

## KINETIC THEORY OF GAS

### Evidences In favour of Molecular Motion

- Diffusion and solution
- Expansion of gases
- Phenomena of evaporation and vapour pressure.
- Brownian movement.

### Assumptions of kinetic Theory

- A gas consists of a large number of identical molecules which are like minute hard elastic spheres constantly moving about in all possible directions with different velocities in a random fashion.
- During the motion, the molecules collide with one another and also with the walls of the container, the collisions being perfectly elastic; in other words, there is no loss of kinetic energy during the collisions. As the chance of collision in all directions is the same, the collisions do not affect the molecular density.
- The molecules exert no forces (attraction or repulsion) on each other except when they actually collide; that is, between two successive collisions they move in straight lines with uniform velocity.
- The collisions are essentially instantaneous that is, the duration of a collision is insignificant compared to the time between collisions.
- Since the molecules are like geometrical mass-point, the actual volume occupied by them is negligible compared to the total volume of the gas (that is, of the container).

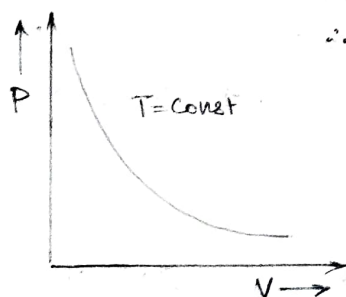
### GAS LAWS

#### (a) Boyle's Law:

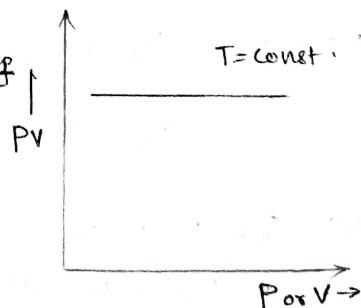
For a given mass of gas the volume of a gas at const. temperature is inversely proportional to its pressure.

$$\therefore V \propto \frac{1}{P} \quad \text{At const } T.$$

$$\therefore PV = \text{const} \quad \text{or} \quad P_i V_i = P_f V_f$$



P-V graph



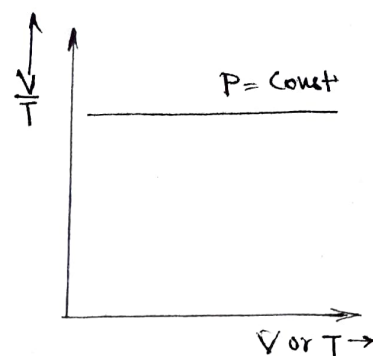
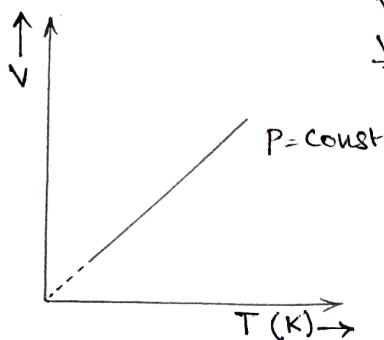
PV - P/V graph.

(b) Charles's Law:

For a given mass of a gas the volume of a gas at const pressure is directly proportional to its absolute temp.

$$V \propto T \quad \text{at Const } P.$$

$$\frac{V}{T} = \text{Const} \quad \text{or} \quad \frac{V_i}{T_i} = \frac{V_f}{T_f}.$$



V-T graph

$\frac{V}{T}$  - P/T graph.

Other form:

When a given mass of a gas is heated at const P then for each  $1^\circ\text{C}$  rise in temp. the volume of the gas increases by a fraction  $\alpha$  of its volume at  $0^\circ\text{C}$ . Thus, if the volume of a given mass of a gas at  $0^\circ\text{C}$  is  $V_0$ , then on heating at const. P to  $t^\circ\text{C}$  its volume will increase by  $V_0 \alpha t$ . Therefore, if its volume at  $t^\circ\text{C}$  be  $V_t$ , then

$$V_t = V_0 + V_0 \alpha t.$$

$$V_t = V_0 (1 + \alpha t)$$

Here  $\alpha$  is called "temp. coefficient of volume" of the gas.

For all gases the experimental value of  $\alpha$  is nearly  $\frac{1}{273} ^\circ\text{C}^{-1}$ .

