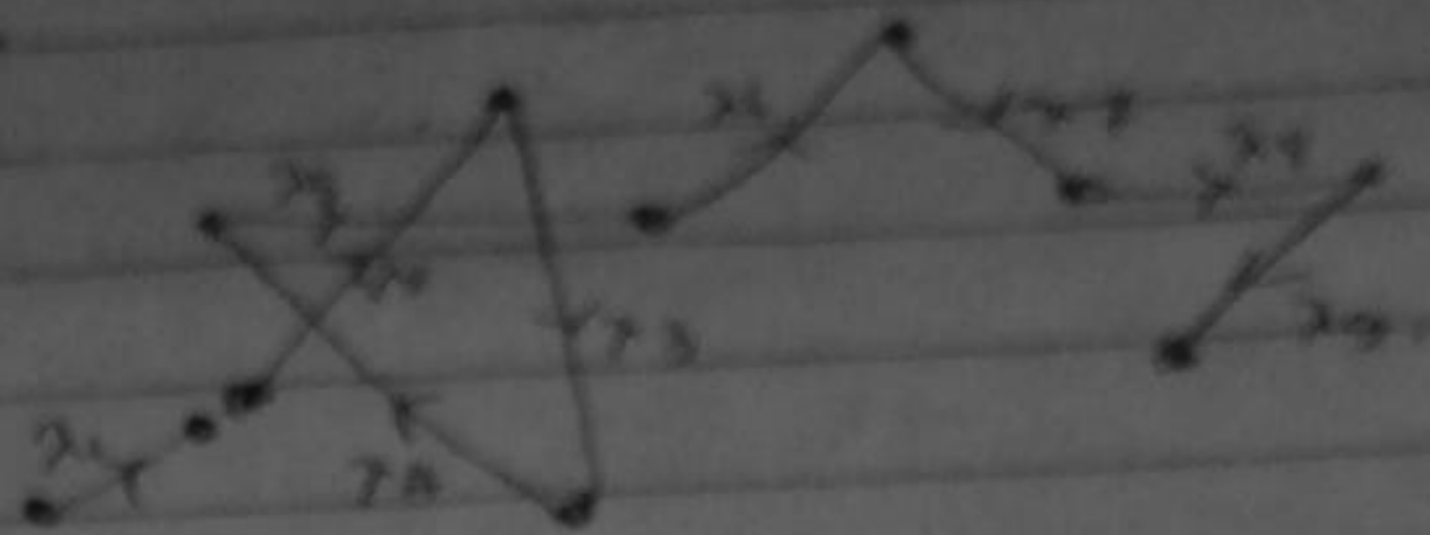


T.D.C. Part-I Chem (Hons.)  
MEAN FREE PATH ( $\lambda$ )  $\rightarrow$

The average distance travelled by a molecule between two successive collisions is known as the 'mean free path'  $\lambda$  is denoted by  $\lambda$ .

The average distance covered by a molecule between two successive collisions, viz. mean free path is given by



$$\lambda = \frac{\text{distance travelled by the molecule per unit time}}{\text{No. of collisions per unit time}}$$

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

Where,  $n$  = total no. of collisions per unit time  
 and  $\lambda_1 + \lambda_2 + \lambda_3 + \dots + \lambda_n$  = total distance traveled by the molecule.

Calculation of  $\lambda$   $\rightarrow$

The value of  $\lambda$  is calculated from the following equation —  $\lambda = \frac{C_{av}}{z}$

or 
$$\lambda = \frac{\frac{C_{av}}{\sqrt{2} \pi \sigma^2 z} N}{kT} \quad \therefore \lambda = \frac{1}{\sqrt{2} \pi \sigma^2 N} \quad \text{--- (I)}$$

$$\lambda = \frac{RT}{\sqrt{2} P \pi \sigma^2} \quad \text{--- (II)}$$

- Where,  $k$  = Boltzmann's const.
- $T$  = Absolute temp.
- $P$  = Pressure

$\sigma$  = diameter of the molecule.

