Pg 294 Reif

$$P(y) \propto \Omega(\bar{E}; y)\, e^{-\beta_0 \bar{E}(y)} \cancel{\propto} = e^{S(y)/k}\, e^{-\beta_0 \bar{E}(y)}$$

$$= e^{-\beta_0\left(-S(y)/k\beta_0 + \bar{E}(y)\right)} = e^{-\beta_0\left(\bar{E}(y) - S(y)T_0\right)} = e^{-\beta_0 F_0}$$

$$\frac{1}{k\beta_0} = T_0$$

Pg 298 Reif

$$\frac{\partial G_0}{\partial T}\Big|_V = \left(1 - \frac{T_0}{T}\right)\left(\frac{\partial \bar{E}}{\partial T}\right)\Big|_V$$

$$\frac{\partial^2 G_0}{\partial T^2}\Big|_V = \left(1 - \frac{T_0}{T}\right)\frac{\partial^2 \bar{E}}{\partial T^2}\Big|_V + \left(\frac{T_0}{T^2}\right)\frac{\partial \bar{E}}{\partial T}\Big|_V$$

Pg 300 Reif

$$G_0(V) = G_{min} - \frac{1}{2}\left(\frac{\partial \bar{p}}{\partial V}\right)_T (\Delta V)^2 = G_{min} - \frac{1}{2}\left(\frac{-1}{Vk}\right)(\Delta V)^2$$

$$= G_{min} = \frac{1}{2Vk}$$

pg 307 Reif

$p < p_1$ 8.4.15 $\Rightarrow$ $\left.\frac{\partial p}{\partial V}\right|_T \lesssim 0$.

$\left.\frac{\partial p}{\partial V}\right|_T \approx 0$

$\kappa \simeq -\frac{1}{V} \left.\frac{\partial V}{\partial p}\right|_T \gg 1$

Pg 308 Rut

$$dg = \underbrace{d\varepsilon - T\,ds} + dp\,v + dv\,p$$

$$= -p\cancel{dV} + p\cancel{dv} + v\,dp = V\,dp$$

Pg 313 Rut

$$d(E - TS) = d(F) = dE - d(TS)$$

$$= T\cancel{dS} - p\,dV + \sum_{i=1}^{m} \mu_i\,dN_i - \cancel{T}dS - S\,dT$$

$$= -S\,dT - p\,dV + \sum_{i=1}^{m} \mu_i\,dN_i$$

Also

$$dG = d(E - TS + pV)$$

$$= dF + d(pV) = -S\,dT - p\cancel{dV} + \sum_{i=1}^{m} \mu_i\,dN_i + p\cancel{dV} + \overset{\text{keep}}{\cancel{V\,dp}}$$

$$= -S\,dT + V\,dp + \sum_{i=1}^{m} \mu_i\,dN_i$$

Pg 314 Reif

$$E(\alpha S, \alpha V, \alpha N_1, \dots, \alpha N_m) = \alpha E(S, V, N_1, \dots, N_m)$$

let $\alpha = 1 + r$

$$\underbrace{E(S + rS, V + rV, N_1 + rN_1, \dots, N_m + rN_m)}_{\text{taylor Expand.}} = (1+r)E$$

$$E(S, V, \cancel{N}_1, \dots, N_m) + \left.\frac{\partial E}{\partial S}\right|_{V,N} rS + \left.\frac{\partial E}{\partial V}\right|_{S,N} rV + \sum_{i=1}^{m} \frac{\partial E}{\partial N_i}(rN_i) \cancel{+} + O(r^2)$$

$$= \cancel{E} + rE$$

$$\Rightarrow \quad E = \left(\frac{\partial E}{\partial S}\right)_{V,N} S + \left.\frac{\partial E}{\partial V}\right|_{S,N} V + \sum_{i=1}^{m} \frac{\partial E}{\partial N_i} N_i$$

By 8.7.7. $\left.\dfrac{\partial E}{\partial S}\right|_{V,N} = T$ $\quad \left.\dfrac{\partial E}{\partial V}\right|_{T,N} = -p$

$$\left.\frac{\partial E}{\partial N_i}\right|_{V,T} = \mu_i$$

$$\therefore \quad E = TS - pV + \sum_{i=1}^{m} \mu_i N_i$$

pg 315 Reif

$$\cancel{dE} = \cancel{TdS} + SdT - \cancel{pdV} - Vdp + \cancel{\sum_i \mu_i dN_i} + \sum_i N_i d\mu_i$$

$$\Rightarrow \quad SdT - Vdp + \sum_i N_i d\mu_i = 0$$

Pg 326 Reif

(8.1) I am going to assume that the probability to find this small vol w/ volume between V & $V+dV$ & temperature between T & $T+dT$ is denoted by

$$P(V,T)\,dV\,dT \;\propto\; e^{-\frac{G(V,T)}{kT_0}}$$

Question:

Note: I am not sure that this is true for arb temp but think so.