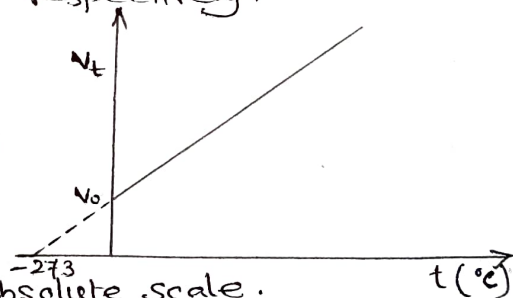
$$V_t = V_0 \left(1 + \frac{t}{273}\right)$$

Let at const P, the volume of a given mass of a gas at  $0^\circ\text{C}$ ,  $t_1^\circ\text{C}$  and  $t_2^\circ\text{C}$  be  $V_0$ ,  $V_1$  and  $V_2$ , respectively.

$$\therefore V_1 = V_0 \left(1 + \frac{t_1}{273}\right) = V_0 \left(\frac{273+t_1}{273}\right)$$

$$V_2 = V_0 \left(1 + \frac{t_2}{273}\right) = V_0 \left(\frac{273+t_2}{273}\right)$$

$$\therefore \frac{V_1}{V_2} = \frac{273+t_1}{273+t_2} = \frac{T_1}{T_2}$$



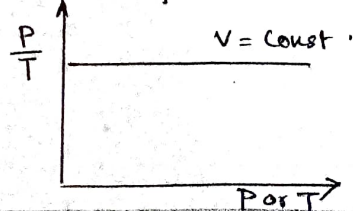
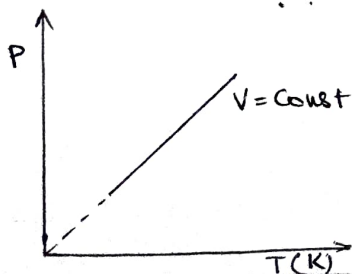
where  $T_1$  &  $T_2$  are temp. in absolute scale.

$$\therefore \frac{V_1}{V_2} = \frac{T_1}{T_2} \quad \text{or} \quad \frac{V_1}{T_1} = \frac{V_2}{T_2} = \text{Const} \quad \text{or} \quad \frac{V}{T} = \text{Const.} \quad \text{or} \quad V \propto T$$

(c) Gay Lussac's Law or Pressure Law

For a given mass of a gas the pressure of a gas at Const volume is directly proportional to its absolute temp.

$$\therefore P \propto T \quad \text{or} \quad \frac{P}{T} = \text{Const} \quad \text{or} \quad \frac{P_i}{T_i} = \frac{P_f}{T_f}.$$



### Other form

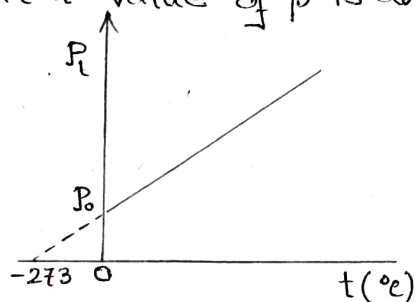
When a given mass of a gas is heated at const volume then for each  $1^\circ\text{C}$  rise in temperature, the pressure of the gas increases by a fraction  $\beta$  of its pressure at  $0^\circ\text{C}$ . Thus, if the pressure of a given mass of a gas at  $0^\circ\text{C}$  be  $P_0$ , then on heating at const volume to  $t^\circ\text{C}$ , its pressure will increase by  $P_0\beta t$ . Therefore, if its pressure at  $t^\circ\text{C}$  be  $P_t$ , then

$$P_t = P_0 + P_0\beta t$$

$$P_t = P_0(1 + \beta t)$$

Here  $\beta$  is called temperature coefficient of pressure of the gas. For all gases the experimental value of  $\beta$  is also  $\frac{1}{273}$  per  $^\circ\text{C}$ .

$$P_t = P_0\left(1 + \frac{t}{273}\right)$$



### (d) Avogadro's Law

At same temperature and pressure equal volume of all gases contain equal number of molecules.

### (e) Ideal Gas Equation

All the above laws can be written in one single equation known as ideal gas equation.

$$PV = nRT = \frac{m}{M}RT \quad \therefore \frac{m}{V} = \rho = \frac{PM}{RT} \quad \therefore \rho = \frac{PM}{RT}$$

Where.  $n = \text{No. of moles} = \frac{m}{M} = \frac{\text{total mass of the gas}}{\text{Molecular mass of the gas}}$

$R = \text{Universal Gas Const } (8.31 \text{ J mol}^{-1} \text{ K}^{-1} \text{ or } 2 \text{ cal mol}^{-1} \text{ K}^{-1})$   
 $0.082 \text{ lit-atm K}^{-1} \text{ mol}^{-1}$

### Derivation of Expression for Pressure due to an Ideal Gas

Consider a cubical vessel of each side  $l$ .