$N$  = No. of molecules, per unit volume  
 and  $C_{av}$  = Average vel. of the molecule  
 $z$  = collision frequency.

From the above equation it is evident that

(i)  $\lambda \propto \frac{1}{p}$  i.e. mean free path decreases at pressure increase.

(ii)  $\lambda \propto T$  i.e. mean free path increases at the temp. increase.

Mean free path has the dimension of length. It is clear that mean free path is independent of average vel. ( $\bar{C}_{av}$ ) and time, so long as  $n$  remains constant. Thus, a knowledge of mean free path gives us an idea about the molecular diameter ( $\sigma$ ).

Dependence of mean free path  $\rightarrow$

The mean free path depends on the following factors —  
size of the molecule  $\rightarrow$  Larger the molecular size, greater will be the no. of collisions. Hence shorter will be the mean free path.

Pressure of the gas  $\rightarrow$  Lower is the pressure of the gas, greater is the mean free path ( $\lambda$ ).

Density of the gas  $\rightarrow$  Higher the density of the gas, shorter is the  $\lambda$ .

Temperature of the gas  $\rightarrow$  Higher the temp. of the gas, greater is the  $\lambda$ .

viscosity of the gas  $\rightarrow$   $\lambda$  increases with increase in viscosity of the gas.

The  $\lambda$  in terms of viscosity coefficient ( $\eta$ ) is given as

$$\lambda = \eta \sqrt{\frac{3}{p \times D}}$$

where,  $p$  = pressure of the gas,

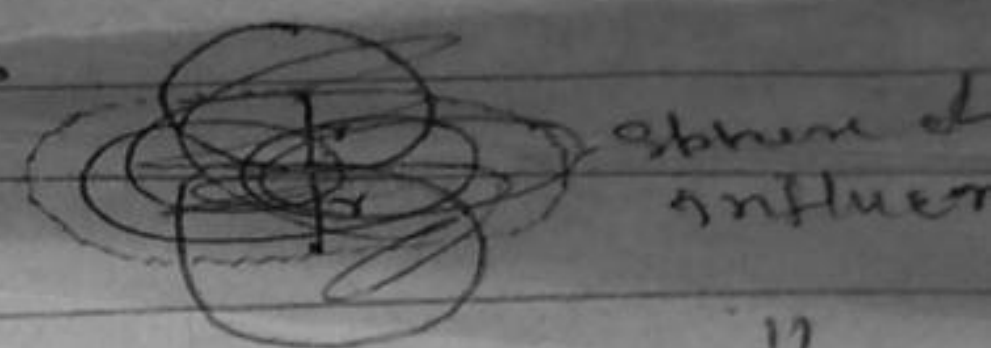
