# Lecture 9

Collision in a gas:

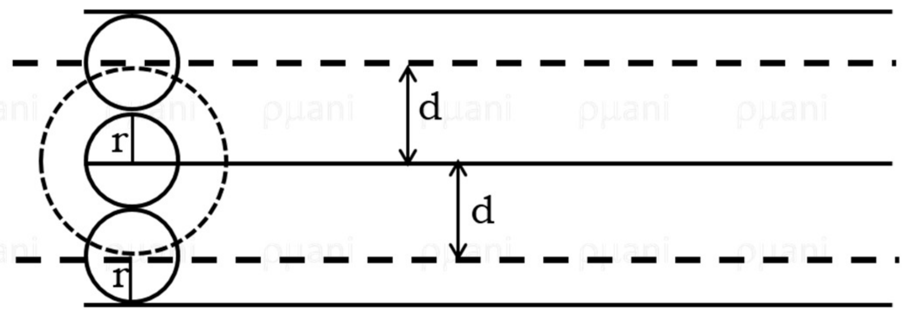
The kinetic model/theory enables us to calculate the frequency with which molecular collisions occur and the average distance a molecule travels between collisions.

Let us assume the molecules to be impenetrable (elastic) hard spheres of diameter ‘d’ (or radius ‘r’)

So, its volume (b) = $\frac{4}{3}\pi\left(\frac{d}{2}\right)^3 = \frac{4}{3}\pi r^3$

[unit? $Å^3$ or $nm^3$]

We count a bimolecular collision when the centre to centre distance is less than (or equal to) d (= 2r)




The sphere of radius ‘d’ surrounding a molecule within Which no centre of another molecule can penetrate is known as “sphere of influence” or effective volume (β).

$$\beta = \frac{4}{3}\pi d^3 = 8b \qquad \text{...........} \text{ (i)}$$

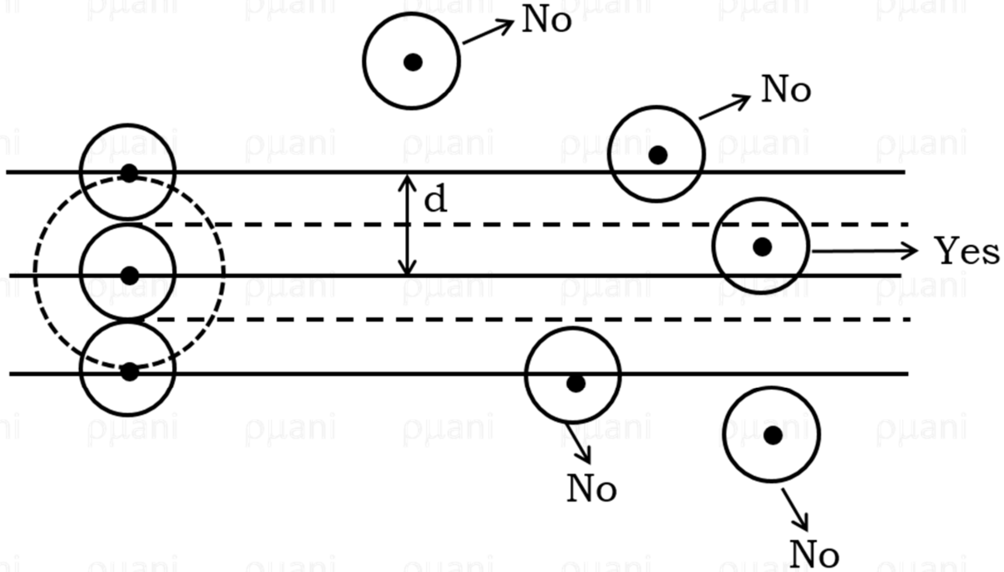
[unit? $Å^3$ or $nm^3$]

and the corresponding area = $\pi d^2 = \sigma$ , where σ is known as the collision cross-section of the molecules.

Unit? $Å^2$ or $nm^2$ [For $N_2$, $\sigma = 0.43\ nm^2$, for benzene, $\sigma = 0.88\ nm^2$]

Let us assume there are ‘n’ no. of molecules per unit volume of a single gas, and they are moving with average speed $\bar{c}$ (per unit time).

Let us calculate how many collisions one particular molecule makes with other molecules per unit time (sec).



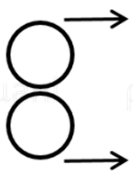
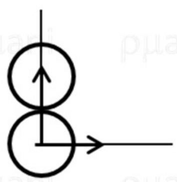

Volume of the colliding space (the molecule need not travel in straight line) = $\pi d^2 . \bar{c}$

Assuming all other molecules to be stationary, the number of molecules with which this molecule will collide with (bimolecular) is $= \pi d^2 . \bar{c} . n$

[Actually (n-1) but as n is large so $(n-1) \simeq n$]

But, this assumption is highly unreasonable.

