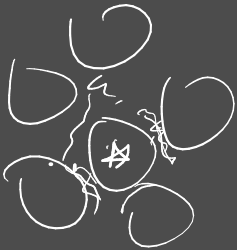
$$P_{\text{ideal}} V_{\text{ideal}} = Nk_B T$$

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

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

b corresponds to
the size of a molecule

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



attractive intermolecular forces

\hookrightarrow lower the potential energy

\hookrightarrow proportional to the number of nearest neighbors

\hookrightarrow proportional to the number
of molecules

\hookrightarrow proportional to
density

$$U_{\text{vdw}} = -a \cdot N \cdot \frac{N}{V} \Rightarrow U_{\text{vdw}} = -a \frac{N^2}{V}$$

$$du = T \cancel{ds} - p dV + \mu \cancel{dN}$$

$$du = -p dV$$

$$p = - \left(\frac{\partial u}{\partial V} \right)_S$$

$$P_{ideal} V_{ideal} = N k_B T$$

$$p = - \left(\frac{\partial u}{\partial V} \right)_S \Rightarrow p = - \left(-a N^2 \frac{\partial \frac{1}{V}}{\partial V} \right) = - \frac{a N^2}{V^2}$$

$$p = P_{ideal} + p_{vdw}$$

$$P_{ideal} = p - p_{vdw}$$

$$P_{ideal} = p - \left(-\frac{a N^2}{V^2} \right) = p + \frac{a N^2}{V^2}$$

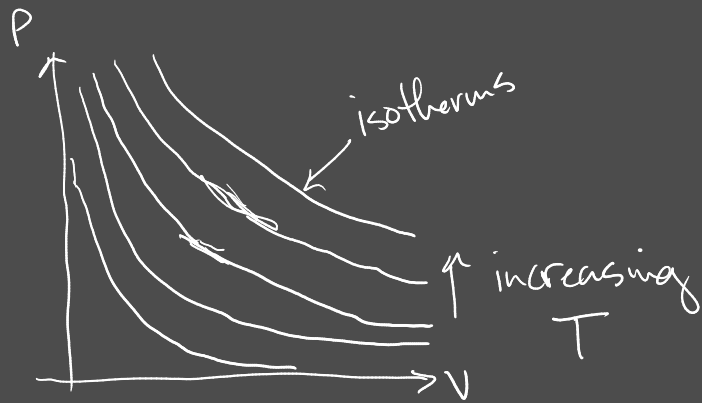
$$a \text{ for } N_2 \sim 4 \cdot 10^{-49} \frac{\text{J}}{\text{m}^3}$$

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

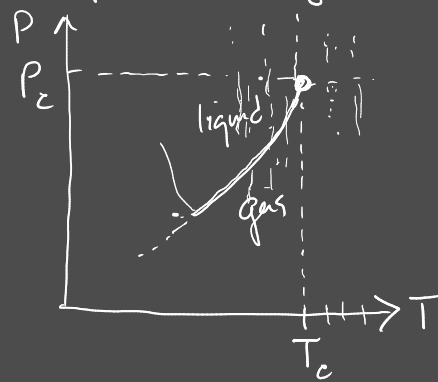
P vs. V

for ideal gas

$$P = \frac{Nk_B T}{V}$$



plot in reduced units } HW
 $\frac{P}{P_c}, \frac{V}{V_c}, \frac{T}{T_c}$
 phase diagram



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

Calculate Gibbs Free Energy

$$dG = -SdT + Vdp + \mu dN$$

$dT = 0$
 $dN = 0$

$$dG = Vdp$$

$$V = \left(\frac{\partial G}{\partial p}\right)_{NT} = \left(\frac{\partial G}{\partial V}\right)_{NT} \cdot \left(\frac{\partial V}{\partial p}\right)_{NT}$$

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

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

$$\left(\frac{\partial G}{\partial V}\right)_{NT} = - \frac{Nk_B T V}{(V - Nb)^2} + 2aN^2 \cdot \cancel{V}$$