Now V & T are ~~[illegible]~~ different from T_0 & $\tilde{V}$ the values at the minimum of $G(V,T)$

Now: taylor expanding G about $\tilde{V}$ & T_0 gives

$$G(V,T) = G_{min} + \frac{\partial G}{\partial T}\Big|_{\tilde{V}}(T-T_0) + \frac{\partial G}{\partial V}\Big|_T (V-\tilde{V})$$

$$G(V,T) = G_{min} + \frac{\partial G_0}{\partial T}\Big|_V (T-T_0) + \frac{\partial G_0}{\partial V}\Big|_T (V-\tilde{V}) + \frac{1}{2!}\left(\frac{\partial^2 G_0}{\partial V^2}\Big|_T (V-\tilde{V})^2 + 2\frac{\partial^2 G_0}{\partial V\,\partial T}(V-\tilde{V})(T-T_0) + \frac{\partial^2 G_0}{\partial T^2}(T-T_0)^2\right) + O(\Delta^3)$$

As G_{min} is the minimum $\frac{\partial G}{\partial T}\Big|_V = 0$

$$\frac{\partial G}{\partial V}\Big|_T = 0$$

Then

$$P(V,T)\,dV\,dT = A\exp\left\{-\frac{G_{min}}{kT_0}\right\}$$

$$\cdot\exp\left\{-\frac{1}{2kT_0}\frac{\partial^2 G_0}{\partial V^2}\Big|_T (V-\tilde{V})^2 - \frac{\partial^2 G_0}{\partial V\,\partial T}\frac{(V-\tilde{V})(T-T_0)}{kT_0} - \frac{1}{2}\frac{\partial^2 G_0}{\partial T^2}\Big|_V \frac{(T-T_0)^2}{kT_0}\right\}$$

$$P(V,T)\,dV\,dT = A'\exp\left\{\;\ldots\ldots\;\right\}$$

total specific heat. ↓ specific heat per unit mass. ↓

From pg 298 Reif Book $\left.\frac{\partial^2 G_0}{\partial T^2}\right|_V = \frac{1}{T_0}\left.\frac{\partial \bar{E}}{\partial T}\right|_V = \frac{C_V}{T_0} = \frac{c_V M}{T_0}$

$$\therefore\quad P(V,T)\,dV\,dT = A'\exp\left\{-\frac{C_V}{2kT_0^2}(T-T_0)^2 - \frac{1}{2kT_0}(V-\tilde{V})^2\left.\frac{\partial^2 G_0}{\partial V^2}\right|_T - \frac{(V-\tilde{V})(T-T_0)}{kT_0}\frac{\partial^2 G_0}{\partial V\partial T}\right\}$$

Now from pg 299 Reif Book $\left.\frac{\partial^2 G_0}{\partial V^2}\right|_T = -\left(\frac{\partial p}{\partial V}\right)_T = \frac{1}{VK}$

↑ Should be $\tilde{V}$. Why?

$$G_0 = \bar{E} - T_0 S + p_0 V \qquad\qquad = \frac{1}{\tilde{V}K} = \frac{\rho_0}{MK}$$

$$\left.\frac{\partial G_0}{\partial V}\right|_T = \frac{\partial E}{\partial V} - T_0\frac{\partial S}{\partial V} + p_0$$

$$\frac{\partial^2 G_0}{\partial T\partial V} = \underline{\frac{\partial^2 E}{\partial T\partial V}} - T_0\frac{\partial^2 S}{\partial T\partial V} = 0\ ?$$ How show? Or why not present?

$$\therefore\quad P(V,T)\,dV\,dT = A'\exp\left\{-\frac{C_V}{2kT_0^2}(T-T_0)^2 - \frac{1}{VKkT_0}(V-\tilde{V})^2\right\}$$

$$\tilde{V} = \frac{M}{\rho_0}$$

$$P(V,T)\,dV\,dT = A' \exp\left\{-\frac{C_V M}{2kT_0^2}(T-T_0)^2 - \frac{\rho_0}{2M\kappa k T_0}\left(V-\frac{M}{\rho_0}\right)^2\right\}$$

$$\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} P(V,T)\,dV\,dT = 1 \quad \text{By Normalization}$$

$$\parallel$$

$$= A' \int_{-\infty}^{\infty} \exp\left\{-\frac{C_V M}{2kT_0^2}(T-T_0)^2\right\} dT \int_{-\infty}^{\infty} \exp\left\{\frac{-\rho_0}{2M\kappa k T_0}\left(V-\frac{M}{\rho_0}\right)^2\right\} dV$$

