

coldness of a substance. / measure of K.E. of the molecules.

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## Chapter-01: The Kinetic Theory of Gases and Transport phenomenon

### \* Gas

Gas is a state of matter that has no fixed shape and no fixed volume.

### \* Physical properties of gases

1. No fixed shape and no fixed volume. Acquires the shape of the container. (অন্তরণ)
2. Highly compressible (সংকোচিত).
3. Not rigid. (গাঢ়িতে) ৰ
4. Diffusion is very fast. (সামুদ্রিক)
5. Lower density.
6. The particles move very fast and collide into one another.
7. Intertparticle force is negligible.
8. There is a great deal of empty space between particles, which have a lot of kinetic energy.

\* Pressure (Pressure is defined as force per unit of area, unit N/m<sup>2</sup>)  
When more gas particles enter a container, there is less space for the particles to spread out, and they become compressed. The particles exert more force on the interior volume of the container. The force is called pressure.

### \* Real gas

A real gas is a gas that does not behave as an ideal gas due to interactions between gas molecules.  
(Repulsion)

A gas that obeys the van der waal's equation,  
 $(P + \frac{a}{v^2}) (v - b) = RT$  is defined as a real gas and also called van der waal's gas.

All kind of gases are real. At high temperature and low pressure, all the real gas behaves like an ideal gas. A real gas is also known as a non-ideal gas.

### \* Ideal gas

Ideal gases are defined as having molecules of negligible size with an average molar kinetic energy dependent only on temperature. On,

An ideal gas defined as one that obeys the Boyle's and charles law that is the relation,  $PV = RT$ , under all conditions. There is no such gas as a truly ideal gas but it remains a useful and simple concept connected with reality by the fact that all gases approach to the ideal gas if the density is low enough.

Note: An ideal gas is defined as one in which all collisions between atoms or molecules are perfectly elastic and in which there are no intermolecular attractive forces.

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### \* free path (পর্যবেক্ষণ)

The distance travelled by the molecule before collision is termed free path.

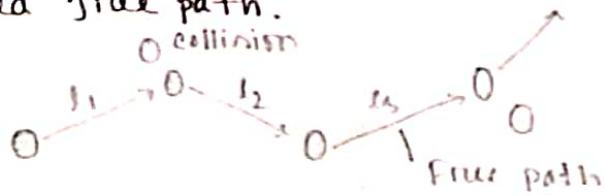


Fig. 1.

### \* Mean free path (মিগুগুণ)

Mean free path is defined as the average distance travelled by a gas molecule between two successive collision.

It is denoted by  $\lambda$ . If  $l_1, l_2$ , and  $l_3$  are the free paths for a molecule of a gas, its mean free path equals,

$$\lambda = \frac{l_1 + l_2 + l_3 + \dots + l_n}{n}$$

$\therefore$  Mean free path,  $\lambda = \frac{S}{\sqrt{2} \pi d^2 N_a}$

well and to understand

## Derivation of gas equation

From kinetic theory,

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

$$= \frac{1}{3} \frac{M}{V} c^2$$

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

Consider, 1 gram molecule of gas  
at absolute temperature  $T$ .

The mean energy of the molecules,

$$= \frac{1}{2} Mc^2$$

$$= \frac{1}{2} Nmc^2$$

$$\therefore PV = \frac{1}{3} Nmc^2$$

$$= \frac{2}{3} \cdot N \cdot \frac{1}{2} mc^2$$

Mean K.E. of a molecule

$$= \frac{1}{2} mc^2$$

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

$$PV = \frac{2}{3} \cdot N \cdot \frac{3}{2} kT$$

$$PV = NkT$$

But,

$$N \times k = R$$

$$PV = RT$$

Note: Dalton's law of partial pressure: The total pressure of a mixture of gasses is equal to the sum of the partial pressures of the component gasses.

$$P_{\text{total}} = P_{\text{H}_2} + P_{\text{O}_2} + P_{\text{N}_2}$$

$$\text{Sub: } P_{\text{total}} = \frac{(n_1 + n_2 + n_3) R T}{V}$$

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pressure law:

At constant volume, the pressure of a given mass of gas is directly proportional to the absolute temperature.

$\therefore P \propto T$ , at constant volume, V.

$$\Rightarrow \frac{P}{T} = \text{constant}$$

Dalton law:

The pressure exerted on the walls containing vessel by a mixture of gasses is equal to the sum of the pressure that would be exerted by the gasses if they were present separately.

Avogadro's law:

At the same temperature and pressure, equal volumes of all gasses have the same number of molecules.  $\therefore V \propto n$  where, ~~P, T, P~~ T, P constant.

In combining the equation of Boyle's and Charles's law:

we may write,

$$\frac{PV}{T} = \text{constant}$$

Boyle's equation,  $PV = \text{constant}$

Charles's equation,  $\frac{V}{T} = \text{constant}$

Replacing this constant by R called universal gas constant.

$$\text{we get, } \frac{PV}{T} = R \Rightarrow PV = RT$$

For, n mole gas, the equation become,

$$PV = nRT$$

This equation is known as equation of state of an ideal gas.

## The Brownian Movement

The random motion of small colloidal particles suspended in a liquid or gas medium, caused by the collision of the medium's molecules with the particles. It's called Brownian movement.



Fig. 1. Brownian movement

### Causes Brownian Motion

- i. The size of the particles is inversely proportional to the speed of the motion.
- ii. The transfer of momentum is inversely proportional to the mass of the particles. Lighter particles obtain greater speeds from collisions.
- iii. The speed of the Brownian motion is inversely proportional to the viscosity of the fluid. The lower the viscosity of the fluid, the faster the Brownian movement.
- iv. Viscosity is a quantity that expresses the magnitude of the internal friction in a liquid. It is the measure of the fluid resistence of flow.

