

Chapter 7

Theory of Gases

Kinetic Theory of Gases:

Kinetic theory of gases provide sound theoretical basis for the various gas laws, mainly Boyle's law, Charles's law, Graham's law and Avogadro's law. These laws were empirical generalization based on experimental observation. There was no theoretical background to justify them.

It is based on following postulates

- (i) Every gas consists of large number of tiny particles called gas molecules.
- (ii) Gas molecules can move rapidly in every possible direction and collide with one another and with walls of container.
- (iii) Their collisions are perfectly elastic i.e. there is no loss of momentum and energy.
- (iv) The volume occupied by the gas molecule is negligible as compared to the total volume of gas.
- (v) There is no attraction or repulsion between gas molecules or gas and walls of vessel.
- (vi) The pressure of the gas is due to bombardment of gas molecules on the walls of vessel.
- (vii) There is no effect of gravity on the distribution of gas in the container.
- (viii) The average kinetic energy of gas molecule is directly proportional to the absolute temperature.

$$\text{K.E.} \propto T$$

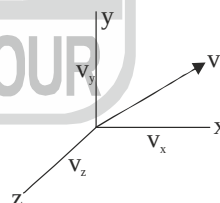
Derivation of Kinetic gas equation :

Let us consider that gas is kept in a cubical box of length 'a' and move with velocity 'v'. The mass of one gas particle be 'm'. The resolution of velocity 'v' along x, y, z axes.

$\therefore$

$$v^2 = v_x^2 + v_y^2 + v_z^2$$

... (1)

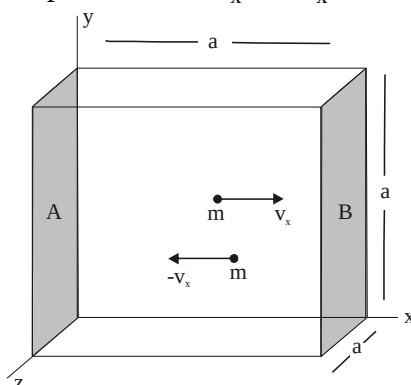


If a gas particle moves in a cubical box along +ve direction of x-axis with v_x velocity between two faces 'A' and 'B'.

momentum of the particle before collision to face 'B' = mv_x

momentum after collision = $-mv_x$.

Therefore, Change in momentum of particle = $-mv_x - mv_x = -2mv_x$



Therefore, Momentum transferred to the face B, $\Delta p = 2mv_x$

On colliding with the same face 'B' the molecule travel $2a$ distance with v_x velocity

$$\therefore \Delta t = \frac{2a}{v_x}$$

$\therefore$ Change in momentum per unit time at B face,

$$\frac{\Delta p}{\Delta t} = \frac{2mv_x}{2a} \cdot v_x = \frac{mv_x^2}{a}$$

Change in momentum between A and B faces

$$= 2 \left(\frac{mv_x^2}{a} \right)$$

According to Newton's law,

Change in momentum per unit time = Force

$$\therefore F = \frac{2mv_x^2}{a}$$

Similarly, along y and z axes $\frac{\Delta p}{\Delta t}$ are $\frac{2mv_y^2}{a}$ and $\frac{2mv_z^2}{a}$ respectively.

$$\therefore \text{Total change in momentum} = \frac{2mv_x^2}{a} + \frac{2mv_y^2}{a} + \frac{2mv_z^2}{a} = \frac{2m}{a} (v_x^2 + v_y^2 + v_z^2)$$

$$\boxed{F = \frac{2mv^2}{a}} \quad \left(\text{from equation(1), } v^2 = v_x^2 + v_y^2 + v_z^2 \right)$$

Area of cube = $6 \times (a)^2$

$$\therefore \text{Pressure, } P = \frac{F}{A} \Rightarrow \frac{2mv^2}{a \cdot 6a^2}$$

$$P = \frac{1}{3} \frac{mv^2}{a^3} \quad \left(\because a^3 = \text{volume of cube } v \right)$$

$$P = \frac{1}{3} \frac{m\bar{v}^2}{V} \quad \left[\bar{v}^2 = \text{Root mean square velocity} \right]$$

For 1 mole, $\boxed{PV = \frac{1}{3} M\bar{v}^2}$, where M is the molar mass of gas

For 'n' mole, $\boxed{PV = \frac{1}{3} Mn\bar{v}^2}$... (2)

Equation (2) is known as kinetic gas equation.

Kinetic Energy of one mole of gas :

From Kinetic gas equation.

$$PV = \frac{1}{3} M\bar{v}^2 \quad (\text{multiply and divide by 2 on R.H.S.})$$

$$PV = \frac{2}{3} \left(\frac{1}{2} M \bar{v}^2 \right) \Rightarrow PV = \frac{2}{3} KE \Rightarrow \left(KE = \frac{1}{2} M \bar{v}^2 \right) \Rightarrow KE = \frac{3}{2} PV$$

From ideal gas equation $PV = RT$ 'for 1 mole'

$$\therefore \boxed{KE = \frac{3}{2} RT} \quad \dots (3)$$

Where, R = universal gas constant.

$$\boxed{KE \propto T}$$

Thus kinetic energy for 1 mole of gas is directly proportional to the temperature

Kinetic energy for 1 molecule:

$$\therefore \text{Kinetic energy for 1 mole} = \frac{3}{2} RT.$$

$$\therefore \text{KE for molecule} = \frac{3}{2} \left(T \frac{R}{N_A} \right) \quad (N_A = \text{Avogadro's number})$$

$$\boxed{KE = \frac{3}{2} kT}$$

$$k = \text{Boltzmann constant } (1.38 \times 10^{-23} \text{ J / K}) \quad \dots (4)$$

$$\boxed{KE \propto T}$$

Thus kinetic energy for one molecule also depends on temperature.

