

Chapter 5 - Free Energy

Apply the laws of thermo to non-cyclic processes

- ↳ most interactions & other transformations are not isolated from surroundings but exchange energy and volume.
- ↳ most at constant temperature + constant pressure

Enthalpy - internal energy plus work to make room for the system under constant pressure from the environment

$$H \equiv U + PV \leftarrow \text{total energy to create the system and put it in an environment}$$
$$\Delta H = \oint Q + \oint W_{\text{other}}$$

New quantity analogous to enthalpy

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

$$F \equiv U - TS$$

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

\hookleftarrow so to get the work w_c must do (to a system at constant pressure & temp)

\hookrightarrow Gibbs Free Energy

$$G = U - TS + PV$$

$$G = \underbrace{H - TS}_{\text{energy to make the system + make room for the system minus the heat we get to subtract from surroundings}}$$

energy to make the system + make room for the system minus the heat we get to subtract from surroundings

Together these are thermodynamic potentials.

$$dF = dU - TdS$$

$$dF = \cancel{dQ} + \cancel{dW} - TdS$$

for a reversible process: (no new entropy created)

$$\cancel{dQ}_{\text{rev}} = TdS$$

then, $dF = \cancel{TdS} + \cancel{dW} - \cancel{TdS}$

$dF = \cancel{dW} \rightarrow$ work done on
the system

otherwise,

$$dF \leq \cancel{dW}$$

Now for the changes in Gibbs

$$dG = dU - TdS + pdV$$

$$dG = \cancel{dQ} + \cancel{dW} - TdS + pdV$$

for reversible processes,

$$\cancel{dQ} = TdS$$

$$\cancel{dW} = \underbrace{-pdV}_{\text{compression work}} + \cancel{dW_{\text{other}}}$$

↳ electrical work, etc

$$dG_r = \cancel{TdS} - \cancel{pdV} + \cancel{dW_{\text{other}}} - \cancel{TdS} + \cancel{pdV}$$

$$dG_r = + \cancel{dW_{\text{other}}}$$

for other than reversible processes

$$dG_r \leq \cancel{dW_{\text{other}}} \text{ at constant } T, p$$

ΔG is very useful so how do you measure it?

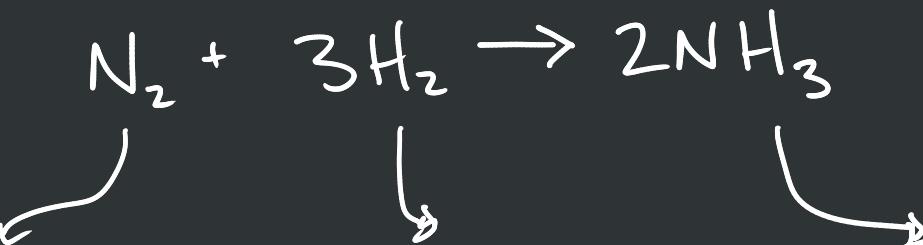
First measure $\Delta H \rightarrow$ heat absorbed/released for a reaction at constant pressure + no other work is done.

Then what? Calculate ΔS from initial + final states using heat capacity data

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

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

Ex: Problem 5.2



$$\Delta H = 0 \text{ kJ/mol}$$

$$S = 191.6 \frac{\text{J}}{\text{K mol}}$$

$$\Delta H = 0 \text{ kJ/mol}$$

$$S = 130.68 \frac{\text{J}}{\text{K mol}}$$

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

$$P = 1 \text{ bar} = 10^5 \text{ Pa} \approx 1 \text{ atm} = 1.01 \cdot 10^5 \text{ Pa}$$

$$\Delta H = -46.11 \text{ kJ/mol}$$

$$S = 192.45 \frac{\text{J}}{\text{K mol}}$$

$$\Delta H = -46.11 \frac{\text{kJ}}{\text{mol}} \cdot 2 \text{ mol} = -92.22 \text{ kJ}$$

$$\Delta S = 2 \text{ mol} \cdot 192.45 \frac{\text{J}}{\text{K mol}} - 3 \cdot 130.68 - 1 \cdot 191.6 \frac{\text{J}}{\text{K}} = -198.75 \frac{\text{J}}{\text{K}}$$

$$\Delta G = \Delta H - T \Delta S = -92.22 \text{ kJ} - 298 \text{ K} \left(-198.75 \frac{\text{J}}{\text{K}} \right)$$

Junk

$$\Delta G = \boxed{-32.99 \text{ kJ}} + 59.23 \text{ kJ}$$

Compare to table $\rightarrow \Delta_f G = -16.45 \times 2 \text{ mol} = \boxed{-32.9 \text{ kJ}}$

Electrolysis, Fuel Cells, Batteries.



electrical work has to be done

$\Delta H = 286 \text{ kJ}$ \rightsquigarrow heat out when
 \equiv
this reaction runs
in reverse

to run forward we have to put
in this much energy

\Rightarrow some of this energy will push
the environment away

$$\begin{aligned} pV_1 &= n_1 RT \\ pV_2 &= n_2 RT \end{aligned} \quad \Rightarrow \quad p\Delta V = \Delta n \cdot R \cdot T = 1.5 \text{ mol} \cdot (8.31 \text{ J/Kmol}) (300 \text{ K})$$