## Effects of Brownian motion

- i. Brownian movement causes the particles in a fluid to be in constant motion.
- ii. This prevents particles from settling down, leading to the stability of colloidal solutions.
- iii. A true solution can be distinguished from a colloid with the help of this motion.

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## \* Vander waal's equation of state for a real gas

The vander waal's equation can be derived by making some modification of the assumption on the kinetic energy theory of gases.

Firstly, In kinetic theory, the size of the gas molecules was ignored. Hence, the available volume occupied by a gas molecule within a container was that of the volume of the container. Actually, the molecules are small but they have some finite size. At low pressure, there are only few gas molecules, hence the volume occupied by them may be ignored. At high pressure, the volume occupied by them cannot be ignored, hence the available volume will be decreased.

Secondly,

We have assumed that there is no force of attraction among the gas molecules. At low pressure, when the gas molecules are far apart it is true. But at high pressure, when the molecules are more closer, there exist force of attraction among

Now, we assume that initially the container was empty and molecules were allowed to enter one by one. Thus, the volume available to 1st molecule =  $V$

$$\text{1st molecule} \rightarrow V - 8s + V_s$$

$$\text{2nd molecule} \rightarrow V - 9s$$

$$\text{N-th molecule} \rightarrow V - (N+1)s$$

$\left[ (N+1)s = \text{occupied by } (N+1) \text{ molecules} \right]$

Average space (in volume) available to each molecule will be,

$$V = \frac{V + (V-s) + (V-2s) + \dots + [V-(N-1)s]}{N}$$

$$= \frac{NV - s \{ (1+2+3+\dots+(N-1)) \}}{N}$$

$$= V - \frac{s}{N} \cdot \frac{N(N-1)}{2}$$

$$= V - \frac{SN}{2} + \frac{s}{2} \approx V - \frac{SN}{2} \quad \left[ \frac{s}{2} \text{ is neglected} \right]$$

$$= V - \frac{8sN}{2}$$

$$= V - 4Ns$$

$s \text{ mole gas} \cdot \text{Na}$   
 $n \text{ " } v = n \text{ Na}$

If there are ' $n$ ' mole of gas,

$$n = n N_A \quad [N_A = \text{Avogadro's number}]$$

Average space available to each molecule will be,

$$= V - 4n N_A s = V - nb, \text{ where, } b = 4 N_A s$$

Thus, the equation of state of the gas will be,

$$P(V-nb) = nRT$$

for one mole of the gas,

$$P(V-b) = RT$$

the gas molecules. A molecule wt within the gas will experience a net force of attraction from all sides. Hence, the net force will be zero. The molecules impinge on the wall of the container will experience a net inward force. Hence the momentum will be reduced. This results in the reduction of pressure.

### Volume correction:

Let, there are  $N$  molecules of gas within a enclosure of volume,  $V$ . If  $r$  be the radius of the each molecule then the volume occupied by each molecule of the gas will be,

$$x = \frac{4}{3} \pi r^3$$

The centers of two molecules can approach to each other upto a minimum distance of  $(2r)$  (minimum)



Now surrounding a molecule, we consider a sphere of radius,  $2r$  which will not be accessible to other molecules. Such a sphere is called sphere of exclusion and the volume occupied by the sphere,

$$S = \frac{4}{3} \pi (2r)^3 = \frac{4}{3} \cdot \pi r^3 8 = 8x$$

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### Pressure correction:

Due to the force attraction between that gas molecules, there will be a reduction of pressure (on the wall). Now, the reduction of pressure is depend on the number of molecules striking the wall per unit time, per unit area and on the number of molecules attracting the from the back. The two numbers are proportional to the square of the density of molecule within the container, i.e,

$$\text{Reduction of pressure} \propto \rho^2$$

$$\propto \frac{1}{V^2}$$

$$= \frac{a}{V^2}$$

$\left[ \rho^2 = \left( \frac{m}{V} \right)^2 \right]$   
— m is constant

After volume correction, the equation of state will be,

$$\Rightarrow P(V-b) = RT \quad [\text{for 1 mole of gas}]$$

$$\Rightarrow P = \frac{RT}{V-b} \quad [\text{when reduction of pressure is not considered}]$$

$$\Rightarrow P = \frac{RT}{V-b} - \frac{a}{V^2} \quad [\text{when reduction of pressure is considered}]$$

$$\Rightarrow \left( P + \frac{a}{V^2} \right) = \frac{RT}{V-b}$$

$$\Rightarrow \left( P + \frac{a}{V^2} \right) (V-b) = RT \quad \text{--- (1)}$$

For n mole of gas,  

$$\left( P + \frac{a}{V^2} \right) (V-nb) = nRT \quad \text{--- (2)}$$
  
 This equation is called the van der waals equation of state for real gas

## \* critical constant (from van der waal's equation)

The critical temperature and the corresponding values of pressure and volume at the critical points are called the critical constant.

