



Kinetic Theory of Gases & Radiation

POSTULATED OR ASSUMPTIONS OF KINETIC THEORY OF GASES : (NOT FOR EXAM)

- 1) Gas consists of large number of small particles called as molecules.
- 2) All molecules of same gas are identical in all respects.
- 3) Molecules of a gas neither attract nor repel each other. Hence their entire energy is kinetic.
- 4) Molecules move with all possible velocities in all possible directions.
- 5) Due to random motion, molecules constantly collide with one another as well as with wall of container. Such a collision is perfectly elastic.
- 6) Between two successive collisions, molecule travels in straight line path called as free path. Average distance covered by molecule between any two successive collision is called as mean free path and it is denoted by λ .
- 7) At constant temperature, average kinetic energy of gas molecule remains constant.
- 8) The actual volume of all molecules together is negligibly small as compared to the total volume of container.
- 9) Force of attraction between molecule of gas is negligible as they are separated by a large distance.
- 10) Gas molecules are rigid and perfectly elastic spheres.
- 11) The time spent in collision is negligible (10^{-8} sec) as compared to the time interval between two successive collision. Gas which obeys all above postulates is called ideal gas or perfect gas.

PERFECT GAS EQUATION :

In practice, the gases do not obey the gas laws at all values of pressure and temperature. It is because of the intermolecular forces between the gas molecules.

A perfect gas is one, whose molecules are free from intermolecular attraction and obeys the gas laws at all values of temperature and pressure.

Perfect Gas equation : Consider one mole of a perfect gas. Let P_1 , V_1 and T_1 be its initial pressure, volume and temperature respectively and P_2 , V_2 and T_2 be their final values. The change of the state of gas from the state (P_1, V_1, T_1) to (P_2, V_2, T_2) may be supposed to be taking place in the following two steps :

Step I : Suppose that the temperature of the gas remains constant at T_1 and the pressure is changed from P_1 to P_2 so that volume of the gas changes from V_1 to say V' . Since the temperature of the gas remains constant, from Boyle's law, we have

$$P_1 V_1 = P_2 V'$$

Setp II : Now, the pressure, volume and the temperature of the gas are P_2 , V' and T_1 respectively. Suppose that the pressure of the gas is kept constant at P_2 and temperature of the gas is changed from T_1 to T_2 , so that volume changes from V' to V_2 . Since the pressure of the gas remains constant, from Charles' law, we have

$$\frac{V'}{T_1} = \frac{V_2}{T_2} \quad \text{or} \quad V' = V_2 \times \frac{T_1}{T_2}$$

Substituting for V' in the equation, we have

$$P_1 V_1 = P_2 \times \left[V_2 \times \frac{T_1}{T_2} \right] \quad \text{OR} \quad \frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2} \quad \text{OR} \quad \frac{P V}{T} = \text{constant}$$

In the above equation, for one mole of the gas, the constant is denoted by R and is called **universal gas constant**. Therefore, the equation becomes

$$P V = R T$$

The equation is called **perfect gas equation** for one mole of a gas. It may be pointed out that in the equation, V is volume of 1 mole of the gas.

For n mole of gas $P V = n R T$



Ex.1. 16 g of oxygen occupy 0.025 m³ at 27°C. If the universal gas constant is 8.4 J/mole K. Find the pressure exerted by it (molecular weight of oxygen = 32)

Sol. $PV = nRT$

$$P \times 0.025 = \frac{16}{32} \times 8.4 \times 300$$

$$\therefore P = 50.40 \times 10^3 \text{ N/m}^2$$

4) Concept of an ideal Gas :-

Definition : “The gas satisfying all the assumptions of kinetic theory of gases at all temperature and pressure is known as ideal gas.” **OR**

“A gas is said to be ideal if it obeys the gas law at all temperatures and pressure.”.

- In ideal gas intermolecular forces are absent.
- At high temperature and low pressure Real gas behave as an Ideal gas.
- All real gases are not perfect as they do not obey gas laws perfectly. However at extremely low pressure and high temperature, some real gases like hydrogen, oxygen, nitrogen, helium etc. obey the gas law to a fair degree of accuracy and hence behaves as nearly perfect gas.
- At low temperature and high pressure behaviour of real gas is different from the ideal gas due to deviation.