?

$$\begin{aligned} &= 3739 \text{ J} \\ &= 3.7 \text{ kJ} \approx 4 \text{ kJ} \leftarrow \end{aligned}$$

So 282 kJ will remain in the system
in the form of potential energy in chemical bonds

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

What is the change in entropy for the system?

$$S_{\text{H}_2\text{O}} = 70 \text{ J/K}$$

$$S_{\text{H}_2} = 131 \text{ J/K}$$

$$S_{\text{O}_2} = 205 \text{ J/K}$$

products

$$S_p = 131 \text{ J/K} + \frac{1}{2} \cdot 205 \text{ J/K} = 233.5 \text{ J/K}$$

$$\Delta S_{\text{reaction}} = 233.5 \text{ J/K} - 70 \text{ J/K} = \underbrace{163.5 \text{ J/K}}.$$

entropy increase

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

$$Q = T\Delta S = 300 \text{ K} \cdot 163.5 \frac{\text{J}}{\text{K}}$$
$$= 49 \text{ kJ}$$

So of 286 kJ that go in, 49 kJ come from the surroundings

$$286 \text{ kJ} - 49 \text{ kJ} = 237 \text{ kJ} \rightarrow \text{comes from electrical work}$$
$$\Delta H - T\Delta S = \Delta G$$

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

→ 49 kJ waste heat goes to the environment

→ $\Delta U = 282 \text{ kJ} \rightarrow$ comes from chemical reaction

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

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

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

{

this is great!

Carnot \rightarrow o extreme case in
cycle chapter 4 $\rightarrow 66\%$

\rightarrow o car engine
 $\epsilon_{\max} = 50\%$

$\epsilon_{\text{actual}} = 20\%$

Battery reaction



start w/ $\Delta H \rightarrow$ heat in to accomplish the rxn

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

↑
energy out from reaction
at constant pressure

what is the Gibbs?

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

↑ electrical energy out

more than ΔH !

How? Heat coming in to the system from the surroundings. How much?

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

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

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

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

Entropy increases

Energy/charge in this reaction?

voltage

→ need to know how many e^- move during the reaction:

$2e^-$ are given up at the (-) electrode

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

$$\text{So since } \text{Voltage} = \frac{\Delta W_E}{q} = \frac{394000 \text{ J}}{2e \cdot 1.6 \cdot 10^{-19} \frac{\text{C}}{e} \cdot N_A} = 2.04 \text{ V}$$

$$\Delta S = \frac{78000 \text{ J/mol}}{298 \text{ K}}$$

$\Delta S = 261.7 \frac{\text{J}}{\text{K}}$
an entropy increase means the system can absorb heat from the outside.

Thermodynamic identities

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

↑ how the energy changes
when dS , dV , & dN change

what about H , F , and G ?

Enthalpy
 $H = U + PV$

$$dH = dU + pdV + Vdp$$

$$dH = TdS - \cancel{pdV} + \mu dN + \cancel{pdV} + Vdp$$

$$\rightarrow dH = TdS + \mu dN + Vdp$$

variables have changed from dU .

$$\left. \begin{array}{l} dp = 0 \\ dN = 0 \end{array} \right\} dH = TdS \leftarrow \text{heat at constant } p$$

Helmholtz Free Energy

$$F = U - TS$$

$$dF = dU - TdS - SdT$$

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

Gibbs Free Energy

$$G = U - TS + PV$$

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

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

You can use the thermodynamic identities to derive many useful derivative statements

$$\text{take } dF = -SdT - pdV + \mu dN$$

hold $V + N$ constant

$$dV = 0$$

$$dN = 0$$

$$dF = -SdT$$

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

and so on, holding the other combinations constant.

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

Similarly for Gibbs!

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

chemical potential
↓

How does the Gibbs Free Energy change w/ pressure
from the reference data?

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

$\Delta G_c = 0 \text{ kJ}$ ← most stable form

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

$$5.3 \cdot 10^{-6} \cdot \partial P = \partial G$$

↑ increase the gibbs
free energy
a small
increase in pressure

Ex: (5.10)

1 mol H₂O at 25°C (298 K)

Gibb's at 30°C (303 K)?

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

$$S_{H_2O} = 69.91 \text{ J/K}$$

$$\Delta G = -S \cdot \Delta T = -(69.91 \text{ J/K}) \cdot (5 \text{ K}) = -349.55 \text{ J}$$

$$\underbrace{G(303)}_{\downarrow} - G(298) = -349.55 \text{ J}$$

$$\begin{aligned} G(303) &= -349.55 \text{ J} + G(298) \\ &= -349.55 \text{ kJ} + (-237.13 \text{ kJ}) \\ &= -237.48 \text{ kJ} \quad \checkmark \end{aligned}$$