At critical point, the rate of change of pressure with respect to volume,

$$\frac{\partial P}{\partial V} = 0$$

and at critical point, the maximum and minimum coincide and so,

$$\frac{\partial^2 P}{\partial V^2} = 0 \quad \text{and} \quad \frac{\partial^2 P}{\partial V^2} = 0$$

The van der waal's equation is,

$$(P + \frac{a}{V^2}) (V - b) = RT$$

$$\text{or, } P = \frac{RT}{V-b} - \frac{a}{V^2} \quad \text{--- (1)}$$



Hence,

$$\frac{\partial P}{\partial V} = \frac{2a}{V^3} - \frac{RT}{(V-b)^2} = 0 \quad \text{--- (2)}$$

$$\frac{\partial^2 P}{\partial V^2} = \frac{2RT}{(V-b)^3} - \frac{6a}{V^4} = 0 \quad \text{--- (3)}$$

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substituting the values of  $V_c$  and  $T_c$  into equation ① we get,

$$P_c = \left(\frac{R}{2b}\right) \cdot \left(\frac{8a}{27Rb}\right) - \frac{a}{9b^2}$$

$$\Rightarrow P_c = \frac{8a}{54b^2} - \frac{a}{9b^2}$$

$$= \frac{8a - 6a}{54b^2}$$

$$\Rightarrow P_c = \frac{2a}{54b^2}$$

$$\therefore P_c = \frac{a}{27b^2}$$

Thus,

$$\text{the critical temperature, } T_c = \frac{8a}{27Rb}$$

$$\text{critical pressure, } P_c = \frac{a}{27b^2}$$

$$\text{and critical volume, } V_c = 3b$$

Notes

i) Critical Temperature - It is the temperature above which a gas cannot be liquefied.

ii) Critical Pressure - It is minimum pressure required to liquefy a gas at its critical Temperature.

iii) Critical Volume - It is the volume occupied by 1 mole of gas at  $T_c$  and  $P_c$ .

## \* Mean free path ( $\text{मी.फे.पी.पी.}$ )

The path traversed by molecule between two successive collision with other molecules is called free path.

Along a free path the molecules move with uniform velocity, along straight line. The average distance between collision is called the mean free path.

If the total distance travelled after  $N$  collisions is  $s$ , the mean free path  $\lambda$  is given by

$$\lambda = \frac{s}{N}$$

Deduction of  $\lambda$ :

Let the molecules is assumed to be sphere of diameter  $d$ . A collision between two molecules will take place if the distance between the center of two molecules is  $d$ . Collision will also occur if the colliding molecules has a diameter  $2d$  and the other molecule is simply geometrical point.



Fig. 1.

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Thus assuming that all other molecules to be simply geometrical points and the colliding molecules of diameter  $\pi d^2$ , thus molecule will cover a volume  $\pi d^2 v$  in one second, where  $v$  is the velocity of molecule. This corresponds to the volume of a cylinder of diameter  $\pi d$  and length  $v$  in one second.

Let,  $n$  is the number of molecules per  $\text{cm}^3$ .

Then the number of molecules present in a volume,  $\pi d^2 v$  is =  $n \pi d^2 v$

This value also represents the number of collision made by the molecule in one second.

The distance moved in one second =  $v$  [  $s=vt$ ,  $s=v$  in one second ]

and the number of collision in one second =  $n \pi d^2 v$

$$\therefore \text{Mean free path, } \lambda = \frac{s}{N} = \frac{v}{n \pi d^2 v} = \frac{1}{n \pi d^2}$$

Maxwell deduce the expression for mean free path by assuming that all other molecules are not at rest.

$$\lambda = \frac{1}{\sqrt{2} \pi d^2 n}$$

Maxwell calculate the value of  $\lambda$  on the basis of law of distribution of velocities.

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Most of the bullet molecules will pass through the layers, but some will collide with target molecules.

The ratio of the number of collisions  $\Delta N$  to the total number of bullet molecules,  $N$  is equal to the area presented by the target molecules, is the total area presented by the layers.

$$\therefore \frac{\Delta N}{N} = \frac{\text{target area}}{\text{total area}}$$

The target area  $\sigma$  of a single molecule is the area of a circle of radius  $d$ ;

$$\sigma = \pi d^2 \quad \text{--- (1)}$$

The area is called microscopic cross section of one molecule.

If there are  $n$  target molecule per unit volume then the total number of target molecule is  $nL^2 A_x$ .

so, the total target area of the layers is,  $L^2$ . So,

$$\frac{\Delta N}{N} = \frac{n\sigma L^2 A_x}{L^2} = n\sigma A_x \quad \text{--- (2)}$$

The quantity  $n\sigma$  is called macroscopic cross-section of the molecules. The number of density  $n$ , in the MKS system, is the number of molecules per cubic meter and the collision cross section  $\sigma$  is the number of square meters per molecule, the unit of the product  $n\sigma$  is 1 square meter per cubic meter. The unit of macroscopic collision cross section is a reciprocal length, not an area.

Each of the  $n\sigma$  collisions diverts a molecule from its original path or scatters it out of the beam, and decrease the number remaining in the beam. Let us, therefore, interpret  $\Delta N$  not as a "number of collisions" but as the decrease in the number  $N$ , and write,

$$\Delta N = -N n \delta \Delta x$$

$$dN = -N n \delta dx$$

$$\Rightarrow \frac{dN}{N} = -n \delta dx \quad \textcircled{2}$$

if,  $N = N_0, x = 0$

$$\therefore \int_{N_0}^N \frac{dN}{N} = -n \delta \int_0^x dx$$

$$\Rightarrow \ln(N/N_0) = -n \delta x$$

$$\therefore N = N_0 e^{-n \delta x} \quad \textcircled{3}$$

This is known as the survival equation.

Putting this value in equation ②,

$$\Delta N = N_0 n \delta e^{-n \delta x} \Delta x$$

let us calculate the average distance travelled by a group of  $N_0$  molecules before they make their first collision. This average distance is known as mean free path,  $\lambda$ .

$$\lambda = \frac{\sum x \Delta N}{N_0} = \frac{\sum x N_0 n \delta e^{-n \delta x} \Delta x}{N_0}$$

$$= n \delta x e^{-n \delta x} \Delta x : \Delta x$$

$$\therefore \lambda = n \delta x e^{-n \delta x} dx$$

$\rightarrow$  we multiply  $x$  by the number of particles  $N_0$  that travels the distance  $x$  before colliding, sum overall value of  $x$ , and divide by the total number  $N_0$ .