CHARACTERISTIC OF IDEAL GAS -

- 1) Size of gas molecules is negligibly small.
- 2) They neither attract nor repel each other.
- 3) Ideal gas obeys all gas law (i.e. Boyle’s law, Charle’s law and Gay-Iussac’s law) at all temperature and pressure and ideal gas equation for one mole

$PV = RT$ where, R = universal gas constant.

- 4) Total energy of an ideal gas molecule is totally kinetic.
- 5) In nature Ideal gas does not exist.

In practice gases do not obey gas laws of all temperature and pressure. Therefore they are known as real gases.

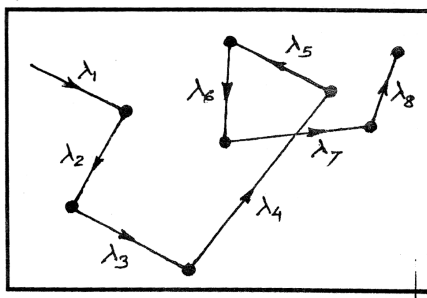
No. of Moles :

$$n = \frac{\text{mass of gas}}{\text{molar mass of gas}} = \frac{M}{M_0}$$

$$n = \frac{\text{No. of molecules}}{\text{Avogadro number}} = \frac{N}{N_A}$$

MEAN FREE PATH (Not For Exam)

1. According to the kinetic theory of gases, gas molecules are always in random motion.
2. During random motion molecules collide with each other and with walls of the container. These collisions are perfectly elastic.
3. Between two successive collisions molecules move along straight line with constant velocity and after each collision, molecules change the direction of the velocity. Hence path of single molecule becomes zigzag as shown in the figure.



4. This motion of molecules was first observed by scientist ROBERT BROWN. Hence it is called as Brownian motion.
5. The distance covered by the molecule between two successive collision is called as “free path” (λ)
6. Average distance covered by the molecule between any two consecutive collision is called as “Mean Free path”.
7. If S is the total distance covered by the molecule and ‘N’ be the number of collisions during this distance then mean free path is given as

$$\lambda = S / N \qquad \lambda = \frac{\lambda_1 + \lambda_2 + \lambda_3 + \dots + \lambda_N}{N}$$

Maxwell on the basis of law of distribution of velocities calculated mean free path as

$$\therefore \lambda = \frac{1}{\sqrt{2} \pi d^2 n_v} \quad \dots\dots\dots(1)$$

where, d -----> molecular diameter

n_v -----> number of molecules per unit volume i.e. (molecular density)

From equation (1) we can say that,

- i) the mean free path is inversely proportional to the square of the molecular diameter (d)
- ii) It is inversely proportional to the number of molecules per unit volume (n_v)

$$n_v = \frac{N}{V}; \quad n_v = \frac{mN}{mV}; \quad n_v = \frac{M}{Vm}; \quad \rho = \frac{M}{V}; \quad n_v = \rho/m \quad (\text{From 1})$$

From equation (2) we can say that

$$\text{But } n_v = \rho/m$$

where, ρ -----> density of gas

m -----> Mass of single gas molecule

$$\therefore \lambda = \frac{m}{\sqrt{2} \pi d^2 \rho} \quad \dots\dots\dots(2)$$

- i) The mean free path is inversely proportional to the density of gas (ρ)

$$n_v = \frac{N}{V} = \frac{P N}{P V} = \frac{P N}{R T}; \quad n_v = \frac{P}{K T} \quad (\text{From 1})$$

$$\text{But, } n_v = P / K T$$

Where, K is the Boltzmann's constant ($K = 1.38 \times 10^{-23} \text{ J/K}$)

P is the Pressure and T is the Absolute temperature

$$\therefore \lambda = \frac{K T}{\sqrt{2} \pi d^2 P} \quad \dots\dots\dots(3)$$

From equation (3) we can say that

- i) Mean free path is directly proportional to the absolute temperature of gas (T).
- ii) It is inversely proportional to pressure of the gas (P).

SI unit of mean free path is metre (m) and dimensions are $[M^0 L^1 T^0]$

Suppose a gas consists of ‘N’ number of molecules moving with velocities C_1, C_2, C_3 respectively. Then

Mean Velocity (v) = The average value of the velocities of all the molecules is called as mean velocity of the molecules of the gas.

$$\text{i.e. } v_{ms} = \frac{v_1 + v_2 + \dots + v_N}{N}$$

SI unit = metre/sec.