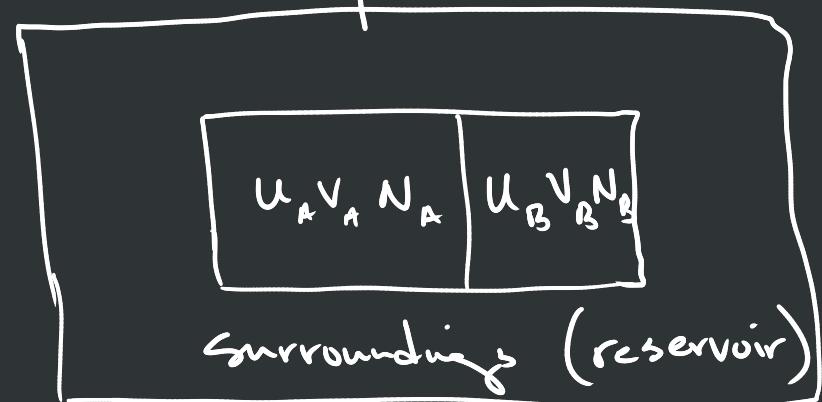
5.2] Free Energy as a Force toward Equilibrium

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

reservoir

↪ Rewrite in

terms of system variable



$$dS_R = \frac{1}{T} dU_R + \cancel{\frac{P}{T} dV_R^0} - \cancel{\frac{\mu}{T} dN_R^0}$$

$$dS_R = \frac{1}{T} dU_R$$

$$dU_R = -dU \Rightarrow dS_R = -\frac{1}{T} dU$$

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

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

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

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

Helmholtz!

$$dF = dU - TdS - \underbrace{SdT}_{\text{assume } dT=0}$$

$$\Delta S_{\text{total}} = - \frac{\Delta T}{T}$$

↑
increas
this

$\frac{-F}{T}$

conditions

$$\Delta T = 0$$

$$\Delta V = 0$$

$$\Delta N = 0$$

↓
decrease → so the system will minimize
that its Helmholtz free energy

What about keeping pressure, temperature, and number of particles fixed?

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

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

$$dU_R = -dU$$

$$dV_R = -dV$$

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

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

dG if hold T, p, N constant

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

System will minimize Gibbs spontaneously

$$dT = 0$$

$$dp = 0$$

$$dN = 0$$

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

5.3] Phase transformations of pure substance

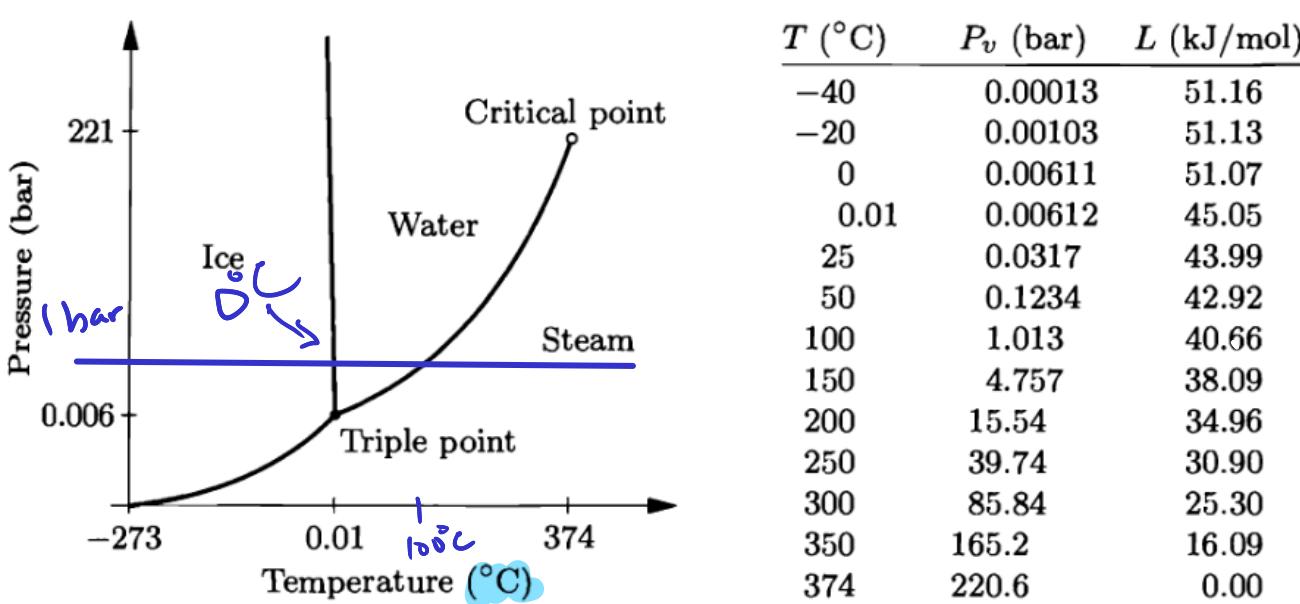


Figure 5.11. Phase diagram for H_2O (not to scale). The table gives the vapor pressure and molar latent heat for the solid-gas transformation (first three entries) and the liquid-gas transformation (remaining entries). Data from Keenan et al. (1978) and Lide (1994).

