

## Mean Free Path

### Molecular Collisions

The molecule of a gas are moving at ordinary temperature with very large velocities, in the case of air it is about 400 m/s. There is no restriction on the motion of the molecules. The molecules were treated as geometrical points which could fly freely from one wall of a container to the other without colliding with other molecules. If such molecules are moving with such a high velocities, the gaseous mass contained in a vessel would disappear in no time. A small amount of gas released in a large room would spread throughout the room practically, instantaneously.

Whereas, we know that when the stopper is removed from a perfume bottle, a considerable time elapses before its smell is detected in a large room. It was soon realised that this relatively slow diffusion of one gas in another resulted from *molecular collisions* such as that shown in figure 1, which cause a molecule to move in an irregular, zig-zag path.

Clausius suggested that slow diffusion of gas is due to a finite, though small, size of gas molecules which undergo random molecular collisions. When a molecule of finite size moves in a gas it collides with other molecules. As a result its direction frequently changes in a series of short zig-zag paths, as shown in figure 1.

Figure 1 Molecular mean free path.

### Mean Free Path

The path covered by a molecule between successive collisions is called a *free path*. From figure 1 we note that *AB*, *BC*, *CD*, etc. are all free paths. Some of these paths will be long, others will be short. The average length of these free paths is referred to as *mean free path*. Thus, *mean free path is the mean distance travelled by a molecule between two successive collisions*.

We can define a mean free path  $\lambda$ . Add up the lengths of a large number of free paths and divide it by the total number; this will give us the mean free path  $\lambda$ . If  $\lambda_1, \lambda_2, \lambda_3, \dots, \lambda_N$  are the successive free paths traversed in time  $t$  and  $N$  is the total number of molecular collisions, then

$$\lambda = \frac{\lambda_1 + \lambda_2 + \dots + \lambda_N}{N} \quad (1)$$

$$\lambda = \frac{\text{total distance traversed}}{\text{total number of molecular collisions}}$$

If  $v$  is the speed of a molecule, then we can write

$$\lambda = \frac{vt}{N} \quad (2)$$

### Estimation of Mean Free Path

Consider a “bullet” molecule traversing the gas with velocity  $v$  and suppose other “target” molecules to be at rest. The moving “bullet” molecule will collide with all such “target” molecules whose centre lie in the region traversed by its *microscopic collision cross section*  $\sigma = \pi d^2$  or by its *sphere of exclusion* of radius  $d$  (diameter of a molecule), as shown in figure 2. The space thus traversed in a time  $t$  is a cylinder of base  $\pi d^2$  and height  $vt$ , and hence of volume  $\pi d^2 vt$ . If there are  $n$  “target” molecules per unit volume, this cylinder will enclose  $\pi d^2 vtn$  number of molecules in this volume and hence the number of collision in time  $t$  is  $\pi d^2 vtn$ . Hence, using eq. (2) we can write

$$\lambda = \frac{vt}{\pi d^2 vtn} = \frac{1}{\pi d^2 n} = \frac{1}{n\sigma} \quad (3)$$

More complete theories of the mean free path take into account the relative motion of all the molecules of a gas, i.e., they consider the “target” molecules, as well as the “bullet” molecules, to be in motion. The only change in the end result is to introduce a small correction factor in eq. (3). The inverse dependence on the number of molecules per unit volume and on the collision cross section remains unchanged.

**Figure 2** The volume swept out by a molecule of radius  $r$  moving with speed  $v$  in time  $t$ .

On the assumption that all molecules have the same speed, *Clausius* obtained the result

$$\lambda = \frac{3}{4} \frac{1}{n\sigma} = \frac{0.75}{n\sigma} \quad (4)$$

If the molecules have a *Maxwellian velocity distribution*

$$\lambda = \frac{1}{\sqrt{2}} \frac{1}{n\sigma} = \frac{0.707}{n\sigma} \quad (5)$$

Note that the value of correction factor decreases with increasing participation of molecules.

One can write the expression for mean free path in terms of the pressure and temperature as

$$\lambda = \frac{1}{\sqrt{2}} \frac{1}{\sigma} \frac{k_B T}{p} \quad (6)$$

Since,  $n = p/k_B T$ . We note that the mean free path is directly proportional to the temperature and inversely proportional to the pressure of the gas. Thus, it will increase as temperature increases and /or pressure decreases, and vice versa.