Mean square velocity ($\overline{v^2}$) = The average (mean) value of square of velocities is called as mean square velocity of the molecules of the gas.

$$\overline{v^2} = \frac{v_1^2 + v_2^2 + \dots + v_N^2}{N}$$

Root mean square velocity (RMS) (v) : The square root of the mean square velocities of the gas molecules is called as root mean square velocity.

$$\text{ie. } v_{\text{rms}} = \sqrt{\overline{v^2}}$$

$$\therefore v_{\text{rms}} = \sqrt{\frac{v_1^2 + v_2^2 + \dots + v_N^2}{N}}$$

SI Unit \Rightarrow metre / sec

Q. Derive an expression for pressure of gas on basis of kinetic theory of gases (4 marks)

Ans : Consider a gas in cubical vessel of each side of length ' l ' then

Surface area of cube (A) = l^2

Volume of Cube (V) = l^3

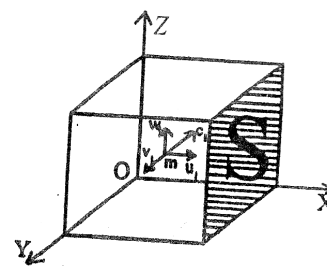
Let ' N ' be total number of gas molecules in a container.

Let ' m ' be mass of each molecule, then

Mass of enclosed gas (M) = mN

$$\text{Density of gas } (\rho) = \frac{M}{V}$$

$$(\rho) = \frac{mN}{l^3}$$



As gas molecules collide frequently, with wall of container, they transfer momentum to the wall during each collision which results into pressure of gas on the walls of container.

Let $v_1, v_2, v_3, \dots, v_N$ be the velocity of ' N ' molecules. Consider any one molecule (say) moving with velocity v_1 . We can resolve this velocity in 3 components parallel to edges of cube. Let these components be v_{x1}, v_{y1}, v_{z1} then we can write,

$$v_1^2 = v_{x1}^2 + v_{y1}^2 + v_{z1}^2$$

Consider a molecule with velocity component u_1 moving in direction OX.

Momentum of molecule having velocity u_1 before collision = mv_{x1}

As collisions perfectly elastic, velocity after collision will be $-v_{x1}$. Hence,

Momentum of molecule after collision = $-mv_{x1}$.

Change in momentum of molecule in one collision = $-2mv_{x1}$.

Negative sign indicates that molecule has lost momentum due to collision. Hence,

Momentum gained by surface in one collision = $+2mv_{x1}$.

Next collision on same wall will take place after travelling a distance of $2l$ (To and fro along length of Cube l) Hence,

$$\text{Time interval between two successive collision } (\Delta t) = \frac{2l}{v_{x1}}$$

$$\text{Hence, number of collision in one second i.e. frequency of collision} = \frac{v_{x1}}{2l}$$

$$\text{Change in momentum per second of Surface 'S' due to one molecule} = 2m \frac{v_{x1}}{2l}$$

$$\text{Change in momentum per second of surface 'S' due to one molecule} = \frac{mv_{x1}^2}{l}$$



There are N molecules. Hence, total change in momentum of surface 'S' due to N molecules is given by

$$\text{Total change in momentum of surface 'S' per second i.e. Rate of change of momentum of surface 'S' } = \frac{mv_{x1}^2}{l} + \frac{mv_{x2}^2}{l} + \frac{mv_{x3}^2}{l} + \dots + \frac{mv_{xN}^2}{l}$$

According to Newton's Second Law of motion, Change in momentum per second on the wall is equal to force exerted by gas molecule on the wall. Hence,

$$F_x = \frac{m}{l} [v_{x1}^2 + v_{x2}^2 + v_{x3}^2 + \dots + v_{xN}^2] \quad \text{Pressure (P)} = \frac{\text{Force}}{\text{Area}}$$

Hence, pressure (P_x) acting on surface 'S' perpendicular to X-axis is given by $P_x = \frac{F_x}{A}$

$$P_x = \frac{m}{Al} [v_{x1}^2 + v_{x2}^2 + v_{x3}^2 + \dots + v_{xN}^2] \quad Al = V \text{ (volume of cube)}$$

$$\therefore P_x = \frac{m}{\text{Volume}(V)} [v_{x1}^2 + v_{x2}^2 + v_{x3}^2 + \dots + v_{xN}^2]$$

