COURSE TITLE : **PHYSICAL CHEMISTRY I**

COURSE CODE : **15U5CRCHE07**

UNIT 1 : **GASEOUS STATE**

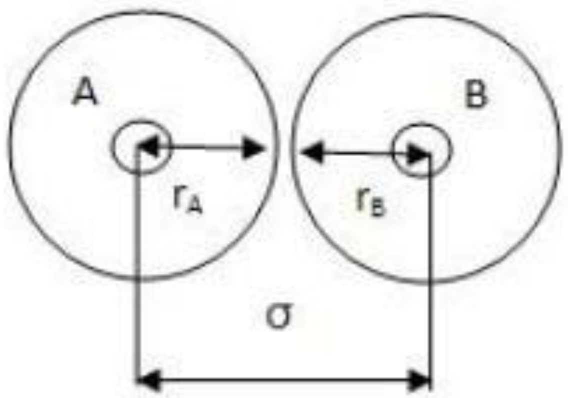
SESSION 8: Collision Parameters

Collision Diameter, σ

- The distance between the centres of two gas molecules at the point of closest approach to each other is called the collision diameter.

- Two molecules come within a distance of σ - *Collision occurs*

- H_2 - 2.74 A^0 N_2 - 3.75 A^0 O_2 - 3.61 A^0



$\sigma = r_A + r_B$

Collision Number, Z

- The average number of collisions suffered by a single molecule per unit time per unit volume of a gas is called collision number.

$$\boxed{Z = \sqrt{2}\pi v \sigma^2 \rho}$$

$$\boxed{\rho = \frac{N}{V}}$$

Number Density (ρ) – Number of Gas Molecules per Unit Volume

Unit of Z = $ms^{-1} \times m^2 \times m^{-3}$ = $\boldsymbol{s^{-1}}$

Collision Frequency, Z_{11}

- The total number of collisions between the molecules of a gas **per unit time** ***per unit volume*** is called collision frequency.

Collision Frequency, Z_{11} = Collision Number $\times$ Total Number of molecules

Collision Frequency, Z_{11} $= \sqrt{2}\pi\nu\sigma^2\rho \times \rho$

Considering collision between like molecules

$$\boxed{\text{Collision Frequency, } Z_{11} = \tfrac{1}{2} \times \sqrt{2}\pi\nu\sigma^2\rho \times \rho = \frac{1}{\sqrt{2}}\pi\nu\sigma^2\rho^2}$$

Unit of Z_{11} = $s^{-1}\ m^{-3}$

The number of bimolecular collisions in a gas at ordinary T and P – 10^{34} $s^{-1}\ m^{-3}$

Influence of T and P

$$Z_{11} = \frac{1}{\sqrt{2}}\pi\nu\sigma^2\rho^2$$

$$\boxed{Z_{11} = 2\sigma^2\rho^2\sqrt{\frac{\pi RT}{M}}}$$

$\boxed{Z_{11} \propto \sqrt{T}}$ at a given P

$\boxed{Z_{11} \propto \rho^2}$ at a given T

$\boxed{Z_{11} \propto P^2}$ at a given T

$\boxed{Z_{11} \propto \sigma^2}$ at a given T , P

For collisions between two different types of molecules.

$$\boxed{Z_{12} = \frac{1}{\sqrt{2}} \pi v^2 \sigma^2 \rho_1{}^2 \rho_2{}^2}$$

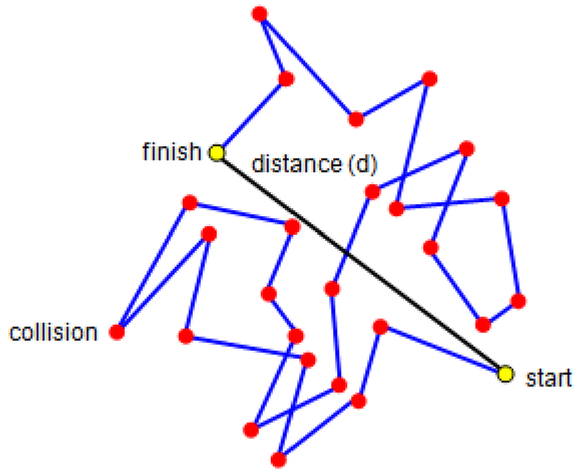
MEAN FREE PATH, λ

FREE PATH – The distance travelled by a molecule between two successive collisions.

