

Expression for Average velocity :-

The average velocity or mean velocity of molecules obeying Maxwell's laws defined by

$$C_{av} = \frac{1}{n} \int_0^{\infty} c \, dn_c$$

where $dn_c = 4\pi n a^3 e^{-bc^2} c^2 dc$

$$\begin{aligned} \text{or, } C_{av} &= \frac{1}{n} 4\pi n a^3 \int_0^{\infty} e^{-bc^2} c^3 dc \\ &= 4\pi a^3 \left[\frac{1}{2b^2} \right] \end{aligned}$$

(Where the value of integral is square bracket)

$$= 4\pi a^3 \times \frac{1}{2b^2} = 2\pi \frac{a^3}{b^2}$$

$$C_{av} \propto \frac{1}{b^2}$$

Now $a = \sqrt{\frac{b}{\pi}}$

then $C_{av} = 2\pi \frac{b^{3/2}}{\pi^{3/2}} \times \frac{1}{b^2}$

$$= 2 \sqrt{\frac{1}{\pi b}} = 2 \sqrt{\frac{2kT}{m\pi}}$$

$$= \sqrt{\frac{8kT}{m\pi}}$$

$$= \sqrt{\frac{2.55 kT}{m}} = 1.596 \sqrt{\frac{kT}{m}}$$

$$a^3 = \frac{b^{3/2}}{\pi^{3/2}}$$

$$\text{and } b = \frac{m}{2kT}$$

where m = molecular mass

T = absolute temp.

k = Boltzmann const.

Root Mean Square velocity:-

The root mean square velocity is the root of average of square of velocity and is defined by

$$C_{r.m.s}^2 = \frac{1}{n} \int_0^{\infty} c^2 dc$$

$$= \frac{1}{n} 4\pi n a^3 \int_0^{\infty} e^{-bc^2} c^4 dc$$

$$= 4\pi a^3 \times \left[\sqrt{\frac{9\pi}{64b^5}} \right]$$

$$= 4\pi a^3 \times \frac{3}{8} \sqrt{\frac{\pi}{b^5}}$$

$$= \frac{3\pi a^3}{2} \sqrt{\frac{\pi}{b^5}}$$

$$= \frac{3}{2} \times \frac{1}{b} = \frac{3}{2} \cdot \frac{2kT}{m} = \frac{3kT}{m}$$

$$\text{Therefore } C_{r.m.s} = \sqrt{\frac{3kT}{m}} = \underline{\underline{1.732 \sqrt{\frac{kT}{m}}}}$$

Most Probable velocity:-

The most probable velocity is that which most of the molecules have. Therefore it is obtained by differentiating $f(c)$ with respect to c and equating the result to zero.

$$\text{Hence } \frac{d}{dc} f(c) = 0$$

$$\text{where } f(c) = 4\pi n a^3 e^{-bc^2} c^2 dc$$

$$\int_0^{\infty} e^{-bc^2} c^4 dc = ?$$

$$\frac{C_{av} = \frac{1.596 \sqrt{kT/m}}{1.732 \sqrt{kT/m}}}{C_{r.m.s}} = \frac{1.596}{1.732} = 0.921$$

$$\text{Or } C_{av} = 0.921 C_{r.m.s}$$

$$= A e^{-bc^2} c^2 dc$$

where $A = 4\pi m a^3$

Hence $\frac{d}{dc} f(c) = A \left[2c e^{-bc^2} + c^2 e^{-bc^2} \times -2bc \right]$

$$= 0$$

or, $2c e^{-bc^2} \times \{1 - bc^2\} = 0$

but $c \neq 0$

Hence $bc^2 = 1$

or $c^2 = \frac{1}{b}$

or $c = \frac{1}{\sqrt{b}}$

∴ therefore $c_{mp} = \sqrt{\frac{2kT}{m}}$

most probable velocity = $\sqrt{\frac{2kT}{m}}$
 $= 1.414 \sqrt{\frac{kT}{m}}$

Thus we see that →

$$c_{rms} > c_{av} > c_{mp}$$

∴ the end

$$\frac{kT}{e_{rms}} = \frac{1.414 \sqrt{\frac{kT}{m}}}{1.732 \sqrt{\frac{kT}{m}}}$$

$$= \frac{1.414}{1.732} = 0.816$$

$$c_{mp} = 0.816 c_{rms}$$