Physical Chemistry

المحـــاضـرة 5

المرحلـة الثانـية
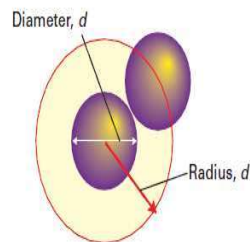
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Molecular collision

The average distance that a molecule travels between collisions is called its **mean free path**, λ (lambda).The mean free path in a liquid is less than the diameterof the molecules, because a molecule in a liquid meets a neighbour even if it moves only a fraction of a diameter. However, in gases, the mean free paths of molecules can be several hundred molecular diameters. If we think of a molecule as the size of a tennis ball, then the mean free path in a typical gas would be about the length of a tennis court.
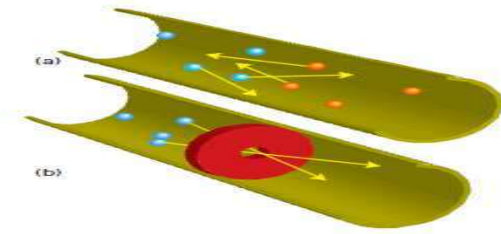
The **collision frequency**, **z**, is the average rate of collisions made by one molecule. Specifically, z is the average number of collisions one molecule makes in a given time interval divided by the length of the interval.

$$c = \frac{\text{mean free path}}{\text{time of flight}} = \frac{\lambda}{1/z} = \lambda z$$

To find expressions for λ and z we need a slightly more elaborate version of the kinetic model. The basic kinetic model supposes that the molecules are effectively point-like; however, to obtain collisions, we need to assume that two 'points' score a hit whenever they come within a certain range d of each other, where d can be thought of as the diameter of the molecules (Fig. 1.11). The collision cross-section, σ (sigma), the target area presented by one molecule to another, is therefore the area of a circle of radius d, so $\sigma = \pi d^2$. When this quantity is built into the kinetic model, it is possible to show that

$$\boxed{\text{Use } z = c/\lambda}$$

$$\lambda = \frac{RT}{2^{1/2} N_A \sigma p} \qquad z = \frac{2^{1/2} N_A \sigma c p}{RT} \qquad (1.19)$$

Diameter, d
Radius, d

$$Z = \frac{\sqrt{2}\ \pi C\, N d_A^2}{V} \qquad \text{------} \qquad \lambda = \frac{C}{\frac{\sqrt{2}\ \pi C\, N d_A^2}{V}} = \frac{V}{\sqrt{2}\ \pi\, N d_A^2}$$

$$V = \frac{nRT}{P} \qquad\qquad \lambda = \frac{nRT}{\sqrt{2}\ \pi\, N d_A^2\, P}$$

Example

Calculate the mean free path λ for Oxygen if d= 3.57× 10^{-10}m at 300K and pressure 101.325 K pa , n= 1?

$$\lambda = \frac{nRT}{\sqrt{2}\ \pi\, N d_A^2\, P} = \frac{8.314 J.K^{-1}\ (300K)}{\sqrt{2}\ \pi\, (3.57\times 10^{-10}m\,)(6.02\times 10^{23} mol^{-1)}\ (101325 pa)} = 7.22\times 10^{-8} m$$

Example :

If the pressure of hydrogen gas in the space 10^{-10}Torr at 1000K, d= 0.2cm, Calculate

1-Number of hydrogen molecues in cm^3 „ 2- Collisions number for one molecules in second (Z s^{-1}) „„ 3- mean free path λ ?

Answer:-

$$\frac{N}{V}$$

PV=nRT ,, $\qquad$ n= $\frac{N}{N_A}$,,,, $\qquad$ $PV = \frac{N}{N_A}$ RT,,,,

$$\frac{N}{V} = \frac{N_A P}{RT} =$$

1atm= 760Torr

1atm = 10^5 Pa

b)) $C = \sqrt{\frac{8RT}{\pi M}}$

$$Z_A = \sqrt{2}\,\pi d_A^2 C\,\frac{N}{V}$$

C)) $\lambda = \dfrac{V}{\sqrt{2}\,\pi\,Nd_A^2} = = \dfrac{1}{\sqrt{2}\,\pi\,d_A^2\,N_{/V}}$

Q1/ Reacted of 2.2g of Fe with addition amoun of HCl to produce H_2 gas, the librated gas has 10 L at 298 k acerding the fallowing eqr.

$$Fe_{(s)} + 2HCl_{(aq)} \longrightarrow FeCl_{2(aq)} + H_{2(g)}$$

Calculate the pressure of librated gas. (A.wt Fe 55.85)

Soln.

$$n_{Fe} = \frac{m}{Mwt} = \frac{2.2}{55.85} = 0.039 \text{ mol}$$

$$n_{Fe} = n_{H_2} = 0.039 \text{ mol}$$

$$PV = nRT \longrightarrow P = \frac{nRT}{V} = \frac{0.039 \times 0.082 \times 298.15}{10.0}$$

$$= 0.095 \text{ atm}$$

Q2/ Gas A diffuses through sand opening at the rate of 30 cm³.min⁻¹. Gas B diffuses through the same openin at the rate of 15 cm³.min⁻¹. which gas is heavier? The density of A is 1 g/L. Calculate the density of B. (pressure & temp. are the same for both gases).