MEAN FREE PATH – The average distance travelled by a molecule between two successive collisions.

$$\boxed{\lambda = \frac{v}{Z} = \frac{v}{\sqrt{2}\pi v \sigma^2 \rho}}$$

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



Larger the size of molecule – Smaller will be the mean free path

Mean freepath is of the order 10^{-7} m

EFFECT OF TEMPERATURE AND PRESSURE ON MEAN FREE PATH

$$\lambda = \frac{1}{\sqrt{2}\pi\sigma^2\rho}$$

'σ' is the collision diameter and 'ρ' is the number density

Relation between Number Density and Pressure:

$$PV = nRT$$

$$\frac{n}{V} = \frac{P}{RT}$$

$$\frac{n}{V} \cdot N_0 = \frac{P}{RT} \cdot N_0$$

$nN_0 =$ Total no. of molecules in n moles of the gas.

$$\rho = \frac{P}{RT} \cdot N_0$$

$\dfrac{nN_0}{V} =$ Total no. of molecules per unit volume of the gas $= \rho$

$$\rho = \frac{P}{(R/N_0)T}$$

$$\boxed{\rho = \frac{P}{kT}}$$

$$\lambda = \frac{1}{\sqrt{2}\pi\sigma^2\rho}$$

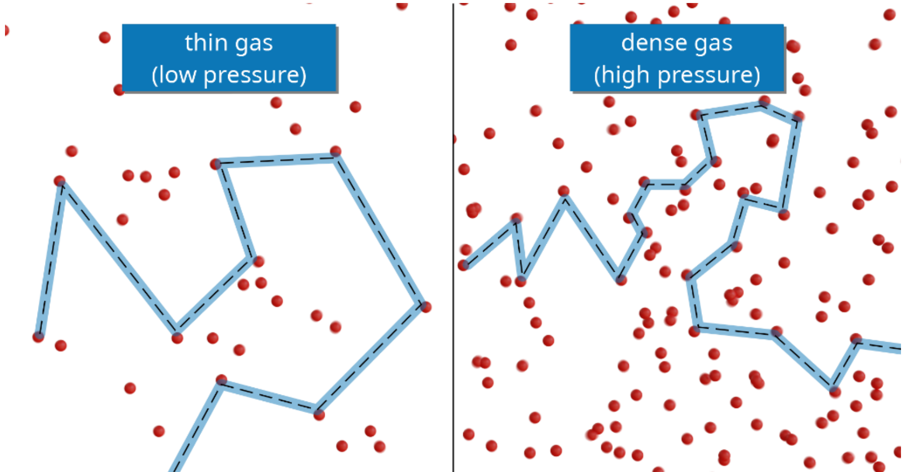
$$\boxed{\rho = \frac{P}{kT}}$$

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

***σ** is independent of temperature and pressure.*

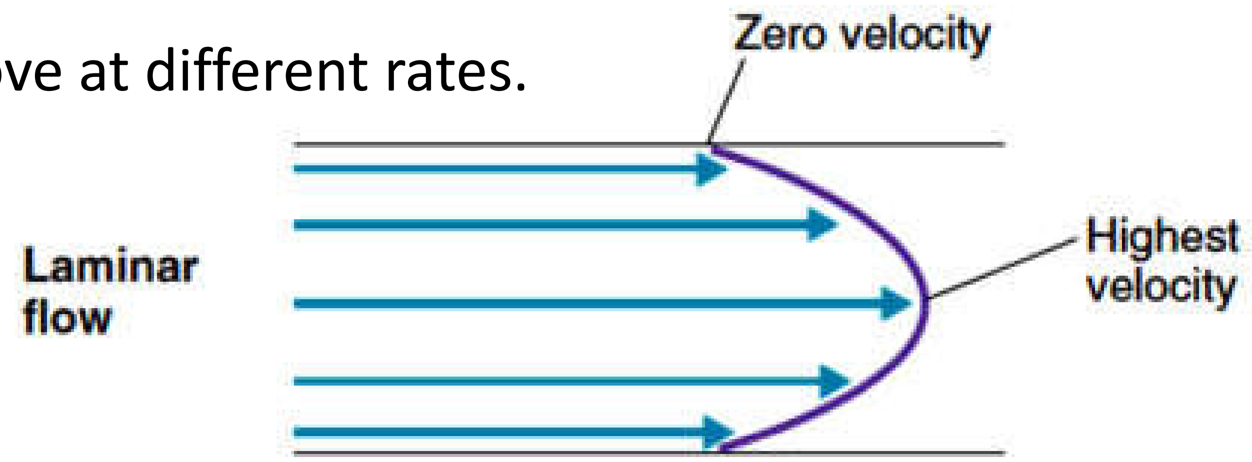
$\lambda \propto T$ *at constant P*

$\lambda \propto \frac{1}{P}$ *at constant T*



VISCOSITY OF GASES

- **Viscosity is the resistance one part of a fluid offers to the flow of another part of it.**
- **Internal friction operating within a fluid due to the shearing effect.**
- Gas is moving in layers – LAMINAR FLOW OR STREAMLINE FLOW
- Adjacent layers of gas molecules move at different rates.



- The velocity changes gradually from one layer to other.
- The velocity increases with increase in distance from the stationary surface.
- Each layer experiences a frictional force called **viscous drag**.