$D$  = density of the gas

and  $\eta$  = viscosity coefficient

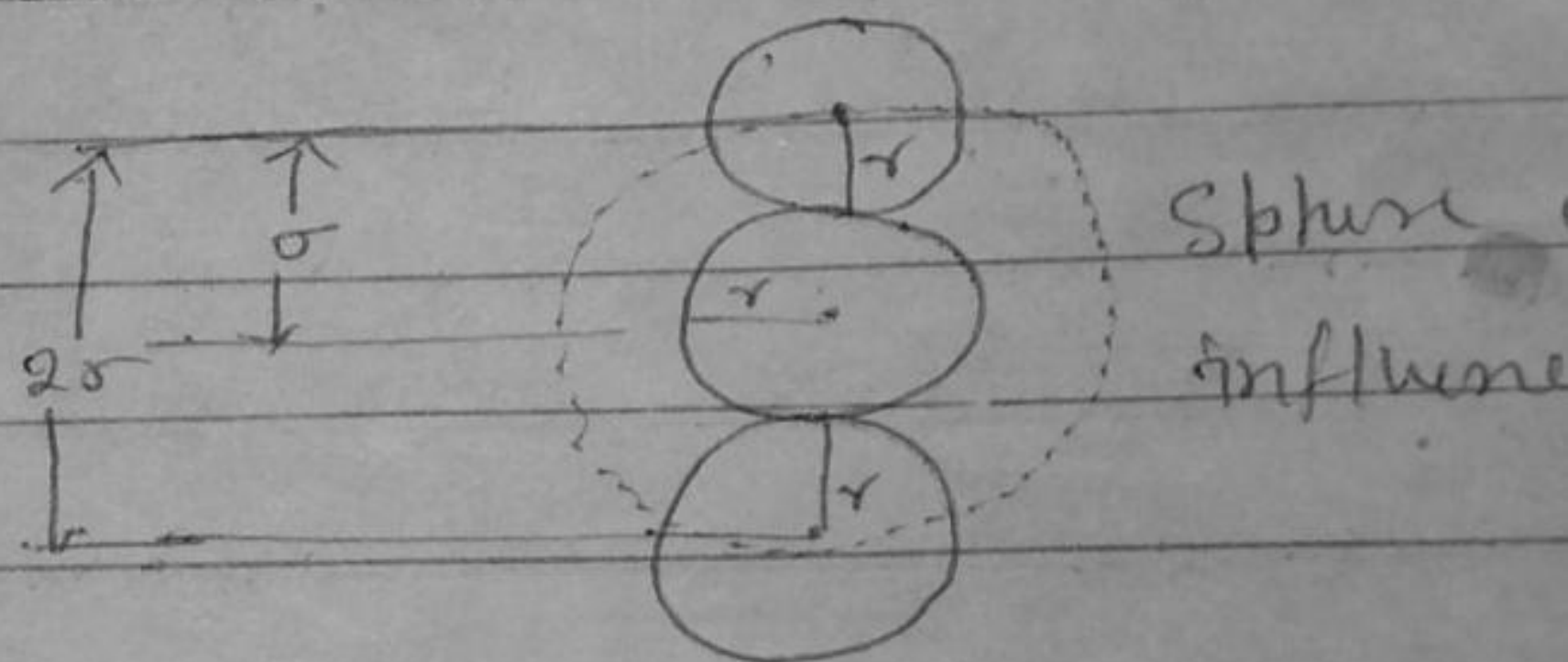
Molecular Diameter or collision diameter ( $\sigma$ )  
 $\Rightarrow$

When two molecules of a gas approach each other, there is a certain distance, beyond which they can not come closer.

"The distance of closest approach between the centres of two molecule is known collision diameter ( $\sigma$ )".



A collision takes place whenever the distance between the centres of two molecules is " $\sigma$ ".



Note

from fig:

Radius of sphere of influence ( $\sigma$ ) = ~~2r~~  $r + r = 2r$ .

The volume of sphere of influence ( $B$ )

$$= \frac{4}{3} \pi \sigma^3 = \frac{4}{3} \pi (2r)^3$$

$$= 8 \cdot \frac{4}{3} \pi r^3$$

$$B = 8 b_i$$

where  $b_i = \frac{4}{3} \pi r^3$

## Collision Frequency or Collision Number

→ The no. of collisions occurring per unit time per unit volume is called collision frequency.

The collision frequency ( $Z$ ) is given by

$$Z = \frac{1}{2} \sqrt{2} \pi \sigma^2 C_{av} n^2 \quad \text{per unit time per unit volume,}$$

since,  $C_{av} = \sqrt{\frac{8KT}{\pi m}}$

$$\therefore Z = \frac{1}{2} \pi \sigma^2 n^2 \cdot \sqrt{2} \sqrt{\frac{KT}{\pi m}}$$

$$Z = \frac{1}{2} \pi \sigma^2 n^2 \sqrt{\frac{2KT}{m}}$$

where,  $\sigma$  = molecular diameter

$C_{av}$  = Average velo. of the molecule

$n$  = No. of molecules per unit volume

$K$  = Boltzmann's const.

$T$  = absolute temp.

and  $m$  = mass of the molecule