Deduction of various gas laws from kinetic gas equation:

(1) Boyle's law:

$$\therefore PV = \frac{1}{3} m.n\bar{v}^2 \Rightarrow PV = \frac{1}{3} m\bar{v}^2 \quad (m.n = M \text{ total mass of gas})$$

$$PV = \frac{2}{3} KE$$

From equation (3),

$$KE \propto T$$

$$PV = \frac{2}{3} T$$

If temperature of gas kept constant

$$PV = \text{constant}$$

$$PV = K \Rightarrow P = \frac{K}{V} \quad \text{Or} \quad \boxed{P \propto \frac{1}{V}} \quad \text{This is Boyle's law.}$$

(2) Charles's law:

$$PV = \frac{1}{3} m.n\bar{v}^2 \Rightarrow PV = \frac{1}{3} M \bar{v}^2 \quad (m.n = M)$$

$$PV = \frac{2}{3} \left(\frac{1}{2} M \bar{v}^2 \right) \Rightarrow PV = \frac{2}{3} KE$$

$$\therefore KE \propto T \Rightarrow PV = \frac{2}{3} T \Rightarrow \frac{V}{T} = \frac{2}{3} P$$

At constant pressure

$$\frac{V}{T} = k \Rightarrow V = kT \Rightarrow \boxed{V \propto T} \quad \text{i.e. Charles's law.}$$

(3) Avogadro's law:

One mole of any substance contains the Avogadro constant (6.022×10^{23}) of molecules. It was Avogadro who discovered the law of nature for gases. This law is known as Avogadro's law, which states:

The volumes of the same number of moles of all gases measured at constant temperature and pressure are the same. That is, at the same temperature and pressure equal volumes of all gases contain equal number of moles or molecules.

Let us consider that two gases having masses m_1 , m_2 and number of moles n_1 and n_2 are at the same temperature pressure and volumes.

$\therefore$ From kinetic gas equation

$$PV = \frac{1}{3} m_1 n_1 v_1^2 \quad \dots (i)$$

$$PV = \frac{1}{3} m_2 n_2 v_2^2 \quad \dots (ii)$$

On comparing equation (i) and (ii), we get

$$\therefore \frac{1}{3} m_1 n_1 v_1^2 = \frac{1}{3} m_2 n_2 v_2^2$$

$$m_1 n_1 v_1^2 = m_2 n_2 v_2^2 \quad \dots (iii)$$

Since both gases are at the same temperature hence they will have same KE.

$$\text{i.e.} \quad \frac{1}{2} m_1 v_1^2 = \frac{1}{2} m_2 v_2^2 \quad \dots (iv)$$

On dividing equation (iii) by equation (iv)

$$\frac{m_1 n_1 v_1^2}{m_1 v_1^2} = \frac{m_2 n_2 v_2^2}{m_2 v_2^2}$$

$$\Rightarrow n_1 = n_2, \text{ this is known as Avogadro's law.}$$

(4) Graham's law of diffusion:

"The rate of diffusion of a gas is inversely proportional to the square root of its density at constant pressure."

From kinetic gas equation.

$$PV = \frac{1}{3} m n v^2 \quad [m \cdot n = M \text{ total mass of gas}]$$

$$PV = \frac{1}{3} M v^2 \Rightarrow v^2 = \frac{3PV}{M} = \frac{3P}{\left(\frac{M}{V}\right)} \Rightarrow v^2 = \frac{3P}{d} \text{ where, } d = \text{density of gas}$$

$$\therefore v = \sqrt{\frac{3P}{d}}$$

If $P = \text{constant}$.

$$v \propto \frac{1}{\sqrt{d}}$$

This equation is known as Graham's law.

Problem-1. The total number of molecules present in a mixture of N_2 and O_2 gases of volume one liter at STP is (assuming ideal behaviour).

(a) 6.02×10^{23}

(b) 2.69×10^{22}

(c) 6.02×10^{22}

(d) 3.01×10^{23}

Soln. $V = 1L$

The total number of molecules = ?

At STP

$$\therefore pV = nRT \text{ (for ideal gas)}$$

$$\Rightarrow 1 \times 1 = n \times 0.083 \times 273.15$$

$$\Rightarrow n = 0.045 \text{ mol}$$

$$\therefore \text{Total number of molecules} = 2.69 \times 10^{22}$$

Correct option is (b)

Problem-2. The average kinetic energy of O_2 molecules at 500K is:

(a) $1.38 \times 10^3 \text{ J.mol}^{-1}$

(b) $1.6 \times 10^4 \text{ J.mol}^{-1}$

(c) $6.24 \times 10^3 \text{ J.mol}^{-1}$

(d) $2.76 \times 10^3 \text{ J.mol}^{-1}$

Soln. Average kinetic energy = $\frac{3}{2}RT$

$$= \frac{3}{2} \times 8.314 \times 500$$

$$= 6.24 \times 10^3 \text{ J mol}^{-1}$$

Correct option is (c)

