* Maxwell's law of Distribution of velocities:-

At a particular tempr., a gas molecule has a fixed mean kinetic energy. After each encounter the speed of molecule changes and due to large no. of collisions, the speed is difference at different instants. But root mean square (r.m.s.) velocity C remains the same at fixed tempr. At any instant, all the molecules are not moving with a same velocity. Some are moving with a velocity higher than C and some are lower than C. But the mean K.E. of all molecules remains constant at a given tempr.

* Derivation of Maxwell's law Distribution of Molecular velocities :-

The r.m.s. velocity of molecules is defined by eqn.

$$C^2 = \frac{1}{N}\int_0^\infty c^2 \cdot dN$$

Here dN is no. of molecules having velocities between C and $C+dC$. If total no. of molecules is N, then a fraction $\frac{dN}{N}$ will have the components of velocities in X-direction in the range u and $u+du$. So, the fraction $\frac{dN_x}{N}$ is a function of u only and is proportional to du.

$$\therefore \frac{dN_x}{N} = f(u)\,du$$

$$\therefore dN_x = N f(u)\,du$$

The eqn. for Y and Z directions are $dN_y = N f(v)\,dv$

$$dN_z = N f(w)\,dw$$

Also the value of N is too large and du is small compared with u but in range u and $u+du$, there are large no. of molecules. The fraction of dN_x molecules whose y components of velocity lie in the range v and $v+dv$ is given by the equation

$$\frac{d^2 N_{x,y}}{dx} = \frac{dN_y}{N} = f(v)\,dv$$

$$\therefore d^2 N_{x,y} = N f(u) f(v)\,du\,dv$$

The no. of molecules represented by $d^2 N_{x,y}$ is still large. Suppose that the fraction of these molecules $d^2 N_{x,y,z}$ whose components of velocity in Z-direction in the range w and $w+dw$ is given by eqn.

$$d^3N_{x,y,z} = N f(u) f(v) f(w)\, du\, dv\, dw$$

The density of velocity points is given by the eqn.

$$f = \frac{d^3N_{x,y,z}}{du \cdot dv \cdot dw} = N f(u) f(v) f(w)$$

As there is no preferred direction of velocities, the density of velocity points f is constant i.e velocity space is isotropic.

Also $\quad c^2 = u^2 + v^2 + w^2$

$$\therefore N f(u) f(v) f(w) = \text{Const.} \quad \text{—} \quad (i)$$

when $\quad u^2 + v^2 + w^2 = \text{Const.} \quad \text{—} \quad (ii)$

These eqns. (i) and (ii) must be similary ~~thisfied~~ satisfied. Eqn (ii) limits the values of variables in eqn (i) and reduces the no. of independent variables to two. Therefore it is called an equation of constraints.

Diff. eqn (i) and (ii)

$$f(v) f(w) \frac{\partial f(u)}{\partial u} \cdot du + f(w) f(u) \frac{\partial f(v)}{\partial v} \cdot dv + f(u) f(v) \frac{\partial f w}{\partial w} \cdot dw = 0 \quad \text{—} \quad (iii)$$

and $\quad 2u \cdot du + 2v \cdot dv + 2w \cdot dw = 0 \quad \text{—} \quad (iv)$

Simplifying eqn (iii) and (iv)

$$\frac{1}{f(u)} \frac{\partial f(u)}{\partial u} \cdot du + \frac{1}{f(v)} \frac{\partial f(v)}{\partial v} \cdot dv + \frac{1}{f(w)} \cdot \frac{\partial f(w)}{\partial w} \cdot dw = 0 \quad \text{—} \quad (v)$$

And $\quad u\,du + v\,dv + w \cdot dw = 0 \quad \text{—} \quad (vi)$

As there are only two independent variables, arbitrary values cannot be given to all the three differentials. Suppose the arbitrary values are given to dv and dw. Multiplying eqn (vi) by $m\beta$ where m is the mass of molecules and β is an arbitrary unknown function. The product of $m\beta$ is called Langrange undetermined multiplier.

$$\therefore m\beta\, [u \cdot du + v \cdot dv + w\, dw) = 0 \quad \text{—} \quad (vii)$$