Volume of the vessel,  $V = l^3$  --- (1)

If  $m$  is the mass of each molecule

$N \rightarrow$  Total number of molecules in the gas.

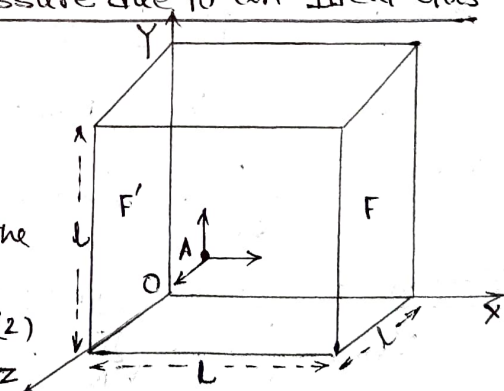
mass of the gas in the vessel  $= Nm$  --- (2)

Consider a molecule A of the gas moving with velocity  $\vec{v}$ .

$$\therefore v^2 = v_x^2 + v_y^2 + v_z^2 \quad \text{--- (3)}$$

Where  $\vec{v}_x, \vec{v}_y, \vec{v}_z$  are the component of velocity along three orthogonal direction.

Assume the molecule collides with face F of the cubical vessel elastically, therefore only  $x$ -component of its velocity ( $v_x$ )





is reversed, whereas the  $y$  and  $z$  components remain unaltered.

$\therefore$  Change in-momentum of A  $= -mv_x - (mv_x) = -2mv_x$

$\therefore$  Momentum imparted to the face F  $= 2mv_x$  (by conservation of momentum)

$\therefore$  time between two successive collision  $(\Delta t) = \frac{2l}{v_x}$

If  $F_x$  is the average force exerted by A along  $ox$  on face F in time  $\Delta t$ .

$\therefore F_x = \frac{2mv_x}{\Delta t} = \frac{2mv_x}{2l/v_x} = \frac{mv_x^2}{l}$

$\therefore$  Total force exerted along  $x$ -axis by all molecules on the face, i.e

$$F_x = \sum \frac{mv_x^2}{l} = \frac{m}{l} \sum v_x^2$$

$\therefore$  Pressure exerted along  $x$ -axis by all molecules on face F.

$$P_x = \frac{F_x}{\text{area}} = \frac{\frac{m}{l} \sum v_x^2}{l^2} = \frac{m}{l^3} \sum v_x^2 = \frac{m}{V} \sum v_x^2$$

Similarly, the pressure exerted by all the molecules along  $y$ -axis and  $z$ -axis are given by

$$P_y = \frac{m}{V} \sum v_y^2 ; \quad P_z = \frac{m}{V} \sum v_z^2$$

Since pressure exerted by the gas molecules is the same in all direction, we have

$$P_x = P_y = P_z = P \text{ (say)}$$

Obviously,  $P_x + P_y + P_z = 3P$ .

or  $P = \frac{P_x + P_y + P_z}{3} = \frac{m}{3V} \sum (v_x^2 + v_y^2 + v_z^2) = \frac{m}{3V} \sum v^2$

or  $P = \frac{Nm}{3V} \frac{\sum v^2}{N}$  or  $P = \frac{1}{3} \left( \frac{Nm}{V} \right) \bar{v}^2$

$\therefore$  or  $P = \frac{1}{3} \rho \bar{v}^2$  } where  $\rho = \frac{Nm}{V}$  density of gas.   
 ----- (1)

or  $PV = \frac{1}{3} Nm \bar{v}^2$

Where  $\frac{\sum v^2}{N} = \text{mean square speed of the molecules.}$

Root mean square (rms) speed :

$$v_{rms} = \sqrt{\bar{v}^2} = \sqrt{\frac{\sum v^2}{N}} = \sqrt{\frac{v_1^2 + v_2^2 + \dots + v_N^2}{N}} \text{ --- (5)}$$