Problem-3. The number of molecules of an ideal gas in a 8.2 l container at 380 torr and 27°C will be

(a) 1.0×10^{23}

(b) 1.0×10^{22}

(c) 6.02×10^{23}

(d) 12.04×10^{23}

Soln. $V = 8.2 \text{ L}$

$P = 380 \text{ torr}$

$T = 27^\circ\text{C} \quad \therefore pV = nRT \text{ (for ideal gas)}$

$$\Rightarrow 380 \times 8.2 = n \times 62.364 \times 300 \Rightarrow n = 0.167 \text{ mol}$$

$$\therefore \text{Total number of molecules} = 1 \times 10^{23}$$

Correct option is (a)

Problem-4. At STP, 1 kmole of a gas occupies 22.4 m^3 . The molecular density (in molecules/ m^3) at STP is

(a) 6.02×10^{26}

(b) 3×10^{10}

(c) 2.7×10^{25}

(d) 10^7

Soln. $V = 22.4 \text{ m}^3$

$$n = 1 \text{ kmol} = 10^3 \text{ mol}$$

$$\text{Number of molecules} = 10^3 \times 6.023 \times 10^{23} = 6.023 \times 10^{26}$$

$$\therefore \text{The molecular density} = \frac{6.023 \times 10^{26}}{22.4} = 2.7 \times 10^{25}$$

Correct option is (c)

Problem-5. When 2g of a gas A is introduced into an evacuated flask kept at 25°C , the pressure is found to be 1 atm. If 3g of another gas B is then added to the same flask, the total pressure becomes 1.5 atm. Assuming ideal gas behaviour, calculate the ratio of the molecular weights $M_A : M_B$.

(a) 1 : 3

(b) 2 : 5

(c) 2 : 3

(d) 3 : 1

Soln.

$$\begin{array}{l|l} W_A = 2g & W_B = 3g \\ T = 25^\circ\text{C} & P_T = 1.5\text{atm} \\ P_A = 1\text{atm} & M_A : M_B = ? \end{array}$$

$$\therefore P_B = P_T - P_A = 1.5 - 1 = 0.5\text{atm}$$

For ideal gas $pV = nRT$

$$\therefore \frac{P_A}{P_B} = \frac{n_A}{n_B}$$

$$\Rightarrow \frac{P_A}{P_B} = \frac{W_A}{M_A} \times \frac{M_B}{W_B} \Rightarrow \frac{1}{0.5} = \frac{2}{M_A} \times \frac{M_B}{3} \Rightarrow \frac{M_A}{M_B} = \frac{1}{3}$$

$$\Rightarrow M_A : M_B = 1 : 3$$

Correct option is (a)

Problem-6. The volume occupied by 7 gm of nitrogen at 27°C and 750.9 mm Hg pressure is :

- (a) 8.24 litres (b) 6.14 litres (c) 6.24 litres (d) 5.24 litres

Soln. $W_{N_2} = 7\text{gm}$

$$T = 27^\circ\text{C}$$

$$P = 750.9\text{mmHg}$$

For ideal gas :

$$pV = nRT \Rightarrow V = \frac{nRT}{p} = \frac{7 \times 62.36 \times 300}{28 \times 750.9}$$

$$V = 6.24\text{L}$$

Correct option is (c)

Problem-7. If the density of air is 1.2 g/lit, what is the volume occupied by 7.8g of air?

- (a) 10.10 lit (b) 10 lit (c) 6 lit (d) 6.5 lit

Soln. $\rho = 1.2\text{g} / \text{L}$

$$\therefore \rho = \frac{w}{v}$$

$$\Rightarrow V = \frac{w}{\rho} = \frac{7.8}{1.2} = 6.5\text{L}$$

Correct option is (d)

REAL GASES

Deviation from ideal behaviour:

Real gases do not obey the ideal gas laws exactly under all conditions of temperature and pressure. Experimental shows that at low pressure and moderately high temperatures, gases obey the laws of Boyle, Charles and Avogadro approximately, but as the pressure is increased or the temperature is decreased, a marked departure from ideal behaviour is observed.

Compression Factor:

The deviations can be displayed more clearly, by plotting the ratio of the observed molar volume V_m to the ideal molar volume $V_{m, ideal}$ as a function of pressure at constant temperature. This ratio is called the compressibility factor Z and can be expressed as

$$Z = \frac{V_m}{V_{m, ideal}} = \frac{P}{RT} V_m$$

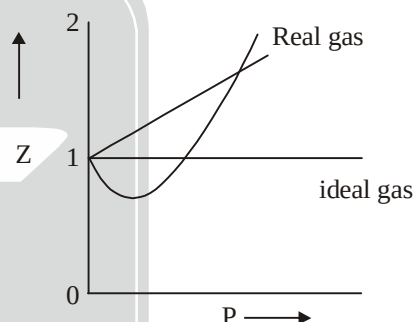
To display the deviation of a gas from ideal behaviour clearly, the ratio of the observed molar volume V , to the ideal molar volume $\left(V_{id} = \frac{RT}{P} \right)$ is plotted against pressure at constant temperature. This ratio is called the compressibility factor, Z ,

$$Z = \frac{V_{real}}{V_{ideal}} = \frac{V_{real}P}{RT}$$

$$\left[V_{ideal} = \frac{RT}{P} \right]$$

For an ideal gas $Z = 1$, For a real gas $Z \neq 1$

- (i) If $Z > 1$, the gas is less compressible compared to an ideal gas.
 - (ii) If $Z < 1$, the gas is more compressible compared to an ideal gas.
- The gas which do not obey ideal gas laws is known as real gas.



