

Chapter 5 - Free Energy

Apply the laws of thermo to non-cyclic processes

↓
chemical reaction

+ other transformations

↳ most interactions

are not isolated from surroundings

↳ but exchange energy and volume.

↳ most are constant temperature + constant pressure

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

$H \equiv U + pV$ ← total energy to create the system and put it in an environment

$$dH = \pm Q + dW_{\text{other}}$$

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

\hookrightarrow to get the work we must do (to a system at constant pressure & temp)

\hookrightarrow Gibbs Free Energy

$$G = U - TS + pV$$

$$G = \underline{H - TS}$$

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

Together there are thermodynamic potentials.

$$dF = dU - TdS$$

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

for a reversible process: (no new entropy created)

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

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

$$dF = \pm W \rightarrow \text{work done on the system}$$

otherwise,

$$dF \leq \pm W$$

Now for the changes in Gibbs

$$dG = dU - TdS + pdV$$

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

for reversible processes,

$$\pm Q = TdS$$

$$\pm W = \underbrace{-pdV}_{\text{compression work}} + \pm W_{\text{other}} \quad \rightarrow \text{electrical work, etc.}$$

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

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

for other than reversible processes

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

ΔG is very useful so how do you measure it?

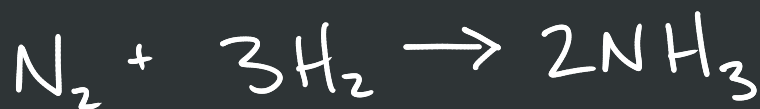
First measure $\Delta H \rightarrow$ heat absorbed/released for a reaction at constant pressure + no other work is done.

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

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

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

Ex: Problem 5.2



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

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

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

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

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

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

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

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

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

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

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

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

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

Electrolysis, Fuel Cells, Batteries.



↑ electrical work has to be done

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

↑ to run forward we have to put
in this much energy

→ some of this energy will push
the environment away

$$\begin{aligned} pV_1 &= n_1RT \\ pV_2 &= n_2RT \end{aligned} \quad \rightarrow \quad p\Delta V = \Delta n \cdot R \cdot T = 1.5 \text{ mol} \cdot (8.31 \text{ J/Kmol}) (300 \text{ K})$$

?

$$= 3739 \text{ J}$$
$$= 3.7 \text{ kJ} \approx 4 \text{ kJ} \leftarrow$$

So 282 kJ will remain in the syst
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?

$$S_{\text{H}_2\text{O}} = 70 \text{ J/K} \quad S_{\text{H}_2} = 131 \text{ J/K} \quad S_{\text{O}_2} = 205 \text{ J/K}$$

products

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

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

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

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

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

$$286 \text{ kJ} - 49 \text{ kJ} = \underline{\underline{237 \text{ kJ}}} \rightarrow \text{comes from} \\ \underline{\text{electrical work}}$$

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

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

→ 49 kJ waste heat goes to the environment

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

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

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

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

⏟
this is great!

Carnot → • extreme case in
cycle chapter 4 → 66%

→ • car engine
 $e_{\text{max}} = 50\%$

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

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?

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

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

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

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

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

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

$$\Delta S = \frac{78,000 \text{ J/mol}}{298 \text{ K}}$$

$$\Delta S = 261.7 \text{ J/K}$$

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

$$G = U - TS + pV$$

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

test Q
↙

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

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

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

hold $V + N$ constant

$$dV = 0$$

$$dN = 0$$

$$dF = -SdT$$

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

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!

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

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

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

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

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

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

\uparrow a small increase in pressure \nwarrow increases the Gibbs free energy

Ex: (5.10)

1 mol H_2O at 25°C (298 K)

Gibbs at 30°C (303 K)?

