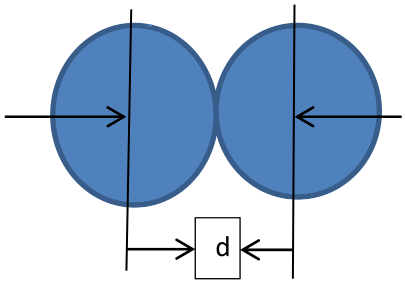
Section B: Physical Chemistry -3

Kinetic Theory of Gases

Collision Parameters

Collision Diameter: The following figure shows the collision of two molecules. Two such molecules approach each other as a result of attractive forces present in these molecules.



However, when they approach quite close to one another, the force of mutual repulsion becomes dominant which causes reversal of direction of motion. *The distance between the centres of the two molecules at the point of their closest approach is known as the **collision diameter***. It is denoted by ***d*** . Since a gaseous molecule can be regarded as a rigid sphere of radius d, the volume of the sphere $(4/3)\pi d^3$ is known as the effective volume of the molecule.

Collision Cross-Section: When two molecules collide, it is assumed that an imaginary sphere exists surrounding the molecule into which the centre of another molecule cannot penetrate. *This imaginary area of the sphere is called the cross sectional area or **collision cross-section***, denoted by σ and $\boldsymbol{\sigma = \pi d^2}$ **.**

Collision Number: The number of collisions suffered by a single molecule per unit time per unit volume of the gas is known as the ***collision number***. Thus,

$$Z_1 = \sqrt{2}\,\pi d^2 < c > \rho$$

< c > is the average velocity of the molecules

ρ is the number density, i.e number of molecules per unit volume of the gas.

Therefore, the total number of molecules colliding per unit time per unit volume of the gas is given by = $\sqrt{2}\,\pi d^2 < c > \rho^2$

Now, each collision involves two molecules. In case the collision is between two like molecules occurring per unit time per unit volume of the gas, the collision number will be

$$Z_{11} = \frac{1}{2}(\sqrt{2}\,\pi d^2 < c > \rho^2\ ) = \frac{1}{\sqrt{2}}(\,\pi d^2 < c > \rho^2\ )$$

Collision Frequency: It is defined as the number of molecular collisions occurring per unit time per unit volume of the gas.

For the molecules of type 1 with that of type 2, the number of collisions would be

$$Z_{12} = \frac{1}{\sqrt{2}}(\,\pi d^2 < c > \rho_1 \rho_2$$

Where ρ_1 *and* ρ_2 are the number densities of molecules of type 1& 2 respectively.

- ***To prove that number density ρ = P/ kT***

For an ideal gas,

$$PV = nRT = nN_AkT$$

$$P = nN_AkT / V = NkT/V \qquad \text{-------(i)}$$

where, $N = nN_A$ is the total number of molecules in n moles of gas.

ρ = N/V, i.e number of molecules per unit volume.

Thus, equation (i) becomes P = ρkT i.e ρ = P/kT ----------(ii)

Thus, collision number can also be written as

$$Z_1 = \sqrt{2}\,\pi d^2 < c > P/kT \qquad \text{-------- (iii)}$$

$$\text{And}\quad Z_{11} = \frac{(\,\pi d^2 <c> P^2\ )}{\sqrt{2}\,(kT)^2} \qquad \text{------- (iv)}$$

N.B ***The units of Z_1 are s^{-1} and those of Z_{11} are s^{-1} m^{-3}.***

Mean Free Path: It is defined as the mean distance travelled by a gas molecule between two successive collisions, denoted by λ.

$$\lambda = \frac{<c>}{Z_1} = \frac{<c>}{\sqrt{2}\,\pi d^2 <c> P/kT} = \frac{kT}{\sqrt{2}\,\pi d^2 P} \qquad \text{-------(a)}$$

From the above equation (a), we see that λ ∝ 1/P, i.e the mean free path of a gas molecule is inversely proportional to pressure.