Van der Waals Equation of State for a Real Gas

Causes of deviations from ideal behaviour

- (i) The volume occupied by the molecules is negligible in comparison to the total volume of the gas
- (ii) The molecules exert no forces of attraction upon one another

- Correction for volume

$$V_i = V - nb \quad b \rightarrow \text{excluded volume; } n \rightarrow \text{number of moles}$$

$$b = 4(\text{volume occupied by a molecule})$$

$$= 4 \left(\frac{4}{3} \pi r^3 \right)$$

- Correction for forces of attraction

$$P_i = P + \frac{an^2}{V^2}$$

$a \rightarrow$ measure the forces of attraction between the molecules

Expression of Van der Waals Equation of State:

$$\left(P + \frac{an^2}{V^2} \right) (V - nb) = nRT$$

Reduction of Van der Waals equation to Virial Equation:

All equations of state can be expressed approximately in one common form called the virial equation of state. Van der waals equation can be reduced to virial equation as

$$Z = 1 + \frac{1}{RT} \left(b - \frac{a}{RT} \right) P + \frac{a}{(RT)^3} \left(2b - \frac{a}{RT} \right) P^2 + \dots$$

The slope of Z versus P curve is obtained by differentiating the above virial equation in Z with respect to pressure at constant temperature.

$$\left(\frac{\partial Z}{\partial P} \right)_T = \frac{1}{RT} \left(b - \frac{a}{RT} \right) + \frac{2a}{(RT)^3} \left(2b - \frac{a}{RT} \right) P + \dots$$

$$\text{At } P = 0; \quad \left(\frac{\partial Z}{\partial P} \right)_T = \frac{1}{RT} \left(b - \frac{a}{RT} \right)$$

Thus, the Van der waals equation, which includes both the effects of size and of intermolecular forces, can interpret both the positive and negative slopes of the Z versus P plots.

Boyle Temperature: At some intermediate temperature T_B , called Boyle temperature, the initial slope of Z versus P curve is zero.

$$\therefore T_B = \frac{a}{Rb}$$

At the Boyle temperature, the Z versus P line of an ideal gas is tangent to that of a real gas when P approaches zero.

Thus, at the Boyle temperature, the real gas behaves ideally over a wide range of pressure, because the effects of the size of molecules and intermolecular forces roughly compensate each other.

Problem-8. Compared to C_2H_6 , the value of vander waal's constants 'a' and 'b' for He will be

- (a) both will be smaller (b) 'a' will be larger but 'b' will be smaller
(c) 'b' will be larger but 'a' will be smaller (d) both will be larger

Soln. Due to small size of He both attractive force and excluded volume will be small.

Correct option is (a)

Problem-9. The vander Waals constant 'b' for a certain gas is 4.42×10^{-2} L/mol. How near can the centers of two molecules approach each other?

- (a) 1.636 Å (b) 3.272 Å (c) 6.525 Å (d) 2.134 Å

Soln. The vander waals constant 'b' = 4.42×10^{-2} L/mol

Two gas molecules centers approach each other = $2r$

$r \rightarrow$ radius of a molecule $\therefore b = 4 \times \text{volume of a gas molecule}$

$$\Rightarrow b = 4 \times \frac{4}{3} \pi r^3 \Rightarrow r = \sqrt[1/3]{\frac{3b}{16\pi}}$$

$$= \sqrt[1/3]{\frac{3 \times 4.42 \times 10^{-2}}{16 \times \pi \times 6.023 \times 10^{23}}} = 1.636 \times 10^{-9} \text{ dm} = 1.636 \text{ Å}$$

$$\therefore 2r = 3.272 \text{ Å}$$

Correct option is (b)

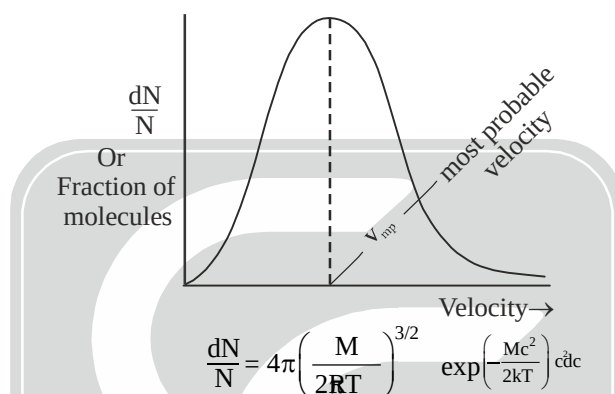
MAXWELL'S DISTRIBUTION OF MOLECULAR VELOCITIES

According to assumption of kinetic theory of gases, molecules of gas collide with one another and with the walls of vessel, thus their velocities keep on changing which results in different speeds for different fraction of molecules at a given temperature.

If N is the total number of molecules in a gas out of which ΔN molecules have the same speed, the fraction of molecules having same speed is given by $\frac{\Delta N}{N}$ or $\frac{dN}{N}$.