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

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

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

$$\begin{array}{c} \swarrow \quad \searrow \\ \underline{\underline{G(303)}} - G(298) = -349.55 \text{ J} \end{array}$$

$$\begin{aligned} G(303) &= -349.55 \text{ J} + G(298) \\ &= -0.34955 \text{ kJ} + (-237.13 \text{ kJ}) \\ &= -237.48 \text{ kJ} \quad \checkmark \end{aligned}$$

5.2) Free Energy as a Force toward Equilibrium

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

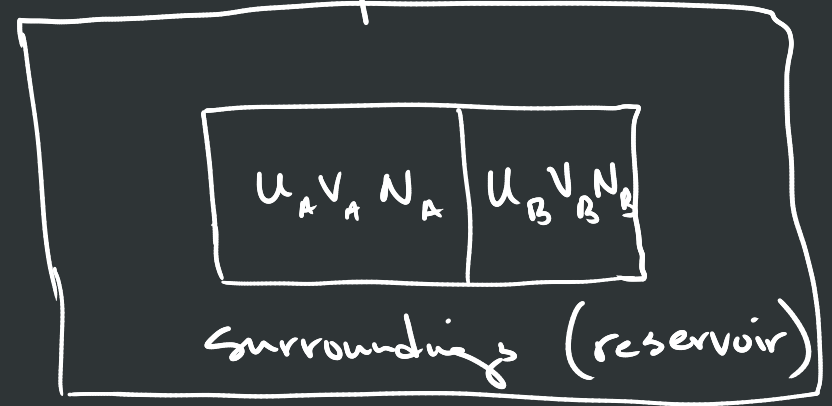
↳ rewrite in
terms of system variable

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

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

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

$$\begin{aligned} dS_{\text{total}} &= dS - \frac{1}{T} dU \\ &= \frac{1}{T} dS - \frac{1}{T} dU \end{aligned}$$



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

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

Helmholtz!

$$dF = dU - T dS - \underbrace{S dT}_{\text{assume } dT=0}$$

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

↑
increase
this

↓
decrease
that

conditions

$$dT=0$$

$$dV=0$$

$$dN=0$$

→ so the system will minimize its Helmholtz free energy

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

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

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

$$dU_R = -dU$$

$$dV_R = -dV$$

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

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

dG if hold T, p, N constant

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

System will minimize Gibbs spontaneously

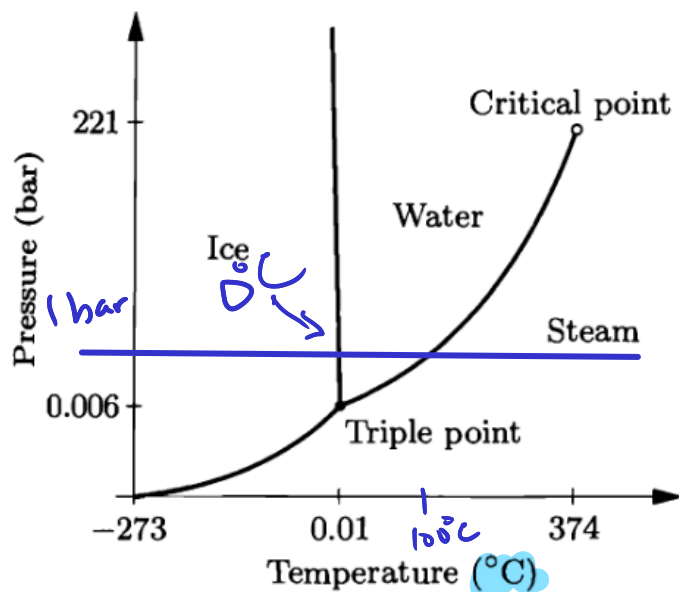
$$dT = 0$$

$$dp = 0$$

$$dN = 0$$

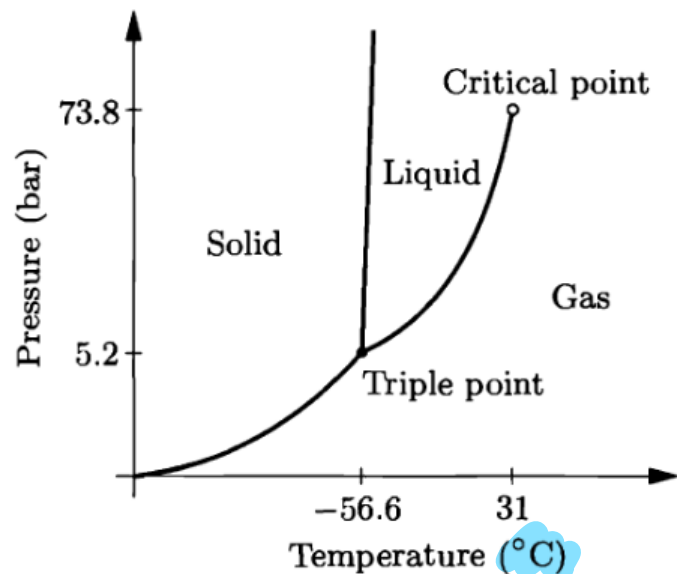
- At constant energy and volume, S tends to increase
- At constant temperature & volume, F tends to decrease
- At constant temperature & pressure, G tends to decrease

