Chapter –1
Kinetic Theory of Gases

By

Dr V.D.Kulkarni

HUTATMA RAJGURU MAHAVIDYALAYA

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Introduction

Solids :- The molecules are closely packed , Intermolecular Force is large. Cannot move from one place to another.Definite shape and volume.

Liquids:- Intermolecular Force is small. Can move from one place to another in liquid.Definite volume but not the shape.

Gases:- Intermolecular Force is small. Can move from one place to another. Not definite volume and shape.

Assumptions of kinetic theory of gases

- A gas consist a large no. of extremely small molecules.At NTP, 1cc = 2* 10 19 molecules
- Molecules are rigid , perfectly elastic, spherical identical w.r.t. mass and volume etc.
- Size of individual gas molecule < volume of gas
- Negligible force of attraction or repulsion between gas Molecules.
- Molecules move in all possible directions.
- Molecules collide with another. Such collision are perfectly elastic. (no loss of KE)
- Time of impact is negligible w r t time interval between successive collisions.
- Between successive collisions, Molecule travels in straight line

- The distance travelled by a molecule between two successive collisions is free path
- The average distance travelled by a molecule between successive collisions is mean free path
- Molecules are constantly moving. No.of molecules Per unit volume of gas =constant.

All assumptions obeyed by the gas is called as the ideal or perfect gas.

On the basis of kinetic theory of gases, ①
Pressure is

$$P = \frac{1}{3}\frac{Nmc^2}{V} \quad -① \quad = \frac{1}{3}\frac{M}{V}c^2 = \frac{1}{3}\rho c^2$$

$N \rightarrow$ Total no. of gas molecules in vol. V.
$m \rightarrow$ mass of each gas molecule
$M \rightarrow$ Total mass
$\rho \rightarrow$ density of gas
$c \rightarrow$ RMS velo.

For perfect or ideal gas eqn $\rightarrow$

$$PV = RT \quad -②$$

From ① & ②

$$\frac{1}{3}Nmc^2 = RT \quad -③ \Rightarrow c^2 = \frac{3RT}{Nm}$$

Since $Nm = M$

$$\Rightarrow c^2 = \frac{3RT}{m} \rightarrow c = \sqrt{\frac{3RT}{m}}$$

$$\Rightarrow \boxed{c \propto \sqrt{T}}$$

From eqn ③

$$\frac{1}{3}Nmc^2 = RT$$

$$\Rightarrow \frac{2}{3}N\left(\frac{1}{2}mc^2\right) = RT$$

$$\Rightarrow \frac{1}{2}mc^2 = \frac{3}{2}\frac{RT}{N} \Rightarrow K.E. = \frac{3}{2}\frac{R}{N}$$

$$\boxed{K.E. \propto Temp(T)}$$

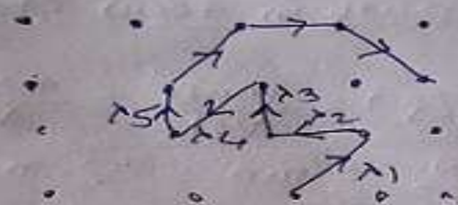
$\frac{R}{N}$ = const (k_B) = Boltzmann const

$$K.E = \frac{1}{2} m\bar{c}^2 = \bar{E} = \frac{3}{2} k_B T$$

where $k_B = 1.38 \times 10^{-23}\ J K^{-1}$

At $T = 0$, $\bar{E} = 0$

Meanfree path :- molecules moves with velocity $= 10^3$ m/s



The distance travelled by a molecule between its two successive collisions is called free path of the molecule.

Let $\lambda_1, \lambda_2, \lambda_3 \cdots \lambda_N \cdots$ free paths during N successive collisions $\therefore$ meanfree path is

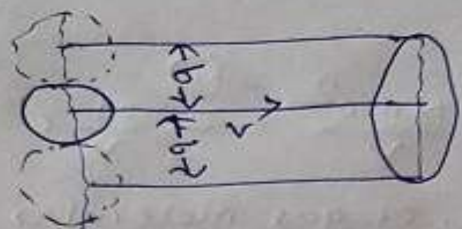
$$\lambda = \frac{\lambda_1 + \lambda_2 + \lambda_3 + \cdots + \lambda_N}{N}$$

λ = $\frac{\text{Total distance travelled by a molecule in N collisions (S)}}{\text{No. of collision (N)}}$

= average distance travelled by a molecule between two successive collisions

Calculation of mean free path :—

③



n = No. of molecules per unit vol. of gas

In one second, molecule will travell a distance (V) ∴ it will collide with all molecules whose centres lie in a cylinder of radius (σ) & length V

$$\therefore \text{vol. of cylinder} = \pi \sigma^2 V$$

∴ mean free path (λ) is

$$\lambda = \frac{\text{Distance travelled in one second}}{\text{No. of collision in one sec.}}$$