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(cross section area)

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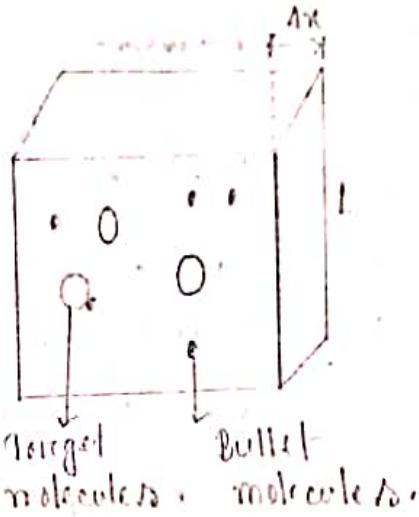
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are,

Let us consider, a thin layer of gas of dimensions  $L$ ,  $L$ , and  $\Delta x$  as shown in Fig. 1.

Let us refer to one of the colliding molecule as the target molecule and

to others as the bullet molecule.



The collision occurs whenever the distance between the centres of the molecules equal to molecular diameter,  $d$  as in Fig. 2.

since it is only the centre to centre distance that determines a collision if does not matter whatever the target is large and the bullet is small or vice versa.

Now, we imagine that a very large number,  $N$  of bullet molecules,

represented by the black dots, is projected toward the face of the layers in such a way that they distributed at random over the face of the layers. If the thickness of the layers is so small that no large target molecule can hide behind another.



Fig. 2.

## III Mathematical expression of Mean free path

In a time interval  $\Delta t$ , the molecule travels a distance  $v\Delta t$ .

$$\therefore N = \pi d^2 \cdot v\Delta t$$

The no. of point

it collides with

$$= \frac{N}{\sqrt{v}} \cdot \pi d^2 \cdot v\Delta t$$

$$\lambda = \frac{\text{length of the path during } \Delta t}{\text{the number of collision}}$$

$$= \frac{v\Delta t}{\frac{N}{\sqrt{v}} \cdot \pi d^2 \cdot v\Delta t} = \frac{1}{\pi d^2 \cdot \frac{N}{\sqrt{v}}}$$

$$\therefore v_{\text{rel}} = \sqrt{2} \cdot v_{\text{avg}}$$

$$\therefore \lambda = \frac{1}{\sqrt{2} \cdot \pi d^2 \cdot \frac{N}{\sqrt{v}}}$$

⇒ Clausius expression  $\rightarrow$

$$\lambda = \frac{1}{\pi d^2 n}$$

⇒ Maxwell's

formula

$$\rightarrow \lambda = \frac{1}{\sqrt{2} \cdot \pi d^2 n}$$

Note: The centre of any two molecules can approach each other only by a minimum distance of  $2d$ .

At critical point,

$$T = T_c, \quad p = p_c \text{ and } V = V_c$$

Then the equations ①, ②, and ③ become

$$p_c = \frac{RT_c}{V_c - b} - \frac{a}{V_c^2} \quad \text{--- ④}$$

$$\frac{RT_c}{(V_c - b)^2} = \frac{2a}{V_c^3} \quad \text{--- ⑤}$$

and,

$$\frac{RT_c}{(V_c - b)^3} = \frac{3a}{V_c^4} \quad \text{--- ⑥}$$

from equation ⑤ ÷ ⑥, we get

$$\frac{\frac{RT_c}{(V_c - b)^2} \times \frac{(V_c - b)^3}{RT_c}}{\frac{RT_c}{(V_c - b)^3}} = \frac{\frac{2a}{V_c^3} \times \frac{V_c^4}{3a}}{\frac{RT_c}{(V_c - b)^3}}$$

$$\Rightarrow 2V_c - 2b = 2V_c$$

$$\Rightarrow 2b = 0$$

putting the value of  $V_c$  into equation ⑥ we get,

$$\frac{RT_c}{(2b - b)^2} = \frac{2a}{(2b)^3}$$

$$\Rightarrow \frac{RT_c}{b^2} = \frac{2a}{16b^3}$$

$$\therefore T_c = \frac{8a}{27pb}$$

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

The equation can be reduced to an ideal gas equation, if—

- (i) The size of the gas molecules is negligible, hence the volume correction will be zero, i.e.,  $nb = 0$
- (ii) There will be no force of attraction among the gas molecules, hence the pressure correction will be zero,  
i.e.,  $\frac{a}{V^2} = 0$

Then, the equation state of the gas will be  $PV = nRT$ ,  
This is the equation of state of an ideal gas.

## Maxwell's law of equipartition of energy

### & principle of equipartition of energy (classical mechanics)

Statement:

If during the motion, the molecules obey ordinary laws of mechanics, then the total energy of a system is equally divided among all the degrees of freedom of the system. This is called the principle of equipartition of energy.

Proof:

This principle can be deduced from symmetry consideration. For a gas in thermal equilibrium, the velocities are evenly distributed along the three co-ordinates (that is x, y, z components of velocity) on the average are equal. In this case, the energies associated with component velocities u, v, and w, which are proportional to  $u^2$ ,  $v^2$ , and  $w^2$  are on an average equal.

$$\text{Thus, } \frac{1}{2}mv^2 = \frac{1}{2}m(u^2 + v^2 + w^2) \cdot \frac{1}{3}mu^2 = \frac{1}{2}mv^2 + \frac{1}{2}mw^2$$

$$= \frac{3}{2}KT$$

$$\Rightarrow \frac{1}{2}mu^2 + \frac{1}{2}mv^2 = \frac{1}{2}mw^2 = \frac{1}{2}KT$$

$$\left| \begin{array}{l} u^2 = v^2 = w^2 = \frac{1}{3}c^2 \\ \therefore m(u^2 + v^2 + w^2) = 3 \cdot \frac{1}{2}mc^2 \\ = 3 \cdot \frac{1}{2}KmT \end{array} \right.$$

That is the energy corresponding to each of the three translational degrees is equal to  $\frac{1}{2}KT$ .

any of various types of movement in which atoms appear to be constantly undergoing small, random fluctuations.

