Class ⇒ B.Sc. (Hons.) Part - I
Subject ⇒ Chemistry
Chapter ⇒ Gaseous state (Group-A)
Topic ⇒ Maxwell distribution of velocities and energies.
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Maxwell Distribution of Velocities

Molecules of a gas are moving continuously in different direction with different velocities. Hence they keep on colliding with one another. However, the collisions are supposed to be perfectly elastic and there is no net loss of kinetic energy.

In other words, whereas some molecules are speeded up, the others are slowed down after collision.

Maxwell suggested that at a particular temperature, the fraction of molecules possessing particular velocities remain almost constant. Such a state is called a steady state.

On the basis of the laws of probability, Maxwell calculated that the fraction of molecules having velocities between c and c+dc is given

$$\frac{dn_c}{n} = 4\pi\left(\frac{M}{2\pi RT}\right)^{3/2} e^{-Mc^2/2RT} c^2 dc \quad \text{—— (1)}$$

where dn_c = No. of molecules having velocities between c and (c+dc).
n = Total no. of molecules of the gas
M = Molecular Mass of the gas.
T = Absolute temperature of the gas.

This eqn. is called Maxwell law of distribution of velocites.

The above equation may be rewritten as

$$\frac{1}{n} \cdot \frac{dn_c}{dc} = 4\pi \left(\frac{M}{2\pi RT}\right)^{3/2} e^{-Mc^2/2RT} c^2 \quad \text{——— (2)}$$

The quantity $\frac{1}{n} \cdot \frac{dn_c}{dc}$ is called the probability (P) of finding molecules with velocity c.

The significance of the Maxwell distribution of velocities equation may be seen by Plotting the probability $\left(P = \frac{1}{n} \cdot \frac{dn_c}{dc}\right)$ versus the velocity c at a particular Temperature T. Such Plot is called Maxwell's distribution of velocities.

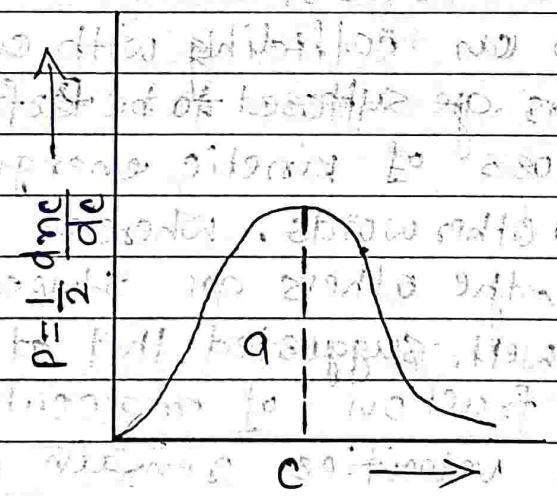

Fig:- Maxwell distribution of velocities.

from Plot it will be noticed that

(i) A very small fraction of molecules has either very low (close to zero) or very high velocities.

(ii) Most intermediate fraction of molecules have velocities close to an average velocity represented by the peak of the curve. This velocity is called Most probable velocity.

(iii) At higher temp. more molecules have higher velocities and fewer molecules have lower velocities.

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Maxwell distribution of energies

The Maxwell distribution of velocities can be converted to represent the distribution of energies as follows:

$\frac{1}{2}Mc^2$ is replaced by E, the kinetic energy of the gas per mole.

$$\frac{1}{2}Mc^2 = E \quad \text{——} \quad (1)$$

To change $c^2 dc$ into the energy terms. Eqn. (1) is rewritten as

$$Mc^2 = 2E \quad \text{——} \quad (2)$$

Differentiating both sides, we get

$$2Mc\,dc = 2dE$$

or, $$Mc\,dc = dE \quad \text{——} \quad (3)$$

Taking square root of both sides of eqn. (2), we get

$$M^{1/2}c = (2E)^{1/2} \quad \text{——} \quad (4)$$

Multiplying eqn. (3) and (4), we get

$$M^{3/2}c^2dc = (2E)^{1/2}dE$$

or, $$c^2dc = \frac{(2E)^{1/2}dE}{M^{3/2}} \quad \text{——} \quad (5)$$

Substituting the value of $\frac{1}{2}Mc^2$ from eqn. (1) and that of c^2dc from eqn. (5) in Maxwell distribution of velocities eqn. we get

$$\frac{dn_c}{n} = 4\pi\left(\frac{M}{2\pi RT}\right)^{3/2} e^{-E/RT}\frac{(2E)^{1/2}dE}{M^{3/2}}$$

or, $$\frac{dn_c}{n} = \frac{2\pi}{(\pi RT)^{3/2}} e^{-E/RT} E^{1/2}dE \quad \text{——} \quad (6)$$

Where $\frac{dn_c}{n}$ now represent the fraction of the total no. of molecules having kinetic energies between E and dE

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Eqn. 6 can be rewritten as

$$P' = \frac{1}{n}\frac{dn_c}{dE} = \frac{2\pi}{(\pi RT)^{3/2}} e^{-E/RT} E^{1/2} \quad \text{—(7)}$$

Where P' represents the probability of molecules having energy E.

The plot of Probability (P') ~~ev~~ vs E obtained are similar to those for the distribution of velocities.

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