$$= A' \int_{-\infty}^{\infty} \exp\left\{-\frac{C_V M}{2kT_0^2}(T-T_0)^2\right\} dT \int_{-\infty}^{\infty} \exp\left\{\frac{-\rho_0}{2M\kappa k T_0}\left(V-\frac{M}{\rho_0}\right)^2\right\} dV$$

$$= A' \sqrt{\pi}\left(\frac{C_V M}{2kT_0^2}\right)^{-1/2} \sqrt{\pi}\left(\frac{\rho_0}{T_0 2M\kappa k}\right)^{-1/2}$$

$$= \pi A' \left(\frac{2kT_0^2}{C_V \cancel{M}} \cdot \frac{T_0 2\cancel{M}\kappa k}{\rho_0}\right)^{1/2} = 2\pi A' \left(\frac{k^2 \kappa T_0^3}{C_V \rho_0}\right)^{1/2}$$

$$\Rightarrow \quad P(V,T)\,dV\,dT = \frac{1}{2\pi}\left(\frac{C_V \rho_0}{k^2 \kappa T_0^3}\right) \exp\left\{\frac{-MC_V}{2kT_0^2}(T-T_0)^2 - \frac{\rho_0}{2M\kappa k T_0}\left(V-\frac{M}{\rho_0}\right)^2\right.$$

Questions: 1) When do we use $-\frac{G(V,T)}{kT_0}$ To vs. T?

2) How does the 2nd derivative of $\frac{\partial^2 G_0}{\partial V \partial T} = 0$?

3) What is the difference between G_0 & G?

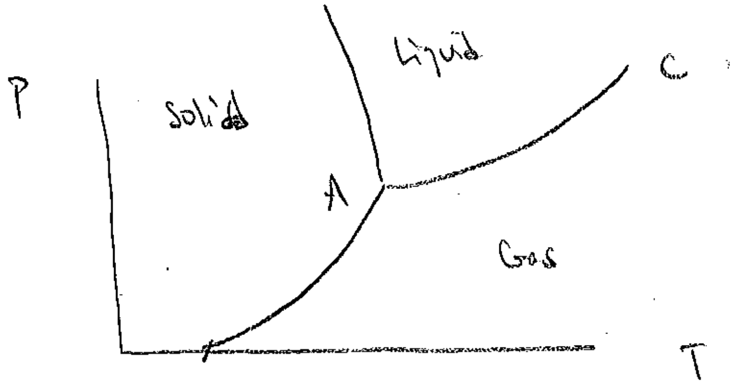
(8.2) Using the Clausius-Clapeyron eq to derive vapor pressure one assumes ΔV = change in vol from solid (liquid) = vol of gas. $p = p_0 e^{-l/RT}$

Guess: $[T]$ = kelvin

Solid Ammonia:
$\ln p = 23.03 - \frac{3754}{T}$

Liquid Ammonia:
$\ln p = 19.49 - \frac{3063}{T}$

(a) Both these curves give the approximate phase diagram in the p,T plane



Thus the ~~stopp~~ triple pt is at the intersection of these two curves

by subtracting

$$0 = 3.54 - \frac{3754}{T} + \frac{3063}{T} \Rightarrow 0 = 3.54 - \frac{691}{T}$$

$$T = \frac{691}{3.54} = 195.19 \text{ kelvin}$$

then $\ln p = 3.798 \Rightarrow p = 44.6$

(b) $l = ?$ For sublimation $\ln p = 23{,}03 - \frac{3754}{T}$

$$p = e^{23{,}03}\, e^{-\frac{3754}{T}}$$

$$\Rightarrow -\frac{l}{R\cancel{T}} = -\frac{3754}{R\cancel{T}} \rightarrow l = 3754(R) \qquad [3754] = \text{kelvin}$$

