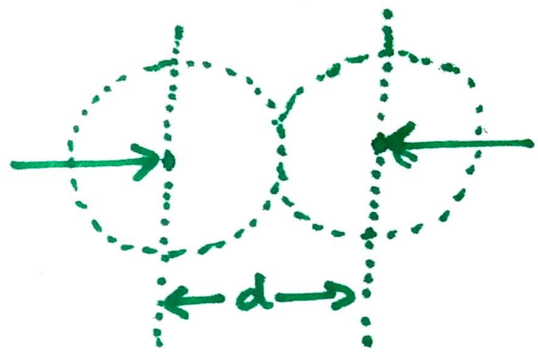
B.Sc. (Hons) Part III

The Gaseous State

Collision Parameters:-

1) Collision diameter: The kinetic theory of gases treat molecules as point masses. When such two molecules approach each other, a point is reached where mutual repulsion between the molecules, due to electronic and nuclear repulsion, becomes so strong that it causes to reverse the direction of their motion.



The distance between the centres of two molecules at the point of their closest approach is known as collision diameter. It is denoted by d.
The volume $(\frac{4}{3}\pi d^3)$ is known as effective volume of the molecule.

If the distance between two molecules is less than d there would be collision between them

Thus, collision is an event in which the centres of two identical molecules comes within a distance d from them.

Collision cross section:-

The model of gaseous molecules as hard, non-interacting spheres of diameter d can satisfactarily account for various gaseous properties such as viscosity, diffusion or thermal conductivity, the mean free path and the number of collisions the molecules undergo.

When two molecules collide the effective area of ~~da~~ target is πd^2.
The quantity πd^2 is called collision cross-sections. σ, of the molecule because it is the cross-sectional area of an imaginary sphere surrounding the molecules into which the centre of another molecule cannot penetrate.

Collision number:-

$$Z_1 = \sqrt{2}\,\pi d^2 \langle c \rangle \rho$$

In a gas, the number of molecules with a single molecule will collide per unit time is given as in equation above.
Here
$\langle c \rangle$ is the average velocity of the molecule
and ρ is the number density i.e the number of molecules per unit volume of gas.
Since each collision involves two molecules, the number of collisions of like molecules occuring per unit time per unit volume of gas is given by equation

Collision frequency:-

$$Z_{11} = \frac{1}{2}(\sqrt{2}\pi d^2 \langle c\rangle \rho^2) = \frac{1}{\sqrt{2}}(\pi d^2 \langle c\rangle \rho^2)$$

Collision frequency:-

The number Z_{11} equation above gives the collision frequency of the gas. Thus collision frequency is the number of molecular collisions occuring per unit time per unit volume of the gas.

For collisions of two types of molecules labelled as 1 and 2 the equation changes to:-

$$Z_{12} = \frac{1}{\sqrt{2}}(\pi d_{av}^2 \langle c\rangle \rho_1 \rho_2) \quad \left[d_{av} = \frac{(d_1+d_2)}{2}\right] \quad -(1)$$

Here ρ_1 and ρ_2 are number densities of two types of molecules. The number densities ρ is given as P/KT

Hence for ideal gas:-

$$PV = nRT = nN_AKT \quad -(2)$$

$$\text{or } P = \frac{nN_AKT}{V} \quad -(3)$$

As $N = nN_A$, $P = \frac{NKT}{V}$ — (4)

N is the total number of molecules in n moles of the gas.

since ρ is the number of molecules per unit volume, therefore

$$\frac{N}{V} = \rho \quad \text{—} \ (5)$$

and equation (4) becomes

$$P = \rho kT \quad \text{—} \ (6)$$

or

$$\boxed{\rho = \frac{P}{kT}} \quad \text{—} \ (7)$$

so values of Z_{11} and Z_{12} can be rewritten as

$$Z_{11} = \sqrt{2}\,\pi d^2 \langle c \rangle \, P/kT$$

and $$Z_{12} = \frac{\pi d^2 \langle c \rangle P^2}{\sqrt{2}\,(kT)^2}$$

For Z_{11} unit is s^{-1} and for Z_{12} the unit is $s^{-1}\,m^{-3}$.

<u>Mean free path:</u>

The mean distance travelled by a gas molecules between two successive collisions.
It is denoted by λ.

$$\lambda = \frac{\langle c \rangle}{Z_{11}} = \frac{\langle c \rangle}{\sqrt{2}\,\pi d^2 \langle c \rangle \, P/kT} = \frac{kT}{\sqrt{2}\,\pi d^2 P}$$

It is quite evident from the equation that

$$\lambda \propto \frac{1}{P}$$

i.e. mean free path is inversely proportional to the pressure of gas.

" Knudsen gas: In a good vacuum the gas molecules collide far more frequently with the walls of container rather than with one another.

The gases under such conditions become Knudsen gases.

NOTICE: All the students of B.Sc. (Chem.) Hons. Part III, Maharaja College are requested to register their e-mail ID on ankitaojha26@gmail.com for registering them for online classes.

Kindly mention your name, Roll no., scanned ID of college and send them as mail.

All the best.

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