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

ccording to maxwell's velo. distribution

$$\boxed{\lambda = \frac{1}{\sqrt{2}\, \pi \sigma^2 n}}$$

① mean free path in terms of pressure & temp. (4)

$P = nkT \Rightarrow n = \frac{P}{kT}$

∴ mean free path :-

$$\lambda = \frac{1}{\sqrt{2}\pi\sigma^2 n} = \frac{1}{\sqrt{2}\pi\sigma^2 P/kT}$$

$$\lambda = \frac{kT}{\sqrt{2}\pi\sigma^2 P}$$

$\boxed{\lambda \propto T}$ & $\boxed{\lambda \propto \frac{1}{P}}$

② mean free path in terms of density of gas :-

$$\text{Density}(\rho) = \frac{\text{mass}}{\text{vol.}} = \frac{mN}{V}$$

$\rho = \frac{mN}{V} = mn \quad \because n = N/V$

$\Rightarrow n = \rho/m.$

$$\Rightarrow \lambda = \frac{1}{\sqrt{2}\pi\sigma^2 n} = \frac{1}{\sqrt{2}\pi\sigma^2 \rho}m.$$

$$\lambda = \frac{m}{\sqrt{2}\pi\sigma^2\rho}$$

$$\boxed{\lambda \propto \frac{1}{\rho}}$$

Transport phenomenon :-

A gas molecule ⟶ mass, momentum, Energy

A gas molecules moves from one place to another

The velocity of gas molecules increases with temp.

During collision, momentum & energy conserved

But certain amount of momentum/energy transferred during collision.

(1) Transport of momentum → velo. of mass motion is not same, viscosity.

(2) Transport of energy →

Temp. is not same

Thermal energy from higher temp. to lower temp. ⇒ Thermal conduction.

Thermal conductivity due to transport of energy

(3) Molecular density of gas is not same.

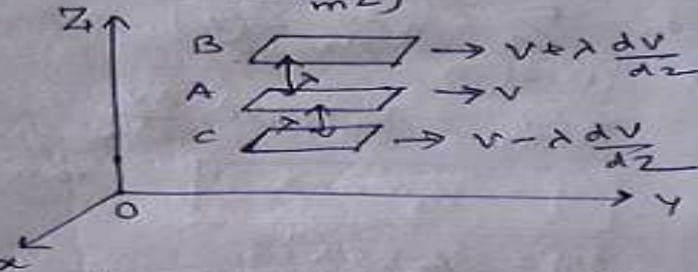
molecules diffused from higher conc. to lower conc. region ⇒ diffusion

The phenomenon of diffusion of a gas is due to transport of mass.

Coefficient of viscosity (η) of gases :- (6)

coeff of viscosity $\Rightarrow$ viscous force per unit area per area per unit velo. gradient.

$\left(\frac{Ns}{m^2}\right)$



Let n — no. of molecules per unit vol.

$m \rightarrow$ mass of each gas molecule

$c \rightarrow$ rms velo.

No. of molecules from layer B crossing unit area of A in a unit time in downward direction $= \frac{1}{6} nc$

mass $= \frac{1}{6} mnc$

Total momentum $= \frac{mnc}{6}\left(v+\lambda \frac{dv}{dz}\right)$

lly total momentum in upward direction from layer C crossing layer A

$$= \frac{mnc}{6}\left(v-\lambda \frac{dv}{dz}\right)$$

$\therefore$ net momentum lost by B & gain by C per unit area per unit time

$$= \frac{mnc}{6}\left(v+\lambda \frac{dv}{dz}\right) - \frac{mnc}{6}\left(v-\lambda \frac{dv}{dz}\right)$$

$$= \frac{1}{3} mnc\lambda \frac{dv}{dz} \quad \text{(1)}$$

Viscous force

$$F \propto A \frac{dv}{dz}$$

(7)

$$F = \eta A \frac{dv}{dz} \quad -(2)$$

$$f = F/A = \eta \frac{dv}{dz} \quad -(2)$$

Equate (1) & (2)

$$\eta \frac{dv}{dz} = \frac{1}{3} m n c \lambda \frac{dv}{dz}$$

$$\boxed{\eta = \frac{1}{3} m n c \lambda}$$ $mn = \rho$ = density

$$\boxed{\eta = \frac{1}{3} \rho c \lambda}$$

(1) $c \propto \sqrt{T} \Rightarrow \eta \propto \sqrt{T}$

(2) $\rho \propto P$ but $\lambda \propto \frac{1}{P} \Rightarrow \rho \propto \frac{1}{\lambda}$

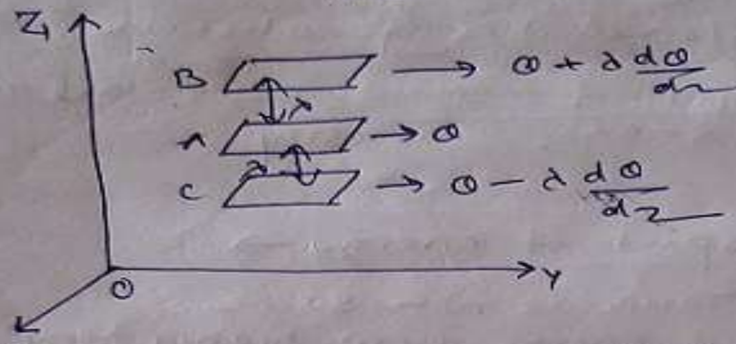
$$\Rightarrow \boxed{\rho \lambda = \text{const}}$$

As temp = const then η does not depend upon Press. (P).

