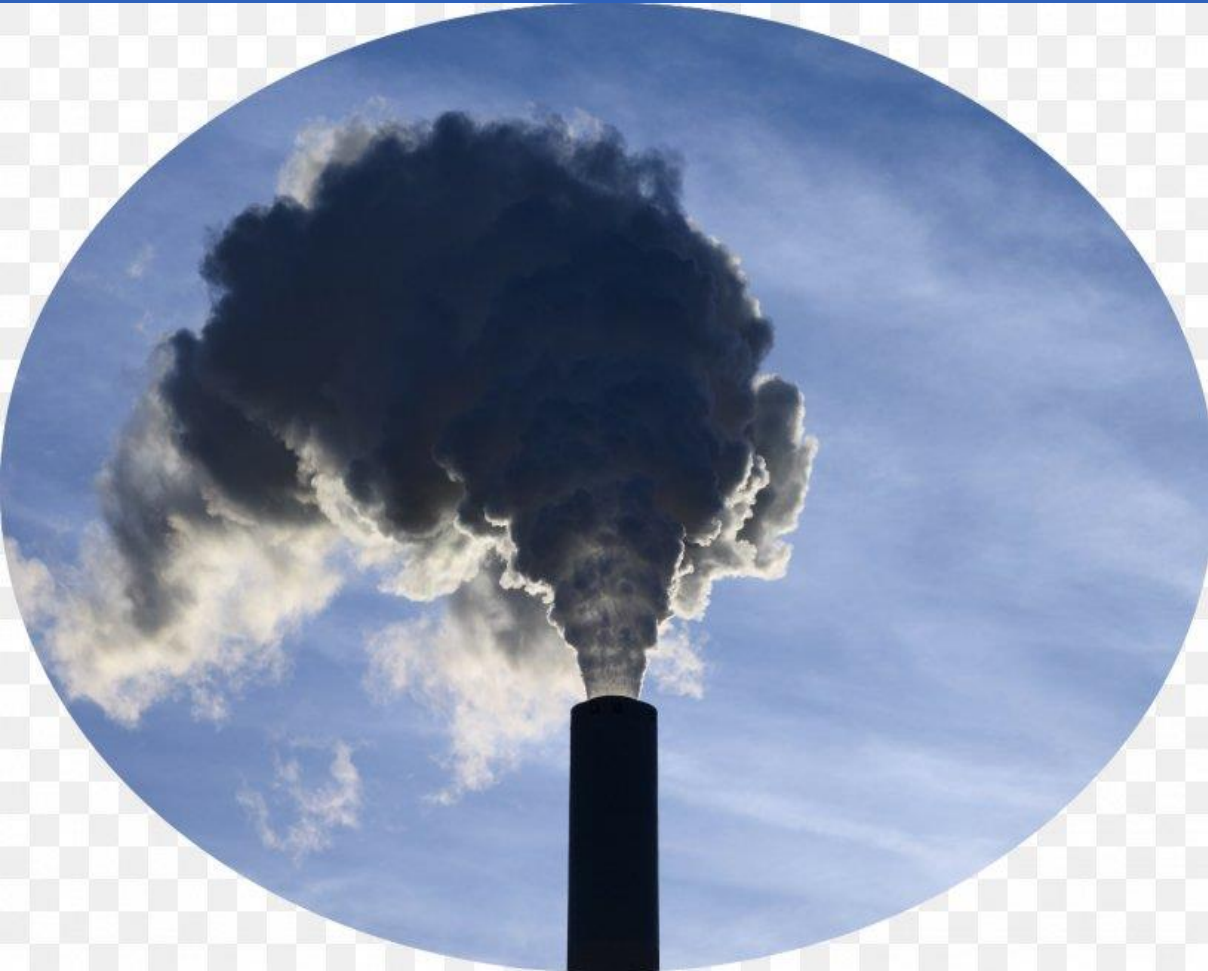
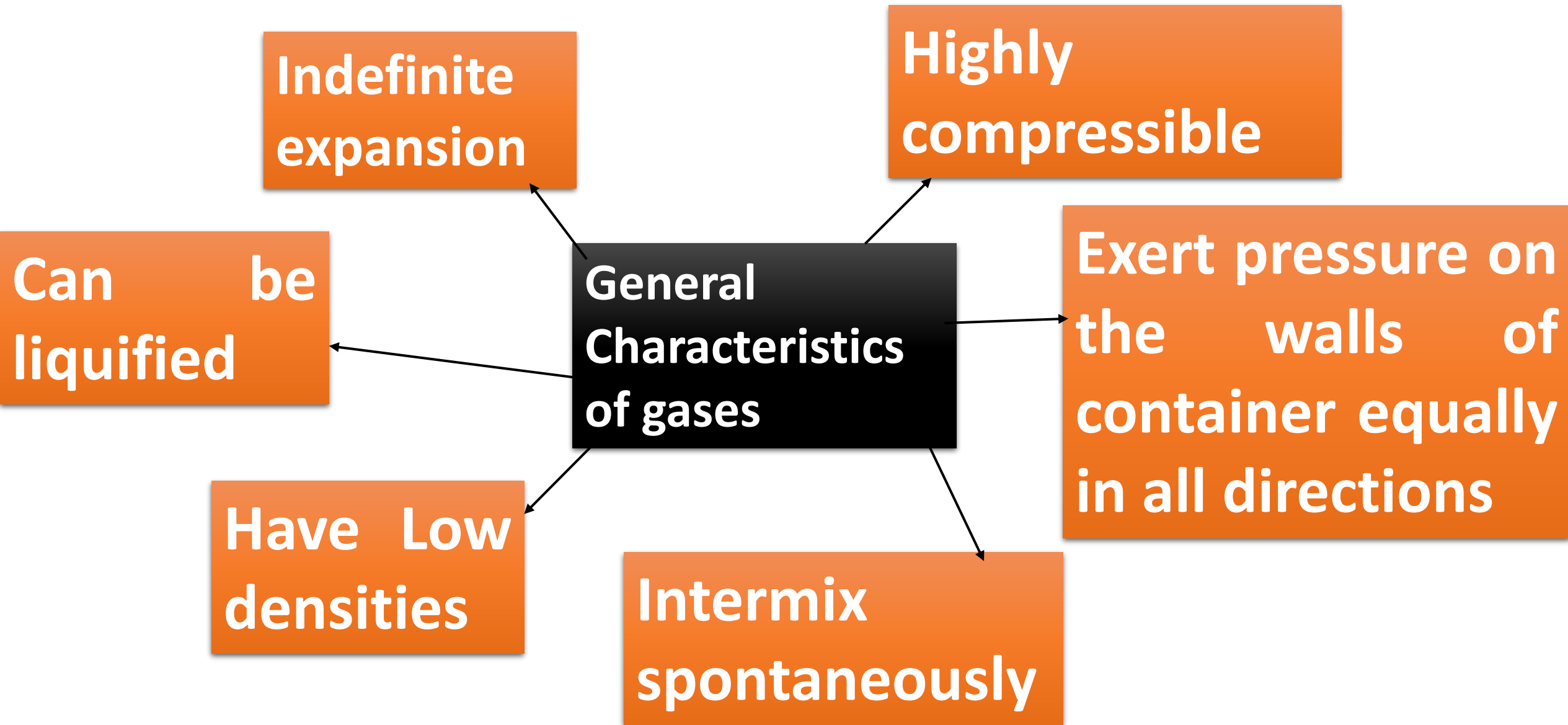


Gaseous State



Gaseous State



Gaseous State

❑ Behaviour of gases is described by variables P, V, T and mass

➤ These variables are inter connected by gas laws

❖ Boyles Law

➤ The volume of given mass of a gas is inversely proportional to its pressure at constant temperature

➤ $PV = \text{constant}$ (at constant temperature)

➤ $P_1V_1 = P_2V_2$

$$V \propto \frac{1}{P} \text{ at const } T$$

❖ Charles Law

➤ At constant pressure, the volume of a given mass of a gas increases or decreases by $1/273$ of its volume at 0°C for each one degree fall or rise of temperature

For 1°C rise in temperature

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

For $t^\circ\text{C}$ rise in temperature

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

Gaseous State

❖ Charles Law contd....

