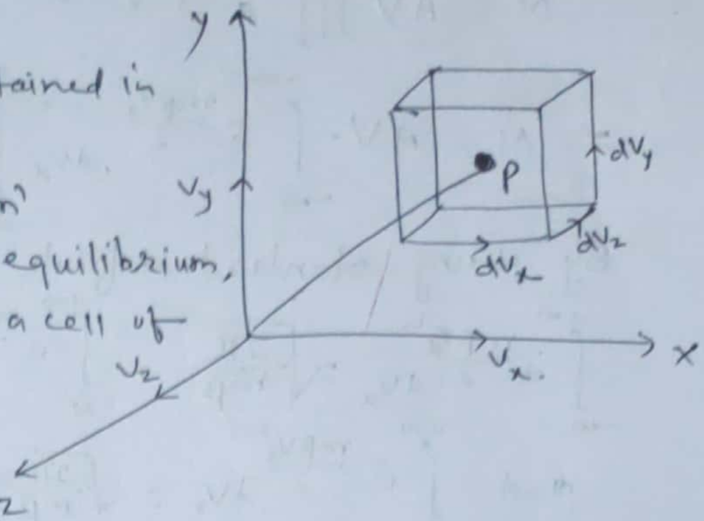
Ques: Deduce Maxwell's law of distribution of molecular velocities. (2016).

Ans:– Consider an ideal gas contained in a container of volume V.

By applying Maxwell-Boltzmann' canonical distribution law in equilibrium, the number of molecules in a cell of energy E_i will be



$$n_i = A \cdot e^{-\beta \cdot E_i} \quad \text{——— ①}$$

where A = constant, $\beta = \frac{1}{KT}$ and E_i = Energy of the particle $= \frac{1}{2}mv^2$

The number of molecules having position coordinates in the range x to $x+dx$, y to $y+dy$, z to $z+dz$ and velocity components in the range V_x to V_x+dV_x, V_y to V_y+dV_y, V_z to V_z+dV_z will be proportional to the element of phase of volume $dx\,dy\,dz \cdot dV_x\,dV_y\,dV_z$.

Therefore, according to Maxwell-Boltzmann's canonical distribution law, the number of molecules having energy E_i and position coordinates between x and $x+dx$, y and $y+dy$, z and $z+dz$ and velocity components between V_x and V_x+dV_x, V_y and V_y+dV_y, V_z and V_z+dV_z is given by

$$n_i\, dx\,dy\,dz \cdot dV_x\,dV_y\,dV_z = A \cdot e^{-\beta E_i} \cdot dx\,dy\,dz \cdot dV_x\,dV_y\,dV_z \quad \text{——— ②}$$

But E_i = Energy of particle $= \frac{1}{2}mv^2 = \frac{1}{2}m(V_x^2+V_y^2+V_z^2)$ put in eqⁿ ②

$$n_i\, dx\,dy\,dz \cdot dV_x\,dV_y\,dV_z = A\, e^{-m\beta \cdot \frac{1}{2}(V_x^2+V_y^2+V_z^2)} \cdot dx\,dy\,dz\, dV_x\,dV_y\,dV_z \quad \text{——— ③}$$

for evaluating constant A, eqⁿ ③ is integrated overall available volume and all ranges of velocities,

$$N = \iiiiiint A\, e^{-m\beta \cdot \frac{1}{2}(V_x^2+V_y^2+V_z^2)} \cdot dx\,dy\,dz\, dV_x\,dV_y\,dV_z$$

$$\Rightarrow N = A \cdot \iiint dx \cdot dy \cdot dz \cdot \iiint e^{-m\beta \cdot \frac{1}{2}(V_x^2+V_y^2+V_z^2)} \cdot dV_x\,dV_y\,dV_z$$

But $\iiint dx \cdot dy\, dz = V$ = volume of the container containing gas

So

$$N = A\cdot V \iiint e^{-m\beta\cdot\frac{1}{2}(V_x^2+V_y^2+V_z^2)}\cdot dV_x dV_y dV_z$$

$$\Rightarrow N = A\cdot V\cdot \int_{-\infty}^{+\infty} e^{-\frac{m\beta V_x^2}{2}}\cdot dV_x \int_{-\infty}^{+\infty} e^{-\frac{m\beta V_y^2}{2}}\cdot dV_y\cdot \int_{-\infty}^{+\infty} e^{-\frac{m\beta V_z^2}{2}}\cdot dV_z \quad \text{—— (4)}$$

By using standard definite integral,

$$\int_{-\infty}^{+\infty} e^{-\frac{m\beta V_x^2}{2}} dV_x = \sqrt{\frac{2\pi}{m\beta}}, \quad \int_{-\infty}^{+\infty} e^{-\frac{m\beta V_y^2}{2}} dV_y = \sqrt{\frac{2\pi}{m\beta}}$$

and $\int_{-\infty}^{+\infty} e^{-\frac{m\beta V_z^2}{2}} dV_z = \sqrt{\frac{2\pi}{m\beta}}$ putting these all values in equ^n (4)

$$N = A\cdot V\sqrt{\frac{2\pi}{m\beta}}\cdot\sqrt{\frac{2\pi}{m\beta}}\cdot\sqrt{\frac{2\pi}{m\beta}} = A\cdot V\left(\frac{2\pi}{m\beta}\right)^{3/2}$$

$$\Rightarrow A = \frac{N}{V}\left(\frac{m\beta}{2\pi}\right)^{3/2} \text{ or } A = \frac{N}{V}\left(\frac{m}{2\pi KT}\right)^{3/2} \quad \text{—— (5)}$$