### \* Brownian motion/movement

If small particles suspended in a liquid or in a colloidal solution illuminated by a strong light be examined under a powerfull microscope, the particles appears to move to and fro rapidly and continuously in an irregular manner.

Each particle ~~repeatedly~~<sup>(repeated)</sup>, rises, sinks, and rises again. Such a haphazard motion is known as Brownian motion/movement, after the name of Robert Brown, an english botanist who first observed this effect when studying with a microscope, a small pollen grains suspended in a liquid.

The following important facts about Brownian movement between have been subsequently observed by various scientist as a result of experimental study.

- (i) The motion of the particles are perpetual and continuous.
- (ii) The smaller the particles the quicker are the motion.
- (iii) They are independent of the jarring and shaking of the vessel.
- (iv) The particles of the same size move equally fast, at the same temperature.
- (v) Particles of gas move randomly, in straight lines and in all direction.

## The Principle of equipartition of energy

Statement :-

The mean Kinetic energy of the system of molecule in thermal equilibrium at the temperature,  $T$  is uniformly (equally) distributed among all the degree of freedom and for each other degree of freedom of a molecule its equals  $\frac{1}{2}KT$ .

Where,  $K$  is Boltzmann constant.

Explain :

The Kinetic energy of a single molecule

$$E_t = \frac{1}{2}mv_x^2 + \frac{1}{2}mv_y^2 + \frac{1}{2}mv_z^2$$

For a gas in thermal equilibrium at temp  $T$ , The average value of energy denoted by  $\langle E_t \rangle$  is;

$$\langle E_t \rangle = \langle \frac{1}{2}mv_x^2 \rangle + \langle \frac{1}{2}mv_y^2 \rangle + \langle \frac{1}{2}mv_z^2 \rangle$$

Since there is no preferred direction

$$\langle \frac{1}{2}mv_x^2 \rangle = \frac{1}{2}K_B T = \langle \frac{1}{2}mv_y^2 \rangle$$

$$= \frac{1}{2}K_B T$$

$$\langle \frac{1}{2}mv_z^2 \rangle = \frac{1}{2}K_B T$$

Note:

The average K.E of the molecule is

$$\langle E_t \rangle = KE = \frac{3}{2} \cdot K_B T$$

$$\therefore \langle \frac{1}{2}mv_x^2 + \frac{1}{2}mv_y^2 + \frac{1}{2}mv_z^2 \rangle = \frac{3}{2}K_B T$$

where,  $\langle \frac{1}{2}mv_x^2 \rangle = \langle \frac{1}{2}mv_y^2 \rangle = \langle \frac{1}{2}mv_z^2 \rangle \therefore \frac{1}{2}mv_x^2 = \frac{3}{2} \cdot \frac{1}{3}m$

$$\therefore \frac{3}{2} \cdot \frac{1}{3}m = \frac{3}{2}K_B T \therefore \frac{1}{2}mv_x^2 = \frac{1}{2}K_B T$$

## Derivation of Gas law

(i) Boyle's law -

According to K.E. theory,

$$P = \frac{1}{3} \rho c^2 = \frac{1}{3} \cdot \frac{M}{V} c^2 =$$

$$\text{At constant } T, \frac{M}{V} c^2 \text{ is constant.}$$

$$\therefore \frac{1}{3} M c^2 = \text{constant}$$

$$\therefore P V = \text{constant.}$$

(ii) Charles's law -

$$P = \frac{1}{3} \rho c^2 = \frac{1}{3} \cdot \frac{M}{V} c^2 =$$

$$PV = \frac{1}{3} M c^2$$

$$\therefore M = m N$$

$$PV = \frac{1}{3} N m c^2 \quad \text{--- (1)}$$

The mean K.E. of  $n^\circ$  molecules,

$$\frac{1}{3} m c^2 = \frac{1}{2} n k T$$

$$m c^2 = 3 k T$$

Substituting their value in (1)

$$PV = N k T \quad \text{--- (2)}$$

$$V \propto T$$

(iii) Regnault's law -

From (1).

When  $V$  is constant  
 $P \propto T$

## \* Equation of state for an ideal gas

The mathematical expression of Boyle's law, Charles law, pressure law, Dalton's law of partial pressure, Avogadro's law are commonly known as equation of state of an ideal gas. They are discussed below:

Boyle's law:

When temperature remains constant, the volume of a given mass of gas is inversely proportional to the pressure.

i.e.,  $v \propto 1/p$ , at constant temperature,  $T$

$$\Rightarrow Pv = \text{constant}$$

where,  $T$  = absolute temperature

$p$  = pressure

and  $v$  = volume.

Charles' law:

At constant pressure, the volume of a given mass of gas is directly proportional to the absolute temperature.

i.e.,  $v \propto T$ , at constant pressure,  $P$ .

$$\Rightarrow \frac{v}{T} = \text{constant}$$

Note: The total number of independent co-ordinate required to describe dynamics of system is called degree of freedom.

Sub: Degree of freedom =  $\frac{N-1}{(R-1)} \times (C-1)$

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## \* Degree of freedom (गतिशील विषय)



Definition:

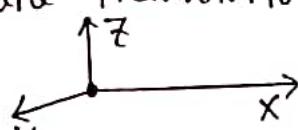
Molecular degree of freedom refers to the number of ways a molecule in the gas phase may move, rotate, or vibrate in space.