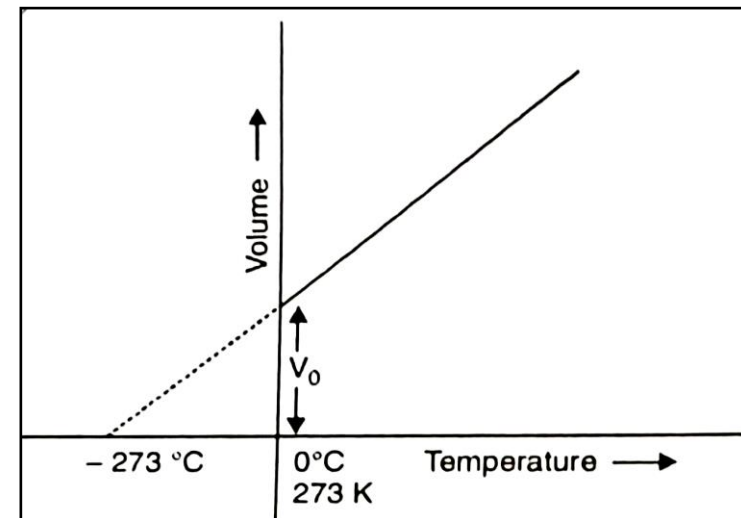
- The volume of the given mass of the gas is directly proportional to the absolute temperature at constant pressure

$$V_t = V_0 \left(1 + \frac{t}{273} \right) = V_0 \left(\frac{273+t}{273} \right) = V_0 \left(\frac{T}{T_0} \right) = V_0 \frac{T}{T_0}$$

$$\frac{V_t}{V_0} = \frac{T}{T_0} \quad \text{or} \quad \frac{V_t}{T} = \frac{V_0}{T_0} \quad \text{So } \frac{V}{T} = \text{constant (V \& T at const P)}$$

❖ Absolute zero temperature

- Absolute or Kelvin scale of temperature
- ✓ $-273^\circ\text{C} = 0 \text{ K}$
- ✓ $0^\circ\text{C} = 273 \text{ K}$
- ✓ $T(\text{K}) = t(^{\circ}\text{C}) + 273$



Gaseous State

□ Avogadro's Law

- Equal volume of all gases contain equal number of molecules under similar conditions of temperature and pressure irrespective of the nature of the gas
- $V \propto N$ at constant T & P
- $V \propto n$ as $n \propto N$

□ 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

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

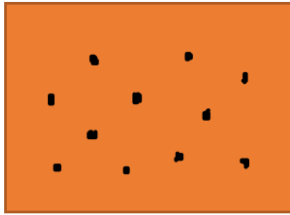
$$\frac{r_1}{r_2} = \sqrt{\frac{d_2}{d_1}}$$

$$\frac{r_1}{r_2} = \frac{P_1}{P_2} \sqrt{\frac{d_2}{d_1}} = \frac{P_1}{P_2} \sqrt{\frac{M_2}{M_1}}$$

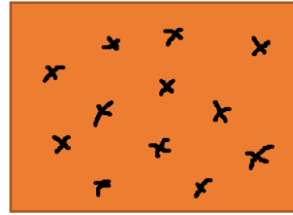
Gaseous State

□ Dalton's Law of Partial pressures

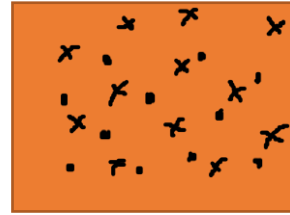
- At constant temperature, the total pressure exerted by a mixture of two or more non-reacting gases is equal to the sum of their partial pressures



p_1



p_2



$P = p_1 + p_2$

□ Ideal Gas Equation

- Obtained by combining Boyle's law, Charle's law, and Avogadro's law

- $V \propto \frac{nT}{P}$ or $PV \propto nT$ $PV = nRT$

Gaseous State

□ Nature of Gas Constant R

$$\text{➤ } R = \frac{PV}{nT} = \frac{\text{Pressure x Volume}}{\text{Moles x Temperature(K)}} = \frac{\frac{F}{A} \text{ x Volume}}{\text{Moles x Temperature(K)}} = \frac{\frac{F}{L^2} \text{ x } L^3}{\text{Mole x TK}}$$

$$\text{➤ } = \frac{F \text{ x } L}{\text{Mole x TK}} = \frac{\text{Work or Energy}}{\text{Mole x TK}}$$

❖ So R represents work done per degree per mole

□ Numerical value of R depends upon the units in which P and V are expressed

➤ 0.0821 L atm K⁻¹ mol⁻¹

➤ 8.314 JK⁻¹ mol⁻¹ = 8.314 Pa m³ K⁻¹

➤ 8.314 x 10⁷ ergs K⁻¹ mol⁻¹

➤ 1.99 calK⁻¹mol⁻¹

1 Atm = 760 mm of Hg = 76 cm of Hg = 101325 Pa = 101325 Nm⁻²

1 Atm = 760 mm of Hg = 76 cm of Hg = 1013961.6 dynes cm⁻²

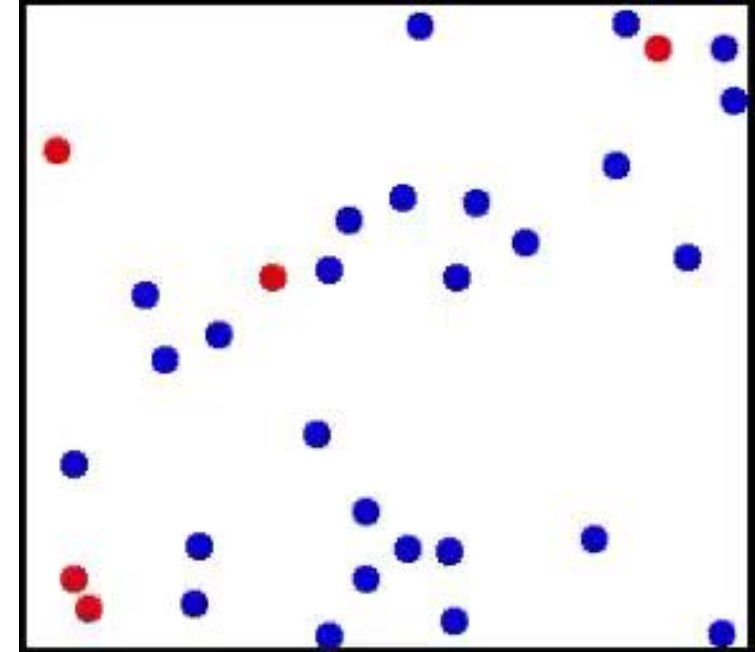
4.183 X 10⁷ ergs = 1 calorie

Kinetic Theory of Gases

- Given by Maxwell, Boltzmann and Clausius
- Also known as Dynamic particle model or Kinetic gas model

□ Postulates

1. Gases consist of tiny particles known as molecules
2. Volume actually occupied by gas molecules is very small as compared to the total volume occupied by gas molecules
3. Molecules are in constant rapid motion in all directions and during motion they collide with one another as well as with the walls of the container