Similarly, pressure ' P_y ' acting on surface perpendicular to y-axis is given by

$$\therefore P_y = \frac{m}{\text{Volume}(V)} [v_{y1}^2 + v_{y2}^2 + v_{y3}^2 + \dots + v_{yN}^2]$$

and pressure P_z acting on surface perpendicular to z-axis is given by

$$\therefore P_z = \frac{m}{\text{Volume}(V)} [v_{z1}^2 + v_{z2}^2 + v_{z3}^2 + \dots + v_{zN}^2]$$

As pressure exerted by gas molecules is same in all directions, average pressure (P) is given by,

$$P = \frac{P_x + P_y + P_z}{3} \text{ putting values,}$$

$$\therefore P = \frac{\frac{m}{V} [v_{x1}^2 + v_{x2}^2 + v_{x3}^2 + \dots + v_{xN}^2] + \frac{m}{V} [v_{y1}^2 + v_{y2}^2 + v_{y3}^2 + \dots + v_{yN}^2] + \frac{m}{V} [v_{z1}^2 + v_{z2}^2 + v_{z3}^2 + \dots + v_{zN}^2]}{3}$$

$$\therefore P = \frac{m}{3V} (v_1^2 + v_2^2 + v_3^2 + \dots + v_N^2)$$

$$\text{Multiplying and Division by N} \quad P = \frac{mN}{3V} \left(\frac{v_1^2 + v_2^2 + v_3^2 + \dots + v_N^2}{N} \right)$$

$$\text{But } \left(\frac{v_1^2 + v_2^2 + v_3^2 + \dots + v_N^2}{N} \right) = \overline{v^2} \dots \dots \dots \text{ (mean square velocity)}$$

$$\therefore P = \frac{mN \overline{v^2}}{3V}$$

$$\therefore v_{\text{rms}} = \sqrt{\overline{v^2}} \quad \text{(C-Root Mean Square Velocity (RMS velocity))}$$

$$\therefore P = \frac{mN v^2}{3V}$$

This is an expression for pressure exerted by gas molecules on the wall of container.

$mN = M$ (Mass of enclosed gas)



$$\frac{M}{V} = \rho \text{ (Density of gas)}$$

$$\therefore P = \frac{1}{3} \left(\frac{M}{V} \right) v^2 \quad \therefore P = \frac{1}{3} \rho v^2$$

This is an expression for pressure exerted by gas molecules in terms of density on the basis of kinetic theory of gases.

$$\frac{3P}{\rho} = v_{rms}^2 \quad \sqrt{\frac{3P}{\rho}} = v_{rms}$$

Ex. 2. Find the number of molecular in 1 cm³ of oxygen at N.T.P. if mass of a oxygen molecular is 5.28×10^{-28} kg and RMS velocity of oxygen molecular at N.T.P. is 426 m/s (Take pressure at N.T.P = 10^5 N/m²)

Sol.

$$V = 1 \text{ cm}^3 = 10^{-6} \text{ m}^3$$

$$m = 5.28 \times 10^{-28} \text{ kg}$$

$$C_{rms} = 426 \text{ m/s}$$

$$P = 10^5 \text{ N/m}^2$$

To find : No. of molecules (N)

$$\begin{aligned} P &= \frac{1}{3} \frac{m N c^2}{V} & P &= \frac{1}{3} \frac{N m_0}{V} C_{rms}^2 & N &= \frac{3PV}{m_0 C_{rms}^2} \\ &= \frac{3 \times 10^5 \times 10^{-6}}{(5.28 \times 10^{-28}) (426)^2} & &= \frac{3 \times 10^{-1}}{958193.28 \times 10^{-28}} \\ &= 0.00000313 \times 10^{27} & \therefore N &= 3.13 \times 10^{21} \end{aligned}$$

Ex. 3. Determine the pressure of oxygen at 0°C, if the density of oxygen at NTP = 1.44 Kg/m³ and RMS speed of the molecules at NTP = 456.4 m/s

Sol. Given : $\rho = 1.44 \times \text{kg/m}^3$ $C = 456.4 \text{ m/s}$

To find : P $C = \sqrt{\frac{3P}{\rho}}$ Squaring

$$C^2 = 3P/\rho \quad \therefore P = \frac{\rho C^2}{3}$$

$$\begin{aligned} &= \frac{1.44 \times (456.4)^2}{3} & &= \frac{1.44 \times 208300}{3} \\ &= \frac{299953.3}{3} & &= 99984.46 \text{ N/m}^2 \\ P &\cong 10^5 \text{ N/m}^2 \end{aligned}$$