

## Chapter-01: The kinetic theory of Gases and transport phenomenon

Heat:

Heat is the transfer of kinetic energy from one medium or object to another, or from an energy source to a medium or object.

Heat is the form of energy that is transferred between systems or objects with different temperature (flowing from the high-temperature system to the low-temperature system).

Temperature:

Temperature refers to the hotness or coldness of a body.

Temperature is a measure of the average kinetic energy of the particles in an object. When the temperature increases, the motion of these particles also increase.

Faster the movement of particles, more the temperature, and vice versa.

### Gas:

A gas is one of the four fundamental states of matter consisting of particles that have neither a defined volume nor shape.

### Physical properties of gases:

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

Pressure :

The force which the substance exerts on another substance per unit area is known as pressure. The pressure of the gas is the force that the gas exerts on the container's boundaries.

The gas molecules move randomly along the given volume. During this movement, they collide with the surface and also with each other. The impact of every individual gas molecules is too small and difficult to visualize. But the impact of all the gas molecules considered together constitutes the gas pressure.

Greater the numbers of collisions, greater the would be the pressure.

## Macroscopic Thermodynamics:

Macroscopic thermodynamics refers to the relationship between the large-scale bulk properties of a system.

The typically ~~thermodynamics~~ considered bulk properties such include volume, elastic moduli, temperature, pressure and specific heat.

These are parameters that are easily measurable. Therefore, the macroscopic thermodynamics approach concerns the gross or average effects of many molecules' interactions as a bulk.

## Microscopic Thermodynamics:

Microscopic thermodynamics refers to the relationship between the small-scale properties of a system. This phenomenon includes the behavior of every molecule by using statistical methods.

The properties considered in the microscopic

thermodynamics include the properties of atoms that are on a very small scale; for example, intermolecular forces, chemical bonding, atomicity etc.

### Macroscopic cross-section :

The Macroscopic cross-section represents the effective target area of all of the nuclei contained in the volume of the material, the units are given in  $\text{cm}^{-2}$ .

$$\Sigma = \sigma \cdot N \quad I = I_0 e^{-\Sigma N t}$$

Here,  
 $\sigma$  = microscopic cross-section

### Microscopic Cross-section :

The microscopic cross-section represents the effective target area of a single target nucleus for an incident particle.

$$\sigma = \pi d^2$$

$\text{cm}^2$

Microscopic,  
 $I = I_0 e^{-\sigma N t}$

Macroscopic,  
 $\Sigma = \sigma \cdot N$

## ~~Basic~~ Basic assumptions of the kinetic theory of gases:

- ✓1. A confined gas of a material consists of an extremely large numbers of identical molecules.
- ✓2. The gas molecules can be treated as an ideal particle, i.e., it has mass but its structure and size can be ignored as compared with the intermolecular separation in a dilute gas and the dimensions of the container.
- ✓3. The molecules ~~of~~ <sup>are</sup> continuously moving at random with velocities colliding with each other and with the walls of the container and the motion obey Newton's law of motion.
- ✓4. The pressure exerted by a gas due to the continuous movement of the molecules with the walls of the container.

- ✓ 5. Between the successive collisions the molecules move in straight line uniform velocities.
- ✓ 6. The molecules are perfectly hard and elastic spheres and all of their energy is kinetic.
- ✓ 7. The molecules are sufficiently far apart so that they do not exert any force of attraction or repulsion between them.
8. The dimensions of the molecules may be neglected in comparison with the distance traversed (पातःगति, अनुप्रवृत्ति पातःगति, यात्रा गति) by the molecule between two successive collision called its free path.
9. The distribution of velocities among the molecules do not change with time.
10. When molecules collide with each others, no energy is gained or lost.
11. The kinetic energy of gases are increase ~~will~~ increase with increased temperature.

~~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.

Boyle's law:

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

$$V \propto \frac{1}{P} ; \text{ [At constant temperature, } T \text{]}$$

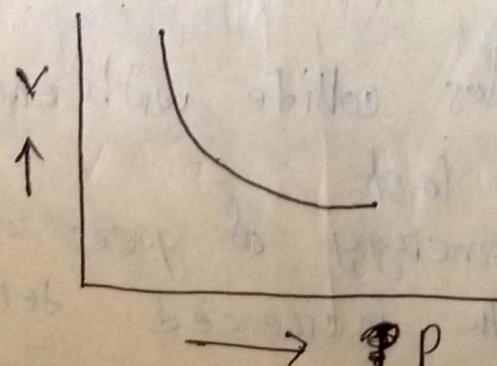
$$\Rightarrow PV = \text{constant}$$

where,

$P$  = Absolute pressure

$V$  = Volume

$T$  = Absolute temperature



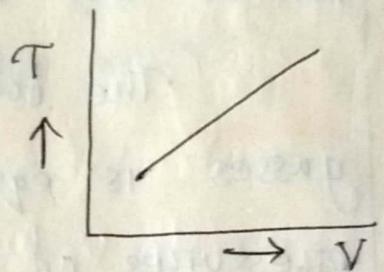
Charles's law :

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

i.e.,

$$V \propto T ; \quad [\text{At constant pressure, } P]$$

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



Pressure law :

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

i.e.,

$$P \propto T ; \quad [\text{At a constant Volume, } V]$$

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

Dalton law :

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

Dalton's law of partial pressure :

The total pressure of a mixture of gasses is equal to the sum of partial pressures of the component gases.

$$P_{\text{total}} = \sum_{j=1}^n P_j$$

$$= P_{\text{gas}_1} + P_{\text{gas}_2} + P_{\text{gas}_3} + \dots + P_{\text{gas}_n}$$

$$= \frac{(n_1 + n_2 + n_3 + \dots + n_n)}{V} RT$$

Avegadro's law :

At the same temperature and pressure, equal volumes of all gases have the same numbers of molecules. i.e.,

Volume : [At constant temperature and pressure]

~~Q~~ Derive the gas equation  $PV=RT$  from the kinetic theory:

Ans:

From kinetic theory,

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

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

$$\Rightarrow PV = \frac{1}{3} M \bar{c}^2 \quad \text{(i)}$$

Consider one gram molecule of a gas at an absolute temp.  $T$ . The mean energy of the molecule,

$$= \frac{1}{2} M \bar{c}^2$$

$$= \frac{1}{2} N m \bar{c}^2$$

No need

where,  $m$  = mass of each molecule

$N$  = Number of molecules in volume  $V$ .