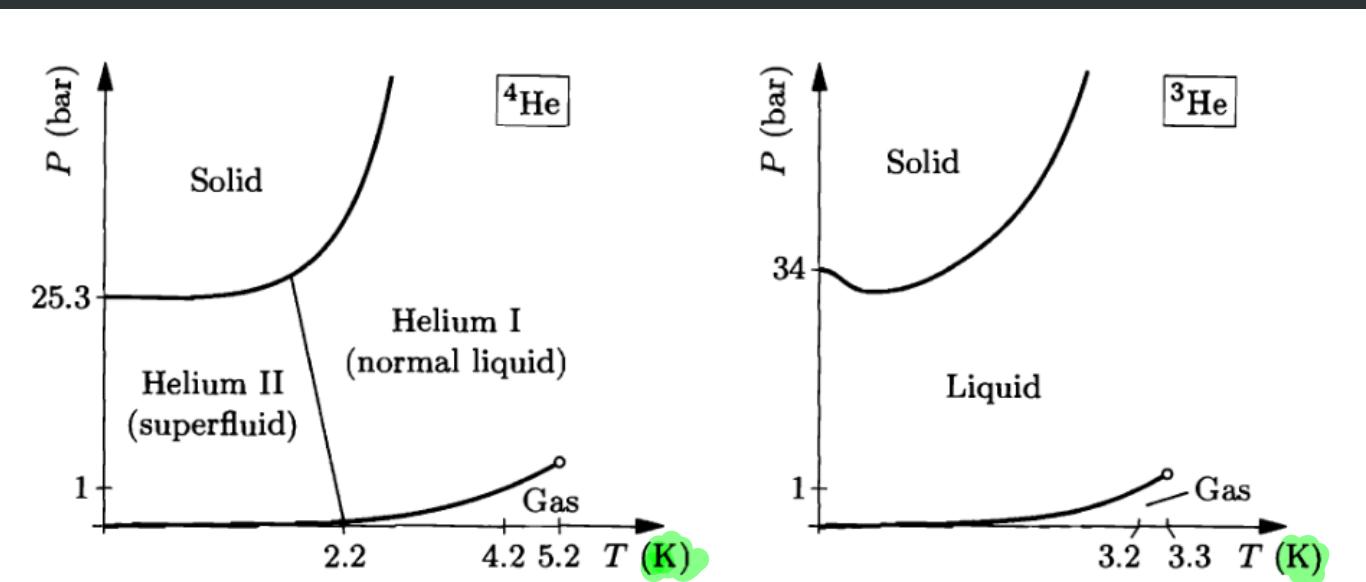
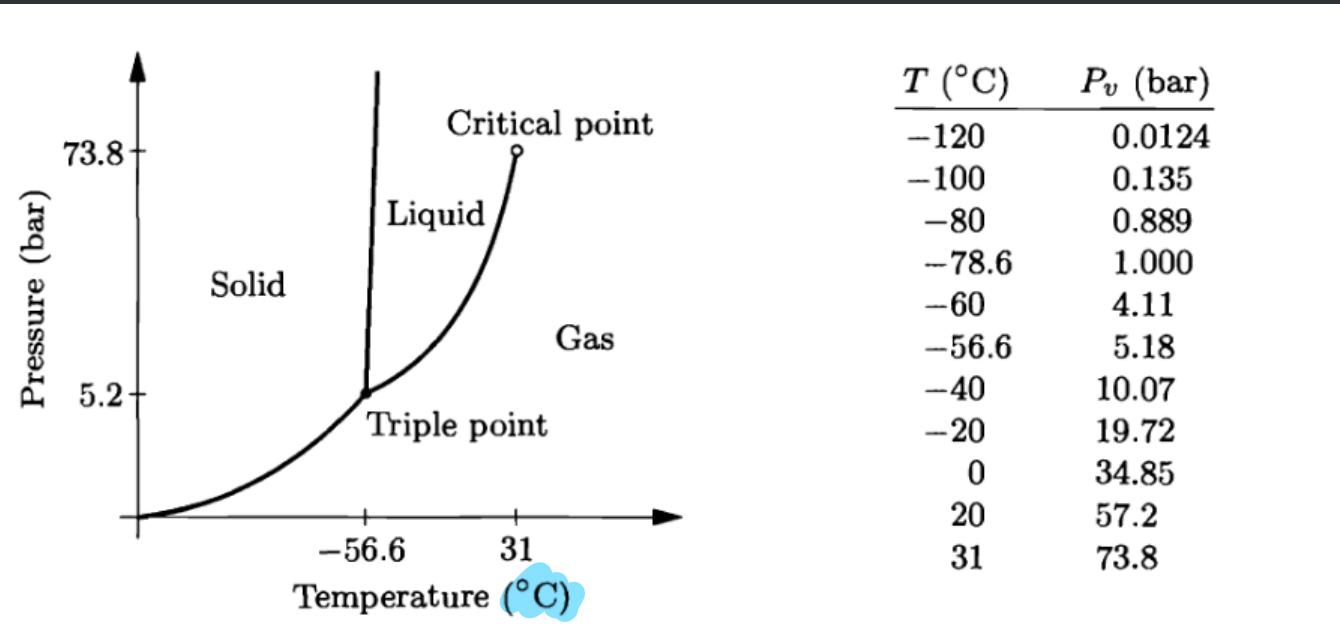