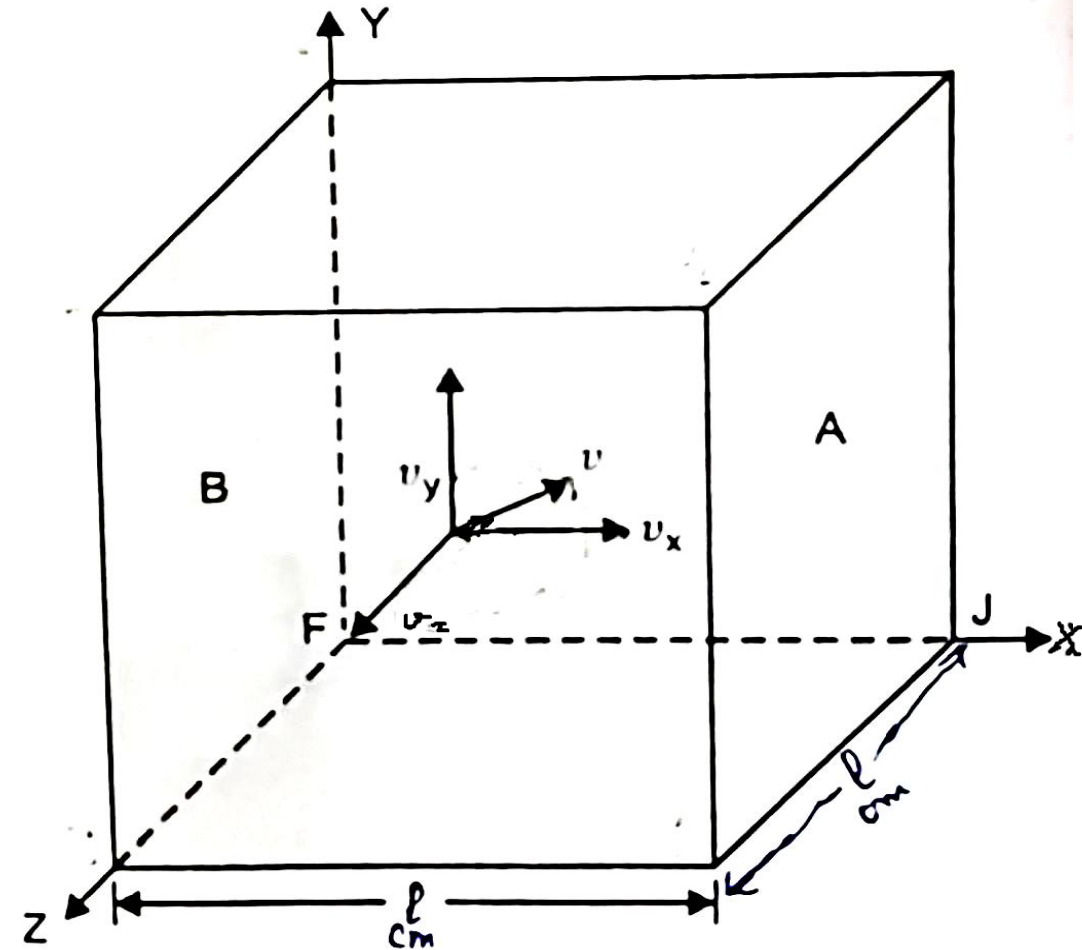
Kinetic Theory of Gases

□ Postulates contd.

- 4. Collisions are perfectly elastic**
- 5. Molecules move independently of one another(No attractive force)**
- 6. Pressure is due to collisions of molecules on the wall of the container per unit area per second**
- 7. KE of gas molecules is proportional to the absolute temperature**
- 8. Force of gravitation on the molecules is negligible**

Derivation of Kinetic gas equation

- Consider n molecules of a sample of gas contained in a cubical vessel of edge length l cm
- Let each molecule is moving with a speed of v cm/s
- $V^2 = v_x^2 + v_y^2 + v_z^2$
- Now let a molecule moves along the X axis with v_x speed and strike faces A and B of the vessel
- At face A, Momentum of the gas molecule before collision = mv_x



Derivation of Kinetic gas equation

- Momentum of molecule after collision = $-mv_x$
- Change in momentum of the molecule = $-mv_x - mv_x = -2mv_x$
- So momentum transferred to the face A = $2mv_x$
- To strike face A again the molecule has to cover a distance of $2l$ cm
- So time taken = $2l/v_x$
- Now number of such collisions on face A in one second = $v_x/2l$
- Change in momentum at face A in one second = Momentum transferred in one collision x No. of collisions in one second
- $2mv_x \times v_x/2l = mv_x^2/l$
- Similarly same amount of momentum will be transferred to the face B
- So total momentum transferred along X axis = $mv_x^2/l + mv_x^2/l = 2mv_x^2/l$

Derivation of Kinetic gas equation

➤ Same amount of momentum will be transferred along Y axis and along Z axis

➤ So total momentum transferred along all directions due to one molecule
$$= \frac{2mv_x^2}{1} + \frac{2mv_y^2}{1} + \frac{2mv_z^2}{1} = \frac{2m}{1} (v_x^2 + v_y^2 + v_z^2) = \frac{2mv^2}{1}$$

➤ And net momentum transferred along all directions due to n molecules
$$= \frac{2mv^2}{1} + \frac{2mv_1^2}{1} + \frac{2mv_2^2}{1} + \frac{2mv_3^2}{1} \dots \dots \dots \frac{2mv_n^2}{1}$$

$$= \frac{2m}{1} (v^2 + v_1^2 + v_2^2 + \dots v_n^2) = \frac{2m \times n}{1} \left(\frac{v^2 + v_1^2 + v_2^2 + \dots v_n^2}{n} \right)$$
$$= \frac{2mnu^2}{1}$$

$$u = \sqrt{\frac{v^2 + v_1^2 + v_2^2 + \dots v_n^2}{n}}$$

Derivation of Kinetic gas equation

Net momentum transferred due to all molecules on all faces is the force exerted according to Newton's second Law

$$F = \frac{2mnu^2}{l}$$

$$\text{So } P = \frac{\text{Force}}{\text{Area}} = \frac{2mnu^2}{l} \times \frac{1}{6l^2} = \frac{1}{3} \frac{mnu^2}{l^3} = \frac{1}{3} \frac{mnu^2}{V}$$

$$PV = \frac{1}{3} mnu^2$$

This is Kinetic gas equation

Average KE of gas molecules

❖ We can use the Kinetic gas equation to calculate KE of a gas molecule at temperature T

➤ $PV = \frac{1}{3} mnu^2 = \frac{2}{3} \cdot \frac{1}{2} mnu^2 = \frac{2}{3} \text{K.E}$ or $\text{KE} = \frac{3}{2} PV$ KE = 1/2 mnu²

➤ Now $PV = RT$ for One mole so $\text{KE} = \frac{3}{2} RT$

➤ For one molecule $\text{KE} = \frac{3RT}{2N} = \frac{3kT}{2}$ where k is Boltzmann constant

$$\frac{R}{N} = k$$

➤ Here we can show that $\text{KE} \propto T$

❖ Molecular motion is said to be thermal motion

➤ $\text{KE} = \frac{1}{2} mnu^2$ So $\text{KE} \propto u^2$ Also $\text{KE} \propto T$ Hence $u^2 \propto T$ or $u \propto \sqrt{T}$

➤ Further at absolute zero, u become zero and all type of molecular motion ceases

Derivation of gas laws from Kinetic gas equation

□ Boyle's Law

$$PV = \frac{1}{3} m n u^2 = \frac{2}{3} \cdot \frac{1}{2} m n u^2 = \frac{2}{3} \text{K.E}$$

➤ $KE \propto T$ so $KE = kT$ Hence $PV = \frac{2}{3} kT$ and at constant temperature $PV = \text{constant}$

□ Charle's Law

➤ As derived above $PV = \frac{2}{3} kT$ or $V = \frac{2kT}{3P}$ so at constant pressure $V \propto T$

□ Avogadro's Law

$$\begin{array}{l} P_1 V_1 = \frac{1}{3} m_1 n_1 u_1^2 \\ P_2 V_2 = \frac{1}{3} m_2 n_2 u_2^2 \end{array} \left. \begin{array}{l} \rightarrow \\ \rightarrow \end{array} \right\} \begin{array}{l} \frac{1}{3} m_1 n_1 u_1^2 = \frac{1}{3} m_2 n_2 u_2^2 \\ m_1 n_1 u_1^2 = m_2 n_2 u_2^2 \end{array} \left. \begin{array}{l} \rightarrow \\ \rightarrow \end{array} \right\} \begin{array}{l} \frac{1}{2} m_1 u_1^2 = \frac{1}{2} m_2 u_2^2 \\ m_1 u_1^2 = m_2 u_2^2 \end{array}$$

$$\text{So } n_1 = n_2$$

Derivation of gas laws from Kinetic gas equation

❑ Ideal gas equation

$$PV = \frac{1}{3} mnu^2 = \frac{2}{3} \cdot \frac{1}{2} mnu^2 = \frac{2}{3} \text{K.E}$$

➤ $KE \propto T$ so $KE = kT$ Hence $PV = \frac{2}{3} kT$ if $\frac{2}{3} k = R$ then $PV = nRT$