Thermal conductivity of gases. (8)

Coeff. of thermal conductivity → quantity of heat energy in steady state thro' unit area per unit area per unit time per unit temp. gradient

$$Q = K \frac{d\theta}{dz} \quad \text{—(1)}$$



No. of molecules in downward dir^n = $\frac{1}{6} nc$

mass = $\frac{1}{6} mnc$

Total heat energy from B to C thro' A = $\frac{mnc}{6} C_v \left(\theta + \lambda \frac{d\theta}{dz}\right)$

Illy

total heat energy from C to B thro' A = $\frac{mnc}{6} C_v \left(\theta - \lambda \frac{d\theta}{dz}\right)$

net heat energy (Q) transferred per unit area per unit time in downward dir^n

$$Q = \frac{mnc}{6} c_v \left(\theta + \lambda \frac{d\theta}{dz}\right) - \frac{mnc}{6} c_v \left(\theta - \lambda \frac{d\theta}{dz}\right)$$

$$= \frac{1}{3} mnc\, c_v \lambda \frac{d\theta}{dz} \quad \text{—(2)}$$

① = ②

$$k \frac{d\theta}{dz} = \frac{1}{3} m n c \, c_v \lambda \frac{d\theta}{dz}$$

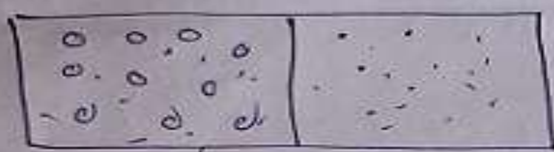
$$k = \frac{1}{3} m n c \, c_v \lambda \qquad \because mn = \rho$$

$$k = \frac{1}{3} \rho c \, c_v \lambda$$

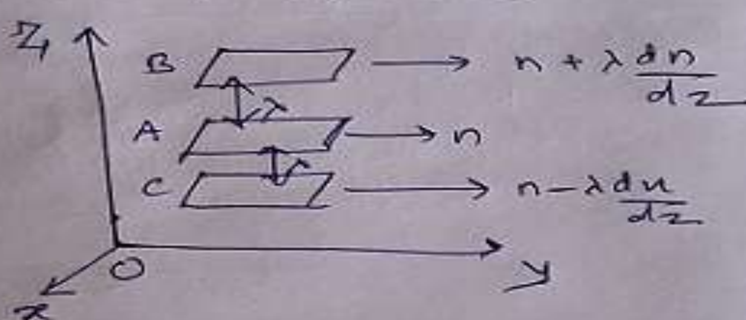
$$k = \left(\frac{1}{3} \rho c \lambda\right) c_v$$

$$\boxed{k = \eta \, c_v}$$

Transport of Matter (Diffusion) :-



O_2 (oxygen) & Hydrogen (H_2)



Let n be molecular concentration along horizontal plane A & $\frac{dn}{dz}$ — rate of change of conc. with distance in upward direction $\perp^{ar}$ to plane A along Z-axis

(10)

conc^n at B $= n + \lambda \frac{dn}{dz}$

conc. at C $= n - \lambda \frac{dn}{dz}$

No. of molecules coming from B & crossing the plane A in downward per unit area per unit time $= \frac{1}{6} c \left(n + \lambda \frac{dn}{dz}\right)$

No. of molecules from C & crossing A upward per unit area per unit time $= \frac{1}{6} c \left(n - \lambda \frac{dn}{dz}\right)$

Net no. of molecules crossing plane A per unit area per second in downward dir^n

$$= \frac{1}{6} c \left(n + \lambda \frac{dn}{dz}\right) - \frac{1}{6} c \left(n - \lambda \frac{dn}{dz}\right)$$

$$= \frac{1}{3} c \lambda \frac{dn}{dz}$$

Coeff. of diffusion (D) $= \dfrac{\text{No. of molecules crossing per unit area in one sec.}}{\text{Rate of change of conc. with dist}}$

$$D = \frac{\frac{1}{3} c \lambda \frac{dn}{dz}}{dn/dz} = \frac{1}{3} c \lambda$$

Reference: A Text book of Thermodynamics and Statistical Physics by V.K.Dhas, Dr.S.D.Aghav, Dr.P.S. Tambade, B.M.Laware : Nirali Prakashan, Pune (Second edition) November-2017