Let us consider three different types of collisions:

| Type of collision | Pictorial | Angle | Relative speed |
|---|---|---|---|
| Head on |  | 180° | $2\,\bar{c}$ |
| Grazing |  | 0° | 0 |
| Assuming average angle of collision to be 90 °C |  | 90° | $\sqrt{2}\,\bar{c}$ |

[Since we are calculating binary collision, so we need to calculate relative speed]

Therefore, the number of collision (bimolecular) suffered by this molecule in unit time (collision frequency)

$$Z = \pi\, d^2 \,.\, \sqrt{2} \,.\, \bar{c} \,.\, n \qquad \text{[ Actually it should be (n-1) but as } n >> 1 \text{ so } (n-1) \simeq n \text{ ]}$$

$$= \sqrt{2} \,.\, \pi\, d^2 \,.\, \bar{c} \,.\, \left(\frac{p}{k\,T}\right)$$

As there are ‘n’ molecules per unit volume,

So, the total number of collisions (by all molecules) per unit volume, per unit time (for ‘n’ molecules)

$$Z_{AA} = Z \cdot n \cdot \frac{1}{2}$$

[Factor $\frac{1}{2}$ arises because we have assumed bimolecular collision only]

$$= \frac{\pi\, d^2 \cdot \bar{c} \cdot n^2}{\sqrt{2}}$$

If there are $n_A$ and $n_B$ no. of molecules of gas A and B per unit volume, then total no. of molecules per unit volume = $n_A + n_B$

If their respective radius are $r_A$ and $r_B$ then the no. of collisions per cc per second

$$Z = \frac{1}{\sqrt{2}} \cdot \pi\, d^2 \cdot \bar{c} \cdot (n_A + n_B)^2$$ [This is the no. of all collisions (between A-A, B-B and A-B)]

No. of collisions between A & B i.e. between dissimilar molecules is given by

$$Z_{AB} = \frac{1}{\sqrt{2}} \cdot \pi\, d^2 \cdot \bar{c} \cdot [(n_A + n_B)^2 - n_A^2 - n_B^2\,]$$

$$= \frac{1}{\sqrt{2}} \cdot \pi\, d^2 \cdot \bar{c} \cdot 2\, n_A \cdot n_B$$

$$= \sqrt{2} \cdot \pi\, d^2 \cdot \bar{c} \cdot n_A \cdot n_B$$

$$= \sqrt{2} \cdot \pi \cdot (r_A + r_B)^2 \cdot \sqrt{\frac{8\,k\,T}{\pi\,\mu}} \cdot n_A \cdot n_B \;=\; = 4 \cdot (r_A + r_B)^2 \cdot \sqrt{\frac{\pi\,k\,T}{\mu}} \cdot n_A \cdot n_B$$

For a mixture of two dissimilar gases, relative speed $= \sqrt{\frac{8\,k\,T}{\pi\,\mu}}$

where $\mu$ = reduced mass = $\frac{m_A\, m_B}{m_A + m_B}$

Question: Calculate the collision frequency & total number of binary collision per cc per second of $N_2$ gas at 1 atm and 25 °C. (d of $N_2$ = 3.74 Å)

Question: What is the effect of increasing temperature on collision frequency? (Keeping numbers of molecules fixed and volume fixed)

Ans. $Z \propto \sqrt{T}$

Question: What is the effect of increasing pressure on collision frequency?

How is the pressure increased?

Ans. (a) If pressure is increased by increasing temperature, i.e. if the numbers of molecules fixed and volume fixed, then

$p \propto T$ i.e. $Z \propto \sqrt{T}$

(b) If pressure is increased by decreasing volume i.e. if the numbers of molecules and temperature fixed, then $Z \propto p$

In the above two questions: → Question should be asked: How temperature / pressure is changed ?

Mean free path:

The average distance covered by a molecule between two successive collisions is known as mean free path.

If collision frequency is 'Z' , then the molecule spends a time $\frac{1}{Z}$ in free flight between collisions.

Therefore, distance travelled = $\frac{1}{Z} \cdot \bar{c}$

So, the mean free path ($\lambda$) = $\frac{\bar{c}}{Z} = \frac{k \cdot T}{\sqrt{2} \cdot \sigma \cdot p}$ [as $\sigma = \pi\, d^2$ , $Z = \sqrt{2} \cdot \pi\, d^2 \cdot \bar{c} \cdot n$ , $n = \frac{p}{kT}$ ]

$\Rightarrow \boxed{\lambda = \frac{k \cdot T}{\sqrt{2} \cdot \sigma \cdot p}}$ unit?

Typical values of $\lambda$ , say for $N_2$ at 1 atm. at room temperature = 70 nm

Doubling the pressure (volume halved, temperature constant) reduces mean free path by a factor of two.

Question: What is the effect of temperature on $\lambda$? Plot.

Ans. For a gas of constant volume, $T \propto p$, therefore $\lambda$ remains constant although temperature is increased (at constant V). Therefore the distance travelled between collisions is dependent on the no. of molecules present at a given volume but not by the speed at which they travel.

$\bar{c} \simeq 500$ m/s , $\lambda \simeq 100$ to 1000 molecular diameter

Each molecule makes a collision within ~ 1 ns

$d << \lambda \Rightarrow$ Kinetic model is valid !

Question: Calculate mean free path of molecules of a gas (d = 4 Å) at 1 atm and 300 K.

Question: Total no. bimolecular collisions (at room temperature and 1 atm pressure) per unit volume per unit time $\simeq 10^{28}$ . So, then all chemical reaction should be over within 1 sec. That does not happen. Why?

Question: Calculate mean free path of molecules of a gas (d = 4 Å) at $10^{-9}$ atm and 300 K. Compare the result with that obtained in (Q. 19).