Adding eqn (v) and (vii)

$$\left[\frac{1}{f(u)} \cdot \frac{\partial f(u)}{\partial u} + m\beta u\right] du + \left[\frac{1}{f(v)} \cdot \frac{\partial f(v)}{\partial v} + m\beta v\right] \cdot dv + \left[\frac{1}{f(w)} \cdot \frac{\partial f(w)}{\partial w} + m\beta w\right] dw = 0 \quad (viii)$$

As the two variables v and w are considered to be independent, their differentials are arbitrary and the values $du = 0$

and $d\omega = 0$ may be assigned to them. From eqn (viii)

$$\frac{1}{f(u)} \cdot \frac{\partial f(u)}{\partial u} + m\beta u = 0 \quad \text{— (ix)}$$

Taking $du = 0$ and $d\omega \neq 0$, we get

$$\frac{1}{f(\omega)} \cdot \frac{\partial f(\omega)}{\partial \omega} + m\beta\omega = 0 \quad \text{— (x)}$$

Taking $d\omega = 0$ and $dv \neq 0$

$$\frac{1}{f(v)} \cdot \frac{\partial f(v)}{\partial v} + m\beta v = 0 \quad \text{— (xi)}$$

To satisfy eqn (ix), (x) and (xi), β would either be a constant or a function of the variables in that eqn. A constant value of β is only value that can satisfy all the eqns. It is cleared from the above eqn. that the function f satisfied the same differential eqn. irrespective of the components.

For the x - components

$$\frac{d}{du}[\log f(u)] = -m\beta u$$

$$\int d[\log f(u)] = -m\beta \int u \cdot du$$

$$\log f(u) = -\beta\left(\tfrac{1}{2}mu^2\right) + \log A \quad \text{— (xii)}$$

where A is a Integral constant.

From eqn (xii)

$$f(u) = A e^{-\beta\left(\frac{1}{2}mu^2\right)} \quad \text{(xiii)}$$

Similarly, $$f(v) = A e^{-\beta\left(\frac{1}{2}mv^2\right)} \quad \text{— (xiv)}$$

And $$f(\omega) = A e^{-\beta\left(\frac{1}{2}m\omega^2\right)} \quad \text{— (xv)}$$

From these three eqn. the density of velocity points is given by

$$f = NA^3 e^{-\beta\left[\frac{1}{2}m\left(u^2+v^2+\omega^2\right)\right]}$$

$$f = NA^3 e^{-\beta\left(\frac{1}{2}mc^2\right)} \quad \text{— (xvi)}$$

But $$f = \frac{d^2 N_{x,y,z}}{du \cdot dv \cdot d\omega} \quad \text{— (xvii)}$$

i.e. the no. of molecules with components of velocity lying in a small cubical volume divided by the volume element. However f is constant within the infinitesimal spherical shell within the radii c and $c + dc$. The volume of this element is

$4\pi c^2 dc$. This volume element contains dN molecules.

$$\therefore f = \frac{dN}{4\pi c^2 dc} \quad \text{--- (xviii)}$$

From eqn. (xvi) and (xviii)

$$\frac{dN}{4\pi c^2 . dc} = NA^3 e^{-B(\frac{1}{2}mc^2)}$$

$$\frac{dN}{dc} = 4\pi NA^3 c^2 e^{-B(\frac{1}{2}mc^2)} \quad \text{--- (XIX)}$$

$$\therefore dN = 4\pi NA^3 e^{-bc^2} c^2 . dc \quad \text{--- (XX)}$$

where N represents the no. of molecules per CC &

$$A = \sqrt{\frac{b}{\pi}} \quad \text{and} \quad b = \frac{Bm}{2}$$

$$\therefore b = \frac{m}{2KT} \quad B = \frac{1}{KT}$$

Here K is Boltzmann's constant

The graph representing dN/dc and speed is shown in fig - 2.

The shaded area in the figure represents the no. of molecules dN having velocities between c and c+dc. The no. of molecules possessing the r.m.s. velocity C is maximum. The no. of molecules having very low or very high velocity is small. The total area under the curve represents the total no. of molecules.