From (i),

$$PV = \frac{1}{3} N m \bar{c}^2$$

$$= \frac{2}{3} N \cdot \frac{1}{2} m \bar{c}^2 \quad \text{(ii)}$$

Mean kinetic energy of a molecule,

$$\Rightarrow \frac{1}{2} m \bar{c}^2 = \frac{3}{2} kT$$

where,  $k$  is Boltzmann's constant.

Now from, (ii),

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

$$\Rightarrow PV = NK\bar{T}$$

But,  $Nk = R$

Therefore

$$PV = RT$$

This is the gas equation for one mole of ideal gas.

For  $n$  mole of gas,

$$PV = nRT.$$

~~Q4~~ Combining the equation of Boyle's and Charles's law:

According to Boyle's law,

$$PV = \text{constant}$$

and according to Charles's law,

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

Now, we may write,

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

Replacing this constant by  $R$  called universal gas constant, we get,

$$\frac{PV}{T} = R$$

$$\Rightarrow PV = RT$$

$$\Rightarrow PV - RT = 0$$

$$\Rightarrow f(P, V, T) = 0$$

this is called the equation of state.

For  $n$  mole gas, the equation becomes

$$PV = nRT$$

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

**Equation of state for a perfect gas:**  
 (Pressure exerted by a perfect gas)

Let us consider an ideal gas inside a cube of side  $l$ . Let each molecule has velocity  $c_1, c_2, \dots, c_n$  the velocity of its  $n$  molecules of mass  $m$ .

each.  $(u_1, v_1, w_1),$

$(u_2, v_2, w_2), \dots \dots$

$(u_n, v_n, w_n)$  be the

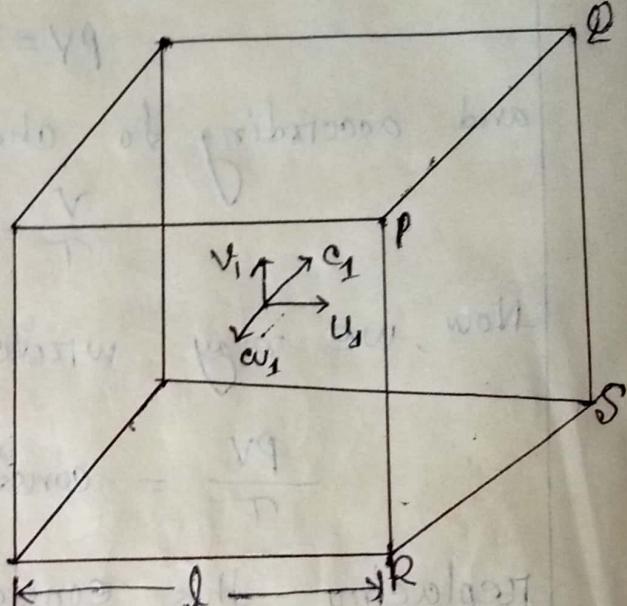
rectangular components of  $c_1, c_2, c_3, \dots, c_n$  respectively. Then,

$$c_1^2 = u_1^2 + v_1^2 + w_1^2 \quad \text{and} \quad c_2^2 = u_2^2 + v_2^2 + w_2^2 \quad \text{and}$$

so on.

Now momentum of the first molecules along  $x$ -axis,  
 $= m u_1$

After collision with Face PQR, it come back with same velocity. So momentum after collision,  
 $= m u_1$



Now, The change in momentum of the molecule,

$$= -mu_1 - (mu_1)$$

$$= -2mu_1$$

The momentum imparted to the face PQRS is

$$= 2mu_1$$

Time taken by the molecule between two successive collisions,

$$t = \frac{2l}{u_1}$$

Force on the surface PQRS, due to 1st molecule,

$$F_1 = \frac{dp}{dt} = \frac{2mu_1}{2l/u_1} = \frac{mu_1^2}{l}$$

Similarly, Force due to the 2nd molecule,

$$F_2 = \frac{mu_2^2}{l}$$

Force on the surface due to the nth molecule

$$F_n = \frac{mu_n^2}{l}$$

Total force along x-axis,

$$F_x = F_1 + F_2 + \dots + F_n$$

$$F_x = \frac{m}{l} (u_1^2 + u_2^2 + \dots + u_n^2)$$

Pressure exerted along x-axis,

$$P_x = \frac{F_x}{l^2}$$

$$\Rightarrow P_x = \frac{m}{l^3} (u_1^2 + u_2^2 + \dots + u_n^2)$$

Similarly pressure exerted along y-axis,

$$P_y = \frac{m}{l^3} (v_1^2 + v_2^2 + \dots + v_n^2)$$

and pressure exerted along z-axis,

$$P_z = \frac{m}{l^3} (w_1^2 + w_2^2 + \dots + w_n^2)$$

The gas is uniform throughout the tube.

Therefore,  $P_x = P_y = P_z = P$

Then, Average pressure,

$$P = \frac{P_x + P_y + P_z}{3}$$

$$\Rightarrow P = \frac{m}{3V} \left[ (u_1^2 + u_2^2 + \dots + u_n^2) + (v_1^2 + v_2^2 + \dots + v_n^2) + (w_1^2 + w_2^2 + \dots + w_n^2) \right]$$

$$= \frac{m}{3V} \left[ (c_1^2 + c_2^2 + \dots + c_n^2) + (c_1^2 + c_2^2 + \dots + c_n^2) + \dots + (c_1^2 + c_2^2 + \dots + c_n^2) \right]$$

$$= \frac{m}{3V} \left( c_1^2 + c_2^2 + \dots + c_n^2 \right)$$

$$= \frac{nm}{3V} \cdot \left( \frac{c_1^2 + c_2^2 + \dots + c_n^2}{n} \right)$$

Here,  
 $3V = V$   
 $= \text{Volume}$

(i)

We know that,

$$\text{rms velocity, } c = \sqrt{\frac{c_1^2 + c_2^2 + \dots + c_n^2}{n}}$$

$$\therefore c^2 = \frac{c_1^2 + c_2^2 + \dots + c_n^2}{n}$$

Now from eqn (i),

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

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

Here,  
 $nm = M$   
 $= \text{Total mass}$   
 and,  
 $\rho = \frac{M}{V}$

It can also be written as,

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

$$\therefore c = \sqrt{\frac{3P}{\rho}}$$

✓.