❑ Graham's Law of diffusion

$$PV = \frac{1}{3} mnu^2 = \frac{1}{3} Mu^2$$
$$u^2 = \frac{3PV}{M} = \frac{3P}{M/V} = \frac{3P}{d}$$

$$u = \sqrt{\frac{3P}{d}}$$

Now ^{rate} $r \propto u$ So $r \propto \sqrt{\frac{3P}{d}}$

and at constant P $r \propto \sqrt{\frac{1}{d}}$

Derivation of gas laws from Kinetic gas equation

□ Dalton's Law partial pressures

- As already derived $KE = \frac{3}{2} PV$
- If we have two gases at same temperature then
- For gas 1 $KE_1 = \frac{3}{2} p_1 V$
- For gas 2 $KE_2 = \frac{3}{2} p_2 V$
- If these two gases are put in together in the same vessel then total KE
- $KE = KE_1 + KE_2$
- $\frac{3}{2} PV = \frac{3}{2} p_1 V + \frac{3}{2} p_2 V$
- $\frac{3}{2} PV = \frac{3}{2} V (p_1 + p_2)$ Or $P = p_1 + p_2$

Maxwell's distribution of molecular speeds

- The molecules of a gas have wide range of velocities due to molecular collisions
- According to Maxwell the fraction of molecules having velocities in the range c to $c + dc$ remains constant at a constant temperature

$$\frac{dn_c}{n} = 4\pi \left[\frac{M}{2\pi RT} \right]^{3/2} e^{-Mc^2/2RT} c^2 \cdot dc$$

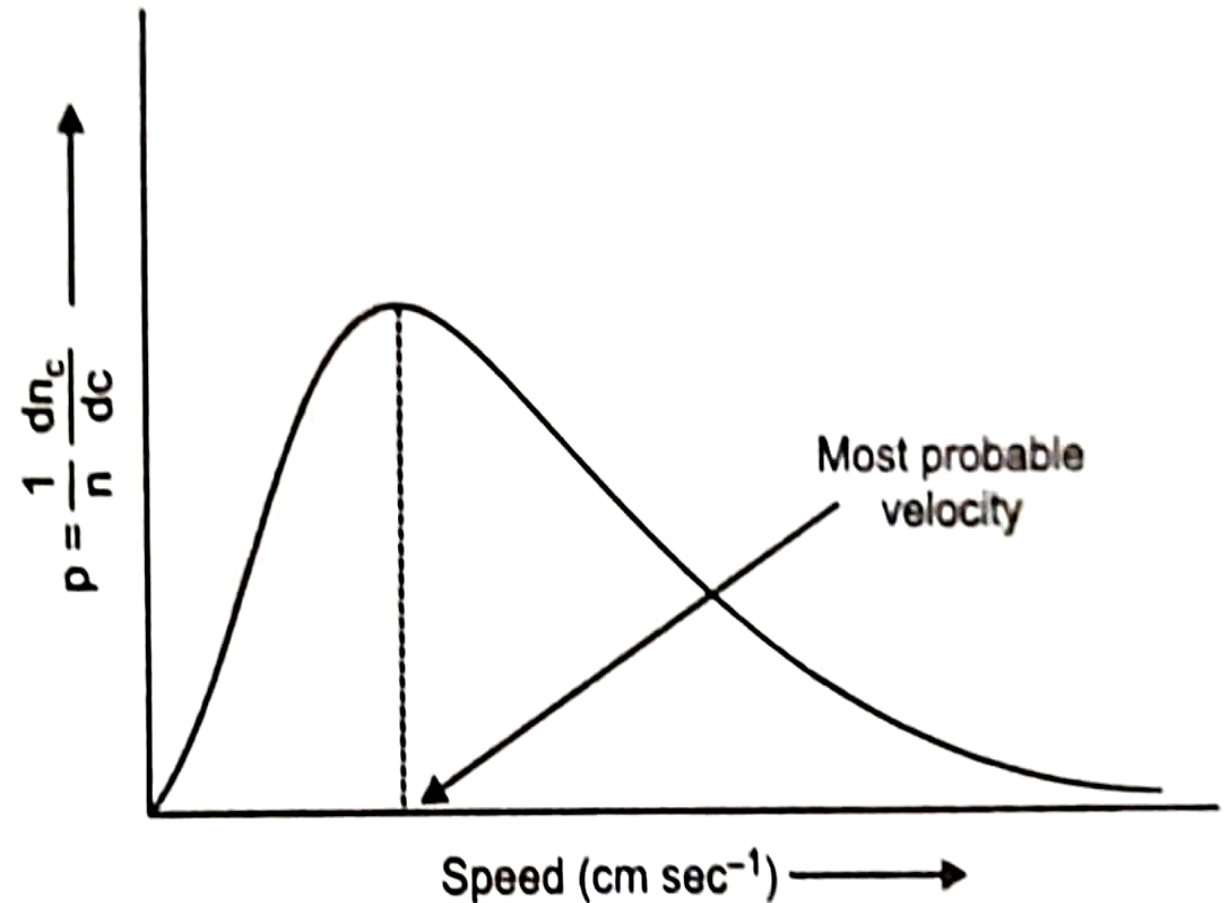
$$\frac{1}{n} \cdot \frac{dn_c}{dc} = 4\pi \left[\frac{M}{2\pi RT} \right]^{3/2} e^{-Mc^2/2RT} c^2$$

$P \rightarrow$ Probability of finding molecules with speed c

Maxwell's distribution of molecular speeds

□ Features of Maxwell distribution curves

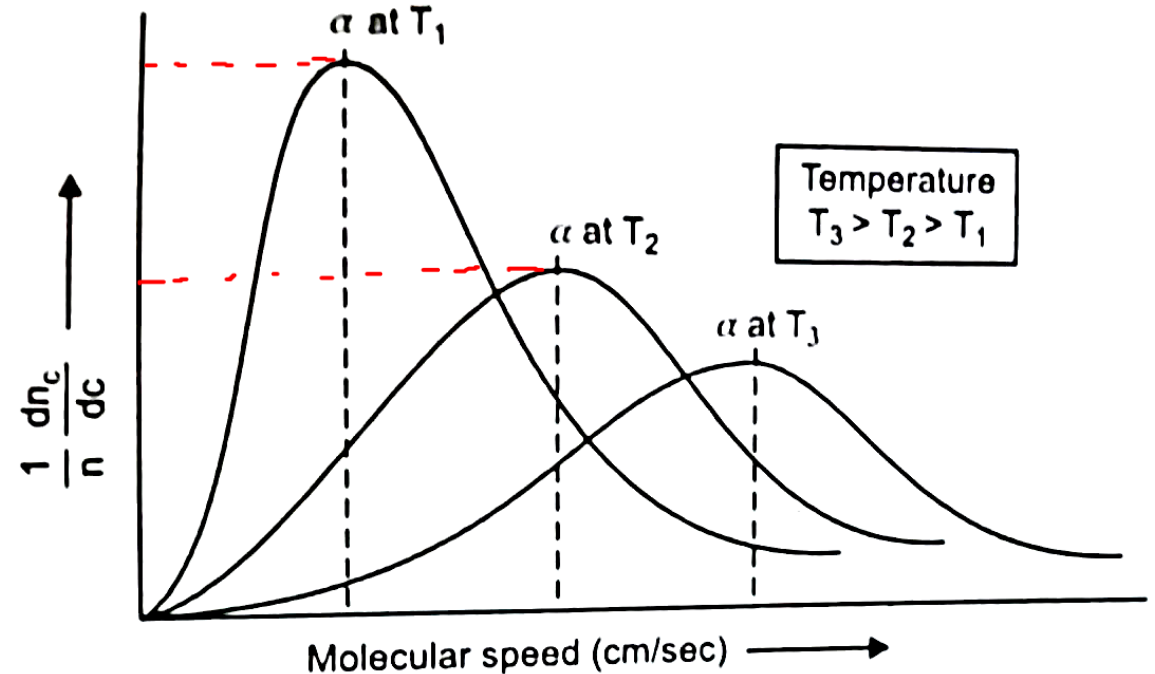
- Fraction of molecules with very low and very high speeds is low
- The fraction of molecules having higher and higher velocities goes on increasing till it reaches maximum and then starts decreasing
- The velocity possessed by maximum fraction of gas molecules is called as most probable speed
- Area under the curve gives total number of gas molecules