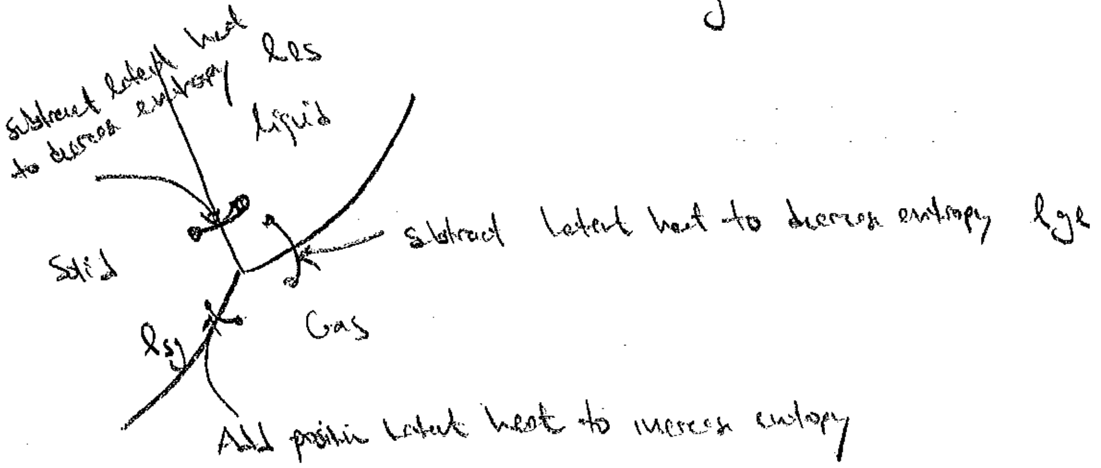
$R = 8{,}3143 \times 10^{7}$ ergs deg^{-1} mole^{-1}

$\therefore\ l_{\text{sublimation}} = 3754(8{,}3143 \times 10^{7})$ ergs · mole^{-1}

$= 3{,}12 \times 10^{11}$ ergs/mole $\frac{1\text{J}}{10^{7}\text{ergs}} = 3{,}12 \times 10^{4}$ Joules

For vaporization

$l = 3063$ deg · $8{,}3143$ J/deg·mole $= 2{,}546 \times 10^{4}$ Joules/mole.



$$\therefore\ l_{sg} - l_{gl} - l_{ls} = 0$$

and back in same state.

$$l_{ls} = l_{sg} - l_{gl}$$

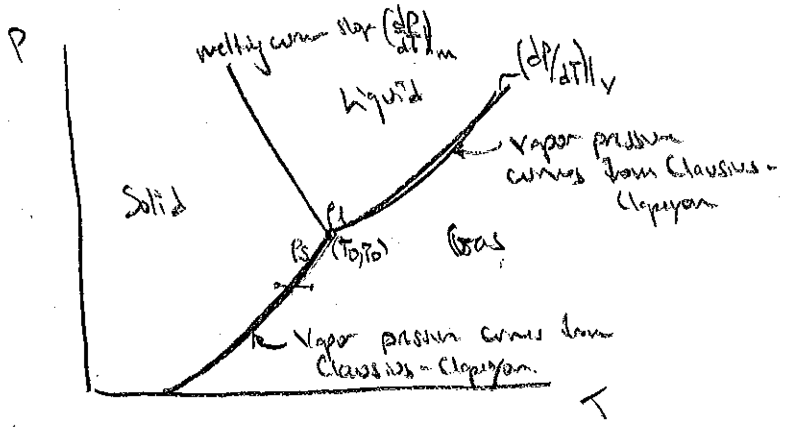
$$= 3{,}12 \times 10^{4} \text{ Joules/mole} - 2{,}546 \times 10^{4} \text{ Joules/mole}$$

$$= 5{,}74 \times 10^{3} \text{ Joules/mole}$$

Pg 326 Reif

1

(B.3)



Clausius-Clapeyron eq:

$$\frac{dP}{dT} = \frac{\Delta S}{\Delta V} = \frac{L_{12}}{T\Delta V}$$

ℓ = latent heat per mole

μ = molecular wt.

$\Rightarrow [\mu] = g/\text{mole}$

$\therefore \left[\frac{\ell}{\mu}\right] = \frac{\text{Heat}/\text{mole}}{g/\text{mol}}$

= Heat/gram

$\ell/\mu = L$

∴ Clausius clapeyron applied along sublimation curve gives

$$\left(\frac{dP}{dT}\right)_S = \frac{1}{T}\left(\frac{\ell_{sg}}{\Delta v}\right)$$

ℓ = latent heat per mole & Δv = vol change per mole

$$\Delta v \approx v_g - v_s \approx v_g$$

$$\left(\frac{dP}{dT}\right)_S = \frac{1}{T}\left(\frac{\ell_{sg}}{v_g}\right) \quad (1)$$

~~ℓ = latent heat/vol.~~

$[\mu\rho_s] = g/\text{mole} \cdot g/L^3$ [illegible]

