

Lecture 18

In this lecture we will learn about “Vapour Pressure”

If a liquid is kept in a closed vessel with some free space over it then liquid will start evaporating. If sufficient time is allowed then an equilibrium will be reached between liquid and vapour.

⇒ What kind of equilibrium is it? Static or dynamic?

As more and more molecules accumulate in the vapour phase with time, the tendency of vapour molecules getting condensed to liquid increases. At equilibrium rate of condensation equals to that of vaporisation. Thus the equilibrium is a dynamic one.

The pressure at which liquid and vapour coexist in equilibrium is known as vapour pressure of that liquid at that particular temperature.

Vapour pressure depends only on temperature and not on the quantity of liquid or the space.

⇒ Why heat is required to form the vapour? Do we need to heat the liquid to form vapour?

Magnitude of cohesive force of liquid is higher than that in vapour phase. A molecule in the bulk possesses force of attraction from all directions. But a molecule on/near the surface experiences greater force of attraction inward than toward the free space. In order to overcome the force sufficient energy (in the form of heat) must be supplied to go to vapour phase.

If E_a be the excess energy (per gm-mole) necessary to overcome force of attraction and vaporise, then the number of molecules n_1 having energy more than E_a (per gm-mole) is given by

$$n_1 = n_L \times e^{-\frac{E_a}{RT}} \quad \text{..... (1) [Assuming Boltzmann distribution to be valid]}$$

n_L = number of molecules per cc of liquid.

If n_g be the number of molecules per cc of vapour, then rate of condensation will be $\lambda' n_g$, where λ' is a constant.

At equilibrium, rate of evaporation = rate of condensation

$$\lambda' \times n_g = n_L \times e^{-\frac{E}{RT}} \quad \text{..... (2)}$$

No. of molecules evaporating = no. of molecules getting condensed.

If n_a no. of molecules is present in V cc, then $\frac{n_a}{V}$ = no. of molecules/cc

n_g = no. of molecules/cc of vapour, $\frac{n_g}{N_0}$ = no. of moles/cc of vapour (N_0 = Avogadro number)

We know, $p V = n R T$ (assuming ideal vapour, here n is the number of moles), $\Rightarrow p = \frac{n}{V} R T$

Thus, Vapour pressure, p (assuming ideal behaviour) can be expressed as

$$p V = n R T \text{ (here } n \text{ is the number of moles)}$$

$$\Rightarrow p = \frac{n}{V} R T \text{ (here } (n/V) \text{ is the number of moles per cc)}$$

$$\Rightarrow p = \frac{n_g}{N_0} \times R T$$

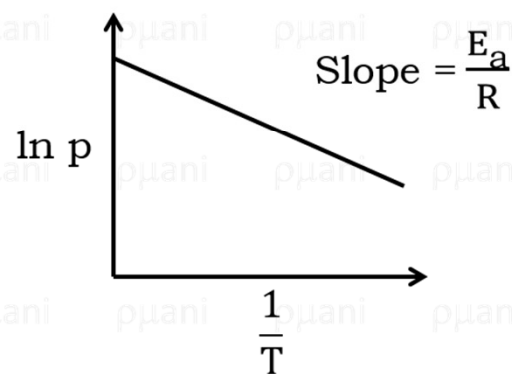
$$\Rightarrow \text{From equation (2), } n_g = \left(\frac{n_L}{\lambda'}\right) \times e^{-\frac{E_a}{RT}}$$

So, $p = \left(\frac{n_L}{\lambda} \times \frac{R}{N_0}\right) \times T \times e^{-\frac{E_a}{RT}}$ [n_L = no. of molecules/cc = constant]

$$p = \lambda T \times e^{-\frac{E_a}{RT}} \quad [\text{where } \lambda \text{ is a constant}]$$

$$\Rightarrow \ln p = -\frac{E_a}{RT} + \underbrace{\ln T + \text{constant}}_{\text{Constant}}$$

Thus, by plotting $\ln p$ against $\frac{1}{T}$ we get,



Thus, from the slope it is possible to calculate E_a .

\Rightarrow When vapour pressure is equal to 1 atmosphere, then the corresponding temperature is known as boiling point.

⇒ How does the magnitude of cohesive force control vapour pressure or heat of vaporisation?

At a fixed temperature, a liquid with greater cohesive force will have smaller vapour pressure than one with smaller cohesive force and hence have higher heat of vaporisation.

At 20°C, heat of vaporisation of water is 44 kJ/mole and that of CCl₄ is 32 kJ/mole, corresponding vapour pressure at this temperature is 2.33 kPa for water and 12.13 kPa for CCl₄.

Reason for higher cohesive force for water: H-bonding

Sublimation point:

Some solids are sufficiently volatile to produce measurable vapour pressure even at ordinary temperature. If it happens that at a particular temperature the vapour pressure reaches 1 atm. below the melting point of the solid, then the solid sublimates and the corresponding temperature is called normal sublimation point.

Boiling point and sublimation point depend on the pressure imposed upon the substance.

Does the Vapour pressure depend on External pressure?:

When the liquid is subjected to a higher external pressure, its vapour pressure changes. Thermodynamically, it can be shown that

$$V_g dp = V_L dP$$

p = vapour pressure, P = external pressure

V_g = molar volume of vapour and V_L = molar volume of liquid [at given temperature]

As $V_g = \frac{RT}{p}$ [assuming ideal gas behaviour for vapour] , $\Rightarrow \frac{RT}{p} dp = V_L \times dP$

$$\Rightarrow \frac{dp}{p} = \frac{V_L}{RT} \times dP \quad [\text{ideal behaviour}]$$

$$\Rightarrow \boxed{\ln \frac{p_2}{p_1} = \left(\frac{V_L}{RT} \right) \times (P_2 - P_1)}$$

p_1 and p_2 are vapour pressure at external pressure of P_1 and P_2 respectively. V_L is regarded as independent of pressure.

Question: Calculate increase of vapour pressure of water per atmosphere rise in external pressure at 10°C . [Given: Vapour pressure of water at $10^\circ\text{C} = 9.2 \text{ mm}$]

$$\text{Ans: } \ln \frac{p_2}{p_1} = \frac{18(2-1)}{82.05 \times 283} \quad [V_L = 18 \text{ cc/mole, } R = 82.05 \text{ cc atm. per degree}]$$

$$\log \frac{p_2}{p_1} = 0.0004$$

$$p_2 = 1.001 p_1$$

$$\Delta p = p_2 - p_1 = 0.001 p_1$$

That is vapour pressure increases by 0.1% of its magnitude for one atmosphere rise in external pressure.