Where,  $v_1, v_2, \dots, v_N$  are the velocities of the molecules

$\therefore$  from eqn (1)  $P = \frac{1}{3} \rho \bar{v}^2$  or  $\bar{v}^2 = \frac{3P}{\rho}$

or  $v_{rms} = \sqrt{\frac{3P}{\rho}}$

## Deduction from pressure expression.

### 1. R.M.S velocity

Since the pressure  $P$  is given by

$$P = \frac{1}{3} \rho v_{rms}^2$$

$$\therefore v_{rms}^2 = \sqrt{\frac{3P}{\rho}} \quad \text{--- (1)}$$

It is apparent that lighter the gas, faster would be its motion. Let us consider a gramme-molecule of the gas. Then  $\rho = M/V$  where  $M$  is the molecular weight and  $V$  the volume occupied by one gram-mole of the gas

$$\therefore P = \frac{1}{3} \frac{M}{V} v_{rms}^2$$

$$\text{or } PV = \frac{1}{3} M v_{rms}^2 \quad \text{--- (2)}$$

But for one gram-mole  $PV = RT$  so that we may write

$$\frac{1}{3} M v_{rms}^2 = RT$$

$$\text{or } v_{rms} = \sqrt{\frac{3RT}{M}} \quad \text{--- (3)}$$

for  $n$  gram-mole

$$v_{rms} = \sqrt{\frac{3nRT}{M}} \quad \text{--- (4)}$$

$$\therefore v_{rms} \propto \sqrt{T}$$

### 2. Average translation kinetic energy per molecule

$$\text{As we know } P = \frac{1}{3} \rho v_{rms}^2 = \frac{1}{3} \left( \frac{Nm}{V} \right) v_{rms}^2 \quad \text{--- (1)}$$

$$\text{But for } n \text{ mole of gas } PV = nRT \quad \text{--- (2)}$$

$$\therefore \frac{1}{3} Nm v_{rms}^2 = nRT$$

$$\frac{1}{2} m v_{rms}^2 = \frac{3}{2} \frac{nRT}{N} = \frac{3}{2} \left( \frac{R}{N_A} \right) T \quad \text{--- (3)}$$

as  $N_A = \text{Avogadro's number} = N/n$

$$\therefore \frac{1}{2} m v_{rms}^2 = \frac{3}{2} K_B T \quad \text{--- (4)}$$

where  $K_B = \frac{R}{N_A}$  Boltzmann Const. ( $1.38 \times 10^{-23} \text{ JK}^{-1}$ )

$\therefore$  Average translational Kinetic energy of a gas molecule

$$\bar{K} = \frac{1}{2} m v_{rms}^2 = \frac{3}{2} K_B T.$$

$\therefore$  Average translational Kinetic energy of a gas molecule depends only on its temperature and is independent of pressure, volume or nature of the gas.

$$\text{Again } P = \frac{1}{3} \rho v_{rms}^2 = \frac{2}{3} \times \frac{1}{2} \rho v_{rms}^2 = \frac{2}{3} \bar{K} \quad \text{--- (5)}$$

$\therefore$  The pressure of a gas is therefore equal to two-third of the mean kinetic energy of translation of the molecules per unit volume.

### 3. Boyle's Law

from pressure eqn

$$p = \frac{1}{3} \rho v_{rms}^2$$

If  $M$  be the mass of a gas that occupies a volume  $V$ ,  $\rho = \frac{M}{V}$ .

$$\therefore p = \frac{1}{3} \frac{M}{V} v_{rms}^2$$

$$\text{or } pV = \frac{1}{3} M v_{rms}^2$$

At const temperature  $T$ ,  $v_{rms}$  is constant.

$$\therefore pV = \text{Const.}$$

### 4. Gay-Lussac Law (and Charles' Law)

As we know  $pV \propto v_{rms}^2$  but  $v_{rms}^2 \propto T$ .

$$\therefore pV \propto T \quad \text{or} \quad \frac{V}{T} = \text{Const at Const } p.$$

$$\text{or } \frac{p}{T} = \text{Const at Const } V.$$

### 5. Dalton's law of partial pressure

Let,  $m_1, m_2, m_3, \dots$  be the molecular masses of different gases 1, 2, 3,  $\dots$  and  $n_1, n_2, n_3, \dots$  their respective number of molecules per unit volume. The total pressure will be due to all the different types of molecules, assuming no interaction and state of thermal equilibrium.

$$p = \frac{1}{3} m_1 n_1 v_{1rms}^2 + \frac{1}{3} m_2 n_2 v_{2rms}^2 + \frac{1}{3} m_3 n_3 v_{3rms}^2 + \dots$$

$$\text{But } \frac{1}{3} m_1 n_1 v_{1rms}^2 = p_1, \text{ partial pressure of gas 1.}$$

$$\bullet \quad \frac{1}{3} m_2 n_2 v_{2rms}^2 = p_2, \text{ partial pressure of gas 2, and so on}$$

$$\therefore p = p_1 + p_2 + p_3 + \dots = \sum p_i$$

$\therefore$  The pressure of a mixture of gases equals the sum of the partial pressure of its components. (only true for ideal gases).