Three kinds of degrees of freedom -

- (i) Translational
- (ii) rotational
- (iii) vibrational

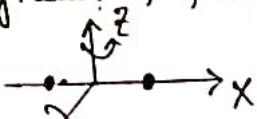
### \* Mono-atomic molecules:

A mono-atomic molecule, e.g. Ne, He etc has 3 degrees of freedom. (all are translational)



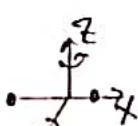
### \* Di-atomic molecules

A di-atomic molecule having a dumb-bell shape e.g. HCl, Cl<sub>2</sub>, O<sub>2</sub>, CO etc has 5 degrees of freedom (3 translational + 2 rotational)



### \* Tri-atomic molecule

A tri-atomic molecule if it is non-linear e.g. H<sub>2</sub>S, SO<sub>2</sub> etc. has 6 degrees of freedom (3 translational + 3 rotational).



If it is linear e.g. CO<sub>2</sub>, CH<sub>4</sub> etc has 5 degrees of freedom (3 translational + 2 rotational).



f. Non-linear

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## \* Difference between a real gas and an ideal gas

### Ideal gas

- Ideal gas obeys all gas laws under all conditions of temperature and pressure.
- Assumptions: kinetic molecular theory

### Real gas

- Real gas obeys gas laws only under low pressure and high temperature.
- Does not follow all assumptions of the kinetic molecular theory

- In ideal gas, the volume occupied by molecules is negligible as compared to the volume occupied by the gas. (Particles have zero volume)

- In real gas, the volume occupied by the molecules is significant in comparison to the total volume occupied by the gas. (Particles occupy a fixed volume)

- The force of attraction among the molecules of gas are negligible.

- The force of attraction among the molecules are significant at all temperature and pressure.

- It obeys the ideal gas equation:

$$PV = nRT$$

- Ideal gases cannot be liquified or solidified.

\* elastic collision

- It obeys the van der waals equation:

$$\left(P + \frac{a}{V^2}\right) (n - b) = RT$$

- (S) Example: most gasses can be liquified  
and often turn solid  
 Nitrogen, Oxygen,  
 carbon di-oxide, helium etc.  
 \* Non-elastic collision

5. The molecules are perfectly hard and elastic spheres and all of their energy is kinetic.
6. The molecules are sufficiently <sup>(optically)</sup> <sup>(optically)</sup> apart so that they do not exert any force of attraction or repulsion between them. <sup>(attract)</sup>
7. The dimensions of the molecules may be neglected in comparison with the distance traversed by the molecules between two successive collision called its free path.
8. The distribution of velocities among the molecules do not change with time.
9. The kinetic energy of gases are increase with increased temperature.
- \* Kinetic energy per unit volume of a gas

According to kinetic energy,

$$P = \frac{1}{3} \cdot \rho c^2 = \frac{1}{3} \cdot \frac{1}{V} P \cdot V^2 = \frac{1}{3} \cdot E$$

Where,  $E = \frac{1}{2} \rho V^2$  and is equal to the kinetic energy per unit volume of the gas.  $\rho$  is the mass per unit volume. Hence, the pressure of a gas is numerically equal to two-thirds of the mean kinetic energy of translation of a unit volume of the molecules.

*Refined*

## \* Basic assumptions of the Kinetic theory of gases

The kinetic theory of gases is based on the following simplifying fundamental assumptions of first stated by clausius in 1860.

1. A gas consist of a large number of molecules. All having the same mass and obeying Newton's law of motion.
2. The volume occupied by the gas molecules may be neglected in comparison with the volume of the container of the gases.
3. The molecules of continuously moving at random with high velocities colliding with each other and with the walls of the container. The pressure exerted by a gas is due to the continuous bombardment of the molecules with the walls of the container.
4. Between the successive collisions the molecules move in straight line with uniform velocities.

\* Math

Suppose the molecular diameter equals  $2 \times 10^{-10}$  m.  
 At standard conditions, if there are about  $3 \times 10^{25}$  molecules/m<sup>3</sup> in a gas, calculate the microscopic, macroscopic cross-section and mean free path.

Solution:

We know that

i) microscopic cross-section,

$$\begin{aligned}\sigma &= \pi d^2 \\ &= 3.1416 \times (2 \times 10^{-10})^2 \\ &= 1.25 \times 10^{-19} \text{ m}\end{aligned}$$

We have,

molecular diameter;  
 $d = 2 \times 10^{-10}$  m

number of molecules,

$$n = 3 \times 10^{25} \text{ molecules/m}^3$$

ii) Macroscopic cross section,

$$\begin{aligned}\Sigma &= n\sigma \\ &= 3 \times 10^{25} \times 1.25 \times 10^{-19} \\ &= 3.75 \times 10^6 \text{ m}\end{aligned}$$

iii) Mean free path,

$$\begin{aligned}\lambda &= \frac{1}{n\sigma} \\ &= \frac{1}{3 \times 10^{25} \times 1.25 \times 10^{-19}} \\ &= 8.0 \times 10^{-26} \text{ m}\end{aligned}$$

$$\Delta N = -N n \sigma A x$$

$$dN = -N n \sigma dx$$

$$\Rightarrow \frac{dN}{N} = -n \sigma dx \quad \text{--- (3)}$$

if,  $N = N_0, x = 0$

$$\therefore \int_{N_0}^N \frac{dN}{N} = -n \sigma \int_0^x dx$$

$$\Rightarrow \ln(N/N_0) = -n \sigma x$$

$$\therefore N = N_0 e^{-n \sigma x} \quad \text{--- (4)}$$

This is known as the survival equation.

