Bsc. II (H), Paper - III A

## Clausius-clapeyron equation

From definition of Gibb's free energy.

$$G = H - TS \quad \text{---} \quad (i)$$

or $\cancel{G = dE + Pdv - T}$

$$G = E + PV - TS$$

differentiating we get

$$dG = dE + Pdv + Vdp - Tds - SdT \quad \text{---} \quad (ii)$$

and from definition of entropy.

$$ds = \frac{q_{rev}}{T} \; \cancel{or} \; \frac{dE + Pdv}{T}$$

As $q_{rev} = dE + Pdv$

$$\text{or} \quad Tds = dE + PdV \quad \text{---} \quad (iii)$$

Putting value of (iii) in (ii) we get

$$dG = \cancel{Tds} + Vdp - \cancel{Tds} - SdT$$

$$\text{or} \quad dG = Vdp - SdT \quad \text{---} \quad (iv)$$

~~And~~ at equilibrium $dG = 0$

Let Two phase I and II are at equilibrium at temperature T and pressure P. In this state the phase I of free energy is $G_1$ and free energy of phase II is $G_2$. The temperature of

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the equilibrium is changed by $dT$ and pressure is changed by $dp$.

hence

$$dG_1 = V_1 dp - S_1 dT \quad \text{—} \quad (V)$$

and

$$dG_2 = V_2 dp - S_2 dT \quad \text{—} \quad (VI)$$

At equilibrium $\Delta G = 0$

i.e. $G_2 - G_1 = 0$

or $dG_2 - dG_1 = 0$

or $dG_2 = dG_1 \quad \text{—} \quad (VII)$

or $V_2 dp - S_2 dT = V_1 dp - S_1 dT$

or $(V_2 - V_1) dp = (S_2 - S_1) dT$

or $\Delta V dp = \Delta S dT$

or $$\frac{dp}{dT} = \frac{\Delta S}{\Delta V} \quad \text{—} \quad (VIII)$$

Here $\Delta V = V_2 - V_1$ i.e. molar volume change and $\Delta S = S_2 - S_1$ i.e. molar entropy change

$$\Delta S = \frac{\Delta H}{T} \quad (IX)$$ where $\Delta H$ is latent heat of transformation and $T$ is i.e. m.p or boiling point etc.

putting value of (IX) in (VIII)

$$\frac{dp}{dT} = \frac{\Delta H}{T \Delta V} \quad \text{—} \quad (X)$$

equation (X) is called clapeyron equation. This is used for physical equilibrium like melting, vapourisation and sublimation.

For solid $\rightleftharpoons$ liquid equilibrium, the eq (X) will be written as

$$\frac{dp}{dT} = \frac{\Delta H_m}{T_m(V_L - V_S)} \quad \text{(XI)}$$

Where Vs is molar volume of solid, $V_L$ is molar volume of liquid $\Delta H_m$ is latent heat of melting.

For liquid $\rightleftharpoons$ vapour equilibrium, the eqn (X) will be written as

$$\frac{dp}{dT} = \frac{\Delta H_V}{T_b(V_V - V_L)} \quad \text{(XII)}$$

Where $T_b$ = boiling temperature, $V_V$, $V_L$ and $\Delta H_V$ are molar volume of vapour, molar volume of liquid and latent heat of vapourisation.

As $V_L \ll V_V$ eq (XII) will be -

$$\frac{dp}{dT} = \frac{\Delta H_V}{T_b V_V} \quad \text{(XIII)}$$

From ideal gas equation

$PV = RT$ for one mole.

and hence the eqn (XIII) will be written as

$$\frac{dp}{dT} = \frac{\Delta H_v}{RT^2} p$$

or $\cancel{\frac{dp}{p} = \frac{\Delta H_v}{RT^2} dT}$

or $\frac{1}{p} \cdot dp \cdot \frac{1}{dT} = \frac{\Delta H_v}{RT^2}$

or $$\boxed{\frac{d\ln p}{dT} = \frac{\Delta H_v}{RT^2}}$$

This equation is derived by clausius as ~~it was~~ on basis of clapeyron equation and hence it is called clausius - clapeyron equation.

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