As a material goes from liquid to a solid, it loses entropy by emitting heat

this is latent heat

$$Q = T\Delta S = mL$$

intensive quantity J/kg

$$\Delta S = \pm\frac{mL}{T} = S_\ell - S_s$$

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

$$\boxed{\frac{dP}{dT} = \frac{L}{T\Delta\left(\frac{1}{\rho}\right)}}$$

$$\frac{m}{\Delta V} = \frac{m}{V_f - V_i} = \frac{1}{\frac{V_f}{m} - \frac{V_i}{m}} = \frac{1}{\frac{1}{\rho_f} - \frac{1}{\rho_i}} = \frac{1}{\Delta\left(\frac{1}{\rho}\right)}$$

NOTE: $\Delta\left(\frac{1}{\rho}\right) = \frac{1}{\rho_f} - \frac{1}{\rho_i}$

NOT $\frac{1}{\rho_f - \rho_i}$

e.g. water-ice

$L = 333$ kJ/kg

$T = 273$K

$\rho_{ice} = 917$ kg/m^3 $\rho_{water} = 1000$ kg/m^3

$$\Delta\left(\frac{1}{\rho}\right) = \frac{1}{\rho_{water}} - \frac{1}{\rho_{ice}} = \frac{1}{1000} - \frac{1}{917} = -9.05\times10^{-5}\ \text{m}^3/\text{kg}$$

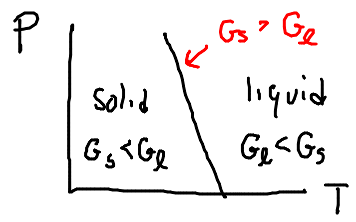
$$\frac{dP}{dT} = \frac{L}{T\Delta\left(\frac{1}{\rho}\right)} = \frac{333\times10^3\ \text{J/kg}}{(273)(-9.05\times10^{-5})} = -1.35\times10^7\ \text{Pa/K}$$

e.g. if to apply 135 atm to a 2cm × 2cm surface

requires 5405 N to drop freezing temperature by 1C°

$1.37\times10^7\ \frac{N}{m^2} \times (0.02)^2\ m^2$

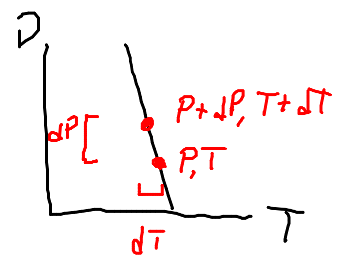
weight of 550kg.



Phase boundaries are where $G_1 = G_2$

all extensive variables in the following are "per mole"

- Choose one point on P,T diagram where $G_s(P,T) = G_\ell(P,T)$
- Suppose that $P + dP$, $T + dT$ is on phase boundary too



$$G_s(P+dP, T+dT) = G_s(P,T) + dG$$

$$dG = -S\,dT + V\,dP + \mu\,dN$$

$$G_s(P+dP, T+dT) = G_s(P,T) - S_s\,dT + V_s\,dP$$

$$G_\ell(P+dP, T+dT) = G_\ell(P,T) - S_\ell\,dT + V_\ell\,dP$$

$$\therefore \quad -S_s\,dT + V_s\,dP = -S_\ell\,dT + V_\ell\,dP$$

$$\xrightarrow[\text{happens}]{\text{algebra}} \quad \frac{dP}{dT} = \frac{S_s - S_\ell}{V_s - V_\ell}$$

gives the slope of the phase boundary

Clausius – Clapeyron relation

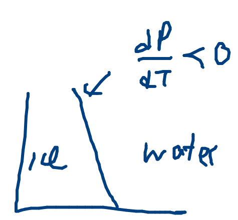
e.g. ice & water : $S_s < S_\ell$ water has more entropy

ice & water : $V_s > V_\ell$

water at $0^\circ C$ is more dense than ice.

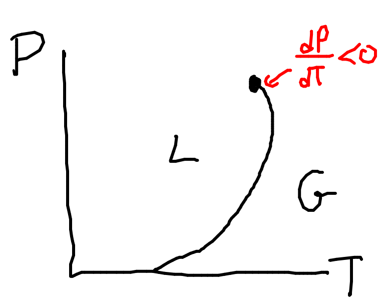
– takes up less space

$$\frac{dP}{dT} = \frac{S_s - S_\ell}{V_s - V_\ell} = \frac{-}{+} < 0$$



Because slope of phase boundary is negative, ice floats on water

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



What's wrong with this picture?

either

- $V_g < V_\ell$ — **No!** gases are much bigger than liquids

or $S_g < S_\ell$ — gases have more entropy than liquids