From eqn (XX)

$$\frac{dN}{dc} = 4\pi N\left[\frac{m}{2\pi KT}\right]^{3/2} c^2 e^{-\frac{mc^2}{2KT}}$$

$$\therefore \frac{dN}{dc} = \frac{4N}{\sqrt{\pi}}\left(\frac{m}{2KT}\right)^{3/2} c^2 e^{-\frac{mc^2}{2KT}} \quad \text{- (xxi)}$$

Taking $\frac{1}{2}mc^2 = E$, where E is the mean kinetic energy of a molecule,

$$\frac{dN}{dc} = \frac{4N}{\sqrt{\pi}}\left(\frac{m}{2KT}\right)^{3/2} c^2 e^{-\frac{N}{KT}} \quad \text{--- (XXII)}$$

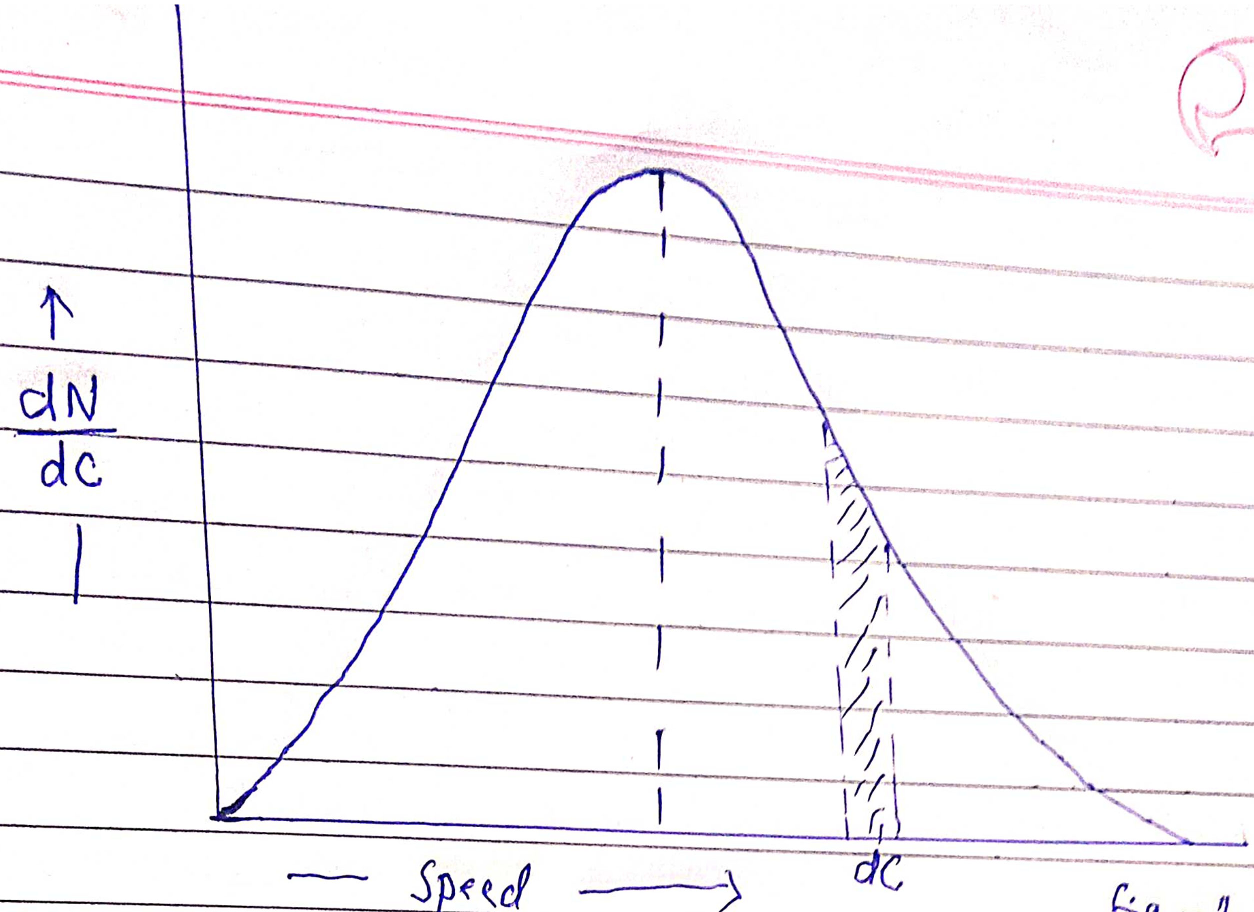

fig – 1

Thus, Maxwell's law of distribution of velocities shows that the mean kinetic energy of all the molecules of a gas remains constant at a fixed tempr, through at any instant the molecules are moving with different velocities.