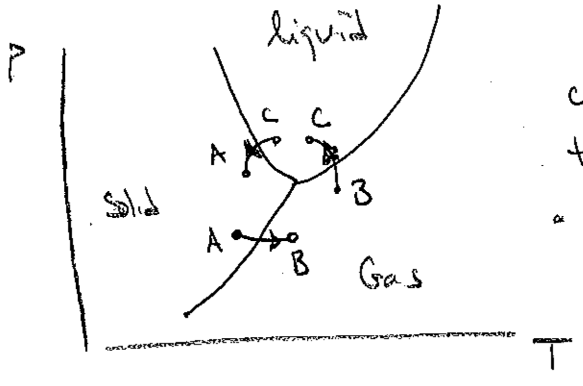
$$\left[\frac{\mu}{\rho_s}\right] = \frac{g/\text{mole}}{g/L^3} = L^3/\text{mole}$$

$\therefore \left[\frac{\mu}{\rho_s}\right]$ = vol of the substance (solid) per mole

$$\left(\frac{dP}{dT}\right)_V = \frac{1}{T}\left(\frac{\ell_{\ell g}}{\Delta v}\right)$$

$$\Delta v = v_g - v_\ell \approx v_g$$

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



completing one cycle around the triple point, should give us a net of no heat/loss gain?

From A to B ⇒ $\Delta S > 0$.

$\left\{ \Delta S = l_{12} / \Delta V \right\}$

[illegible] $\Delta V = V_{gas} - V_{solid} \simeq V_{gas} \geq 0$

$l_{12} \geq 0 \quad \therefore \quad \left(\frac{dP}{dT}\right)_S = \frac{1}{T}\frac{l_{sg}}{V_{gas}}$

From B to C $\quad \Delta S < 0$

$\Delta V = V_{liq} - V_{gas} \simeq -V_{gas}$

$\left(\frac{dP}{dT}\right)_V = -\frac{1}{T}\left(\frac{l_{lg}}{V_{gas}}\right)$

$L_{12} \equiv T\Delta S$ Thus the ~~[illegible]~~ latent heat carries the same sign as the change in entropy

$[L]$ = either latent heat/mole or latent heat per gram.

From C to A $\quad \Delta S < 0$

ΔV

* Note that $L_{AB} + L_{BC} + L_{CA} = 0$

$$\shortparallel$$

$$\cancel{T}\,\Delta V_{AB}\left(\frac{dP}{dT}\right)_S + \cancel{T}\,\Delta V_{BC}\left(\frac{dP}{dT}\right)_V$$

$$+\cancel{T}\,\Delta V_{CA}\left(\frac{dP}{dT}\right)_m = 0$$

By summing entropy changes around this triple point. entropy is a fn of the state of the system

$\Delta V_{AB} = V_{gas} - V_{solid} \simeq V_{gas} = V_B$

$\Delta V_{BC} = V_l - V_g \simeq -V_{gas} = -V_B$

$[V]$ is either molar volume or volume per gram.

$\Delta V_{CA} = V_A - V_C$

$\therefore$

$$\left(\frac{dP}{dT}\right)_M = -\frac{\Delta V_{AB}}{\Delta V_{CA}}\left(\frac{dP}{dT}\right)_S - \frac{\Delta V_{BC}}{\Delta V_{CA}}\left(\frac{dP}{dT}\right)_V$$

$$= \frac{-V_B}{V_A - V_C}\left(\frac{dP}{dT}\right)_S + \frac{V_B}{V_A - V_C}\left(\frac{dP}{dT}\right)_V$$

takin $[V]$ = molar volume $\Rightarrow$

$$= \frac{-V_B}{\left(\frac{\mu}{\rho_S} - \frac{\mu}{\rho_L}\right)}\left(\frac{dP}{dT}\right)_S + \frac{V_B}{\left(\frac{\mu}{\rho_S} - \frac{\mu}{\rho_L}\right)}\left(\frac{dP}{dT}\right)_V$$

$$= \frac{-V_B/\mu}{\left(\frac{1}{\rho_S} - \frac{1}{\rho_L}\right)}\left(\frac{dP}{dT}\right)_S + \frac{V_B/\mu}{\left(\frac{1}{\rho_S} - \frac{1}{\rho_L}\right)}\left(\frac{dP}{dT}\right)_V$$

Now $[V_B/\mu] = \frac{\text{Vol/mole}}{\text{g/mol}} = \frac{\text{Vol}}{\text{g}}$ of gas

$VP = RT$ $\quad n = 1 \quad \Rightarrow [V] =$ Vol/mole.