The quantity $\frac{dN}{N}$ gives the fraction of molecules with speeds between c and $c+dc$. It can also be given by $p(c)dc$.

Maxwell plotted a graph between different values of the speeds and the corresponding molecular fractions which is known as 'Maxwell's distribution curve'.



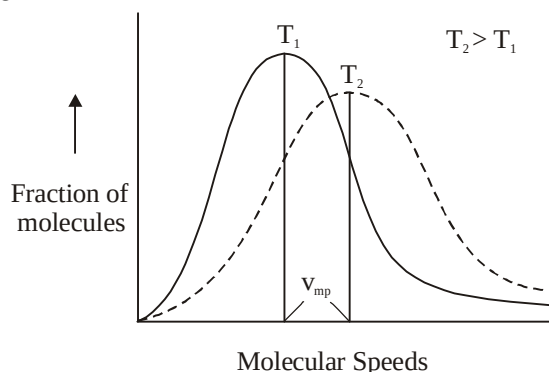
The important features of curve are given as:

- (1) The fraction of molecules with too low or too high velocities are very small.
- (2) The fraction of molecules possessing higher and higher speeds keeps on increasing till it reaches a certain maximum value and then starts decreasing as shown in the curve.
- (3) There is a certain velocity for which the fraction of molecules is maximum. This is called the most probable velocity. Its value at a given temperature depends upon the volume of the gas.

Effect of temperature on distribution of molecular velocities:

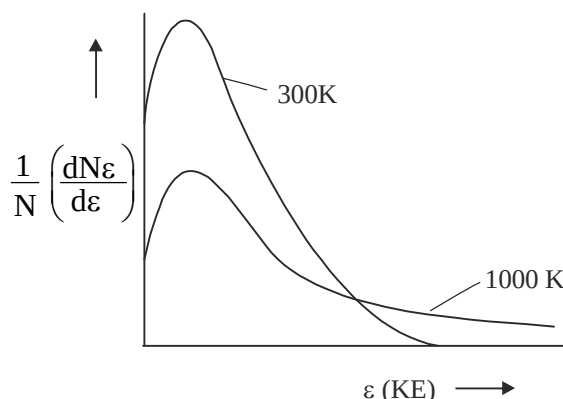
In molecular speeds at x-axes the factor $e^{-(mc^2/2kT)}$ called Boltzmann factor increases with the rise in temperature and thus molecular speeds increase. But the fraction of molecules having most probable velocity decreases with the rise in temperature.

Thus thickness of curve increases along with the decrease in height and curve shifts towards right with the rise of temperature.



Maxwell's distribution of molecules kinetic energies:

It is a curve between the fraction of molecules having kinetic energies in the range of ϵ and $\epsilon + d\epsilon$ i.e. $\frac{dN\epsilon}{N}$ versus kinetic energies ϵ .



The maximum in the probability function corresponds to the most probable kinetic energy.

Most probable kinetic energy

$$\text{per mole} = \frac{1}{2} RT$$

$$\text{per molecule} = \frac{1}{2} kT \quad [k = \text{Boltzmann constant}]$$

Types of Molecular velocities:

Molecular motions are of three types:

(1) Most probable speeds (v_{mp}):

The most probable speed is defined as the velocity possessed by maximum number of molecules of a gas at a given temperature. It is given by

$$v_{mp} = \sqrt{\frac{2RT}{M}} \quad \dots (1)$$

M = molecular mass of gas.

(2) Average Speed (v_{av}):

It is the arithmetic mean of different velocities possessed by the molecules of the gas at a given temperature.

If $c_1, c_2, c_3, \dots, c_n$ are the individual velocities of the gas molecules and 'n' is their total number, then, average velocity is given by.

$$\langle v \rangle = \frac{c_1 + c_2 + c_3 + \dots + c_n}{n} \quad \dots (2)$$

If $c_1, c_2, c_3, \dots$ are the velocities possessed by groups of $n_1, n_2, n_3, \dots$ molecules of the gas respectively, average velocity is given by.

$$\langle c \rangle = \frac{n_1 c_1 + n_2 c_2 + n_3 c_3 + \dots}{n_1 + n_2 + n_3 + \dots}$$

on solving Boltzmann - distribution of molecular velocities, average speed comes out to be

$$\langle v \rangle = \sqrt{\frac{8RT}{\pi M}} \quad \dots (3)$$

(3) Root mean Square velocity:

It is the square root of the means of the squares of the speeds of the different molecules in a gas at a given temperature.

If $c_1, c_2, c_3, \dots$ are the velocities possessed by groups of $n_1, n_2, n_3, \dots$ molecules respectively.

$$\therefore v_{\text{rms}} = \sqrt{\frac{n_1 c_1^2 + n_2 c_2^2 + n_3 c_3^2 + \dots}{n_1 + n_2 + n_3 + \dots}}$$

By solving Boltzmann equation v_{rms} is given by $v_{\text{rms}} = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3PV}{M}} \dots (4)$

Relation between different types of Speeds:

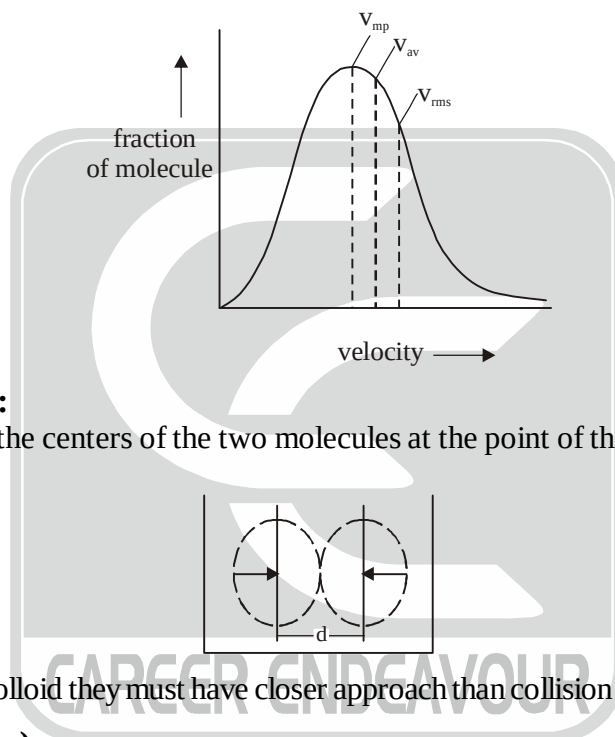
(i) Average speed = $0.9213 \times$ Root mean square speed

(ii) Most probable speed = $0.816 \times$ Root mean square speed.

$$\therefore v_{\text{rms}} : v_{\text{av}} : v_{\text{mp}} = 1.224 : 1.128 : 1 = 1 : 0.92 : 0.82$$

(iii) $v_{\text{rms}} > v_{\text{av}} > v_{\text{mp}}$

Thus, at a given temperature root mean square velocity of a gas is maximum and probable speed is minimum.



Collision diameter:

The distance between the centers of the two molecules at the point of their closest approach is known as collision diameter.

For two molecules to collide they must have closer approach than collision diameter.

Collision number (z_1):

The number of collisions suffered by a single molecule per unit volume of the gas. It is given by

$$z_1 = \sqrt{2} \pi d^2 \langle v \rangle \rho \dots (1)$$

where, ρ = number of molecules per unit volume of the gas

$\langle v \rangle$ = Average velocity

d = collision diameter.

The total number of molecules colliding per unit time per unit volume of the gas

$$= \sqrt{2} \pi d^2 \langle v \rangle \rho^2 \dots (2)$$

Since each collision involves two molecules, the number of collisions of like molecules per unit time per unit volume of gas is given by

$$z_{11} = \frac{1}{2} \sqrt{2} \pi d^2 \langle v \rangle \rho^2$$

$$z_{11} = \frac{1}{\sqrt{2}} \pi d^2 \langle v \rangle \rho^2$$

... (3)

Collision frequency: The number of collisions experienced by molecules per cc of a gas per second is known as collision frequency.

$$\therefore \text{Total no. of molecules colliding per cc per sec. is } z = \sqrt{2} \pi \langle v \rangle N^2 d^2$$

$$\therefore \text{Collision frequency } n = \frac{z}{N} \quad [N = \text{number of gas molecules}]$$

$$n = \frac{\pi \langle v \rangle d^2 N^2}{\sqrt{2}} \quad \dots (4)$$

Mean free path:

The mean free path is defined as the average distance travelled by a molecule between two successive collisions.

$$\lambda = \frac{\text{average distance travelled per sec.}}{\text{number of collisions by a molecule per sec.}} = \frac{\langle v \rangle}{\sqrt{2} \pi \langle v \rangle d^2 N} \Rightarrow \lambda = \frac{1}{\sqrt{2} \pi d^2 N}$$

Assuming that the collision diameter, σ , is independent of temperature, the temperature and pressure dependence of the mean free path is given by ideal gas law as

$$\lambda = \frac{\langle v \rangle}{z_1} \Rightarrow \lambda = \frac{kT}{\sqrt{2} \pi d^2 \cdot p} \quad \dots (5)$$

$$\therefore \begin{cases} \lambda \propto \frac{1}{p} & \text{at constant 'T'} \\ \lambda \propto T & \text{at constant 'p'} \end{cases}$$

Problem-10. The v_{rms} of a gas at 300 K is $30 R^{1/2}$. The molar mass of the gas, in kg mol^{-1} , is

- (a) 1.0 (b) 1.0×10^{-1} (c) 1.0×10^{-2} (d) 1.0×10^{-3}

Soln. $V_{rms} = 30R^{1/2}$

$$T = 300 \text{ K}$$

$$\text{Molar mass (M)} = ?$$

$$\therefore V_{rms} = \sqrt{\frac{3RT}{M}}$$

$$\Rightarrow 30R^{1/2} = \sqrt{\frac{3R \times 300}{M}}$$

$$\Rightarrow M = 1 \text{ kg mol}^{-1}$$

Correct option is (a)

Problem-11. Given that the mean speed of H_2 is 1.78 km s^{-1} , the mean speed of D_2 will be

