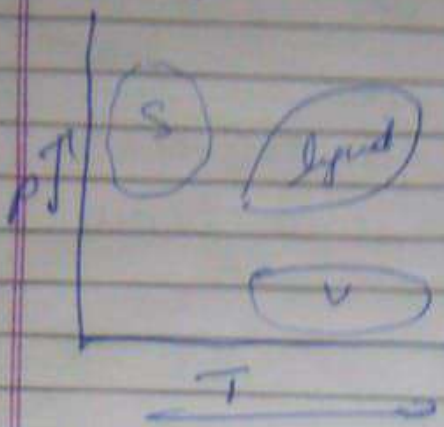
Since it defines a one component system i.e. C = 1, the max degree of freedom is 2, i.e. it, phase diagram can be drawn in 2 dimensions



A single phase can be drawn over a region or area since the given phase can exist under different conditions of T & P, ie. T & P can be varied independently over a range of values without affecting the existing of single phase.

solid phase is stable at low T & high P
liquid phase is in between these 2 extreme
Gases phase is at high T & low P

Two phase in equilibrium can be represented by one line, since only one variable is required either T or P has a definite value of T is stated, the corresponding equilibrium value of P can be determined & vice versa. The no. of lines in a phase diagram will be equal to no. of two phase equilibria which the system can posses.

Since for a pure substance $dG = -S_m dT + V dP$
or in terms of chemical potential $d\mu = -S_m dT + V dP$
At const P

$\left(\frac{\partial \mu}{\partial T}\right)_P = -S_m$ The slope of curve drawn between μ and T is equal to S_m

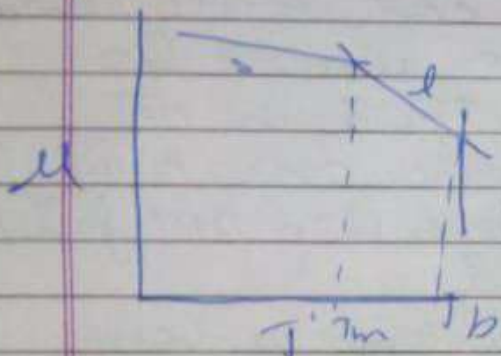
Since S_m of a given substance in any phase is +ve so slope of the curve μ vs T should -ve then.

At any temp $S_{m,s} < S_{m,l} < S_{m,g}$.

Taking -ve it will reverse the sign

$-S_{m,s} > -S_{m,l} > -S_{m,g}$.

ie the slope of μ VS T curve for a substance has small -ve value since $S_{s,m}$ is small value slope of μ VS T for liquid is slightly more -ve and that for gases is large -ve value



The curve where s & l phase intersect each other at temp T_m. At this temp, chemical potential of substance is same in both solid & liquid phase. ie $s \rightleftharpoons l$.

Temp T_m is mpt of the solid.

Curves liquid & gaseous phase intersect each at temp T_b where $\mu_l = \mu_g$. It is called boiling part of liquid.