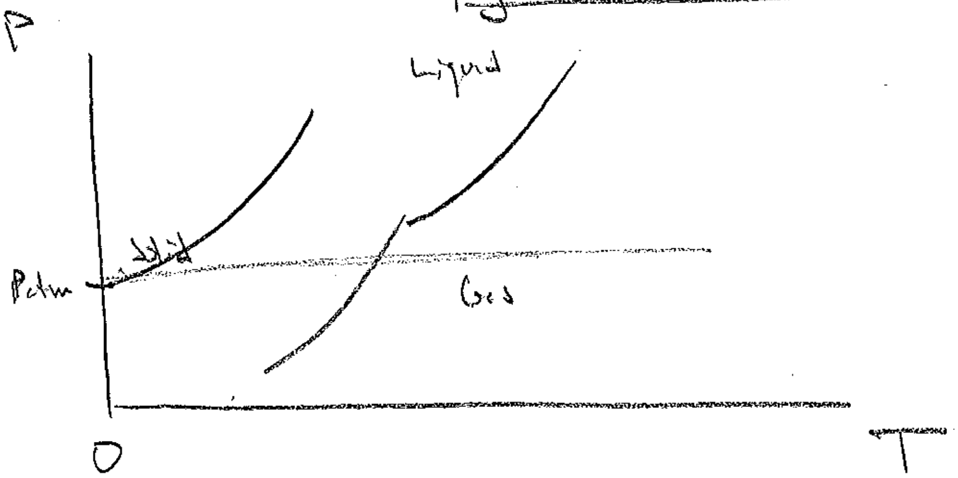
$V = \frac{RT}{P}$

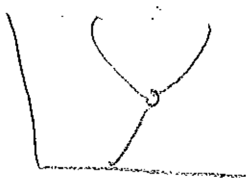
$$\Rightarrow \frac{1}{V_B}\left(\frac{dP}{dT}\right)_M = \frac{1}{\mu}\frac{1}{(1/\rho_S - 1/\rho_L)}\left(\frac{dP}{dT}\right)_S + \frac{1}{\mu(1/\rho_S - 1/\rho_L)}\left(\frac{dP}{dT}\right)_V$$

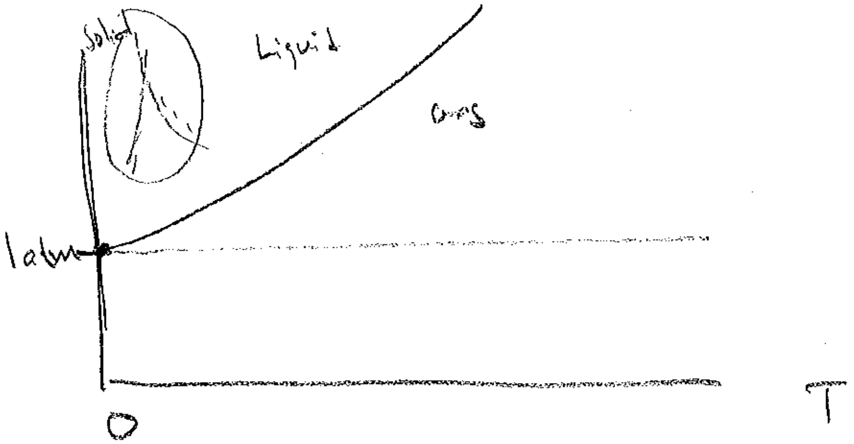
$$= \frac{P}{RT}\left(\frac{dP}{dT}\right)_M = \underline{\qquad\qquad\qquad\qquad}$$

Pg 326 Reif

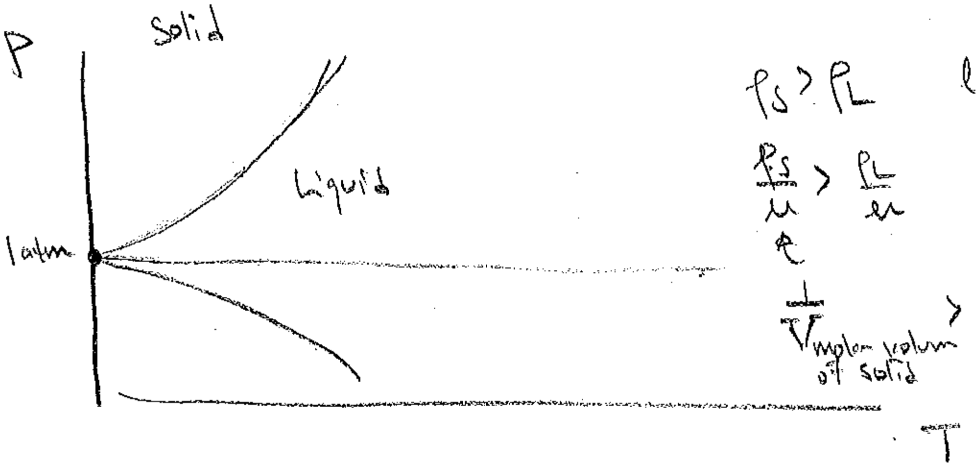
8.4







$$\frac{g/V}{g/mol} = \frac{mol}{V}$$



$\rho_S > \rho_L$ let μ = moleqular weight.

