Clapeyron - clausis Equation:-

An important equation for One Component two-Phase System was derived by Clapeyron from the 2nd law of thermodynamics

Two Phase are in equilibrium may be any one of the following

$S \rightleftharpoons L$, At the melting point of Solid.

$L \rightleftharpoons V$, Equilibrium at the boiling point of Liquid.

$S \rightleftharpoons V$, Equilibrium at the sublimation temp. of the Solid.

$S_{Rhombic} \rightleftharpoons S_{Monoclinic}$ At the transition temp. of the two alltropic forms.

Let us Consider the change of a pure Substance from Phase A to another Phase B in equilibrium with it at a given temp. and Pressure.

G_A and G_B are free energy change per mole in Phase A and B respectively. If a system is in equilibrium without change in temp. and Pressure then $G_A = G_B$, hence there will be no change in free energy.

i.e $\Delta G = G_B - G_A = 0$ ——— (1)

If the temperature rise from T to dT and Pressure from P to dp in Order to maintain the equilibrium.

Now the free energy at the new temp & Pressure in Phase A is $G_A + dG_A$ and in Phase B, $G_B + dG_B$ respectively.

The two Phases are still in equilibrium,

hence, $G_A + dG_A = G_B + dG_B$

We Know $dG = Vdp - SdT$

For Phase A, $dG_A = V_A dP - S_A dT$

For Phase B, $dG_B = V_B dP - S_B dT$

$\because G_A = G_B$

$\therefore dG_A = dG_B$

or, $V_A dp - S_A dT = V_B dP - S_B dT$

or $S_B dT - S_A dT = V_B dP - V_A dP$

$dT(S_B - S_A) = dP(V_B - V_A)$

or $\dfrac{(S_B - S_A)}{(V_B - V_A)} = \dfrac{dP}{dT}$

or $\dfrac{\Delta S}{\Delta V} = \dfrac{dP}{dT}$

$\because \Delta S = q/T$

$\therefore \dfrac{q}{T\Delta V} = \dfrac{dP}{dT}$

or $$\frac{dP}{dT} = \frac{q}{T(V_B - V_A)}$$

Suppose the system consist of water in two phase i.e liquid and vapour are they are in equilibrium with each other at temp. T.

$$\text{Liquid Water} \rightleftharpoons \text{Vapour Water}$$

q, = molar heat of vaporisation, V_B = Volume in vapour state, V_A = volume in liquid state

then, $$\frac{dP}{dT} = \frac{\Delta H_{vap}}{T V_g}$$

[Where $q = \Delta H_{vap}$ i.e molar heat of vaporisation and $V_g >>> V_l$ so V_l may be neglected - V_g = volume in vapour state]

From ideal gas eq^n $V_g = \frac{RT}{P}$

$$\therefore \frac{dP}{dT} = \frac{\Delta H_{vap}}{T} \cdot \frac{P}{RT}$$ [substituting the value of $V_g = \frac{RT}{P}$]

$$\frac{dP}{dT} = P \cdot \frac{\Delta H_{vap}}{RT^2}$$

or $$\frac{1}{P} \cdot \frac{dP}{dT} = \frac{\Delta H_{vap}}{RT^2}$$

$$\frac{d(\ln P)}{dT} = \frac{\Delta H_{vap}}{RT^2}$$

or $$d\ln P = \frac{\Delta H_{vap}}{R} \frac{dT}{T^2}$$

On integrating the above eq^n

$$\int_{P_1}^{P_2} d\ln P = \frac{\Delta H_{vap}}{R} \int_{T_1}^{T_2} \frac{dT}{T^2}$$

or $$\ln \frac{P_2}{P_1} = -\frac{\Delta H_{vap}}{R} \left[\frac{1}{T_2} - \frac{1}{T_1}\right]$$

or, $$\ln \frac{P_2}{P_1} = \frac{\Delta H_{vap}}{R} \left[\frac{1}{T_1} - \frac{1}{T_2}\right]$$

$$\ln \frac{P_2}{P_1} = \frac{\Delta H_{vap}}{R} \left[\frac{T_2 - T_1}{T_1 T_2}\right]$$ This equation is known as Clausius - Clapeyron equation.

Application: - Application of Clausius - Clapeyron Equation for

(A) $L \rightleftharpoons V$ (Equilibrium)

From eq^n $$\ln \frac{P_2}{P_1} = \frac{\Delta H_{vap}}{R} \left[\frac{T_2 - T_1}{T_1 T_2}\right]$$

(1) This can be used for calculating molar heat of vaporisation ΔH_{vap} of a liquid. If we know the vapour pressures at two temperatures
Further if ΔH_{vap} is known, vapour pressure (at describe temp.) can be calculated

(2) Effect of Temp. on vapour pressure of a liquid : - The vapour pressure of a liquid at one temp. is known, that at another temp. the vapour pressure can be calculated

(3) Effect of Pressure on boiling Point : - The boiling point of a liquid at one pressure is known then at another pressure the boiling point may be calculated.

(B) Clausius - Clapeyron eq^n's application : -
Application for Solid $\rightleftharpoons$ Vapour Equilibrium

$$\frac{dP}{dT} = \frac{\Delta H_{sub}}{T(V_g - V_s)}$$

or $$\ln \frac{P_2}{P_1} = +\frac{\Delta H_{sub}}{R} \left[\frac{T_2 - T_1}{T_1 T_2}\right]$$

If P_1, P_2, ΔH_{sub}, & T T_2 is given then T_1 may be calculated.