5.3] Phase transformations of pure substance



| T ($^{\circ}\text{C}$) | 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 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).



| T ($^{\circ}\text{C}$) | P_v (bar) |
|----------------------------|-------------|
| -120 | 0.0124 |
| -100 | 0.135 |
| -80 | 0.889 |
| -78.6 | 1.000 |
| -60 | 4.11 |
| -56.6 | 5.18 |
| -40 | 10.07 |
| -20 | 19.72 |
| 0 | 34.85 |
| 20 | 57.2 |
| 31 | 73.8 |

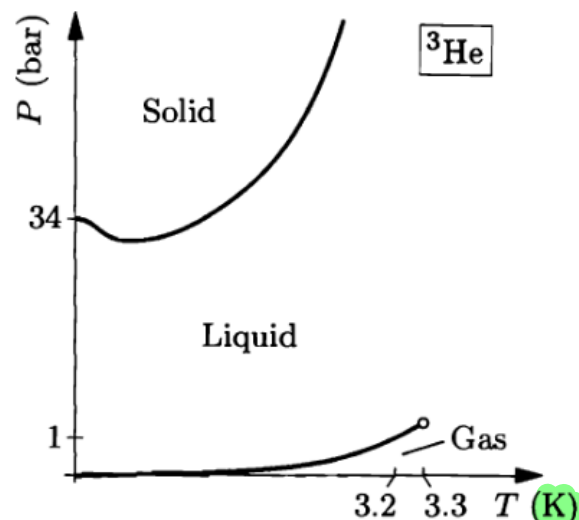
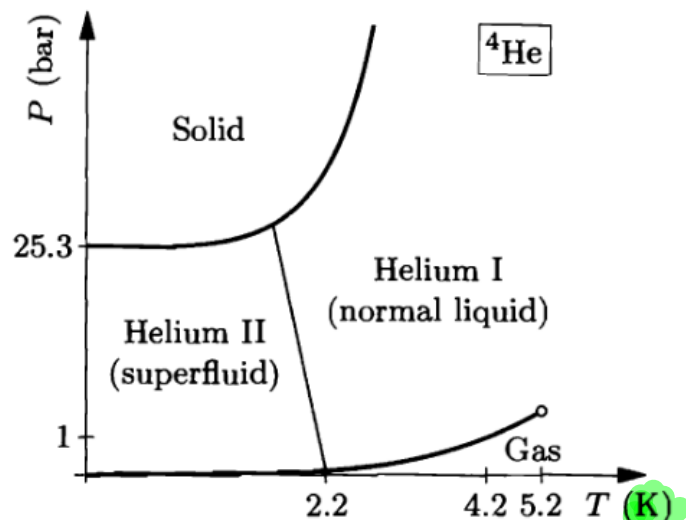


Figure 5.13. Phase diagrams of ^4He (left) and ^3He (right). Neither diagram is to scale, but qualitative relations between the diagrams are shown correctly. Not shown are the three different solid phases (crystal structures) of each isotope, or the superfluid phases of ^3He below 3 mK.