$\frac{\rho_S}{\mu} > \frac{\rho_L}{\mu}$

$\Leftarrow$

$\frac{1}{V_{\text{molar volume of Solid}}} > \frac{1}{V_{\text{molar volume of Liquid}}}$

$\Rightarrow \boxed{V_{\text{molar vol of Liq}} > V_{\text{molar vol of Solid}}}$

Clausius Clapeyron Eq

$$\left(\frac{dP}{dT}\right)_m = \frac{\Delta S}{\Delta V} < 0$$

from Solid to Liquid

$\Delta V > 0$

$+ \Delta S < 0$.

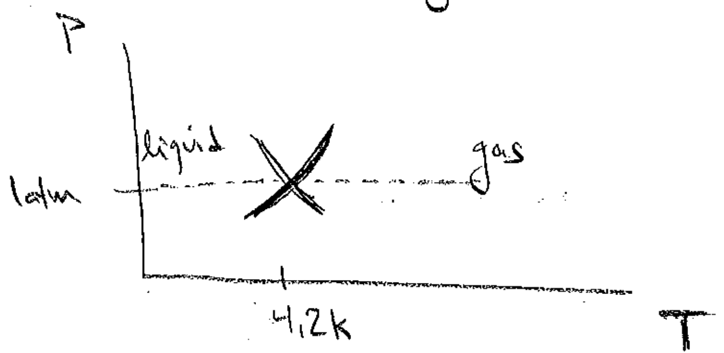
<u>Questions</u>

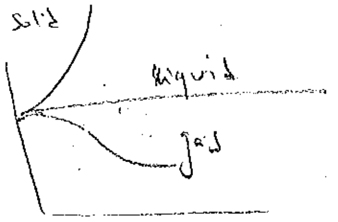
1) If this is true then what does the P & T diagram look like?

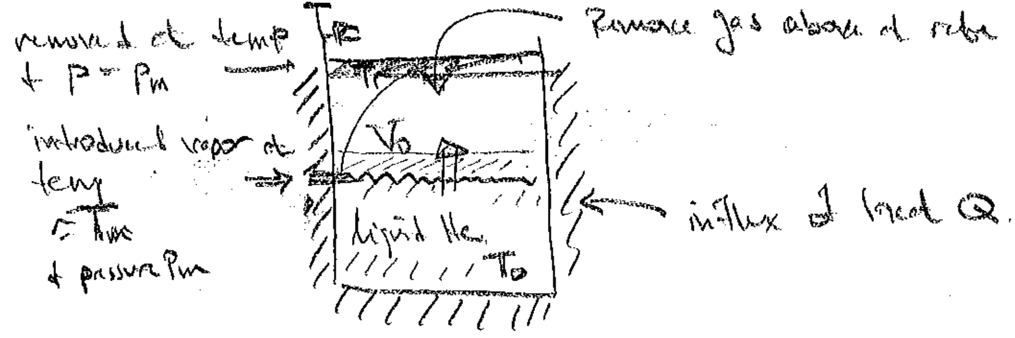
2) How do I know that $\frac{dp}{dT} \neq 0$?

Pg 326 Pr 7

(8.5)







$\frac{dV}{dt} = -\mathcal{V}$ constant

$V(t) = -\mathcal{V}t + V_0$

(a) With heat influx Q, lets assume all this heat goes into changing the liquid He into gasious He

$\Rightarrow$ $\frac{Q}{L}$ = # of moles of He that get converted into gasous He per second.

as ~~μ (molecular weight of He) = 2 g/mole~~

In the top portion 2 effects occur the ss an influx of Gas due to a phase change & an outflux of gas due to the pumping action. 1st the volume of gas produced per second is then

The $P_m V = nRT_{pm}$

$$V = \frac{\left(\frac{Q}{L}\right) R T_{pm}}{P_m} \text{ per second input}$$

set

$= \mathcal{V}$ = amount take out

$$P_m = \frac{Q R T_{pm}}{L \mathcal{V}}$$

Note: we use T_r for the temperature in the ideal gas eq. This is due to the fact that this volume of gas is removed at T_r not at T_{He}. Thus that is where the volume below is achieved.

(b) Calculate T_m the temperature of the He as it melts. From the Clausius-Clapeyron eq one can show

$$p = p_0 e^{-\ell/RT}$$

to get p_0 evaluate at T_r (top of dewar)

$$p_m = p_0 e^{-\ell/RT_r}$$

$$p_0 = p_m e^{\ell/RT_r}$$

Then $p = p_m e^{\ell/RT_r} e^{-\ell/RT}$

at the surface $p_m = p_m e^{\ell/RT_r} e^{-\ell/RT_m}$?