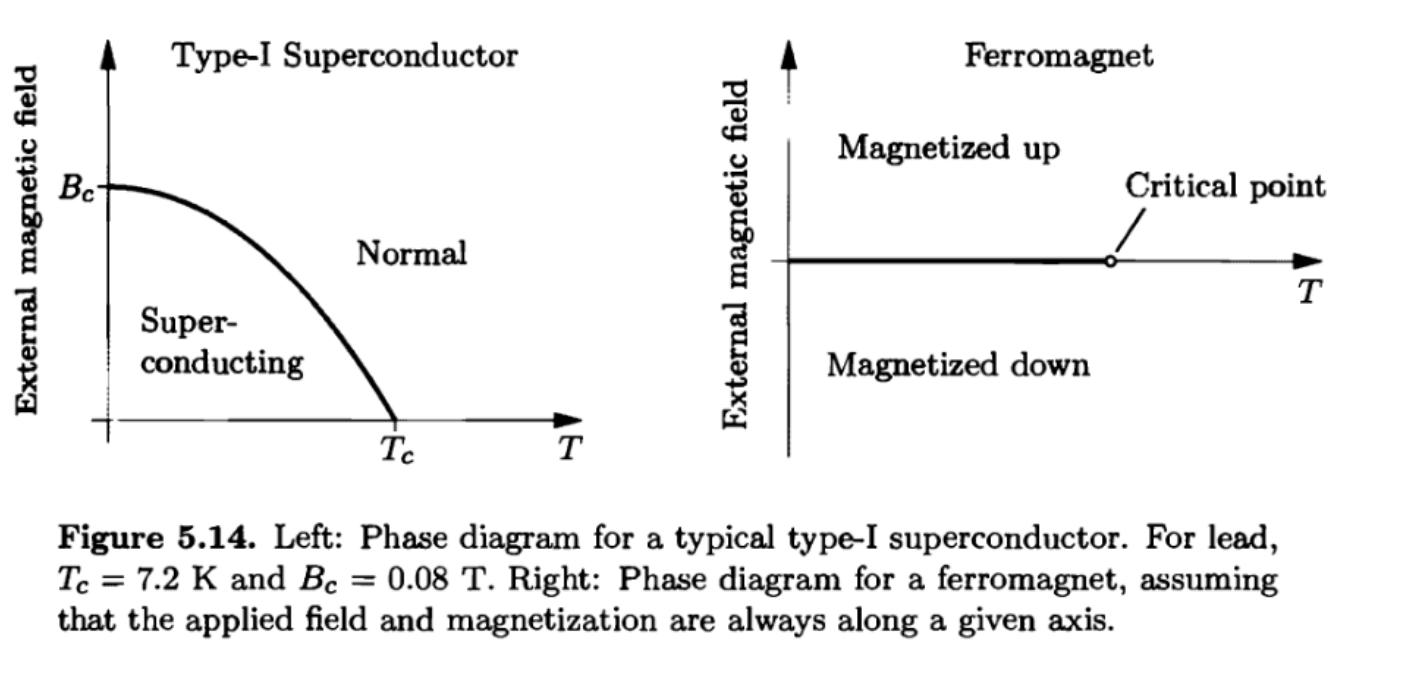
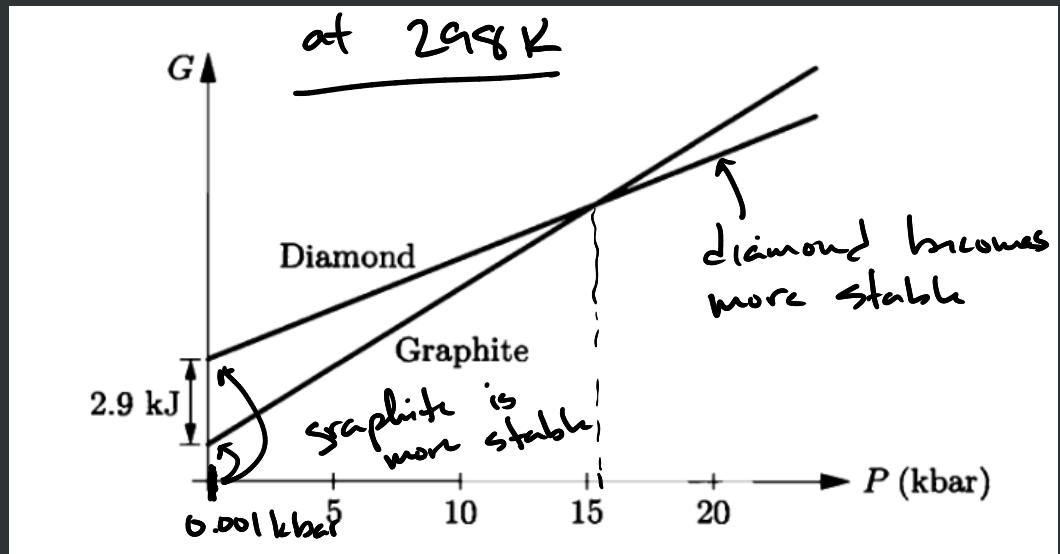


