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Deg II Chem. Hons; Paper- III

Topic :- Thermodynamics

Clapeyron - clausius equation (Rest)

Suppose the system consists of water in two Phases Viz. liquid and vapour in equilibrium with each other at temperature T

Then q = Molar heat of vaporisation
= L_v (say)

V_B = volume of one mole of water in the vapour state = V_g (say)

V_A = volume of one mole of water in the liquid state = V_l (say)

The above equilibrium may then be written as

$$\frac{dp}{dT} = \frac{L_v}{T(V_g - V_l)}$$

Where T is the temperature at which the liquid and vapour exist in equilibrium.

If T is the boiling Point of water then the value of

$L_v = 18 \times 540 = 9,720$ calories

suppose the system consists of water at its freezing point. Then the two phases in equilibrium will be

Water (solid) ice $\rightleftharpoons$ water (liquid)

If again one mole is the quantity involved, q will be the molar heat of fusion of ice = Lf (say)

Then the equation will be

$$\frac{dp}{dT} = \frac{L_f}{T(V_l - V_s)}$$

T is the freezing point of water

The value of $L_f = 18 \times 80 = 1440$ calories

Integration of clapeyron-clausius equati

clapeyron-clausius equation applied to $L \rightleftharpoons V$ equilibrium can only be integrated. $S \rightleftharpoons L$ cannot be integrated since the molar volume of the substance in the gaseous state is considerably greater than that in the liquid state, Vl may be neglected in comparision to Vg.

The clapeyron-clausius equation may then be put as

$$\frac{dp}{dT} = \frac{L_v}{T \cdot V_g}$$

where V_g is the molar volume of the substance in the gaseous state, Assuming that the gas Law ($PV = RT$) is applicable, $V_g = RT/P$ Hence

$$\frac{dp}{dT} = \frac{L_V}{T} \times \frac{P}{RT} = \frac{P \cdot L_V}{RT^2}$$

or $$\frac{dp}{dT} \cdot \frac{1}{P} = \frac{L_V}{RT^2}$$

We know that $\frac{dp}{dT} \cdot \frac{1}{P} = \frac{d(\log P)}{dT}$

$$\therefore \frac{d(\log P)}{dT} = \frac{L_V}{RT^2}$$

Integrating and assuming that L_V remains constant over a small range of temperature, we get

$$\int d(\log P) = \frac{L_V}{R} \int \frac{dT}{T^2}$$

If P_1 and P_2 are the vapour pressure at temperature T_1 and T_2 respectively

Then $$\int_{P_1}^{P_2} d(\log P) = \frac{L_V}{R} \int_{T_1}^{T_2} \frac{dT}{T^2}$$

or $$\log \frac{P_2}{P_1} = -\frac{L_V}{R}\left[\frac{1}{T_2} - \frac{1}{T_1}\right]$$

$$\boxed{2.303 \log_{10} \frac{P_2}{P_1} = \frac{L_V}{R}\left[\frac{T_2 - T_1}{T_2 \cdot T_1}\right]}$$

L_V per gram for H_2O = 540 calory