Phase diagram

Def^n:- The effect of changes in temperature, or in pressure or composition on the changes of phase in a system can be easily understood only when these are graphically represented. The conditions under which the different phases can co-exist are conveniently described by graphs called phase diagrams. That is why phase diagrams are universally employed in the application of phase rule to heterogeneous systems.

Some elementary facts about phase diagram:-

I) When the ~~variable~~ variations of two factors (i.e. two degree of freedom) such as pressure & temp. and conc^n is to be observed. The graph can be drawn on a ~~pb~~ plane with two coordinates, this is called two dimensional phase diagram. This is generally occour for one component system.

II) When the three variable (i.e. F=3) such as temp, pr. & composition are needed for studying a polyphase system, we required three axis, as a result of ~~su~~ which a three dimensional solid diagram is obtained, who called phase diagram.

III) Every three dimensional phase diagrams can be split up into three two dimensional phase diagrams.

IV) Time is not a variable, since phase diagrams are concerned with systems in equilibria & total quantities of the components are also not of any importance, but their conc^n are, Total quantity is always same but conc. may vary.

v. The phase diagram shows at a glance the properties of the substance, eg - melting, boiling, transition & triple points.

vi) Bivarient eq^m is therefore represented by an area in T-P/T-C/P-C diagram, ~~but~~ the univarient eq^m by a line & the invarient by a point.

vii) Every point on the phase diagram represents a state of the system since it describes values of T & P.

viii) The line on the phase diagram divide it into regions lebelled solid, liq. & gas.

ix) The area bounded by the lines indicates the existance of a single homogeneous phase.

x) The point of the intersection of any two curves will indicate co-existance of all the three phases, solid-liquid - vapour in eq^m. The point is called triple point.

Clapeyron Equation

The condition of eq^m, between two phase (say α, β) of a pure substance is

$$\mu_\alpha(T, P) = \mu_\beta(T, P) \quad \text{---}(1)$$

If the temp. is changed to $(T + dT)$ and pressure 'p' to $(P + dP)$, then ~~under~~ of chemical potential (μ) will be change to $(\mu + d\mu)$. After change of temp & pressure the system attain eq^m, so the conditions of eq^m is,

$$(\mu + d\mu)_\alpha = (\mu + d\mu)_\beta$$

$$\text{or, } d\mu_\alpha = d\mu_\beta \quad [\text{since } \mu_\alpha = \mu_\beta] \text{---}(11)$$

From second law of thermodynamics we can write,

$$d\mu = -\bar{S}dT + \bar{V}dP$$

For phase α, $d\mu_\alpha = -\bar{S}_\alpha dT + \bar{V}_\alpha dP$

" " β, $d\mu_\beta = -\bar{S}_\beta dT + \bar{V}_\beta dP$

For eq^n (II),

$$-\bar{S}_\alpha dT + \bar{V}_\alpha dP = -\bar{S}_\beta dT + \bar{V}_\beta dP$$

$$\boxed{\frac{dP}{dT} = \frac{\bar{S}_\beta - \bar{S}_\alpha}{\bar{V}_\beta - \bar{V}_\alpha} = \frac{\Delta\bar{S}}{\Delta\bar{V}} = \frac{\Delta\bar{H}}{T.\Delta\bar{V}}} \quad \left[\begin{array}{l}\text{Since } \Delta G = \Delta H - T\Delta S \\ \text{at } eq^m,\ \Delta G = 0 \\ \therefore \Delta S = \frac{\Delta H}{T}\end{array}\right] \quad \text{--- (III)}$$

This is called clapeyron eq^n.

Case - I :

1) Now consider eq^n (III) for solid ⇌ liq.

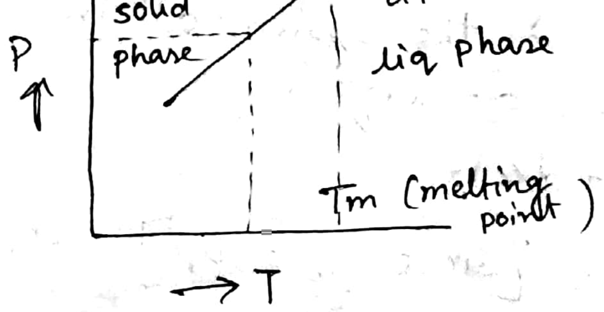
$\Delta\bar{S} = \bar{S}_L - \bar{S}_{solid} = \Delta\bar{S}_{fus} = +ve$ [Since $\bar{S}_L > \bar{S}_{solid}$]

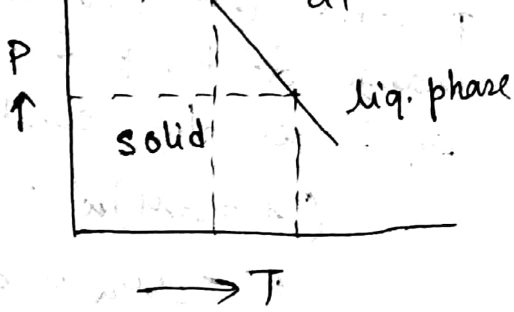
$\Delta V = \bar{V}_L - \bar{V}_{solid} = \Delta\bar{V}_{fus} = +ve$ [for maximum cases]

or $= -ve$ [for ice or Bi]

$\therefore \frac{dP}{dT} = +ve$ or, $= -ve$ Melting point increases with pr. for most substance & decreases with pr. ~~pr~~ for ice, Bi etc.