Figure 5.13. Phase diagrams of ^4He (left) and ^3He (right). Neither diagram is to scale, but qualitative relations between the diagrams are shown correctly. Not shown are the three different solid phases (crystal structures) of each isotope, or the superfluid phases of ^3He below 3 mK.





At what depth would this happen?



$$\text{Pressure} = \frac{\text{Force}}{\text{Area}} = \frac{mg}{A} = \frac{\rho \cdot V \cdot g}{A}$$

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

$$\rho_{H_2O} = 1000 \text{ kg/m}^3$$

$$P = \rho dg$$

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

$$\frac{15000 \cdot 10^5}{1.6 \cdot 10^4} = 3 \cdot 10^3 \cdot 10 \cdot d$$

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

↳ slope of the graph to the left
 ↳ does not change much
 So this would predict a straight-ish line for each of these materials

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

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

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

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

Temperature Dependence of gibbs follows entropy

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

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

$$-S_{\text{gr}} = 5.74$$

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

$$-S_{\text{dia}} = -2.38$$

as temperature increases
 Gibbs goes down, but
 graphite goes down more
 quickly

So what about the shape
 of the phase boundary line?

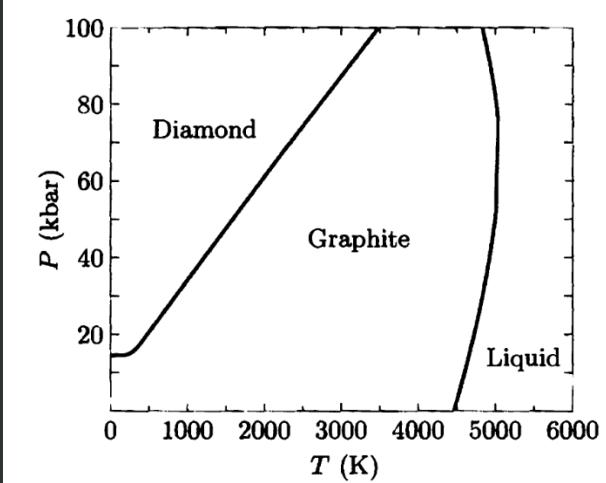
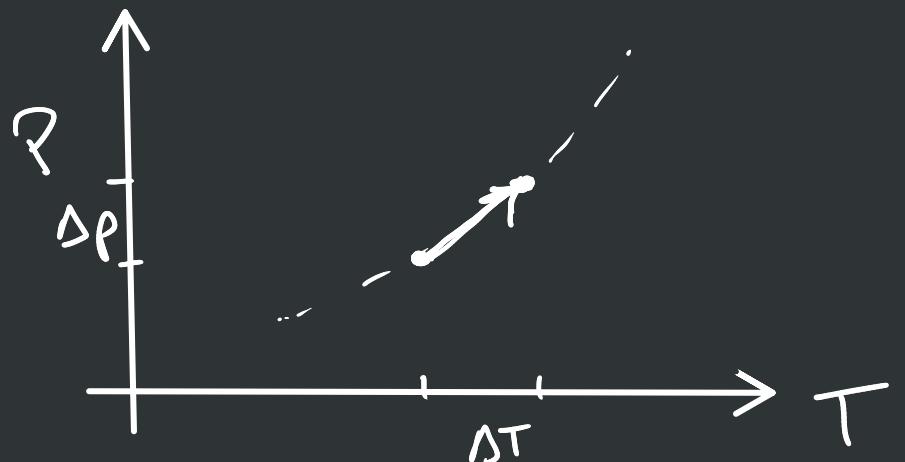


Figure 5.17. The experimental phase diagram of carbon. The stability region of the gas phase is not visible on this scale; the graphite-liquid-gas triple point is at the bottom of the graphite-liquid phase boundary, at 110 bars pressure. From David A. Young, *Phase Diagrams of the Elements* (University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

$G_l = G_g$
 and if we increase pressure
 and Temp we will stay on
 that line



$$dG_e = dG_{eq}$$

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

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

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

$$(S_g - S_e) dT = (V_g - V_e) dP$$

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

Special Q
↓

$$\Delta S = \frac{L}{T} \quad \leftarrow \text{Latent Heat (per mol)}$$

$$\boxed{\frac{\Delta S}{\Delta N} = \frac{dP}{dT}}$$

Clausius - Clapeyron relation

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

(applies to
any phase boundary.)

So go back to diamond vs. graphite

Slope of
the phase boundary
line

$$V_{\text{graphite}} = 5.31 \cdot 10^{-6} \text{ m}^3 \quad \Delta V = 1.9 \cdot 10^{-6} \text{ m}^3$$

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

$$S_{\text{graphite}} = 5.74 \text{ J/K} \quad \Delta S = 3.4 \text{ J/K}$$

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

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

$$\frac{dP}{dT} = 1.8 \cdot 10^6 \frac{\text{Pa}}{\text{K}}$$

So at 298 K, we found 15 kbar
to be where phase change occurs,
but what about 100°C higher?

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

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

Lab diamonds

one way ↳ { 1800 K
and 60 kbar

$$\Delta P = 1.8 \cdot 10^6 \frac{Pa}{K} (100 K)$$

$$\Delta P = 1.8 \cdot 10^8 \frac{Pa}{K}$$

↓

$$\Delta P = 1800 \text{ bar}$$

$$\rightarrow \Delta P = 1.8 \text{ kbar}$$

higher pressure than
at room temperature

farther down
more depth 100-200 km

van der Waals Model \rightarrow equation of state - slight correction to ideal gas.