Maxwell's distribution of molecular speeds

Effect of temperature on distribution of speeds

- With increase in temperature, the curve flattens and the peak shifts forward and downward
- The most probable speed increases
- The fraction of molecules possessing most probable speed decreases
- The fraction of molecules having lower speeds decreases but having higher speeds increases
- The total number of molecules remains the same i.e. area under the curve remains unchanged



Maxwell's distribution of molecular Energies

Acc. to distribution law of velocities.

$$\frac{dN_c}{N} = 4\pi \left(\frac{M}{2\pi RT} \right)^{3/2} e^{-Mc^2/2RT} c^2 dc \quad \text{--- (i)}$$

This equation can be changed to represent distribution of energies as

$$E = \frac{1}{2} Mc^2 \quad \text{KE per mole} \quad \text{--- (ii)}$$

$$2E = Mc^2 \quad \text{--- (iii)}$$

Diff. eqn (iii)

$$2dE = 2Mc dc \quad \text{--- (iv)}$$

Take sq. roots of both sides of eqn (iii)

$$(2E)^{1/2} = (M)^{1/2} c \quad \text{--- (v)}$$

Multiply eqn (iv) & (v)

$$(2E)^{1/2} dE = M^{3/2} c^2 dc \quad \text{--- (vi)}$$

$$\text{or } c^2 dc = \frac{(2E)^{1/2} dE}{M^{3/2}}$$

Maxwell's distribution of molecular Energies

Now substitute

value of $m c^2$ from eqn (iii) & $c^2 dc$ from (vi) in eqn (i)

$$\frac{dN_c}{N} =$$

$$4\pi \left(\frac{m}{2\pi RT} \right)^{3/2} e^{-E/RT} \cdot \frac{(2E)^{1/2} dE}{m^{3/2}}$$

$$\left[2^{1/2} \cdot \frac{2^{1/2}}{2} = \frac{2}{2} = 1 \right]$$

=

$$\frac{2\pi}{(\pi RT)^{3/2}} e^{-E/RT} \cdot E^{1/2} dE \quad \text{--- (vii)}$$

P' =

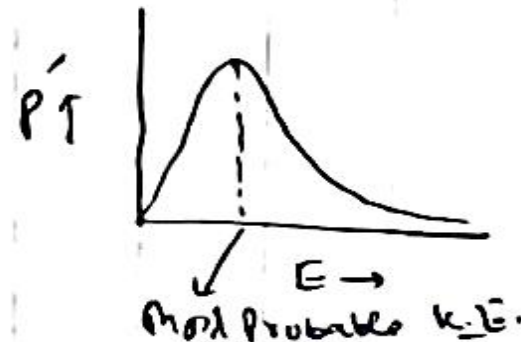
$$\frac{1}{N} \frac{dN_c}{dE}$$

$$= \frac{2\pi}{(\pi RT)^{3/2}} e^{-E/RT} E^{1/2} \quad \text{--- (viii)}$$

Above eqn. represents probability of molecules having energy E .

Now if we plot P' vs E we get similar distribution curves

for velocities.



Different types of molecular speeds

Most probable velocity (α)

- It is the speed possessed by maximum fraction of the gas molecules at a particular temperature

$$\alpha = \sqrt{\frac{2RT}{M}}$$

Average velocity or mean velocity (v or \bar{c})

- It is the average of different velocities possessed by all the molecules of a gas at a particular temperature

$$v = \frac{v_1 + v_2 + v_3 + \dots}{n}$$

$$v = \frac{n_1 v_1 + n_2 v_2 + n_3 v_3 + \dots}{n_1 + n_2 + n_3 + \dots}$$

$$v = \sqrt{\frac{8RT}{\pi M}}$$

Root mean square velocity (u or c_{rms} or $\langle c^2 \rangle^{1/2}$)

- It is the square root of the mean of the squares of different velocities possessed by various gas molecules at particular temperature

$$u = \sqrt{\frac{v_1^2 + v_2^2 + v_3^2 + \dots}{n}}$$

$$u = \sqrt{\frac{n_1 v_1^2 + n_2 v_2^2 + n_3 v_3^2 + \dots}{n_1 + n_2 + n_3 + \dots}}$$

$$u = \sqrt{\frac{3RT}{M}} \text{ or } \sqrt{\frac{3PV}{M}} \text{ or } \sqrt{\frac{3P}{\rho}}$$

Relation between different types of molecular velocities

$$\alpha = \sqrt{\frac{2RT}{M}}$$

$$v = \sqrt{\frac{8RT}{\pi M}}$$

$$u = \sqrt{\frac{3RT}{M}}$$

$$\frac{\alpha}{u} = \sqrt{\frac{2}{3}}$$

$$\alpha = \sqrt{\frac{2}{3}} u$$

$$\alpha = 0.816 u$$

$$v = \sqrt{\frac{8}{3\pi}} u$$

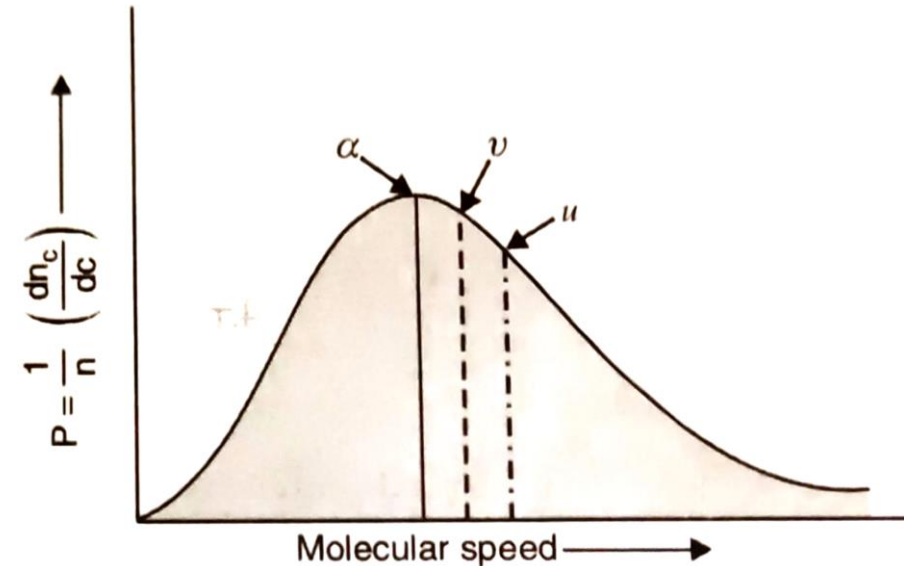
$$v = 0.921 u$$

$$\alpha : v : u = \sqrt{\frac{2RT}{M}} : \sqrt{\frac{8RT}{\pi M}} : \sqrt{\frac{3RT}{M}}$$

$$= \sqrt{2} : \sqrt{\frac{8}{\pi}} : \sqrt{3} = 1.414 : 1.595 : 1.732$$

$$= 1 : 1.128 : 1.224$$

$$\text{SO } u > v > \alpha$$



Numerical problems on molecular velocities

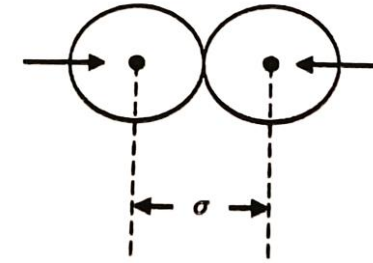
- 1) Calculate the root mean square velocity, average velocity, and most probable velocity of SO_2 gas at 427°C
- 2) At what temperature, the RMS velocity of SO_2 molecule will be equal to the RMS velocity of O_2 molecule at 27°C
- 3) At what temperature the rms velocity of methane becomes double of its value at N.T.P.?
- 4) Calculate the rms speed of argon gas at N.T.P.
- 5) Calculate the rms speed of nitrogen gas at 27°C and 700 mm pressure
- 6) Oxygen gas has a density of 1.429 g/L at N.T.P. Calculate the rms and average speeds of oxygen molecules.
- 7) Prove that rms velocity of hydrogen gas at any temperature is 4 times that of oxygen gas at that temperature.
- 8) At what temperature, the rms speed of CO_2 is same as that of Cl_2 at 293K?