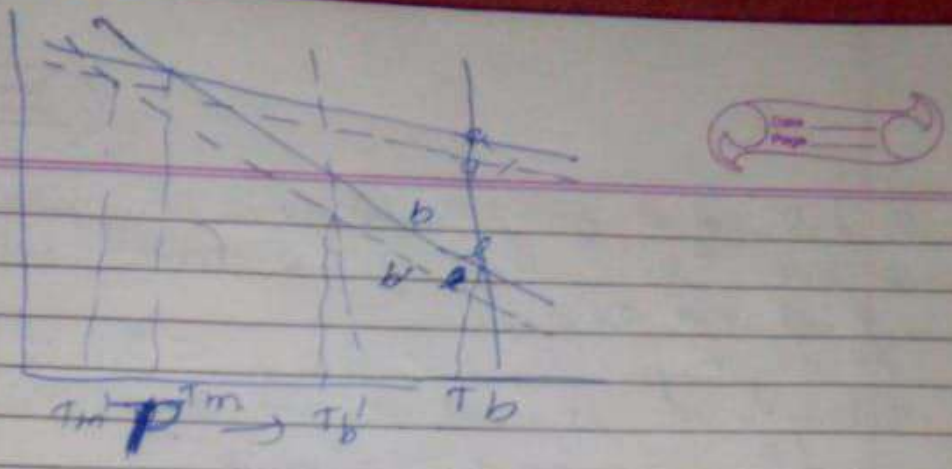
$d\mu = -S_m dT + V dP$

At constt T, $d\mu = V_m dP = \left(\frac{\partial \mu}{\partial P}\right)_T = V_m$

$V_{m,g} > V_{m,l} > V_{m,s}$ order of decreasing chemical potential.

$|d\mu_g| >> |d\mu_l| > |d\mu_s|$

when pressure of system is reduced. The decrease of chemical with ↓ of P is maximum for solid phase & largest for gaseous phase eg in the graph, the ↓ in chemical potential for solid phase is from a to a' liquid phase b to b' & gases c to c'



The mpt & bpt shifts to lower values as P is decreased, the shift is more for boiling pt The temp difference betn T_m & T_b ↓ with ↓ in P. This shows the temp range over which liquid phase can exist is decreased If P is decreased to a sufficient low value it may happen liquid is not formed, solid directly passes over to the gaseous phase. This happens when tpt falls below the mpt of solid

Temp T_s at sublimating temp is very sensitive to change of P

when P is ↑ed, the effects are exactly opposite. There is ↑ in mpt & boiling pt of the substance. The ↑ in bpt is large & enhances the stability of liquid phase.

The effect of P on mpt & bpt of substance which shows a ↓ in volume on melting.

↓ of chemical potential of solid will be larger than that of liquid There occurs ↑ in mpt as P is ↓ed. The ↑ of P will ↓ the mpt. eg Hg, Bi, Sb

Clapeyron Equation

Let us consider a system in which a pure substance B is present in 2 phases

α and β. Two phases can be $s \rightleftharpoons l$, $l \rightleftharpoons v$ & $s \rightleftharpoons v$

At equilibrium $\mu_{B(\alpha)} = \mu_{B(\beta)}$ — (1)

Let temp is changed by small amt, new equilibrium is established & P also changes by small amount

Chemical pot. can change by small amt

$\mu_{B(\alpha)} + d\mu_{B(\alpha)} = \mu_{B(\beta)} + d\mu_{B(\beta)}$ — (2)

Sub from (1) eq (2) reduce to

$$d\mu_{B(\alpha)} = d\mu_{B(\beta)} \quad \text{— (3)}$$

α phase: $d\mu_{B(\alpha)} = -S_{m,B(\alpha)}\,dT + V_{m,B(\alpha)}\,dP$ — (4)

β phase: $d\mu_{B(\beta)} = -S_{m,B(\beta)}\,dT + V_{m,B(\beta)}\,dP$ — (5)

sub (4) & (5) in (3)

$$-S_{m,B(\alpha)}\,dT + V_{m,B(\alpha)}\,dP = -S_{m,B(\beta)}\,dT + V_{m,B(\beta)}\,dP$$

$$S_m \frac{dP}{dT} = \frac{S_{m,B(\beta)} - S_{m,B(\alpha)}}{V_{m,B(\beta)} - V_{m,B(\alpha)}}$$

$$\frac{dP}{dT} = \frac{\Delta S_{m,\beta}}{\Delta V_{m,\beta}} \quad \frac{\text{change in entropy}}{\text{change in volume}}$$

This is known as Clapeyron equation

Application of clapeyron equation $s \rightleftharpoons l$

$$\frac{dP}{dT} = \frac{\Delta S_{fus}}{\Delta V_{melt}} = \frac{\Delta H_{fus}}{T \Delta V_{m,fus}}$$