$\because \beta = \frac{1}{KT}$

putting values of A and β in equ^n (2), we get

$$n_i dx dy dz\cdot dV_x dV_y dV_z = \frac{N}{V}\left(\frac{m}{2\pi KT}\right)^{3/2} e^{-\frac{m}{2KT}(V_x^2+V_y^2+V_z^2)}\cdot dx dy dz\, dV_x dV_y dV_z \quad \text{—— (6)}$$

The number of molecules having velocity coordinates in the range V_x to V_x+dV_x, V_y to V_y+dV_y, V_z to V_z+dV_z irrespective of position coordinates, can be obtained by integrating equ^n (6) with respect to position coordinates as

$$n_i\, dV_x dV_y dV_z = \frac{N}{V}\left(\frac{m}{2\pi KT}\right)^{3/2}\cdot e^{-\frac{m}{2KT}(V_x^2+V_y^2+V_z^2)}\cdot dV_x dV_y dV_z\cdot \iiint dx\, dy\cdot dz$$

$$= \frac{N}{V}\cdot\left(\frac{m}{2\pi KT}\right)^{3/2}\cdot e^{-\frac{m}{2KT}(V_x^2+V_y^2+V_z^2)}\cdot dV_x\cdot dV_y\cdot dV_z\cdot V$$

$\because \iiint dx\cdot dy\cdot dz = V =$ volume of the container

$$\Rightarrow n_i\cdot dV_x dV_y dV_z = N\cdot\left(\frac{m}{2\pi KT}\right)^{3/2}\cdot e^{-\frac{m}{2KT}(V_x^2+V_y^2+V_z^2)}\cdot dV_x dV_y dV_z \quad \text{—— (7)}$$

Lastly we want to find number of molecules having velocity component in the range V_x to V_x+dV_x irrespective of V_y and V_z which can be obtained by integrating equ^n (7)

with respect to V_y and V_z i.e,

$$n(V_x)\cdot dV_x = N\cdot\left(\frac{m}{2\pi KT}\right)^{3/2}\cdot dV_x \iint e^{-\frac{m}{2KT}(V_x^2+V_y^2+V_z^2)}\cdot dV_y\, dV_z$$

$$= N\cdot\left(\frac{m}{2\pi KT}\right)^{3/2}\cdot dV_x \cdot e^{-\frac{mV_x^2}{2KT}} \int_{-\infty}^{+\infty} e^{-\frac{mV_y^2}{2KT}} dV_y \cdot \int_{-\infty}^{+\infty} e^{-\frac{mV_z^2}{2KT}}\cdot dV_z$$

$$= N\cdot\left(\frac{m}{2\pi KT}\right)^{3/2}\cdot dV_x \cdot e^{-\frac{mV_x^2}{2KT}}\cdot \sqrt{\frac{2\pi KT}{m}}\cdot \sqrt{\frac{2\pi KT}{m}}$$

$$\left(\because \int_{-\infty}^{+\infty} e^{-\frac{mV_y^2}{2KT}}\cdot dV_y = \int_{-\infty}^{+\infty} e^{-\frac{mV_z^2}{2KT}}\cdot dV_z = \sqrt{\frac{2\pi KT}{m}}\right)$$

$$\Rightarrow n(V_x)\cdot dV_x = N\left(\frac{m}{2\pi KT}\right)^{1/2}\cdot e^{-\frac{mV_x^2}{2KT}}\cdot dV_x \qquad (8)$$

Equ (8) gives the number of molecules having x-components of velocity in the range between V_x and V_x+dV_x. Equ (8) shows that the velocity component V_x is distributed symmetrically about the value $V_x=0$.

The probability that a molecules will have ~~x compon~~ x-component of velocity in the range V_x to V_x+dV_x is given by

$$P(V_x)\cdot dV_x = \frac{n(V_x)\, dV_x}{N} = \left(\frac{m}{2\pi KT}\right)^{\frac{1}{2}}\cdot e^{-\frac{mV_x^2}{2KT}}\cdot dV_x \qquad (9)$$

Equs (8) and (9) represent Maxwell's distribution law of velocities.

The probability function $P(V_x)$ is given by $\frac{P(V_x)\cdot dV_x}{dV_x}$

$$\text{or}\quad P(V_x) = \left(\frac{m}{2\pi KT}\right)^{\frac{1}{2}}\cdot e^{-\frac{mV_x^2}{2KT}} \qquad (10)$$

equ (10) can also be expressed in terms of momentum component P_x. By substituting $mV_x = P_x$ and $m.dV_x = dP_x$ on right hand side of equ (10), we see

$$P(P_x) = \left(\frac{m}{2\pi KT}\right)^{\frac{1}{2}}\cdot e^{-\frac{P_x^2}{2mKT}} \qquad (11)$$