- (a) 1.26 km s^{-1} (b) 2.52 km s^{-1} (c) 5.04 km s^{-1} (d) 3.17 km s^{-1}

Soln. Mean speed $(u) \propto \frac{1}{\sqrt{M}}$

$$\frac{u_{\text{H}_2}}{u_{\text{D}_2}} = \sqrt{\frac{M_{\text{D}_2}}{M_{\text{H}_2}}}$$

$$\Rightarrow u_{D_2} = u_{H_2} \times \sqrt{\frac{M_{H_2}}{M_{D_2}}}$$

$$\Rightarrow u_{D_2} = 1.78 \times \sqrt{\frac{2}{4}}$$

$$= 1.26 \text{ Km s}^{-1}$$

Correct option is (a)

Problem-12. A mixture of He, N₂ and O₂ gases are maintained at a temperature of 300 K. The ratios of their root mean squared velocities, $\bar{C}_{\text{He}} : \bar{C}_{\text{N}_2} : \bar{C}_{\text{O}_2}$ is

(a) 1:1/7:1/8

(b) 8:7:1

(c) 1:1/√7:1/√8

(d) √8:√7:1

Soln. $\bar{C} \propto \frac{1}{\sqrt{M}}$

$$\bar{C}_{\text{He}} : \bar{C}_{\text{N}_2} : \bar{C}_{\text{O}_2} = \frac{1}{\sqrt{4}} : \frac{1}{\sqrt{28}} : \frac{1}{\sqrt{32}}$$

$$= 1 : \frac{1}{\sqrt{7}} : \frac{1}{\sqrt{8}}$$

Correct option is (c)

Problem-13. The velocity of a sound wave in oxygen at STP is 300 m/s. The velocity of the same wave in Helium at STP would be :

(a) 424 m/s

(b) 600 m/s

(c) 1200 m/s

(d) 849 m/s

Soln. $u \propto \frac{1}{\sqrt{M}}$ (velocity of a molecule)

$$\frac{u_{\text{He}}}{u_{\text{O}_2}} = \sqrt{\frac{M_{\text{O}_2}}{M_{\text{He}}}} \Rightarrow u_{\text{He}} = 300 \times \sqrt{\frac{32}{4}} \approx 849 \text{ m/s}$$

Correct option is (d)

Problem-14. If the average speed of hydrogen molecule at a given temperature is c, then the average speed of oxygen molecule at the same temperature will be

(a) 2c

(b) 4c

(c) $\frac{c}{2}$

(d) $\frac{c}{4}$

Soln. $\bar{u}_{H_2} = C ; \bar{u}_{O_2} = ?$

At constant temperature

$$\bar{u} \propto \frac{1}{\sqrt{M}} \Rightarrow \frac{\bar{u}_{O_2}}{\bar{u}_{H_2}} = \sqrt{\frac{M_{H_2}}{M_{O_2}}} \Rightarrow \bar{u}_{O_2} = C \times \sqrt{\frac{2}{32}} = \frac{C}{4}$$

Correct option is (d)

Problem-15. The RMS speed of He(g) at 0°C is 1300 m·s⁻¹. The most probable speed of the gas will be

- (a) 1300 m·s⁻¹ (b) 866.6 m·s⁻¹ (c) 1592.2 m·s⁻¹ (d) 1061.4 m·s⁻¹

Soln. $(u_{rms})_{He} = 1300 \text{ m s}^{-1}$ $(u_{mp})_{He} = ?$ $\because u_{rms} = \sqrt{\frac{3RT}{M}}$

$$\frac{1300}{\sqrt{3}} = \sqrt{\frac{RT}{M}} \quad \dots (i)$$

$$\Rightarrow u_{mp} = \sqrt{\frac{2RT}{M}}$$

From equation (i), $u_{mp} = \frac{\sqrt{2} \times 1300}{\sqrt{3}} = 1061.4 \text{ m s}^{-1}$

Correct option is (d)

Problem-16. The rate of diffusion of methane at a given temperature is twice that of a gas 'P'. The molecular weight of P is

- (a) 64 (b) 36 (c) 40 (d) 16

Soln. Rate of diffusion $\propto \frac{1}{\sqrt{\text{molar mass}}}$

$$\therefore \frac{R_p}{R_{CH_4}} = \sqrt{\frac{M_{CH_4}}{M_p}}$$

$$\Rightarrow \frac{1}{2} = \sqrt{\frac{16}{M_p}} \quad (\because R_{CH_4} = 2R_p)$$

$$\Rightarrow M_p = 64 \text{ g mol}^{-1}$$

Correct option is (d)

Problem-17. Approximately one hydrogen atom per cubic meter is present in interstellar space. Assuming that the H-atom has a diameter of 10⁻¹⁰m, the mean free path (m) approximately is

- (a) 10¹⁰ (b) 10¹⁹ (c) 10²⁴ (d) 10¹⁴.

Soln. Mean free path (m) = $\frac{1}{\sqrt{2}\pi\sigma^2 N^*}$

$\sigma \rightarrow$ collision diameter

$N^* \rightarrow$ Number of molecules per unit volume

$$\text{Mean free path } (m) = \frac{1}{\sqrt{2}\pi \times 10^{-20} \times 1} = 2.25 \times 10^{19} \text{ m}$$

Correct option is (b)

Problem-18. With increase in temperature, the viscosities of gases and liquids respectively :

- (a) Increase, decrease (b) Decrease, increase
(c) Increase, increase (d) Decrease, decrease

Soln. In case of gases, because of their continuous movement, there occurs an interchange of molecules between two layers, with the result that a fraction of momentum of one layer is passed over to the other layer. The net effect is to decrease the relative rate of movement of one layer with respect to the other. On increasing temperature momentum of molecule increases so viscosity of gas increase.