### Ideal gas :

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

It also can be defined as the gases that ~~do not obey~~ all gas laws at all conditions of pressure and temperature. Ideal gases do not condense. They also do not have a triple point. Ideal gases have mass and velocity.

In an ideal gas all collisions between atoms or molecules are perfectly elastic and in which there are no intermolecular attractive forces.

There are no such gases, 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 ~~tensile~~ is low enough.

### 5. Real gas:

Real gases are defined as the gases that do not obey gas laws at all standard pressure and temperature. Real gases condense when cooled to their boiling point. They have velocity, mass and volume.

A real gas does not behave as an ideal gas due to interactions between gas molecules.

It obeys the van der Waals' equation,

$$\left(P + \frac{a}{V^2}\right)(V - b) = RT \text{ and for this it is also called the van der waal's gas.}$$

All kind of gases are real. At high temperature and low pressure, all real gas behaves like an ideal gas.

~~\* Difference between a real gas and an ideal gas:~~

Real Gas	Real Gas
1. Ideal gas obeys all gas laws under all conditions of pressure and temperature.	1. Real gas obeys gas laws only at conditions of low pressure and high temperature.
2. It follows all the assumptions of kinetic molecular theory.	2. It does not follow all assumptions of the kinetic molecular theory.
3. The volume occupied by the molecules is negligible as compared to the total volume.	3. The volume occupied by the molecules is not negligible as compared to the total volume.
4. There are no inter-molecular forces of attraction.	4. Either attractive or repulsive forces are present between the particles.
5. The molecules collide with each other elastically.	5. The molecules collide with each other inelastically.
6. It obeys the ideal gas equation, $PV = nRT$	6. It obey's the van der waal's equation $(P + \frac{a}{V^2})(V - b) = RT$
7. It is a hypothetical gas	7. It exists in nature around us.

### Mean free path :

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

### Mean free path :

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

It is denoted by  $\lambda$ . If  $\lambda_1, \lambda_2$  and  $\lambda_3$  are the free paths for a molecule of a gas, its mean free path equals,

$$\lambda = \frac{\lambda_1 + \lambda_2 + \lambda_3 + \dots + \lambda_n}{n}$$

$$\therefore \text{Mean free path - } \lambda = \frac{1}{\frac{1}{\lambda_1} + \frac{1}{\lambda_2} + \dots + \frac{1}{\lambda_n}}$$

### ■ Degree of freedom :

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

There are three kinds of degrees of freedom -

i) Translational.

ii) Rotational.

iii) Vibrational.

### Translational degree of freedom :

Translational degree of freedom arise from the ability of gas molecules to move freely in space. A molecule may move in the X, Y, Z direction of a cartesian coordinate system. When the centre of mass of a particle moves from its initial position to a new position, we say that the particle is having a translational motion along the X-axis, Y-axis and Z-axis. So, the translational motion of the molecule of gas has three degree of freedom.

## Rotational degree of freedom :

A molecule's rotational degrees of freedom represent the numbers of unique ways the molecule may rotate in space about its center of mass with a change in the molecule's orientation.

## Vibrational degree of freedom :

The atoms of a molecule can also vibrate and these vibrations of the atoms of a molecule slightly change the internuclear distance between the atoms of the molecule. The number of vibrational degrees of freedom of a molecule is determined by examining the number of unique ways the atoms within the molecule may move relative to one another, such as in bond stretches or bends.

(iv) Viscosity is a quantity that expresses the magnitude of the internal friction in a liquid. It is the measure of the fluid resistance of flow.

(v) The important facts about Brownian Movement:

(i) The motion of the particles are <sup>fast</sup> perpetual and continuous!

(ii) The smaller the particles the quicker are the motion.

(iii) They are independent of the stirring 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.

## Effect of Brownian motion :

1. Brownian motion causes the particles in a fluid to be in constant motion.

Avoid to be in constant motion.

2. This prevents particles from settling down, leading to the stability of colloidal solution.
3. A true solution can be distinguished from a colloid with the help of this motion.

## Intermolecular force :

An intermolecular force (secondary force) is the force that mediates interaction between molecules, including the electromagnetic forces of attraction or repulsion which acts between atoms and other types of neighbouring particles.

Intermolecular forces are weak relative to intramolecular forces.

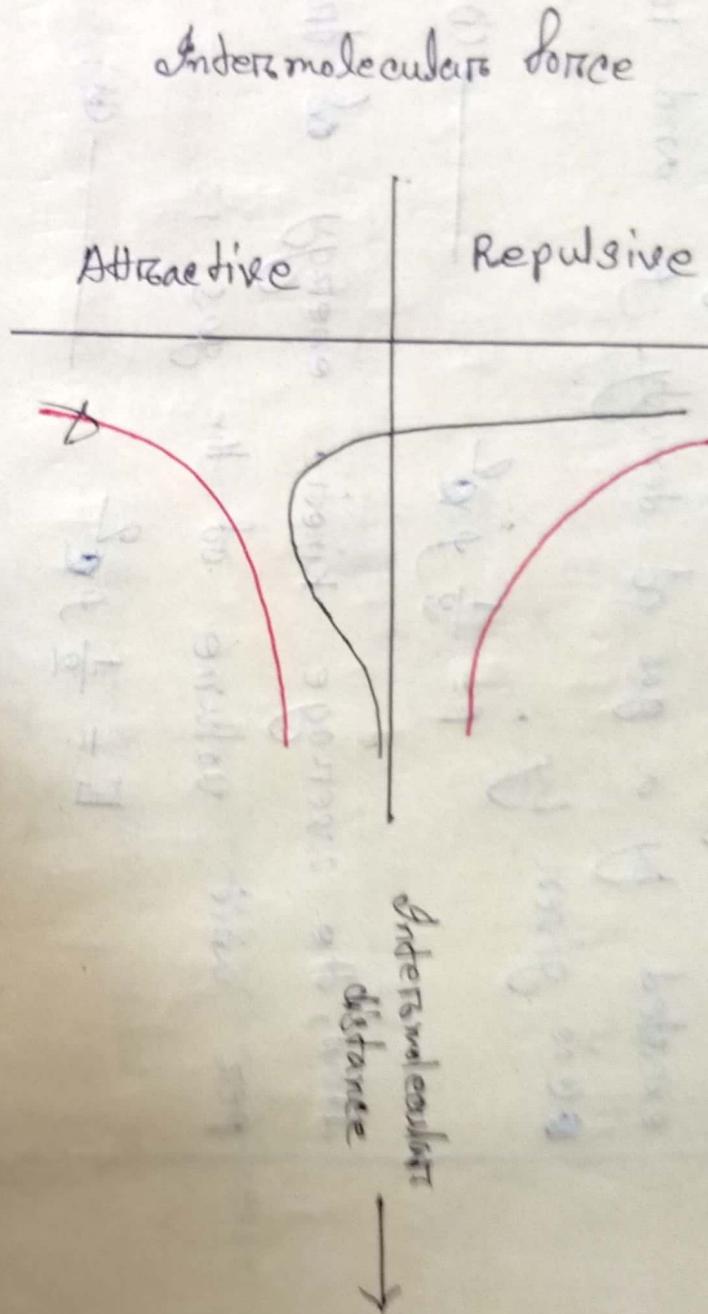
This intermolecular force is created due to two forces