[Redox Titration between \$\text{MnO}_4^-\$ and \$\text{Fe}^{2+}\$ - YouTube](#)

Collision Properties

❑ Collision diameter (σ)

- It is the distance between the centres of two molecules when they are at a closest distance of approach.



❑ Collision number (N_c)

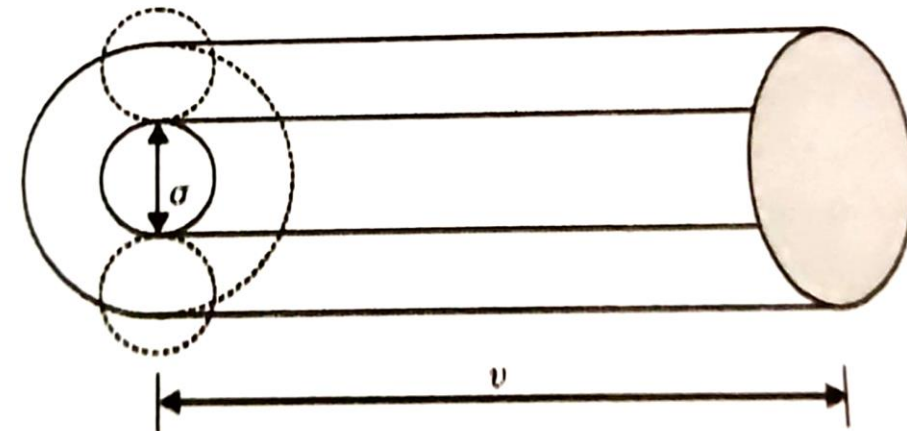
- It is the number of collisions which a molecule makes with the other molecules in one second

❑ Collision frequency (Z)

- It is the number of collisions taking place in 1 cc of a gas in one second

❑ Collision Cross section

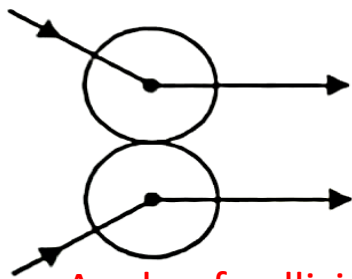
- It is an area of imaginary sphere of radius σ around the molecule into which the centres of other molecules cannot penetrate



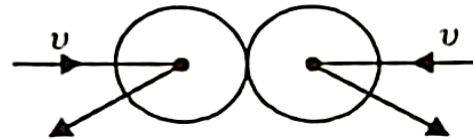
Derivation of expression for Collision number

Collision number (N_c)

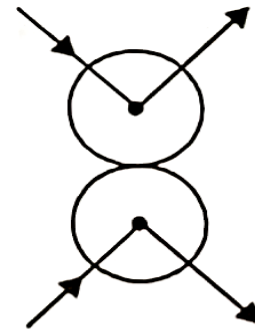
- Consider a cylinder of length ' v ' cm and with radius of cross section as σ
- Volume of cylinder = $\pi\sigma^2v$
- Let ' n ' is the number of molecules per unit volume, so number of molecules in the cylinder = $(\pi\sigma^2v)n$
- Let a molecule moves through the cylinder. It will collide with all the molecules whose centres lie within the cylinder
- So number of collisions undergone by it in one second or $N_c = (\pi\sigma^2v)n$
- Since all the molecules are moving so we have to consider relative velocity and all angles of collision are equally probable and we take average angle of collision ie 90°
- Replacing v with $\sqrt{2}v$ we get $N_c = \sqrt{2} \pi v \sigma^2 n$



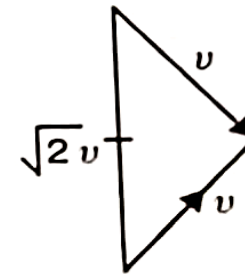
Angle of collision = 0°
(a) Glancing collision
relative velocity = 0



Angle of collision = 180°
(b) Head on collision
relative velocity = $2v$



(c) Collision at right angles
Relative velocity = $\sqrt{2}v$
Angle of collision = 90°



Derivation of expression for collision frequency

❑ Collision frequency (Z)

➤ Since n is the number of molecules per unit volume so total number of collisions taking place in 1 cc of the gas in one second

$$➤ Z = N_c \times n = (\sqrt{2} \pi v \sigma^2 n) \times n = \sqrt{2} \pi v \sigma^2 n^2$$

➤ One collision involves two molecules so total number of collisions will be half i.e.

$$Z = \frac{1}{2}(\sqrt{2} \pi v \sigma^2 n^2) \quad Z = \frac{1}{\sqrt{2}} \pi v \sigma^2 n^2$$

➤ Further if we put the expression for v we get

$$➤ Z = \frac{1}{\sqrt{2}} \pi \left(\frac{8RT}{\pi M} \right)^{1/2} \sigma^2 n^2 \quad \text{OR} \quad Z = 2 \sigma^2 n^2 \sqrt{\frac{\pi RT}{M}}$$

Effect of T and P on Collision number & collision frequency

□ On Collision frequency (Z)

➤ $Z = \frac{1}{\sqrt{2}} \pi v \sigma^2 n^2$ $Z \propto v n^2$ also $PV = n'RT$ or $n'/V = P/RT$ or $n = PN_0/RT$ so $n \propto P/T$ & $v \propto \sqrt{T}$

- ✓ $Z \propto \sqrt{T} \times P^2/T^2$ or $Z \propto P^2/T^{3/2}$ so $Z \propto P^2$ at constant T and $Z \propto 1/T^{3/2}$ at constant pressure
- ✓ and at constant volume $P \propto T$ so $Z \propto T^2/T^{3/2}$ or $Z \propto \sqrt{T}$ and $Z \propto P^2/P^{3/2}$ or $Z \propto \sqrt{P}$

□ Collision number

✓ $N_c = \sqrt{2} \pi v \sigma^2 n$ $N_c \propto v n$ or $N_c \propto \sqrt{T} \times P/T$ or P/\sqrt{T}

- ✓ At constant T, $N_c \propto P$ and at constant pressure $N_c \propto 1/\sqrt{T}$

- ✓ At constant volume $P \propto T$ so $N_c \propto T/\sqrt{T}$ ie $N_c \propto \sqrt{T}$ or $N_c \propto P/\sqrt{P}$ ie $N_c \propto \sqrt{P}$

Mean free path

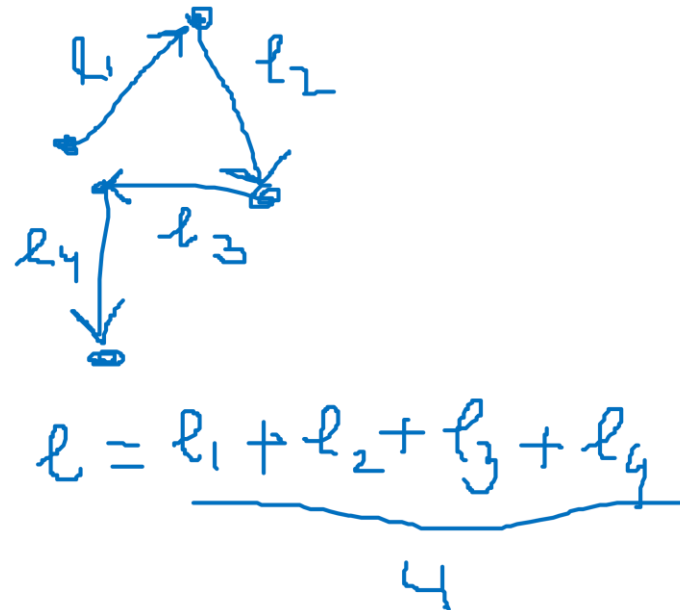
□ Mean free path(l or λ)

- It is the mean distance travelled by a molecule between any two successive collisions.
- The distance travelled by a molecule before it collides with another molecule is called as free path

$$l \text{ or } \lambda = \frac{\text{Distance travelled by a molecule in one second}}{\text{No. of collisions undergone by the molecule in one second}} = \frac{\text{Av. velocity}}{\text{collision number}} = \frac{v}{Nc}$$

$$l = \frac{v}{\sqrt{2} \pi v \sigma^2 n}$$

$$l = \frac{1}{\sqrt{2} \pi \sigma^2 n}$$



Mean free path

□ Effect of temperature and pressure on Mean free path(l or λ)