### 6. Avogadro's Hypothesis:

Let us have two gases contained in separate enclosures, each of volume  $V$ . Let  $n_1, m_1, v_{1rms}$  be the number of molecules, molecular mass and rms velocity respectively of gas 1, let  $n_2, m_2, v_{2rms}$  be the corresponding quantities for gas 2.

$$\frac{1}{3} m_1 \frac{n_1}{V} v_{1rms}^2 = \frac{1}{3} m_2 \frac{n_2}{V} v_{2rms}^2$$

$$\text{or, } \frac{1}{3} m_1 n_1 v_{1rms}^2 = \frac{1}{3} m_2 n_2 v_{2rms}^2 \quad \dots (i)$$

When the temperature is the same, we have

$$\frac{1}{2} m_1 v_{1rms}^2 = \frac{1}{2} m_2 v_{2rms}^2 \quad \dots (ii)$$

on dividing eqn (i) & (ii)

$$n_1 = n_2$$

$\therefore$  Equal volumes of all gases under like conditions of temperature and pressure contain equal number of molecules.



## 7. Graham's Law of diffusion

Let two vessels of equal capacity contain two gases 1 and 2, at the same temperature and pressure. Each gas thus have the same number of molecules. Since the numbers of molecules are the same, the number  $n_1$  and  $n_2$  which diffuse (if allowed) will be in the ratio of their speed, which again will be in the same ratio as rms speeds.

$$\therefore \frac{n_1}{n_2} = \frac{v_{1rms}}{v_{2rms}} \quad \dots \dots \dots (i)$$

Since pressure are equal, we may write.

$$\frac{1}{3} \rho_1 v_{1rms}^2 = \frac{1}{3} \rho_2 v_{2rms}^2$$

$$\text{or } \frac{v_{1rms}}{v_{2rms}} = \sqrt{\frac{\rho_2}{\rho_1}} \quad \dots \dots \dots (ii)$$

$\therefore$  From eqn (i) & (ii)

$$\frac{n_1}{n_2} = \sqrt{\frac{\rho_2}{\rho_1}}$$

## 8. Clapeyron's Equation

From pressure expression

$$p = \frac{1}{3} m n v_{rms}^2 = \frac{1}{3} \frac{n}{N_A} m N_A v_{rms}^2$$

$$= \frac{1}{3} \frac{n}{N_A} M v_{rms}^2 = \frac{n}{N_A} pV \quad \left[ \because M = m N_A = \text{mol. weight} \right]$$

$$= \frac{n}{N_A} RT \quad \left[ pV = \frac{1}{3} M v_{rms}^2 \right]$$

$$p = n K_B T \quad \text{where } K_B = \text{Boltzmann Const} = \frac{R}{N_A}$$

## Average, Root mean square and Most Probable speed.

Average speed:  $\bar{v} = \frac{v_1 + v_2 + v_3 + \dots + v_n}{n}$

By using Maxwell speed distribution Law, it can be shown that

$$\bar{v} = \sqrt{\frac{8 K_B T}{\pi m}} = \sqrt{\frac{8 R T}{\pi M}} = \sqrt{\frac{8 P V}{\pi M}} \quad \left[ \because K_B = \frac{R}{N_A}, m N_A = M \right]$$

$M \rightarrow$  Molecular mass  
 $m \rightarrow$  Mass of single molecule.

## Root mean Square Speed:

$$v_{rms} = \sqrt{\frac{v_1^2 + v_2^2 + v_3^2 + \dots + v_n^2}{n}}$$

From Maxwell's speed distribution Law, it can be shown that

$$v_{rms} = \sqrt{\frac{3 K_B T}{m}} = \sqrt{\frac{3 R T}{M}} = \sqrt{\frac{3 P V}{M}}$$

$$\bullet \quad v_{rms} \propto \sqrt{T}$$

$$\bullet \quad v_{rms} \propto \frac{1}{\sqrt{M}} \text{ for const } T.$$

## Most Probable Speed.

The speed possessed by the maximum number of molecules in a gas sample at a given temperature.

From Maxwell speed distribution Law, it can be shown that

$$v_{mp} = \sqrt{\frac{2 K_B T}{m}} = \sqrt{\frac{2 R T}{M}} = \sqrt{\frac{2 P V}{M}}$$

$$\therefore \quad v_{rms} > \bar{v} > v_{mp}.$$