- Retarding influence of the slower-moving layer on the adjacent faster-moving layer

– Manifested as resistance to flow or **viscosity**.

The viscous force depends on area of contact and velocity gradient

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

$$F = -\eta \cdot A \cdot \frac{dv}{dz}$$

$\eta =$ coefficient of viscosity or viscosity.

$$\frac{F}{A} = \eta \qquad when \ \frac{dv}{dz} = 1$$

Coefficient of viscosity is defined as the force per unit area required to maintain a unit velocity difference between two adjacent parallel layers of a fluid unit distance apart.

Unit of Coefficient of Viscosity

$$\eta = -\cdot\frac{F}{A}\cdot\frac{dz}{dv}$$

Unit of η **= Nm^{-2} s or Pa s**

In CGS system the unit is ***Poise***

1 Poise = 0.1 Pa s

Relationship between Coefficient of Viscosity and Mean Free Path

$$\boxed{\eta = \frac{1}{3} \cdot v \cdot d \cdot \lambda}$$

Where, 'd' is the density of the gas

$$d = \frac{mass}{V} = \frac{mN}{V} = \frac{M}{N_0} \cdot \frac{N}{V} = \frac{M}{N_0} \rho$$

$$\lambda = \frac{kT}{\sqrt{2}\pi\sigma^2 P} \qquad v = \sqrt{\frac{8RT}{\pi M}}$$

$$\boxed{\eta = \frac{2}{3\pi N_0 \sigma^2} \sqrt{\frac{MRT}{\pi}}}$$

Dependence of Viscosity on Temperature and Pressure

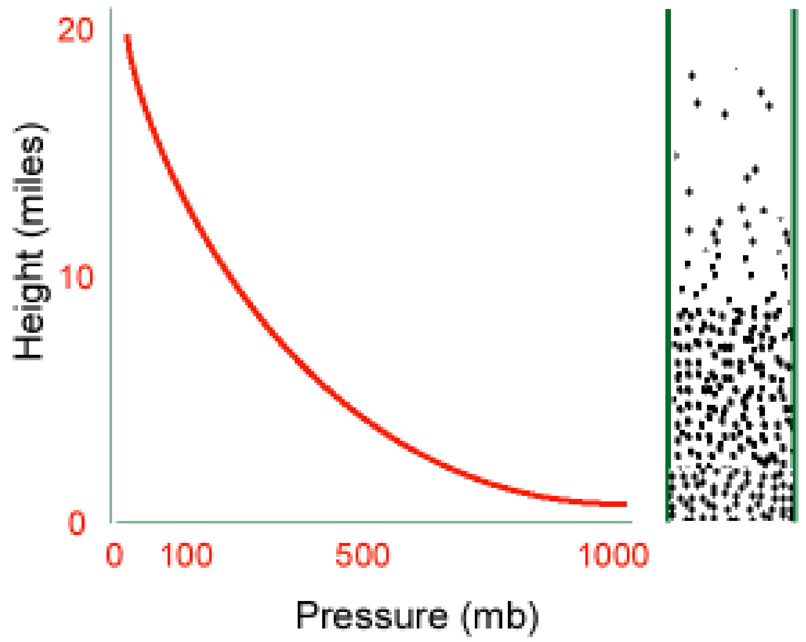
$$\boxed{\eta = \frac{2}{3\pi N_0 \sigma^2}\sqrt{\frac{MRT}{\pi}}}$$

$$\eta \propto \sqrt{T}$$

Viscosity is independent of Pressure

BAROMETRIC DISTRIBUTION LAW

- The molecules in a very large column of gas under the influence of gravity.
- Due to this the molecules are not distributed evenly.
- More molecules at the lower levels than at higher levels.
- Pressure of the gas will be different at different vertical positions in the container.
- Variation in pressure is explained by Barometric Distribution law.