Putting this value in equation (2),

$$\Delta N = N_0 n \sigma e^{-n \sigma x} A x$$

let us calculate the average distance travelled by a group of  $N_0$  molecules before they make their first collision. This average distance is known as mean free path,  $\lambda$ .

$$\lambda = \frac{\sum x \Delta N}{N_0} = \frac{\sum x N_0 n \sigma e^{-n \sigma x} A x}{N_0}$$

$$= n \sigma x e^{-n \sigma x} A x; A x$$

$$\therefore \lambda = n \sigma x e^{-n \sigma x} dx$$

We multiply  $x$  by the number of particles  $\Delta N$  that travels the distance  $x$  before colliding, sum overall value of  $x$ , and divide by the total number  $N_0$ .

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Replacing the sum by an integral, we have,

$$\begin{aligned}\lambda &= \int_0^\infty n\delta x e^{-n\delta x} dx \\ &= n\delta \int_0^\infty x e^{-n\delta x} dx \\ &= n\delta x \cdot \frac{1}{n^2 \delta^2}\end{aligned}$$

$$\therefore \lambda = \frac{1}{n\delta}$$

N.B.:  $\int_0^\infty x e^{-n\delta x} dx$

=

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The mean free path is inversely proportional to the macroscopic collision cross section, since the unit of macroscopic collision cross section is the reciprocal of the unit of length, the unit of mean free path is the unit of length.

Note: The mean free path does not depend on the molecular speed.

\* For classius,

$$\lambda = \frac{3}{4} \cdot \frac{1}{n\delta}$$

and Maxwell's

$$\lambda = \frac{1}{\sqrt{2}} \cdot \frac{1}{n\delta}$$

Note: Thermal conductivity: Thermal conductivity ( $\lambda$ ) is the intrinsic property of a material which relates its ability to conduct heat.

Defn:  $\therefore \text{Thermal conductivity} = (\text{heat} \times \text{distance}) / (\text{area} \times \text{temperature gradient})$

[W K<sup>-1</sup>m<sup>-1</sup>]

## \* Thermal conductivity

Definition:

Thermal conductivity can be defined as the rate at which heat is transferred by conduction through a unit cross-section area of a material, when a temperature gradient exists perpendicular to the area.

Explain:



fig.1

The thermal conductivity of a gas is treated in the same way as its viscosity. Let the upper and lower plate in Fig. 1, be at rest but at different temperatures, so that there is a temperature gradient rather than a velocity gradient in the gas.

If  $dT/dy$  is the temperature gradient normal to a surface within the gas, the thermal conductivity  $\lambda$  is defined by the equation,

$$H = -\lambda \frac{dT}{dy} \quad \text{--- (1)}$$

Q3) Diffusion: Diffusion is the gradual movement of solute particles from an area of high concentration to an area of low concentration.  
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### \* Diffusion

(Biology)  
(y1 pg)

#### Definition:

Diffusion is the net movement of anything from a region of higher concentration to a region of lower concentration.

Or,  
Diffusion is a consequence of random molecular motion and occurs whenever there is a concentration gradient of any molecular species, that is when the numbers of particles of one kind per unit volume on one side of a surface differs from that on the other side.

#### Explain:

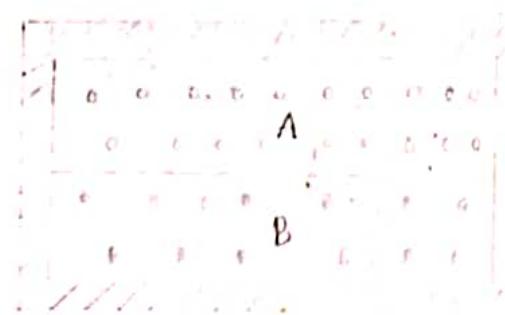


Fig. 1. A vessel containing two different gases separated by a partition.

Consider an imagined horizontal surface S-S within the vessel of Fig. 1. at some stage of the diffusion process.

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We assume as before that each molecule makes its last collision before crossing at a perpendicular distance  $\frac{2L}{3}$  away from the surface. If  $n^*$  is the number of tagged molecules per unit volume at the surface  $S-S$ , the number per unit volume at a distance  $\frac{2L}{3}$  below the surface is,

$$n^* = n_0^* - \frac{1}{3} L \frac{dn^*}{dy}$$

In the expression previously derived for the flux,  $\phi$ , we must replace  $n$  by  $n^*$ , and the upward flux  $\Gamma \uparrow$  is then,

$$\Gamma \uparrow = \frac{1}{4} \bar{v} \left( n_0^* - \frac{1}{3} L \frac{dn^*}{dy} \right)$$

In the same way, the downward flux is

$$\Gamma \downarrow = \frac{1}{4} \bar{v} \left( n_0^* + \frac{1}{3} L \frac{dn^*}{dy} \right)$$

The net flux  $\Gamma$  is the difference between these, so

$$\Gamma = -\frac{1}{3} \bar{v} L \frac{dn^*}{dy}$$

comparison with equation ① shows that,

$$D = \frac{1}{3} \bar{v} L = \frac{1}{3} \frac{\bar{v}}{m \sigma}$$

where,  $m$  is the total number of molecules per unit volume.



## Math

Given that, the density of air  $\text{U}^{235}$  is  $1.29 \text{ kg m}^{-3}$ , mean velocity  $460 \text{ m/s}$  and mean free path  $6.4 \times 10^{-8} \text{ m}$  at standard conditions. Determine the diffusion co-efficient.