1. Potential energy due to the reaction of surrounding molecules.
2. Thermal energy of molecules which is actually kinetic energy of molecules. This energy depends on the temperature of the object.

Intermolecular force changes with change in distance  $r$  between the molecules. The nature of this changes are shown in below. The greater the intermolecular distance i.e. the greater the ~~the intermolecular force~~ value of  $r$ , the intermolecular force become more attractive. And the smaller the intermolecular distance the more the repulsive the intermolecular force.

In the normal condition, the attraction and repulsion forces cancel each other out. So the net force is zero. In this case  $r = r_0$ .

Hence  $r_{\text{eq}} = \text{Equilibrium intermolecular distance}.$



$$10^{-2} \text{ N m}^{-1}$$
$$\frac{\text{N m}}{\text{J}}$$

**E** Kinetic energy per unit volume of a gas:

According to kinetic theory of gases, the pressure exerted by a gas of density  $\rho$  and r.m.s velocity  $v$  is given by,

$$\rho = \frac{4}{3} \rho v^2 \quad \text{(i)}$$

Now, the average kinetic energy of translation per unit volume of the gas is,

$$E = \frac{1}{2} \rho v^2 \quad \text{(ii)}$$

We get from (i)  $\therefore$  (ii),

$$\frac{\rho}{E} = \frac{\frac{4}{3} \rho v^2}{\frac{1}{2} \rho v^2}$$

$$\Rightarrow \frac{\rho}{E} = \frac{2}{3} \cancel{\rho v^2}$$

$$\therefore \rho = \frac{2}{3} \times E$$

$= \frac{2}{3} \times$  Average K.E per unit volume.

The kinetic interpretation of Temperature:

The pressure exerted by a perfect gas, according to the kinetic theory,

$$\begin{aligned} P &= \frac{1}{3} \rho c^2 \\ \Rightarrow P &= \frac{1}{3} \frac{M}{V} c^2 \\ \Rightarrow PV &= \frac{1}{3} M c^2 \end{aligned} \quad \text{--- (i)}$$

The quantity  $\frac{1}{3} M c^2$  is two-thirds the kinetic energy translation of the molecules. That is,

$$\frac{1}{3} M c^2 = \frac{2}{3} \left( \frac{1}{2} M c^2 \right)$$

Putting this value, in eqn (i),

$$PV = \frac{2}{3} \left( \frac{1}{2} M c^2 \right) \quad \text{--- (ii)}$$

The equation of state of an ideal gas is,

$$PV = RT \quad \text{--- (iii)}$$

From (ii) and (iii),

$$\frac{2}{3} \left( \frac{1}{2} M c^2 \right) = RT \quad \left| \begin{array}{l} \text{Considering 1 gram} \\ \text{molecule of the gas at} \\ \text{a temperature } T \\ \text{in Kelvin.} \end{array} \right.$$

Let the mass of each molecule be  $m$  and Avogadro's number be  $N_0$ .

$$\therefore M = m \times N_0$$

Therefore the equation (iv) becomes,

$$\begin{aligned} \frac{1}{2} m N_0 c^2 &= \frac{3}{2} R T \\ \Rightarrow \frac{1}{2} m c^2 &= \frac{3}{2} \frac{R}{N_0} T \\ \Rightarrow \frac{1}{2} m c^2 &= \frac{3}{2} k T \end{aligned} \quad (v)$$

Here  $k$  is called Boltzmann's constant.

Thus from eqn (v) the mean K.E. of a molecule is directly proportional to the absolute temperature of a gas. When the temperature of a gas is increased, the mean kinetic energy of molecule increases. When heat is withdrawn from a gas, the mean kinetic energy of the molecules decreases. Thus, at absolute zero temperature the kinetic energy should be zero. It means at absolute state of rest and have no kinetic energy.

But before the absolute zero temperature is reached, all gases change their state to liquids and solids.

As from eqn (v) we get,

$$\sigma^2 \propto T$$

It means that the root mean square velocity of the molecules is also directly proportional to the square root of the absolute temperature.

### Principle of equipartition of energy:

Statement:

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

Where,  $k$  is Boltzmann constant.

### Explanation

According to kinetic theory of gases, the mean kinetic energy of a gas molecule at a temperature  $T$  is given by,  ~~$\frac{1}{2}mc^2 = \frac{3}{2}kT$~~

$$\frac{1}{2}mc^2 = \frac{3}{2}kT \quad \text{--- (i)}$$

$$\text{But, } c^2 = u^2 + v^2 + w^2$$

As,  $x$ ,  $y$  and  $z$  are all equivalent, mean square velocities along three axes are equal.

$$u^2 = v^2 = w^2 \quad \text{Hence, } \cancel{u^2 = v^2 = w^2} \cancel{\frac{1}{3}c^2}$$

$$\text{Hence, } u^2 = v^2 = w^2 = \frac{1}{3}c^2 \quad \left| \begin{array}{l} \text{Therefore,} \\ c^2 = 3u^2 = 3v^2 = 3w^2 \end{array} \right.$$

$$\text{Or, } \frac{1}{2}m u^2 = \frac{1}{2}m v^2 = \frac{1}{2}m w^2$$

$$\therefore \frac{1}{2}m c^2 = 3\left(\frac{1}{2}mu^2\right) = 3\left(\frac{1}{2}mv^2\right) = 3\left(\frac{1}{2}mw^2\right)$$