$$p = p_0 e^{-\frac{Mgh}{RT}}$$

$p =$ Pressure at height h above the reference level

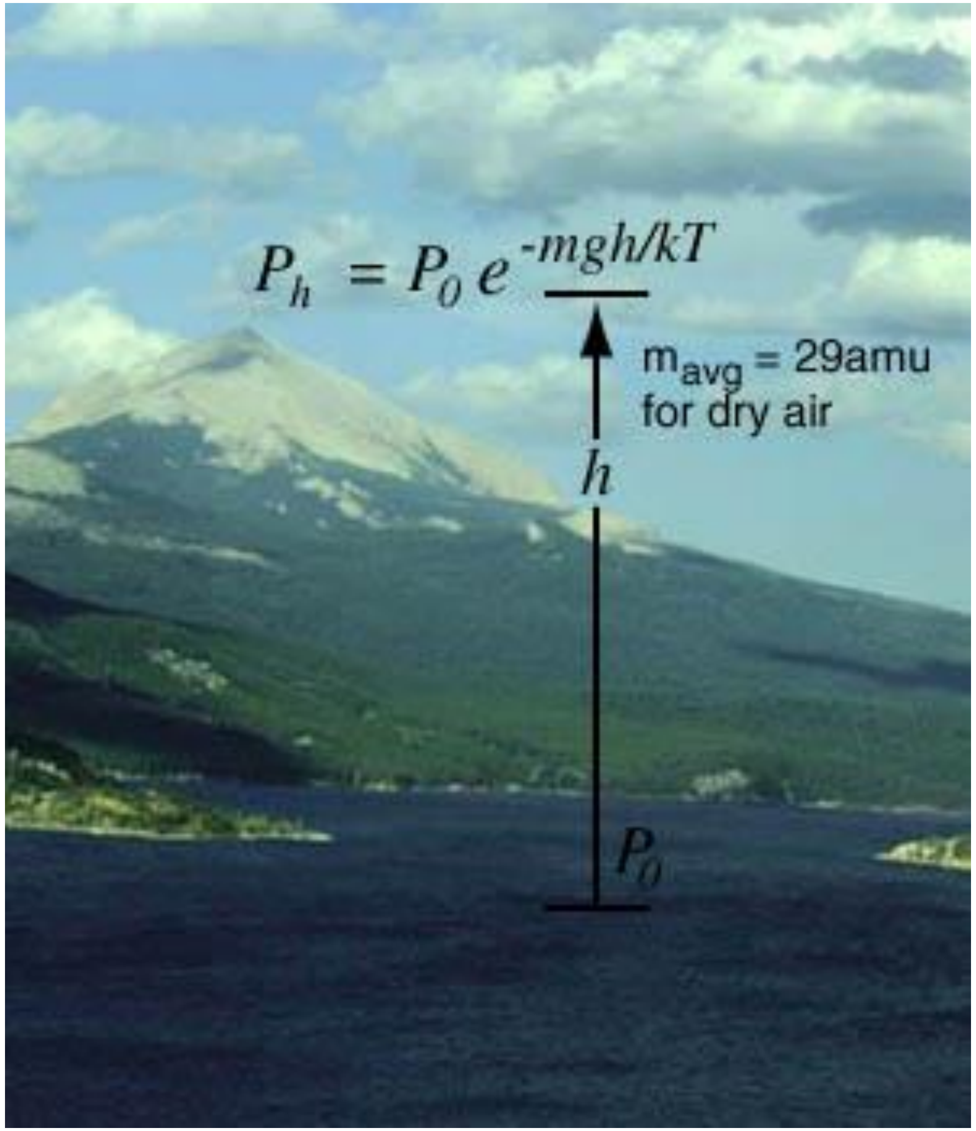
$p_0 =$ Pressure at some reference level

M = Molecular Mass

$g =$ Acceleration due to gravity

R = Universal Gas Constant

T = Kelvin Temperature


$P_h = P_0 e^{-mgh/kT}$
m_{avg} = 29amu
for dry air
h
P_0