## Solution:

We know,

$$\sigma = \frac{1}{n\lambda}$$

$$= \frac{1}{92 \times 6.4 \times 10^{-8}}$$

$$= 1.69 \times 10^5$$

Again, we know that,

$$\begin{aligned}\eta &= \frac{1}{m} \frac{\bar{v} m}{\sigma} \\ &= \frac{1 \times 460 \times 235}{3 \times 1.69 \times 10^5} \\ &= 2.67 \times 10^{-1} \\ &= 0.267\end{aligned}$$

density,  $\rho = 1.29 \text{ kg m}^{-3}$

Mean velocity,  $\bar{v} = 460 \text{ m/s}$

Mean free path,  $\lambda = 6.4 \times 10^{-8} \text{ m}$

mass,  $m = 235$

number of molecules  
in,  $n = 92$

Note. Right

diffusion co-efficient,

$$\begin{aligned}&= \frac{1}{3} \bar{v} \lambda c \\ &= \frac{1}{3} \times 6.4 \times 10^{-8} \times 460 \\ &= \end{aligned}$$

## \* uses of diffusion

- (i) p-n junction - Dopant diffusion for semi-conductor devices.
- (ii) Thermal barrier coatings for turbine blades.
- (iii) Hot dip galvanizing - coatings and thin films.
- (iv) sputtering, Annealing - magnetic materials for hard drives.
- (v) The process such as dialysis, microfiltration, ultrafiltration, osmosis etc. use the principles of diffusion.
- (vi) The molecular weight of polymers can be estimated from diffusion process.

### Note:

- i. Nitriding
- ii. P-n Junction
- iii. Annealing
- iv. Hot dip galvanizing
- v. Thermal barrier coating for turbine blades.
- vi. Manufacturing of plastic Beverage Bottles / Mylar<sup>TM</sup> Balloons.

The vessel contains a mixture of tagged and untagged molecules, the total number of molecules per unit volume being the same at all points so that the pressure is uniform. We assume the temperature to be uniform also. Let  $n^*$  represent the number of tagged molecules per unit volume at any point.

We shall assume that  $n^*$  is function of  $y$  only, where the  $y$ -axis is normal to the surface  $S-S$ .

If  $\frac{dn^*}{dy}$  is positive, the downward flux of tagged molecules across the surface  $S-S$  is then greater than the upward flux. If  $\Gamma$  represents the net flux of tagged molecules across the surface, per unit time and per unit area, the coefficient of self-diffusion  $D$  is defined by the equation,

$$\Gamma = -D \frac{dn^*}{dy} \quad \text{--- (1)}$$

The negative sign is included since if  $\frac{dn^*}{dy}$  is positive, the net flux  $\Gamma$  is downward and is negative.

The energy transported in an upward direction, per unit area and per unit time, is the product of this quantity and the molecular flux,  $\Phi$ .

$$H \uparrow = \frac{1}{4} n \bar{v} \Phi^* \left( T_0 - \frac{2}{3} \lambda \cdot \frac{dT}{dy} \right)$$

In the same way, the energy transported by molecules crossing from above is,

$$H \downarrow = \frac{1}{4} n \bar{v} \Phi^* \left( T_0 + \frac{2}{3} \lambda \cdot \frac{dT}{dy} \right)$$

The net rate of transport per unit area, which we identify with the heat current  $H$ , is

$$H = -\frac{1}{3} n \bar{v} \Phi^* \lambda \frac{dT}{dy}$$

and by comparison with equation ①, we see that the thermal conductivity  $\propto \frac{\bar{v} \Phi^*}{\delta}$ ,

$$\lambda = \frac{1}{3} n \bar{v} \Phi^* \lambda = \frac{1}{3} \frac{\bar{v} \Phi^*}{\delta}$$

$$1 : 6 = \frac{1}{\delta}$$

thus the thermal conductivity, like the viscosity, should be independent of density. This is also in good agreement with experiments down to pressures so low that the mean free path becomes of the same order of magnitude as the dimensions of the container.

The ratio of thermal conductivity to viscosity is,

$$\frac{\lambda}{\eta} = \frac{\bar{v}^*}{m} = \frac{c_v}{m N_A} = \frac{c_v}{M}$$

$$\text{and: } \frac{\lambda M}{\eta c_v} = 1$$

where,  $M$  is the molecular weight of the gas. All gases this combination of experimental properties should equal unity.

## \* Graph of the survival equation



fig.1. Graph of the survival equation

In terms of the mean free path, the survival equation can be written,

$$\begin{aligned} \cancel{N = N_0 e^{-\frac{x}{l}}} \\ N = N_0 e^{-\frac{x}{l}} \\ = N_0 e^{-x/l} \end{aligned}$$

In fig.1. is a graph of this equation, in which the dimensionless ratio  $N/N_0$  is plotted as a function of  $x/l$ . The ordinate of the curve is the fractional number of molecules with free paths longer than any fraction of the mean free path. Note that, the fraction with free paths longer than the mean is  $e^{-1}$  or 0.37%, while the number with free paths shorter than the mean is 63%.

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Where,  $H$  is the heat flow or heat current per unit area and per unit time across the surface. The negative sign is included because if  $dT/dy$  is positive the heat current is downward and is negative.

From the molecular viewpoint, we consider the thermal conductivity of a gas to result from the net flux of molecular kinetic energy across a surface. The total kinetic energy per mole of the molecules of an ideal gas is simply its internal energy  $u$ , which in turn equals  $c_v T$ .

The average kinetic energy of a single molecule is therefore  $c_v T$  divided by Avogadro's number,  $N_A$  and if we define a molecular heat capacity  $c_v^*$  as  $c_v^* = c_v/N_A$ , the average molecular kinetic energy is  $c_v^* T$ .

We assume as before that each molecule crossing the surface made its last collision at a distance ~~of~~  $2L/3$  above or below the surface, and that its kinetic energy corresponds to the temperature at that distance. If  $T_0$  is the temperature at the surface S-S, the kinetic energy of a molecule at a distance  $2L/3$  below the surface is,

$$c_v^* T = c_v^* \left( T_0 - \frac{2}{3} \lambda \frac{\Delta T}{dy} \right)$$