

Clapeyron - Clausius Equation: -

An important equation for one component two-phase system was derived by Clapeyron from the 2nd law of thermodynamics

Two phases 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.

$S_{\text{Rhombic}} \rightleftharpoons S_{\text{Monoclinic}}$ At the transition temp. of the two allotropic 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.

$$\text{i.e. } \Delta G = G_B - G_A = 0 \quad \text{--- (1)}$$

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, $G_A + dG_A = G_B + dG_B$

$$\text{We know } dG = VdP - SdT$$

$$\text{For Phase A, } dG_A = V_A dP - S_A dT$$

$$\text{For Phase B, } dG_B = V_B dP - S_B dT$$

$$\therefore G_A = G_B$$

$$\therefore dG_A = dG_B$$

$$\text{or, } V_A dP - S_A dT = V_B dP - S_B dT$$

$$\text{or } S_B dT - S_A dT = V_B dP - V_A dP$$

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

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

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

$$\therefore \Delta S = q/T$$

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

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

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 .



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

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

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

From ideal gas eqⁿ $V_g = \frac{RT}{P}$

$$\therefore \frac{dp}{dT} = \frac{\Delta H_{\text{vap}}}{T} \cdot \frac{P}{RT}$$

[substituting the value of $V_g = \frac{RT}{P}$]

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

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

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

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

On integrating the above eqⁿ

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

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

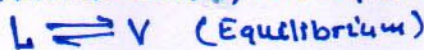
$$\text{or, } \ln \frac{P_2}{P_1} = \frac{\Delta H_{\text{vap}}}{R} \left[\frac{1}{T_1} - \frac{1}{T_2} \right]$$

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

Clausius - Clapeyron Equation.

Application: - Application of Clausius - Clapeyron Equation for

(A)



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

- (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 eqⁿ's application: -

Application for Solid \rightleftharpoons Vapour Equilibrium

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

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

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If $P_1, P_2, \Delta H_{\text{sub}},$ & T_2 is given then T_1 may be calculated.