In liquid intermolecular forces are responsible for internal friction. On increase in temperature intermolecular forces decrease so viscosity decrease.

Correct option is (a)

Problem-19. Which has the maximum value of mean free path?

- (a) CO_2 (b) H_2 (c) O_2 (d) N_2

Soln. Mean free path (λ) = $\frac{1}{\sqrt{2}\pi\sigma^2 N^*}$

$\sigma \rightarrow$ collision diameter

Smaller the collision diameter, higher will be the mean free path.

Correct option is (b)

Problem-20. Calculate the temperature at which the average velocity of oxygen equals that of hydrogen at 20 K.

Soln. $\langle v \rangle = \sqrt{\frac{3RT}{M}} \Rightarrow \langle v \rangle \propto \sqrt{\frac{T}{M}}$; [M = mol. mass of gas]

$$\therefore \frac{\langle v \rangle_{\text{oxygen}}}{\langle v \rangle_{\text{hydrogen}}} = \sqrt{\frac{T_{O_2} \times M_{H_2}}{M_{O_2} \times T_{H_2}}} = \sqrt{\frac{T_{O_2} \times 2}{32 \times 20}}$$

Given that $T_{H_2} = 20K$, $M_{H_2} = 2$ and $M_{O_2} = 32$

$$1 = \sqrt{\frac{T_{O_2}}{320}} \quad \left[\because \langle v \rangle_{O_2} = \langle v \rangle_{H_2} \right]$$

$$[1]^2 = \left[\left(\frac{T_{O_2}}{320} \right)^{\frac{1}{2}} \right]^2 \Rightarrow 1 = \frac{T_{O_2}}{320} \Rightarrow T_{O_2} = 320K$$

Problem-21. Calculate the root mean square velocity of nitrogen at $27^\circ C$ and 70 cm pressure. Density of Hg = 13.6 g.

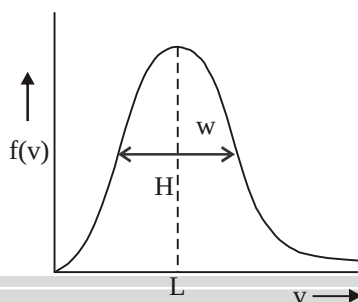
Soln. $\left. \begin{array}{ll} P_1 = 70 \text{ cm} & P_2 = 76 \text{ cm} \\ V_1 = ? & V_2 = .0224 \text{ cm}^3 \end{array} \right\} \text{ at STP}$
 $T_1 = 300 \text{ K} ; T_2 = 273 \text{ K}$

$$\therefore \frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2} \Rightarrow V_1 = \frac{P_2 V_2 T_1}{P_1 T_2} = \frac{76 \times .0224 \text{ m}^3 \times 300}{70 \times 273} \Rightarrow V_1 = 0.026725 \text{ m}^3$$

$$\text{Pressure in MKS unit (P)} = \frac{70}{76} \times 101325 \text{ Nm}^{-2}$$

$$v_{\text{rms}} = \sqrt{\frac{3PV}{M}} = \sqrt{\frac{3 \times (70/76) \times 101325 \times 0.026725 \text{ m}^3 \text{ mole}^{-2}}{28 \times 10^{-3} \text{ kg.mole}^{-1}}} = 517 \text{ ms}^{-1}$$

Problem-22. The maxwell Boltzmann distribution for molecular speeds is shown in the following figure. In the figure, H is the height of the Peak, L is the location at the maxima and W is the width at half height. As the temperature is decreased.



- (a) H increases, L decreases and W increases. (b) H increases, L decreases and W decreases.
(c) H decreases, L decreases and W increases (d) H decreases, L decreases and W decreases.

Soln. Correct answer is (b)

Problem-23. For the distribution of molecules velocities of gases, identify the correct order from following.

- (a) $v_{\text{rms}} > v_{\text{av}} > v_{\text{mp}}$ (b) $v_{\text{mp}} > v_{\text{rms}} > v_{\text{av}}$ (c) $v_{\text{av}} > v_{\text{rms}} > v_{\text{mp}}$ (d) $v_{\text{mp}} > v_{\text{av}} > v_{\text{rms}}$

Soln. Correct answer is (a)

Root mean square velocity from kinetic gas equation :

From kinetic gas equation,

$$PV = \frac{1}{3} mn\bar{v}^2 \quad \dots (1)$$

Where, p = Pressure of gas, v = volume of gas, m = mass of 1 gas molecule
n = number of moles of gas, $\bar{v}$ = Root mean square velocity.

$$PV = \frac{1}{3} M\bar{v}^2; \quad (m.n = M \text{ total mass of gas/mol. mass})$$

$$3PV = M\bar{v}^2; \Rightarrow \bar{v}^2 = \frac{3PV}{M}$$

$$\boxed{V_{\text{rms}} = \sqrt{\frac{3PV}{M}}} \quad \text{or} \quad \boxed{V_{\text{rms}} = \sqrt{\frac{3RT}{M}}} \quad [\because PV = RT]$$

Problem-24. Estimate C_v (molar heat capacity at constant volume) for

- (i) HCl (ii) He (iii) CO_2 (iv) NH_3 (v) CH_4

Soln. (i) HCl - linear diatomic molecule.