- $PV = n'RT$ or $n'/V = P/RT$ or $n = PN_0/RT$
- Put this value of n in the expression for l

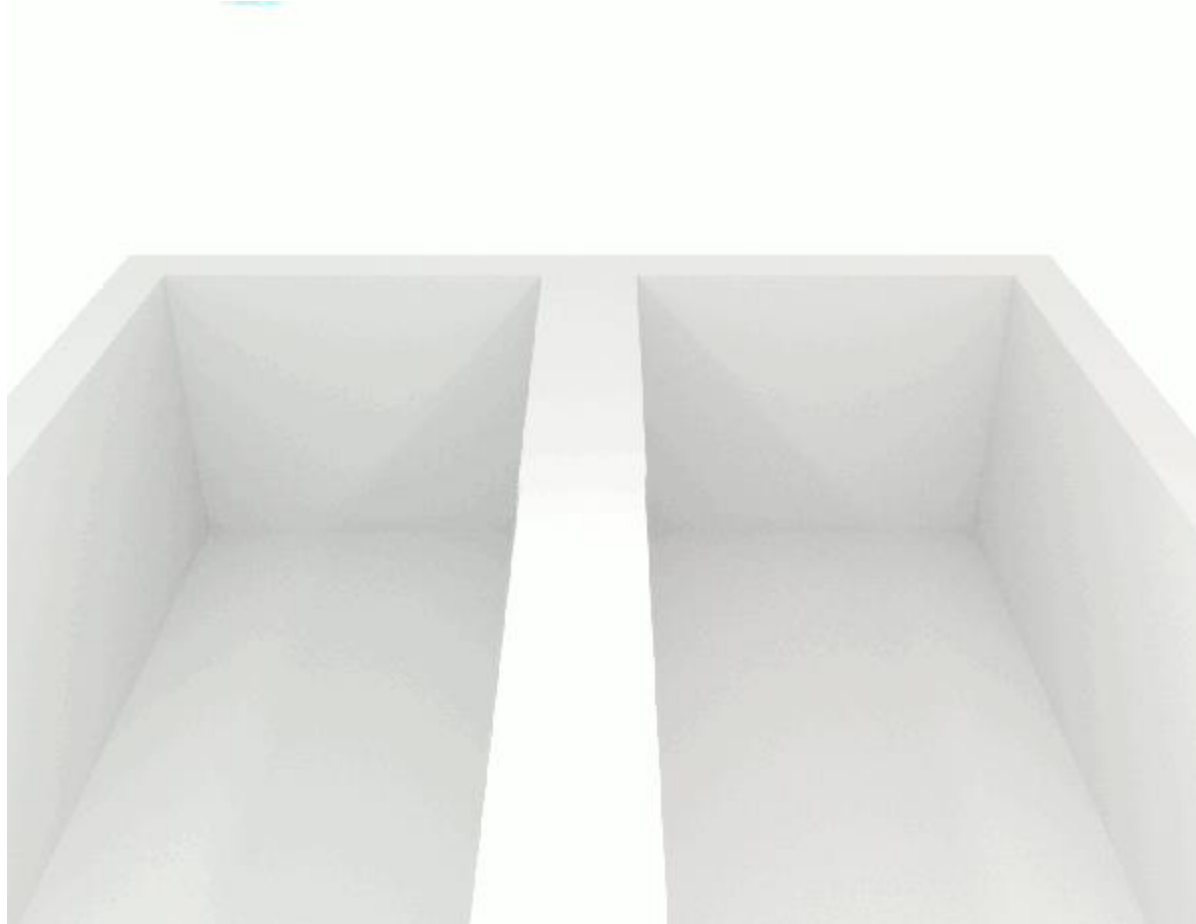
- $l = \frac{1}{\sqrt{2}\pi\sigma^2} \cdot \frac{RT}{PN_0}$ $l = \frac{kT}{\sqrt{2}\pi\sigma^2 P}$ $l \propto T/P$ $l \propto T$ & $l \propto 1/P$

- At constant volume $P \propto T$ so l is independent of T and P at constant. volume

Viscosity in gases

- **Viscosity is property of fluids(Gases or liquids)**
- **The resistance offered by one layer of fluid to the flow of other layer of the fluid is called as viscosity**
- **For gases we can consider laminar flow**
- **The gas molecules are always in motion. There is exchange of molecules between the layers**
- **The layer touching the surface has zero velocity and has least momentum**
- **As we move up the momentum of the layer is retarded by the lower layer**
- **So there is internal friction which retards the relative motion of adjacent layers and is called as viscosity.**

Viscosity in liquids



Viscosity in gases

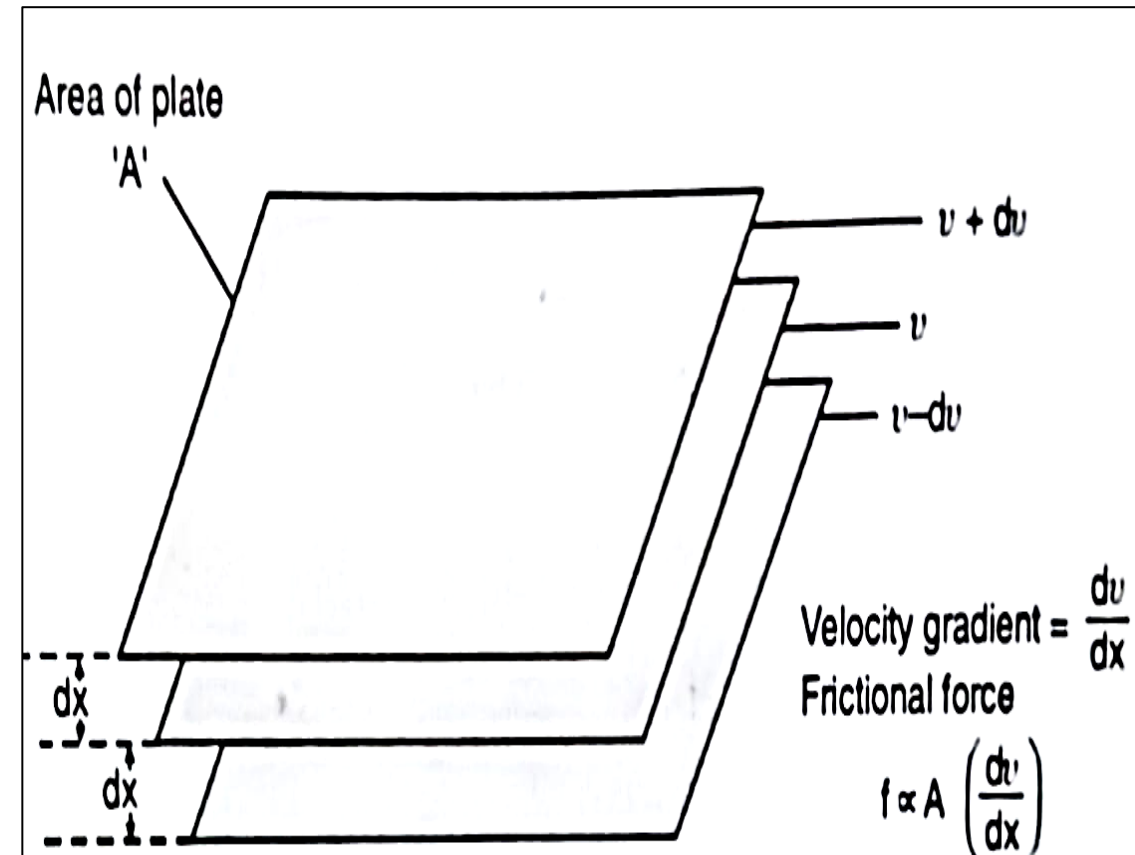
➤ Force is required to maintain a uniform velocity difference between adjacent layers