~~$\Rightarrow \frac{3}{2}mc^2 = 3\left(\frac{1}{2}mu^2\right) = 3\left(\frac{1}{2}mv^2\right) = 3\left(\frac{1}{2}mw^2\right)$~~

$$\Rightarrow \frac{3}{2}kT = 3\left(\frac{1}{2}mu^2\right) = 3\left(\frac{1}{2}mv^2\right) = 3\left(\frac{1}{2}mw^2\right)$$

From above relation, we can write,

$$\frac{3}{2} kT = 3 \left( \frac{1}{2} mu^2 \right)$$

$$\Rightarrow \frac{1}{2} kT = \frac{1}{2} mu^2$$

$$\Rightarrow \frac{1}{2} mu^2 = \frac{1}{2} kT$$

Similarly,

$$\frac{1}{2} mv^2 = \frac{1}{2} kT$$

$$\text{and, } \frac{1}{2} mw^2 = \frac{1}{2} kT$$

Therefore, the average kinetic energy associated with each degree of freedom =  $\frac{1}{2} kT$ .

Thus, the energy associated with each degree of freedom (whether translatory or Rotational) is  $\frac{1}{2} kT$ .

This represents the theorem of equipartition of energy.

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 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

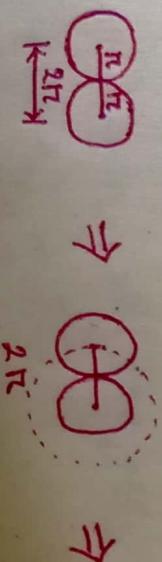
faro apart, it is true. But at high pressure, when the molecules are more closer, there exist force of attraction among the gas molecules. A molecules within the gases will experience a net force of attraction from all sides. Hence the net force will be zero. The molecules impinge on the wall of the container will experience a net inward force. Hence the momentum will be reduced. The 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,

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

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



Now surrounding a molecule, we consider a sphere of radius,  $r_2$  which will not be accessible to other molecules. Such a sphere is called sphere of exclusion and the volume occupied by the sphere,

$$S = \frac{4}{3} \pi (r_2)^3 = \frac{4}{3} \pi r_2^3 \delta = 8\pi$$

Now, we assume that initially the container was empty and molecules were allowed to enter one by one. Thus, the volume available to ~~the~~ molecule  $\rightarrow$

thus,

The volume available to 1st molecule =  $V$

$$V - S = V - 8\pi = V - 8$$

2nd  $\sim$

3rd  $\sim$

$\vdots$

$\dots$

$\dots$

$\dots$

$$\text{The volume } V - N \cdot S = V - (N-1)S$$

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

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

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

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

$$= V - \frac{3N}{2} + \frac{s}{2}$$

$\approx V - \frac{3N}{2}$  [ $\frac{s}{2}$  is neglected]

$$= V - \frac{3N}{2}$$

$$= V - 4Nr$$

If there are 'n' mole of gas,

$$N = nN_A \quad [N_A \Rightarrow \text{Avogadro's number}]$$

Average space available to each molecule will be,

$$V - 4nN_A r = V - nb \quad [\text{where } b = 4N_A r]$$

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

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

For one mole of the gas,

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

Pressure correction:

Due to the force attraction between the 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 from the back. The two numbers are proportional to the square of the density of molecule within the container, i.e.,

Reduction of pressure  $\propto \rho^2$

$$\propto \frac{1}{V^2} \quad \left[ \because \rho = \frac{m}{V} \right]$$

$m$  is constant

$\therefore$  The volume correction  $\propto \frac{1}{V^2}$

$\therefore$  The pressure correction  $= \left( P + \frac{a}{V^2} \right)$

After volume correction, the equation of state will be,

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

$$\Rightarrow P = \frac{RT}{V-b} \quad [\text{when reduction pressure is not considered}]$$
$$\Rightarrow P = \frac{RT}{V-b} - \frac{a}{V^2} \quad [\text{when reduction of pressure is considered}]$$

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

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

For n mole of gas,  $(V-nb)$

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

This equation is called the van der waals equation of state for real gas.

Physical significance of constant a and b in van der waals equation?

Q) Physical significance of constant a and b in van der waals equation?

The van der waal's equation of state for real gas is,

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

This equation can be reduced to an ideal gas equation, if -

- ① The size of the gas molecules is negligible, hence the volume correction will be zero, i.e.  $nb = 0$

- ② There will be no force of attraction among the gas molecules, hence the pressure correction will be zero,

$$\text{i.e., } \frac{a}{V^2} = 0$$

Then the equation state of the gas will be,

$$PV = nRT$$

This is the equation of state of an ideal gas.

The critical constant

\* Critical temperature ( $T_c$ ):

It may be defined as that temperature above which the gas can't be liquefied however

high pressure we may apply on the gas.

For example, the critical temperature of  $\text{O}_2$  is 304.2 K.

\* Critical pressure: The minimum pressure required to liquidify the gas at the critical temperature is called the critical pressure.

\* Critical volume: The volume occupied by one mole of the gas at critical temperature and pressure is called critical volume.

At the critical temperature and the corresponding values of pressure and volume at the critical points are called the critical constant. ( $T_c$ ,  $P_c$ ,  $V_c$ )

The critical constant phenomena and the Vander Waal's

Equation :

For 1 mole of the gas, the Vander Waal's equation is,

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

On simplification, it gives,

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

$$\Rightarrow (PV^2 + a)(V - b) = RT V^2$$

$$\Rightarrow PV^3 - PV^2 b + aV - ab = RT V^2$$

$$\Rightarrow V^3 - V^2 b - \frac{RT}{P} V^2 + \frac{a}{P} V - \frac{ab}{P} = 0$$

$$\Rightarrow V^3 - \left( b + \frac{RT}{P} \right) V^2 + \frac{a}{P} V - \frac{ab}{P} = 0 \quad \text{(ii)}$$

At the critical temperature, all the roots

become equal for a particular value of pressure,

P. Now representing critical volume by  $V_c$ , we should have,

$$V = V_c$$

$$\Rightarrow V - V_c = 0$$

$$\Rightarrow (V - V_c)^3 = 0$$

$$\Rightarrow V^3 - 3V_c V^2 + 3V_c^2 V - V_c^3 = 0 \quad \text{--- (iii)}$$

at the critical point  $P \rightarrow P_c$  or  $T \rightarrow T_c$  the equation (ii) becomes -

$$V^3 - \left(b + \frac{R T_c}{P_c}\right)V^2 + \frac{a}{P_c}V - \frac{ab}{P_c} = 0 \quad \text{--- (iv)}$$

at critical point the eqn (iii) and (iv) must be identical. Hence the coefficient of similar power of  $V$  must be equal in both the equation.