Soln.

$$\frac{r_A}{r_B} = \sqrt{\frac{d_B}{d_A}}$$

$$\left(\frac{30}{15}\right)^2 = \left(\sqrt{\frac{d_B}{1 \text{ g/L}}}\right)^2$$

$$4 = \frac{d_B}{1 \text{ g/L}}$$

$$\therefore d_B = 4 \text{ g/L} \qquad \therefore \text{Gas B is heavier and high densi}$$

Real gases: deviation from ideal gas

Real gases do not conform to ideal gas behaviour. A plot of *PV* against pressure shows that whereas the *PV* is constant for an ideal gas, this is not true for real gases.
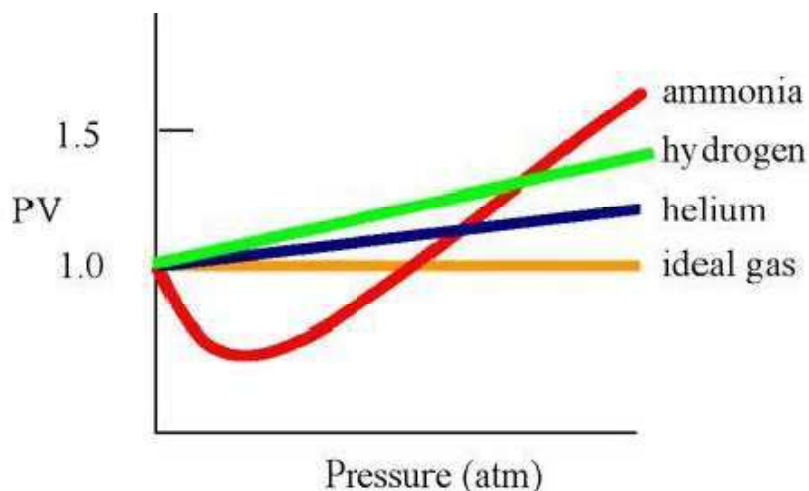
Figure 1.10 Plot of *PV* against pressure showing the behaviour for an ideal gas and real gases. Plot for NH_3, H_2, and He show deviation from the ideal gas curve.

Real gases do not follow the assumptions of the ideal gas behaviour. Deviations from ideal gas behaviour of varying degrees are seen when *PV* is plotted against *P*. Gases with only weak intermolecular forces give straight lines at low pressure and are close to the ideal gas behaviour. Significant deviation is observed for gases with strong intermolecular forces such as oxygen and nitrogen. Another assumption made when dealing with ideal gases is that molecules have no volume whereas real gases have a defined volume.

The compression factor

We can express the extent of deviation from ideal behaviour as a function of pressure (which is related to the density of the gas) by introducing a quantity called the Compressibility or Compression factor Z.

$$Z = \frac{PV}{nRT} = \frac{P\acute{V}}{RT}$$

(1.17)

For an ideal gas Z = 1, and real gases exhibit Z values different from unity. Z values may be explained in terms of the operation of intermolecular forces.

At low pressures the molecules are far apart and the predominant intermolecular interaction is **attraction**. The molar volume V_m is less than that expected for an ideal gas: intermolecular forces tend to draw the molecules together and so reduce the space which they occupy. Under such conditions we expect that $Z < 1$.

As the pressure is increased the average distance of separation between molecules decreases and **repulsive** interactions between molecules become more important. Under such conditions we expect that $Z > 1$. When $Z > 1$, the molar volume is greater than that exhibited by an ideal gas: repulsive forces tend to drive the molecules apart.
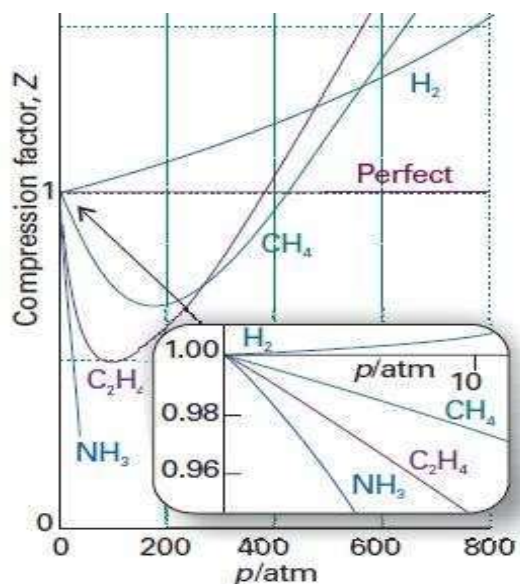

Figure 1.11 The variation of the compression factor, Z, with pressure for several gases at 0°C. A perfect gas has $Z = 1$ at all pressures. Notice that, although the curves approach 1 as $p \rightarrow 0$, they do so with different slopes.

The virial equation of state

The observation of a Z factor different from unity can be used to construct an empirical or observation based equation of state, by supposing that the ideal gas equation of state is only the first term of a more complex expression which can be expressed in terms of a mathematical power series. This is called the Virial equation of state.

$$Z = 1 + \frac{Bn}{v} + \frac{Cn^2}{v^2} + \frac{Dn^3}{v^3} +$$

<div align="center">(1.18)</div>