Transformation of solid into liquid is an endothermic proc & ΔH_{fus} is +ve

ΔV_m can be +ve or -ve dependent upon which is one is more dense

For most substances $\rho_s > \rho_l$ ΔV_{fus} is +ve but H_2O, Si, Sb, ΔV_{fus} is -ve solid phase is less dense than the liquid phase

$\Delta S_{fus} = 8$ to 25 J/K/mole

$\Delta V_m = 1$ to 10 cm^3 mole^{-1}

Typical value $\Delta S_{fus} = 20$ J/K/mole

$\Delta V_{fus} = 5$ cm^3 mole^{-1}

$$\frac{dP}{dT} = \frac{20 \text{ J/K/mole}}{5 \text{ cm}^3 \text{ mole}^{-1}} = \pm 4 \text{ J/K cm}^{-3}$$

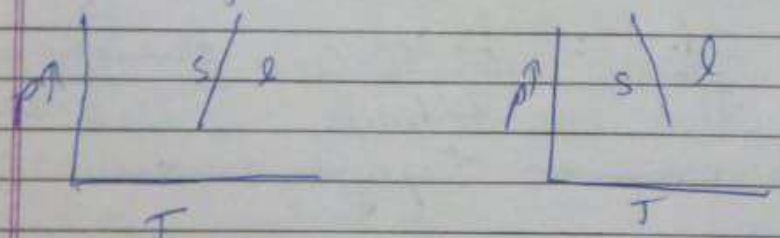
$$= 4 \text{ MPa cm}^3 \text{ K}^{-1} \text{ cm}^{-3}$$

$$= 4 \times 10^3 \text{ K Pa K}^{-1}$$

$$= 4 \times 10^3 \left(\frac{1}{101} \text{ atm}\right) \text{K}^{-1}$$

$$= 395 \text{ atm K}^{-1}$$

Slope of P vs T graph for $S \rightleftharpoons l$ has a large value. Graph is almost vertical. It tilted slightly to left if $\Delta_{fus} V_m$ is -ve



A pt lying anywhere on left of line corresponds to temp below mpT of substance & only solid form exist. A pt on right of line corresponds to temp above mpT, only liquid form exists

$$\frac{dT}{dP} = \frac{1}{395} \text{ K atm}^{-1} = 0.025 \text{ K atm}^{-1}$$

The change in the mpt of a solid
Variation of external P is very small
+ve means for these substances which there
are T in volume on mpT whereas -ve
for a substance where a ↓ in volume
of on melting is observed

$$\frac{dP}{dT} = \frac{\Delta H_{fus}}{T \Delta V_m}$$

$$\int_{P_1}^{P_2} dP = \frac{\Delta H_{fus}}{\Delta V_{m\,fus}} \int_{T_m}^{T_m'} \frac{dT}{T}$$

$$P_2 - P_1 = \frac{\Delta H_{fus}}{\Delta V_{m\,fus}} \ln \frac{T_m'}{T_m}$$

ΔT is -ve if ΔV_{fus} is +ve
ΔT is -ve if ΔV_{fus} is -ve

$l \rightleftharpoons v$. ΔH $\Delta S_{fus} = 90\ J/K/mole$
$\Delta V_m = 24\ dm^3/mole$

$$\frac{dP}{dT} = \frac{90\ J/K/mole}{24\ dm^3\ mol^{-1}}$$

$$= 3.75\ kPa/K$$

$$= 3.75\ kPa/K \left(\frac{1\ atm}{\quad}\right) = 0.037\ atm\ K^{-1}$$

The value is much smaller than 0.1 KR
smaller than $s \rightleftharpoons l$ eqn

$s \rightleftharpoons v$ $\Delta S_{fus\,sub} = +ve$, $\Delta V_m = +ve$

$\Delta H_{sub} > \Delta H_{vap}$

$$\left(\frac{dP}{dT}\right)_{s-v} > \left(\frac{dP}{dT}\right)_{l-v}$$