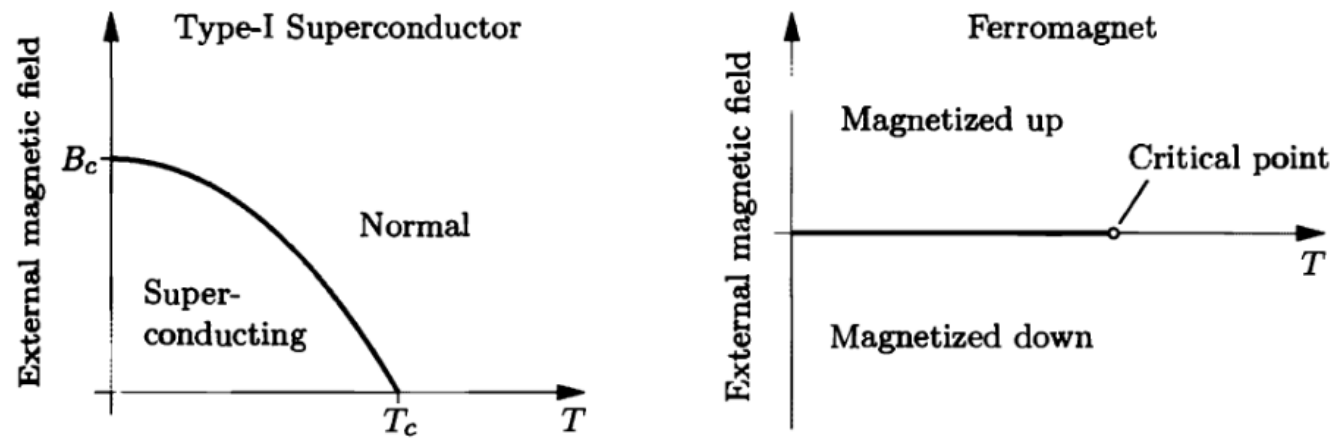
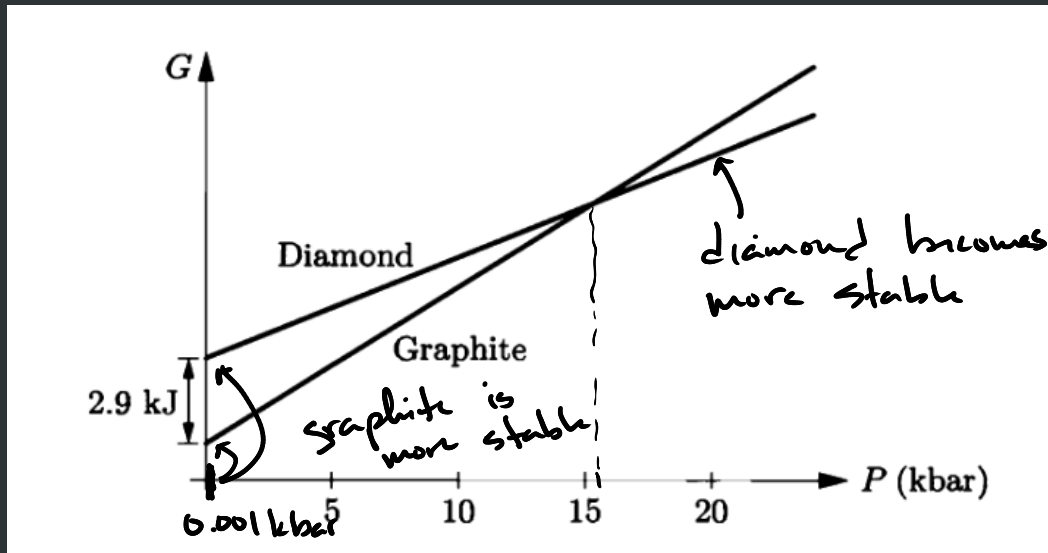


Figure 5.14. Left: Phase diagram for a typical type-I superconductor. For lead, $T_c = 7.2$ K and $B_c = 0.08$ T. Right: Phase diagram for a ferromagnet, assuming that the applied field and magnetization are always along a given axis.



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

→ slope of the graph to the left

→ does not change much
so this would predict a straight-ish line for each of these materials

At what depth would this happen?



$$\begin{aligned} \text{Pressure} &= \frac{\text{Force}}{\text{Area}} = \frac{mg}{A} = \frac{\rho \cdot V \cdot g}{A} \\ &= \frac{\rho \cdot d \cdot \cancel{A} \cdot g}{\cancel{A}} \end{aligned}$$

$$\rho_{\text{H}_2\text{O}} = 1000 \text{ kg/m}^3$$

$$P = \rho d g$$

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

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

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

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