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

$-Nb \rightarrow$ correction since the gas cannot be compressed to zero volume, b represents the size of a molecule

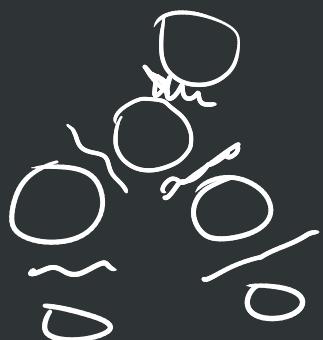
\hookrightarrow attractive intermolecular forces

\hookrightarrow lower the potential energy

\hookrightarrow proportional to the number of nearest neighbours

\hookrightarrow proportional to density

\hookrightarrow proportional to the number of atoms



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

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

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

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

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

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

$$U_{vdw} = -aN^2 \frac{1}{V}$$

$$P_{vdw} = -\left(\frac{\partial U}{\partial V}\right)_S \quad \text{or} \quad \partial U = -P \partial V$$

$$P_{vdw} = -\left(-aN^2 \frac{\partial}{\partial V}\left(\frac{1}{V}\right)\right)$$

$$P_{vdw} = aN^2 \left(-\frac{1}{V^2}\right)$$

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

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



$$P_{ideal} = P - \left(-\frac{aN^2}{V^2}\right) = P + \frac{aN^2}{V^2}$$

Values for "a" and "b"

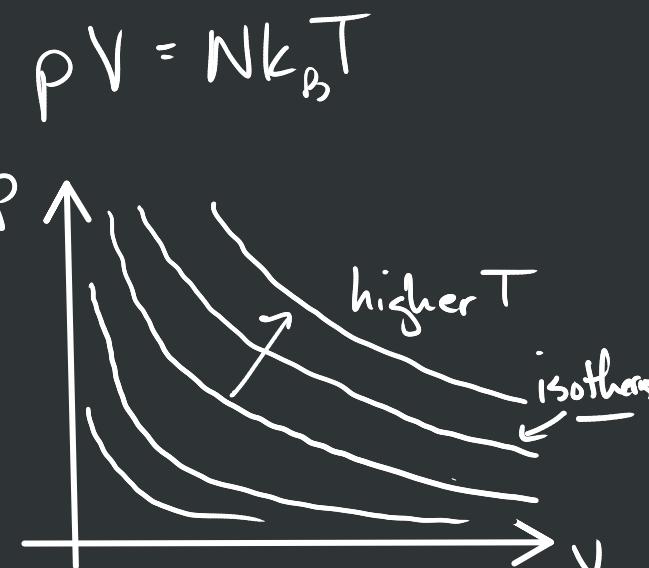
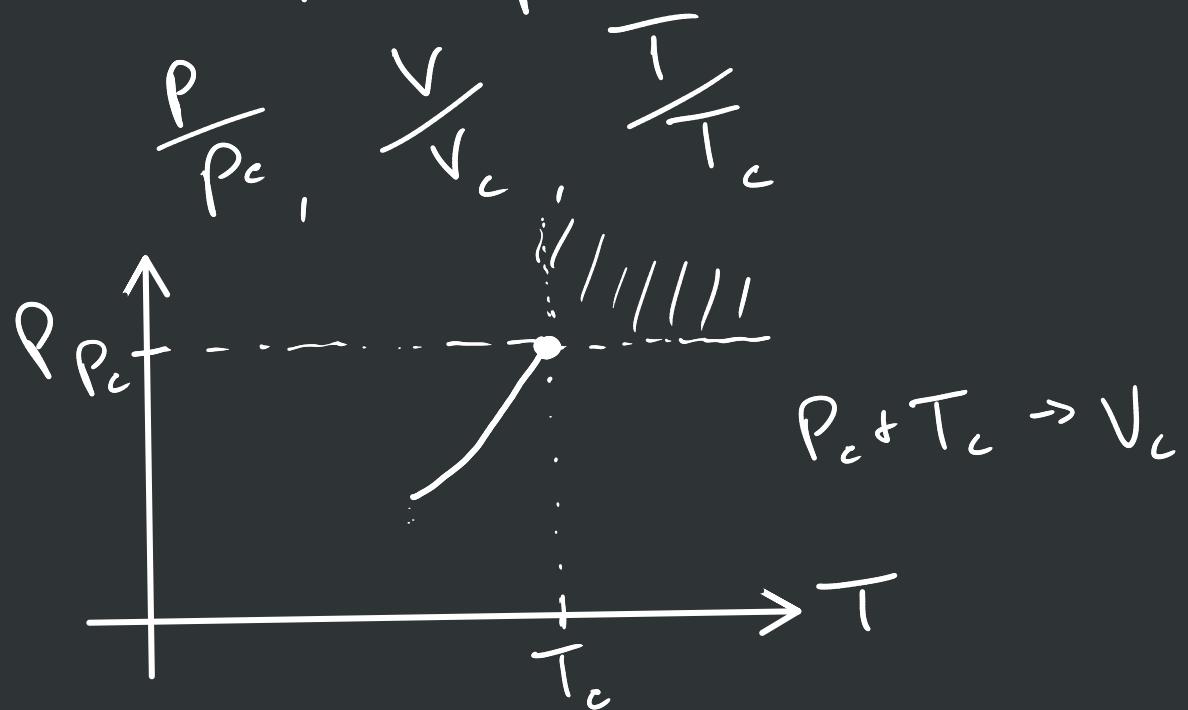
$b \sim$ volume of a molecule

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

$a \sim$ more variable

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

Want: plot P vs. V in reduced units.