➤ $F \propto A \frac{dv}{dx}$

➤ $F = \eta A \frac{dv}{dx}$

➤ If $A = 1 \text{ cm}^2$ & $dv/dx = 1$ then $F = \eta$

➤ So Coefficient of viscosity is the force per unit area required to maintain a unit velocity gradient between two adjacent parallel layers



Viscosity in gases

□ Units of coefficient of viscosity(CGS system)

$$\text{➤ } \eta = \frac{F}{A} \frac{dx}{dv} = \frac{\text{dynes}}{\text{cm}^2} \frac{\text{cm}}{\text{cm sec}^{-1}} = \text{dynes sec cm}^{-2} = 1 \text{ poise}$$

➤ If we put $F = ma$

$$\text{➤ then } \eta = \frac{ma}{A} \frac{dx}{dv} = \frac{\text{g cm sec}^{-2} \times \text{cm}}{\text{cm}^2 \times \text{cm sec}^{-1}} = 1 \text{ g cm}^{-1} \text{ s}^{-1} = 1 \text{ poise}$$

➤ Smaller units are cP or mP 1 P = 100 cP or 1 P = 1000 mP

Viscosity in gases

□ Relation between coefficient of viscosity and mean free path

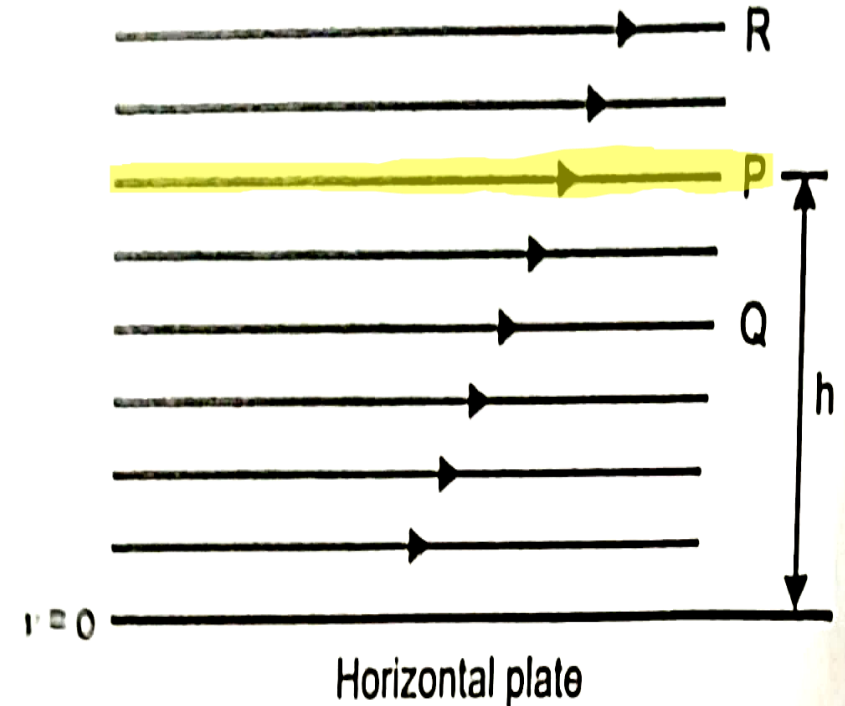
- Consider layer P at height h
- If velocity gradient is dv/dx , then at height h, velocity will

$$v = h \left(\frac{dv}{dx} \right)$$

- If mean free path is l , then the molecules of layer P will collide and interchange with molecules at a distance l above (layer R) and l below (layer Q)

- Now velocity of molecules in layer Q below = $(h - l) \frac{dv}{dx}$

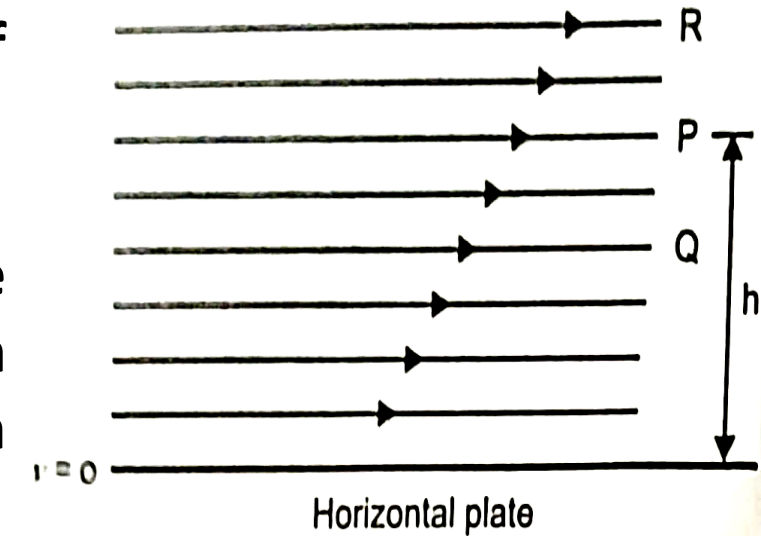
- Now velocity of molecules in layer R above = $(h + l) \frac{dv}{dx}$



Viscosity in gases

□ Relation between coefficient of viscosity and mean free path contd.

- Due to interchange of molecules there is transfer of momentum from one layer to another
- Consider transfer of momentum from layer P to Q and R
- $1/3^{\text{rd}}$ of the molecules in each layer move along three perpendicular directions and $1/6^{\text{th}}$ of the molecules move in upward direction and $1/6^{\text{th}}$ of the molecules move in downward direction



- Number of molecules moving upward or downward = $\frac{1}{6} n v$

Viscosity in gases

□ Relation between coefficient of viscosity and mean free path contd.

➤ From layer Q the momentum transferred upwards towards layer P per square cm per sec = $\frac{1}{6} mnv(h-l) \frac{dv}{dx}$

➤ From layer R the momentum transferred downwards towards layer P per square cm per sec = $\frac{1}{6} mnv(h+l) \frac{dv}{dx}$

➤ Net downward flow of momentum per second toward the layer P

$$= \frac{1}{6} mnv (h+l) \frac{dv}{dx} - \frac{1}{6} mnv (h-l) \frac{dv}{dx}$$

$$= \frac{1}{6} mnv [(h+l)-(h-l)] \frac{dv}{dx} = \frac{1}{6} mnv (h+l-h+l) \frac{dv}{dx} = \frac{1}{6} mnv (2l) \frac{dv}{dx} = \frac{1}{3} mnv l \frac{dv}{dx}$$

Viscosity in gases

□ Relation between coefficient of viscosity and mean free path contd.

➤ Now momentum transferred is equal to the force so $F = \frac{1}{3} mnvl \frac{dv}{dx}$

also $F = \eta \frac{dv}{dx}$ for $A = 1 \text{ sq.cm}$

➤ $\eta \frac{dv}{dx} = \frac{1}{3} mnv l \frac{dv}{dx}$

➤ $\eta = \frac{1}{3} mn v l$ or $\eta = \frac{1}{3} \rho v l$

Viscosity in gases

□ Effect of Temperature & pressure on coefficient of viscosity

➤ $\eta = \frac{1}{3} mnvl$ and putting the expressions for v and l , we get

$$\eta = \frac{1}{3} mn \left(\sqrt{\frac{8kT}{\pi m}} \right) \left(\frac{1}{\sqrt{2}\pi\sigma^2 n} \right) \quad \eta = \frac{2}{3} \frac{\sqrt{mkT}}{\pi^{3/2} \sigma^2} \quad \text{so } \eta \propto \sqrt{T}$$

➤ With increase in temperature, coefficient of viscosity increases because KE of molecules increases which increases transfer of momentum from one layer to another layer.

➤ Sutherland relationship $\eta = \frac{\eta_0 \sqrt{T}}{(1 + C/T)}$

➤ We can see there is no effect of pressure on coefficient of viscosity

Viscosity in gases

□ Calculation of molecular diameter from Coefficient of viscosity

$$\text{➤ } \eta = \frac{1}{3} m n v l$$

Put the expression for l , we get

$$\text{➤ } \eta = \frac{1}{3} \frac{m n v}{\sqrt{2\pi\sigma^2 n}}$$

$$\text{➤ } \eta = \frac{1}{3} \frac{m v}{\sqrt{2\pi\sigma^2}}$$

Knowing m , v , & η , we can calculate molecular diameter