Therefore,

$$3V_c^2 = b + \frac{R T_c}{P_c} \quad \text{--- (v)}$$

and,

$$3V_c^2 = \frac{a}{P_c} \quad \text{--- (vi)}$$

$$\text{and also, } V_c^3 = \frac{ab}{P_c} \quad \text{--- (vii)}$$

Dividing equation (vii) by (vi) we get,

$$\frac{1}{3}V_c = b$$

$$\Rightarrow V_c = 3b \quad \text{--- (viii)}$$

Putting the value of  $V_c$  in eqn (vi), we get,

$$3(3b)^2 = \frac{a}{P_c} \quad (\text{vii})$$
$$\Rightarrow P_c = \frac{a}{27b^2}$$

Putting the value of  $P_c$  and  $V_c$  in eqn (v),

$$3 \times (3b) = b + \frac{RT_c}{27b^2}$$

$$\Rightarrow 9b = b + \frac{27b^2 \cdot RT_c}{a}$$

$$\Rightarrow 8b = \frac{b}{a} + \frac{27b^2 \cdot RT_c}{a}$$

$$\Rightarrow ab =$$

$$\Rightarrow ab = \frac{27b^2 \cdot RT_c}{a}$$

$$\Rightarrow T_c = \frac{8a}{27b^2 R} \quad (\text{viii})$$

Thus,

$$\text{the critical temperature, } T_c = \frac{8a}{27b^2 R} \quad \text{and}$$
$$\text{the critical pressure, } P_c = \frac{a}{27b^2}$$

and the critical volume,  $V_c = 3b$

Relation between  $P_e$ ,  $V_e$  and  $T_o$  :-

Here,

$$V_e = 3b$$

$$\Rightarrow b = \frac{V_e}{3} \quad \dots \quad (i)$$

And,

$$P_e = \frac{a}{2\pi b^2} = \frac{a}{2\pi \left(\frac{V_e}{3}\right)^2} \quad [Putting the value of b]$$

$$\Rightarrow P_e = \frac{a}{3 V_e^2}$$

$$\Rightarrow a = 3 P_e V_e^2 \quad \dots \quad (ii)$$

also,

$$T_c = \frac{8a}{2\pi b R}$$

$$\Rightarrow T_c = \frac{8 \times 3 P_e V_e^2}{2\pi \times \frac{V_e}{3} \times R} \quad [Putting the value of a and b]$$

$$\Rightarrow T_c = \frac{8}{3} \frac{P_e V_e}{R}$$

$$\Rightarrow P_e V_e = \frac{3}{8} R T_c$$

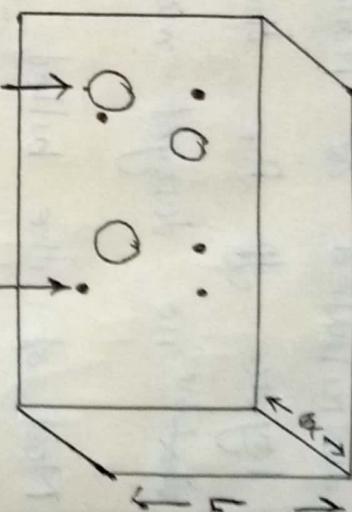
The limitation of van der waal's equation:

At very high temperature the van der waal's equation is inadequate (approx) for calculating the properties of gases. The limitation are given below :

1. Van der waal's theory assumes  $a, b$  to be constant. But the value of  $a$  is found to be depend on the temperature. At very high temperatures, its tend to zero.
2. According to theory,  $V_c = 3b$  but it is found to depend on the nature of the gas. Experimentally, it is found that  $V_c \approx 2b$
3. The theoretical value of critical coefficient  $\frac{R T_c}{P_c V_c}$  is 2.667 for all gases. However, it varies from gas to gas with an average value of 3.7 for most of the gases. This constant appears to depend on the molecular structure of the gas.

Mean free path :

Let us consider, a thin layer of gas of dimensions  $L_x, L_y$ , and  $4\pi$  as shown in fig-1.

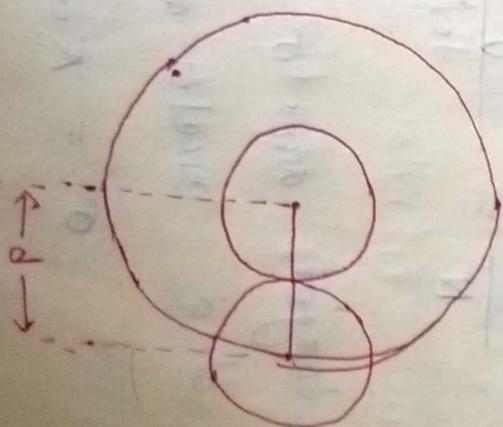


Let us refer to one of the colliding molecule as the target molecule and to others as the bullet molecule. The collision occurs whenever the distance between the centres of the molecules equal to molecular diameter,  $d$  as in fig-2.

Since it's only the centre to centre distance that determines a collision it does not matter whether what ever 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 layer 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 target molecule can hide behind another.

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

The ratio of the number of collisions ~~and~~ the total number of bullet molecules,  $N$ , is equal to the area presented by the target molecules to the total area present 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  $d$ .

$$\sigma = \pi d^2$$

The area is called microscopic cross section of one molecule.

If there are  $n$  largered molecule per unit volume then the total danger area of the layer is,  $\underline{l^2}$ ,

$$\text{So, } \frac{\Delta N}{N} = \frac{n \sigma L^4 x}{l^2} = n \sigma \underline{x} = \underline{\underline{\sigma}}$$

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 meter per cubic meter is the unit of macroscopic collision cross section is a reciprocal length, not an area. Each of the  $\Delta N$  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

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

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

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

$$if, N = N_0 e^{n\sigma x} = 0$$

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

$$\Rightarrow \ln\left(\frac{N}{N_0}\right) = -n\sigma x$$

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

This is known as the survival equation.