Solve for P:

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

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

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

rewrite in terms of γ_{V_c} , $\frac{P}{P_c}$, $\frac{T}{T_c}$

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

$$V_c =$$

$$P_c = ?$$

$$T_c =$$

Calculate the Gibbs for van der Waal fluid.

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

$$dT = 0$$

$$dN = 0$$

$$dG = Vdp$$

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

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

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

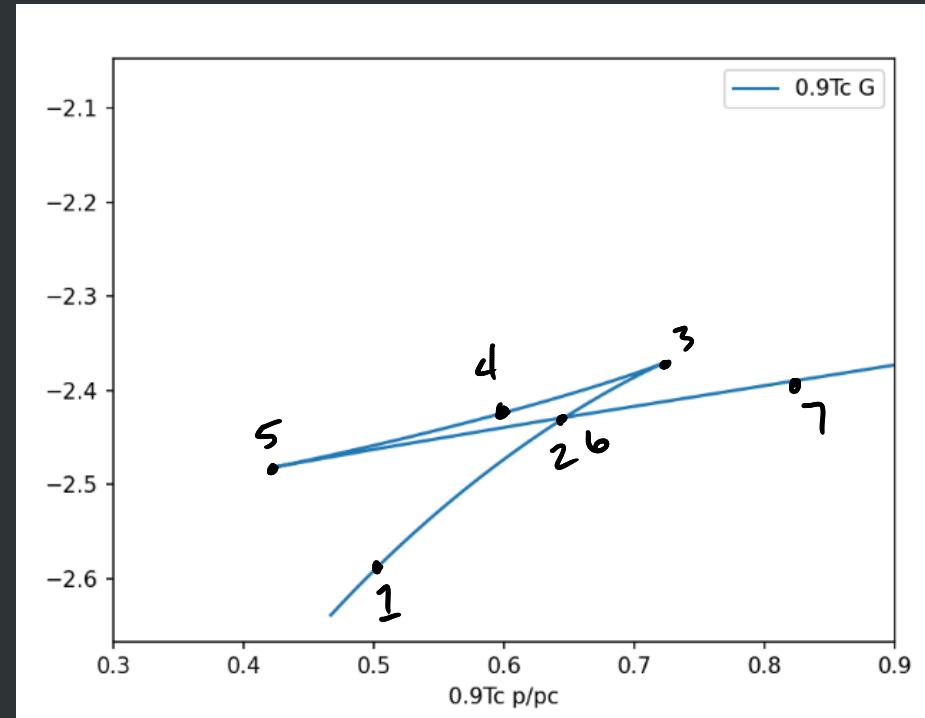
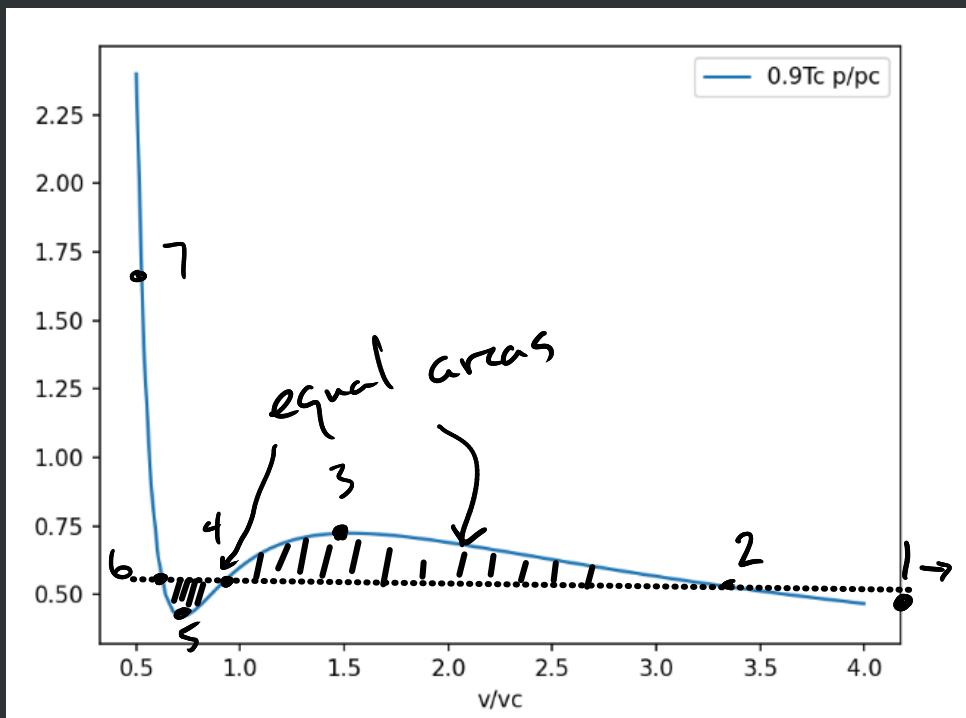
this we can do

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

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

applying $T \neq T_c, V \neq V_c$

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



$$\int_{\text{loop}} dG = 0$$

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

$$\int_{\text{loop}} V dP = 0 \rightarrow \underline{\text{solve for pressure}}$$