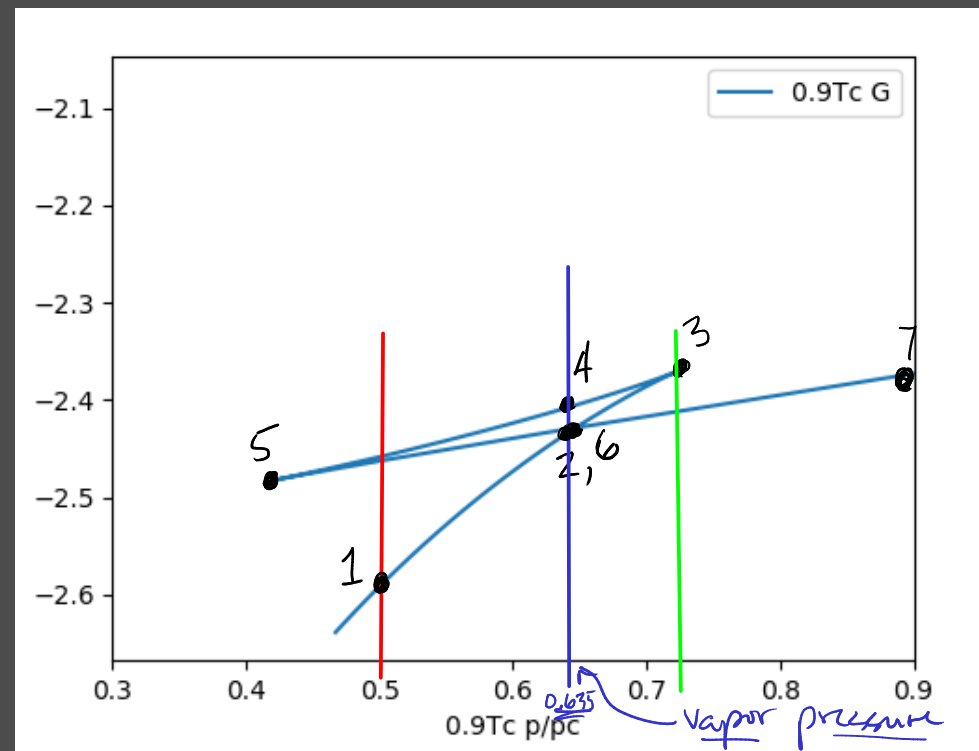
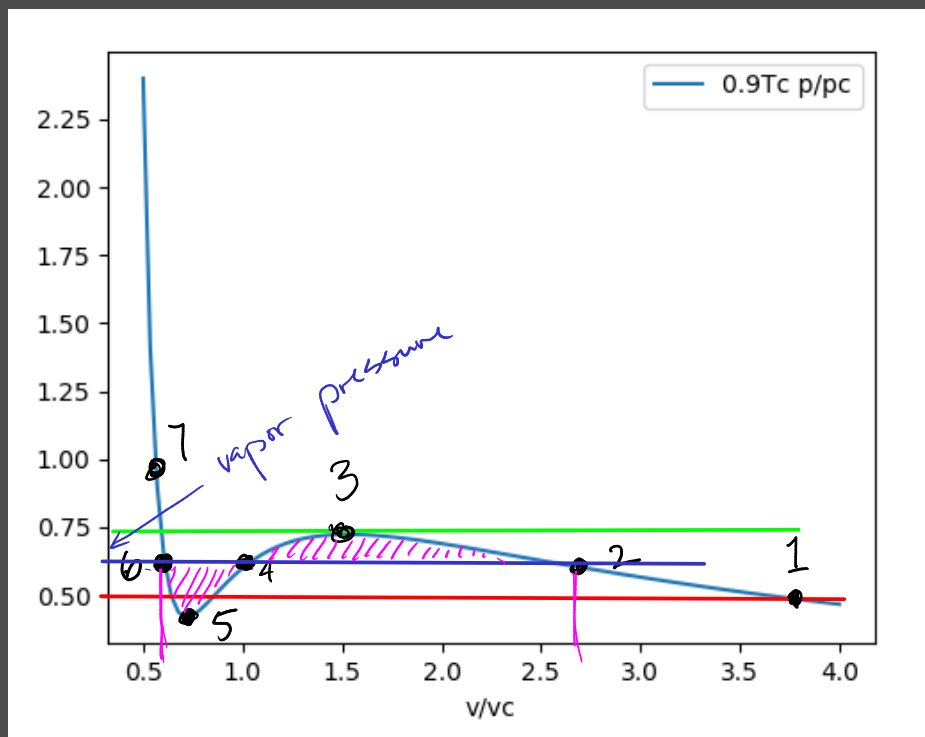
$$\left(\frac{\partial G}{\partial V}\right)_{NT} = \frac{-Nk_B T V}{(V - Nb)^2} + \frac{2aN^2}{V^2}$$

↓ integrating wrt. V

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

#5.48

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



$$\int_{\text{loop}} dG = 0 = \int \left(\frac{\partial G}{\partial p} \right)_T dp = \int v dp$$