Putting this value in equation (2)

$$dN = N_0 n\sigma e^{-n\sigma x} dr$$

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,  $\lambda$

We multiply  $\lambda$  by the numbers of particles  $dN$  that travels the distance  $x$  before colliding, sum over all value of  $x$ , and divide by the total number  $N$ .

$$\lambda = \frac{\int x dN}{N_0}$$

$$= \frac{\int x N_0 n\sigma e^{-n\sigma x} dx}{N_0}$$

$$\therefore \lambda = n \sigma \bar{v} e^{-n\sigma \bar{v}} \cdot d\sigma$$

$\therefore \lambda = n \sigma \bar{v} e^{-n\sigma \bar{v}}$ .  
Replace in the sum by an integral, we have,

$$\lambda = \int_0^\infty n \sigma \bar{v} e^{-n\sigma \bar{v}} d\sigma$$

$$= n \sigma \bar{v} \frac{1}{n^2 \sigma^2}$$

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

This 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 the 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 classing, Mean free path,

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

In Maxwell's, Mean free path,

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

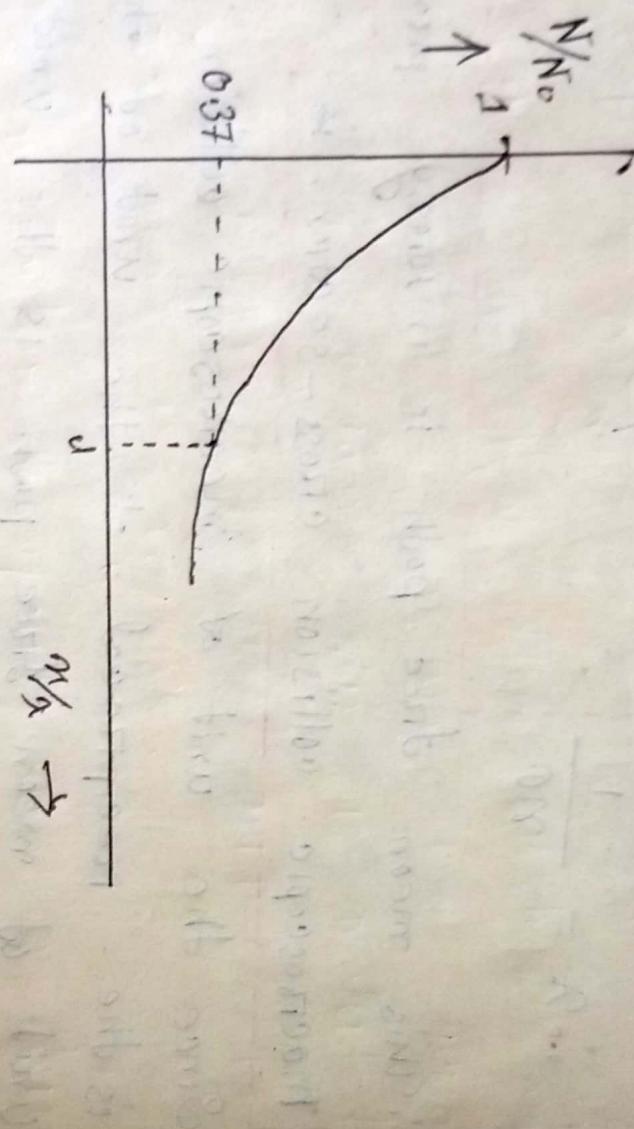
The graph of the survival equation :

The survival equation is,

$$N = N_0 e^{-n\sigma \alpha}$$

In terms of mean free path  $\alpha$  it becomes,

$$N = N_0 e^{-\frac{\alpha}{\lambda}}$$



## Thermal conductivity:

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

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

$$[\text{W K}^{-1} \text{m}^{-1}]$$

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.

### Explanation:

$$\text{the thermal conductivity } \kappa = \frac{T_2 - T_1}{A \cdot S}$$

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

fig-1

is a temperature gradient rather than a velocity gradient in the gas.

If  $\frac{dT}{dy}$  is the temperature gradient normal to the  $\sigma$  surface within the gas, the thermal conductivity  $\kappa$  is defined by the equation,

$$H = -\kappa \frac{dT}{dy} \quad (i)$$

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  $\frac{dT}{dy}$  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  $c_v T$ .

$$\therefore U = c_v T$$

The average kinetic energy of a single molecule, therefore is,

$$U^* = \frac{C_V}{N_A} T = C_V^* T$$

$$C_V^* = \frac{C_V}{N_A}$$

$\geq$  Molecular heat capacity.

We assume as before that each molecule

crossing the surface made its last collision at a distance  $2\frac{2}{3} r$  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 &  $\sigma$  the kinetic energy of a molecule at a distance

$2\frac{2}{3} r$  below the surface is -

$$C_V^* \sigma = C_V^* \left( T_0 - \frac{2}{3} \lambda \frac{dT}{dy} \right)$$

The energy transferred in an upward direction, per unit area and per unit time, is the product of this quantity and the molecular flux of,

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

Here,

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

$$\dot{H}_1 = \frac{1}{4} n \bar{v} c_v^* \left( T_0 + \frac{2}{3} \eta \frac{dT}{dy} \right)$$

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

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

and by comparison with equation ①, we get the thermal conductivity

$$\kappa = \frac{1}{3} n \bar{v} c_v^* \lambda \\ = \frac{1}{3} \frac{\bar{v} c_v^*}{\sigma} \left[ \because n \lambda = \frac{1}{\sigma} \right]$$

thus the thermal conductivity, like the viscosity should be independent of density.

The ratio of thermal conductivity to viscosity is,

$$\frac{\kappa}{\eta} = \frac{c_v^*}{m} = \frac{c_v}{m N_A} = \frac{\alpha}{M}$$

$$\text{Thus, } \frac{\kappa M}{\eta c_v} = 1$$

## Diffusion:

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

(Net / Diffusion)

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

## Self - Diffusion:

The diffusion of molecules of a single species into others of the same species, known as self-diffusion.

### Explanation:-

Let us consider an imagined horizontal surface  $S-S'$  within the vessel of Fig-1.