In the plot of 'P' against, the slope $\left(\frac{dP}{dT}\right)$ of the plot will be large & the curve is nearly vertical. This shown in fig I (a) & fig I (b).





The fig - I (a) & I (b) are phase diagram for solid ⇌ liq. equilibria. Right side of the line represent liq. phase and left side solid phase and line represent solid ⇌ liq. coexist, Any point on the line indicate melting point of the substance corresponding pressure.

Case-II

Now consider liq ⇌ vapour

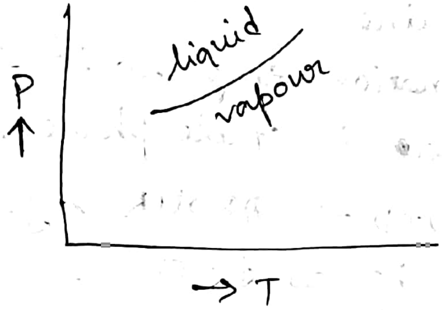
Application of Clapeyron eq^n to liq ⇌ vap.

$\Delta S = \bar{S}_{vap} - \bar{S}_{liq} = +ve$ [Since all cases $\bar{S}_{vap} > \bar{S}_{liq}$]

$\Delta V = \bar{V}_{vap} - \bar{V}_{liq} = +ve$

$\therefore \frac{dP}{dT} = (+)ve$ [for all substance]

The slope of the liq-vap. is small compared with that of solid - liq. curve.



Every point on the curve represent the temp. and press. at which liquid vapour co-exist in eq^m. The curve is called phase diagram of liquid - vapour system.

Case-III

Now consider solid ⇌ vapour

For the transformation solid → vapour

$\Delta S = \bar{S}_{vap} - \bar{S}_{solid} = \frac{\Delta H_{sub}}{T} = (+)ve$ (all substance)

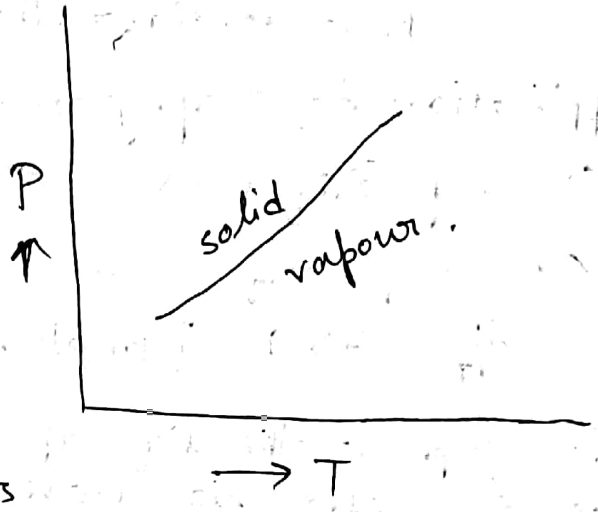
$\Delta V = \bar{V}_{vap} - \bar{V}_{solid} = (+)ve$ (all substance)

and the Clapeyron eq^n is,

$$\left(\frac{dP}{dT}\right)_{solid-vap} = \frac{\Delta S_{sub}}{\Delta V} = \frac{\Delta H_{sub}}{T\Delta V} = \frac{(\Delta H_{fus} + \Delta H_{vap})}{T\Delta V} = (+)ve \text{ [for all substance]} \quad \text{---}(1)$$

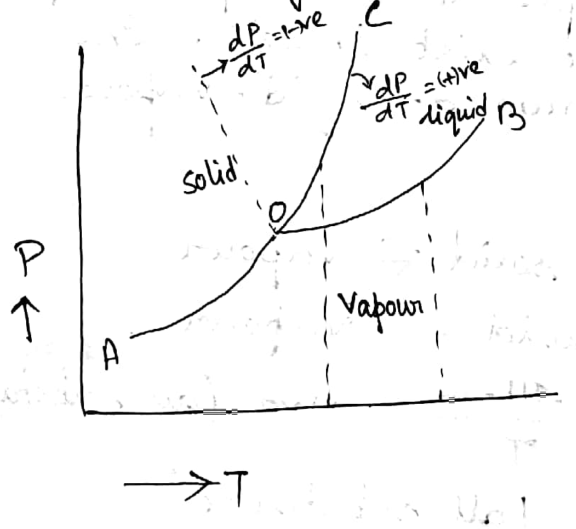
$$\left(\frac{dP}{dT}\right) liq\text{-}vap = \frac{\Delta H vap}{T \cdot \Delta V} \quad \cdots (11)$$

The ΔV's in eq^n (1) & (2) are nearly equal. But ΔS sub. or ΔH sub is greater than ΔS vap or ΔH vap. So solid-vap. curve will be more steeper than liquid - vapour curve.



This is a phase diagram for solid vap. system. Every point on the curve represent the temp. (T) and pressure at which solid-vap. co-exist in eq^m. Points to the left of the line lie below the sublimation temp, solid is stable & at the right vapour is stable phase.

For SOLID ⇌ LIQUID ⇌ VAPOUR system, Phase diagram will be as follows.



The point 'O' is the intersection of three curve. In this point solid - liq - vap. coexist. This is called triple point. Every point on the curve OB indicate the boiling point and OC indicate melting point.