From the information given about the ~~p_0~~ boiling temperature & pressure one can calculate

$$p = p_0 e^{-\ell/RT}$$

w/ $p = p_0$ (1 atm)
& $T = T_0$ (4.2 K)

~~$p_0 = p_0 e^{-\ell/RT_0}$~~

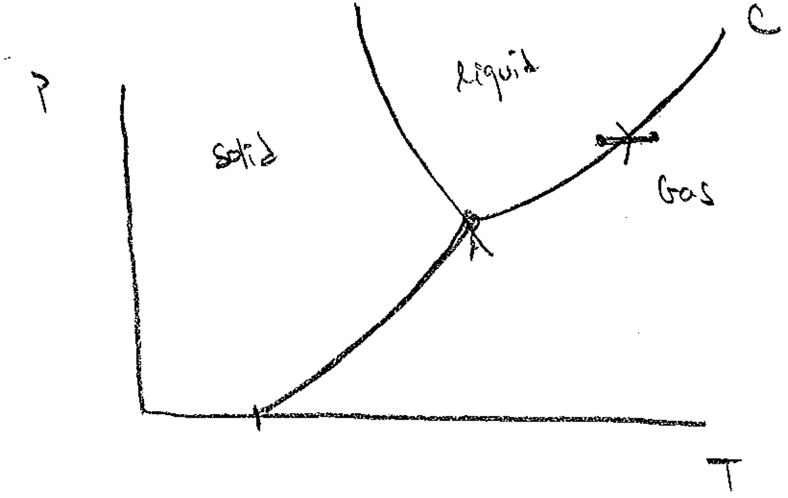
$$p_m = p_0 e^{-\ell/RT_m} \Rightarrow \ln\left(\frac{p_0}{p_m}\right) = -\frac{\ell}{RT_m}$$

$$T_m = -\frac{l}{R\ln(p_0/p)}$$ $l =$ latent heat per mole

Question

<u>How do part (b)??</u>

(b)



$l \equiv T\Delta S$

$l_{eg} \geq 0.$

$$\frac{dp}{dT} = \frac{l}{T\Delta v}$$

$$\Longleftrightarrow \frac{dp}{dT} = \frac{L}{T\Delta V}$$

$l \overset{?}{\propto} L$

$l \downarrow$ latent heat per unit mole

$L \downarrow$ latent heat per unit gram

μ = molecular wt
= g/mol

ΔV = Vol change per gram.

$$\frac{l}{\mu} = L$$

$\frac{L}{n} =$

Clausius Clapeyron ⟹

$$\Delta V\,dp = L\frac{dT}{T}$$

$$\Delta V = V_{gas} - V_{liq} \approx V_{gas} = \frac{nRT}{p}$$

⟹ curves OA & AC are given by $p = p_0 e^{-}$

Confusion is: is that p_0 in problem statement is not

p_0 on pg 306

Thus eq on 306 can be written

$$p = Ae^{-\ell/RT}$$

know at $p = p_0$ & $T = T_0$ from problem statement that is an solution to the Above eq

$$p_0 = Ae^{-\ell/RT_0} \Rightarrow A = p_0 e^{\ell/RT_0}$$

Thus $$p = p_0 e^{\ell/RT_0} e^{-\ell/RT} = p_0 \exp\left\{\frac{\ell}{R}\left(\frac{1}{T_0} - \frac{1}{T}\right)\right\}$$

to find approx temp at pressure p_m

$$\Rightarrow \frac{p_m}{p_0} = \exp\left\{\frac{\ell}{R}\left(\frac{1}{T_0} - \frac{1}{T_m}\right)\right\}$$

$$\frac{R}{\ell} \ln\left(\frac{p_m}{p_0}\right) = \frac{1}{T_0} - \frac{1}{T_m}$$

$$\frac{1}{T_m} = \frac{1}{T_0} - \frac{R}{\ell} \ln\left(\frac{p_m}{p_0}\right)$$

$$\Rightarrow T_m = \frac{1}{\left(\frac{1}{T_0} - \frac{R}{\ell} \ln\left(\frac{p_m}{p_0}\right)\right)} \frac{T_0}{T_0}$$

$$\Rightarrow \quad T_m = T_0\left(1 - \frac{RT_0}{l}\ln\left(\frac{P_m}{p}\right)\right)^{-1}$$

Now $l = \cancel{\mu}L$ ~~Thus in terms of the variables~~ given

~~$T_m = T_0\left(1 - \frac{RT_0}{\mu L}\ln\left(\frac{P_m}{p}\right)\right)^{-1}$~~

l = latent heat per mole ⇒ l above = L in problem.