Dr S. K. Gupta
Deptt. of Chemistry
Marwari College Darbhanga

Deg-I (H) - Physical-Chemistry

Chapter - Gaseous State Topics - Molecular-Velocities.

Maxwell-Distribution of Molecular-Velocities.

Gaseous Particles are moving constantly moving in all-direction. During motion they keep on colliding with one another and also with the walls of the container.

As a result of Collision the speed & direction of the molecule changes. However the distribution of velocities among different molecules remains the same at a particular-Temp. (individual speed may change)

Maxwell-Boltzmann suggested that at particular Temp. the fraction of molecules possess particular velocity remain almost constant. It is known as Steady State.

Upon the basis of law of Probability they establish a relationship b/w fraction of molecules with velocities c & c+dc says

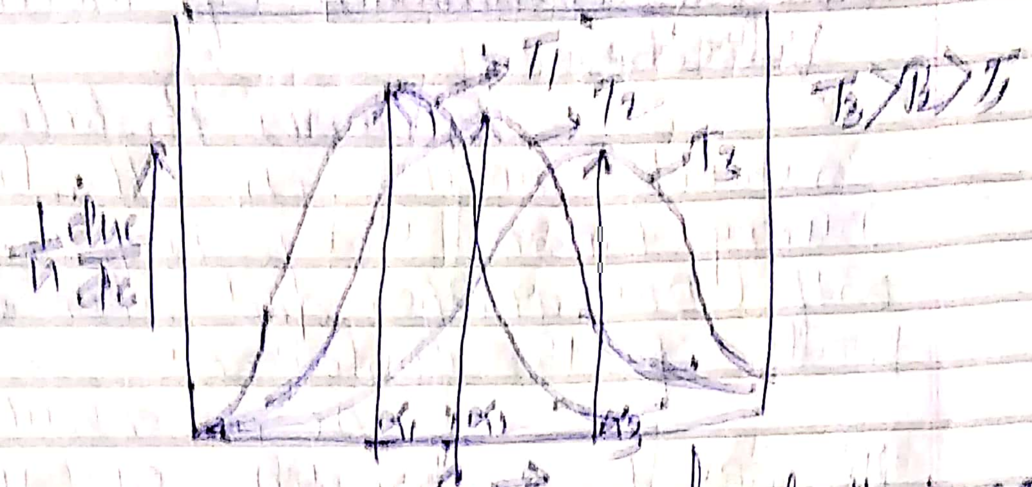
$$\frac{dn_c}{n} = 4\pi \left(\frac{M}{2\pi RT}\right)^{3/2} \cdot e^{-\frac{Mc^2}{2RT}} c^2 dc$$

Where - $\frac{dn_c}{n}$ - fraction of Molecules having different speeds.

M = molar Mass of gas

T = Absolute Temp.

$$\frac{1}{N}\frac{dN_c}{dc} = 4\pi\left(\frac{M}{2\pi RT}\right)^{3/2} e^{-\frac{Mc^2}{2RT}} c^2$$



Distribution of velocities in gas.

$\frac{1}{N}\frac{dN_c}{dc}$ = Probability of finding the gas molecules b/w velocity range c & c+dc.

Conclusion from the Graph Plotted b/w Probability & velocity range.

(1) The number of molecule having speed very low or zero is nil. It concludes that the number of motionless molecule is nil.

(2) The number of molecule having high speed is also very less.

(3) The maximum fraction of molecule possessing a speed (peak on the curve) at particular temp is called most probable velocity (V_{mp}).

The most probable velocity is not constant of any gase, rather it shifts towards the higher values of velocities with rise of Tempr.

(4) The nature of graph does not change with change of Tempr. The curve become more flat & the peak shift toward right at higher Tempr. It indicates the wider distribution of speeds.

There are three type of Molecular Speeds/ velocities

(1) Most Probable Velocities (V_{mp}) –

The velocities possessed by maximum fraction of molecules of a gas at given Tempr.

$$V_{mp} = \sqrt{\frac{2RT}{M}}$$

T = Absolute Tempr
M = Molar Mass of gas
R = universal gas const.

(2) Average Velocities (V_{ave})

It is defined as the simple average of different speeds of all the molecule present in a given sample of gases.

$$V_{ave} = \frac{V_1 + V_2 + V_3 + \cdots + V_n}{n}$$

n = Total no of Molecule

$$= \sqrt{\frac{8RT}{\pi M}}$$

(3) Root mean square velocities (V_{rms})

It is defined as the square root of the average (mean) of squares of different velocities.

$$V_{rms} = \sqrt{\frac{V_1^2 + V_2^2 + V_3^2 + \text{---} V_n^2}{n}}$$

$$= \sqrt{\frac{3RT}{M}}$$

Relation b/w V_{mp}, V_{ave} & V_{rms}.

$$V_{rms} : V_{ave} : V_{mp} = \sqrt{\frac{3RT}{M}} : \sqrt{\frac{8RT}{\pi M}} : \sqrt{\frac{2RT}{M}}$$

$$= \sqrt{3} : \sqrt{\frac{8}{\pi}} : \sqrt{2}$$

$$= 1.732 : 1.595 : 1.414$$

$$= 1.224 : 1.128 : 1$$

These three are related as

$$V_{ave} = 0.921 \times V_{rms}$$

$$V_{mp} = 0.816 \times V_{rms}.$$

Remember — The R.M.S velocity is commonly used having following relations

$$V_{rms} = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3PV}{M}} = \sqrt{\frac{3P}{d}}$$

M = Molar Mass, V = volume, P = Pressure, d = density