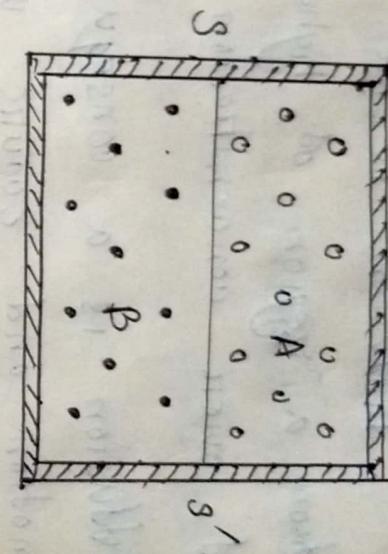
At some stage of

diffusion process.

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 is then greater than the upward flux.



If  $\Gamma$  represents the net flux of staggered molecules across the surface, per unit time and per unit area, the coefficient of self-diffusion  $D$  is defined by the equation,

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

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

We assume as before that each molecule makes its last collision before crossing at a perpendicular distance  $2\sqrt{3}$  below the surface

$$\text{is, } n^* = n_0^* - \frac{2}{3} \lambda \frac{dn^*}{dy}$$

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

$$\Gamma \uparrow = \frac{1}{4} \nabla \left( n_0^* - \frac{2}{3} \lambda \frac{dn^*}{dy} \right)$$

In the same way, the downward flux is,  
 $\Gamma_L = \frac{1}{4} \nabla \left( n_0^* + \frac{2}{3} \lambda \frac{dn^*}{dy} \right)$   
the net flux  $\Gamma$  is the difference between  
these, so,

$$\Gamma = -\frac{1}{3} \nabla \lambda \frac{dn^*}{dy}$$

Comparison with equation (i) shows that,

$$D = \frac{1}{3} \bar{V} \lambda = \frac{1}{3} \frac{\bar{V}}{n_0}$$

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

### (iii) Viscosity:

The property of fluid by virtue of which it opposes relative motion between its different layers is known as viscosity.

Let us consider a particle of two large plates separated by a layers of gas of thickness  $L$ . Because of the viscosity of the gas, a force

$F$  must be exerted on the upper plate to drag it to the right at constant velocity relative to the lower, stationary plate. The molecule

in the layer of  $\Delta y$  of the gas,  $\Delta y$  is defined by

the gas have a

forward velocity

component  $u$  which

increases uniformly

with distance  $y$  above

the lower lower plate.

The coefficient of viscosity gradient at right angles to the plate.

$$\frac{F}{A} = \eta \frac{du}{dy}$$

Here,  $\frac{du}{dy}$  = velocity gradient

The dotted line  $s-s'$  represents an imagined surface within the gas at an arbitrary height  $y$  above the lower plate. Because of their random motion there is a molecular flux  $\phi$  across the dotted surface, both from above and from below.

Molecules arriving at the surface will on the average have started their

last free paths before reaching the surface

at a distance  $\lambda$  away from the surface. The

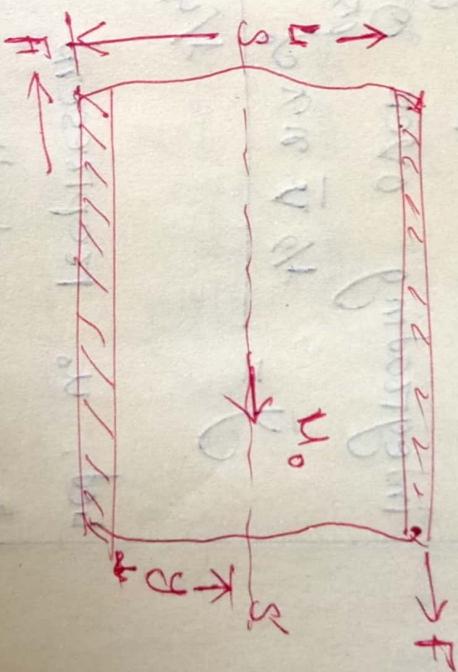
perpendicular distance  $y$

from the surface, for any molecules is

$y = \lambda \cos \theta$ . The average value of  $y$  is  $\bar{y}$

is found by multiplying  $\lambda \cos \theta$  by the flux

$\Delta \phi$ , summing over all values of  $\theta$ , and dividing



by the total flux  $\phi$ , we get,

$$\Delta\phi_0 = \frac{1}{2} \bar{v} n \sin\theta \cos\theta \Delta\theta$$

and we know,

$$\phi = \frac{1}{4} \bar{v} n$$

therefore replacing  $\Delta\theta$  with  $d\theta$  and integrating over  $\theta$  from zero to  $\pi/2$ .

$$\bar{\phi} = \frac{1/2 \bar{v} n \lambda c_0}{1/4 \bar{v} n \lambda} \int_{\pi/2}^{\pi/2} \sin\theta \cos^2\theta d\theta = \frac{2}{3} \lambda$$

Let,  $u_0$  represent the forward velocity of the gas at the  $s-s'$ . At a distance  $\frac{2}{3}\lambda$  above the surface, the forward velocity,

$$u = u_0 + \frac{2}{3} \lambda \frac{du}{dy}$$

Since the forward velocity gradient  $\frac{du}{dy}$  can be considered constant over a distance of the order of a free path. The forward momentum of a molecule with the velocity is,

$$mu = m(u_0 + \frac{2}{3} \lambda \frac{du}{dy})$$

The momentum  $\vec{G}_1 \downarrow$  carried across the surface per unit time and per unit area by the molecules crossing from above,

$$\vec{G}_1 \downarrow = \frac{1}{q} nm \bar{v} \left( u_0 + \frac{2}{3} \lambda \frac{du}{dy} \right)$$

Similarly the momentum  $\vec{G}_1 \uparrow$  carried across the surface per unit time and per unit area by the molecules crossing from below,

$$\vec{G}_1 \uparrow = \frac{1}{q} nm \bar{v} \left( u_0 - \frac{2}{3} \lambda \frac{du}{dy} \right)$$

The net rate of transport of momentum,

$$\vec{G} = \vec{G}_1 \downarrow - \vec{G}_1 \uparrow$$

$$\vec{G} = \frac{1}{3} nm \bar{v} \lambda \frac{du}{dy}$$

Therefore,

$$n = \frac{1}{3} n_m \bar{v} \lambda$$

$\therefore \lambda = \frac{1}{n_m}$