Kinetic Molecular Theory of Gases

The gas laws discussed so far were based on experimental observations. They were not based on any theory. In order to explain the general behaviour of gases, Maxwell, Boltzmann and others put forward a theoretical model of the gas. The theory is known as *Kinetic molecular theory of gases or microscopic model of gases.*

Postulates of kinetic molecular theory

(i). All gases are made up of a large number of extremely small particles called molecules.

(ii) The molecules are separated from one another by large distances so that the actual volume of the molecules is negligible as compared to the total volume of the gas.

(iii) The molecules are in a state of continuous rapid motion in all directions. During their motion, they keep on colliding with one another and also with the walls of the container.

(iv) Molecular collisions are perfectly elastic, *i.e.,* there is no net loss or gain of energy in their collisions. However, there may be redistribution of energy during such collisions.

(v) There are no attractive forces between the molecules. They move completely independent of each other.

(vi) The pressure exerted by the gas is due to the bombardment of its molecules on the walls of the container. The pressure exerted by the gas is due to the bombardment of its molecules on the walls of the container.

(vii) At any instant, different molecules possess different speed and hence different energies. However, the average kinetic energy of the molecules is directly proportional to its absolute temperature.

Kinetic energy and molecular speeds

Molecules of a gas are in continuous motion. During their movement they collide with each other and also with the walls of the container. This results in change of their speed and redistribution of energy. Thus the speed and energy of all the molecules of a gas are not the same. So we can determine only average value of speed of molecules.

Average speed (u_{av})

It is the mean or average of the speeds of different molecules of the gas. If there are n molecules in a sample of gas having individual speed u_1 , u_2 , ... u_n, then the average speed is given by the expression.

$$u_{av} = \frac{u_1 + u_2 + \ldots\ldots\ldots u_n}{n}$$

It is calcualted using the relation

$$\boxed{U_{av} = \sqrt{\frac{8RT}{\pi M}}}$$

Maxwell-Boltzmann distribution of molecular speed

Maxwell and Boltzmann have shown that actual distribution of molecular speeds depends on temperature and molecular mass of a gas. The distribution of molecular speeds at two different temperatures T_1 and T_2 (where $T_2 > T_1$) for a gas is shown in the following graph.

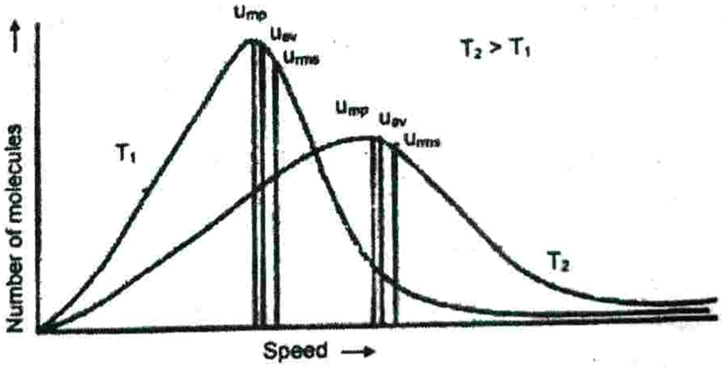

Fig. 5.5

From the above graph, it can be see that

(i) Number of molecules having very low and very high speeds are very small

(ii) The maximum in the curve represents the speed possessed by maximum number of molecules. This speed is called **most probable speed (u_{mp})**

(iii) On increasing the temperature most probable speed increases

Most probable speed is calcualted using the relation

$$\boxed{U_{mp} = \sqrt{\frac{2RT}{M}}}$$

Effect of mass on molecular speed

Speeds of gas molecules also depend on mass of molecules. At the same temeprature molecules with higher mass have lower speed than lighter molecules. For example, at the same temperature N_2 molecules have higher value of most probable speed than heavier Cl_2 molecules.

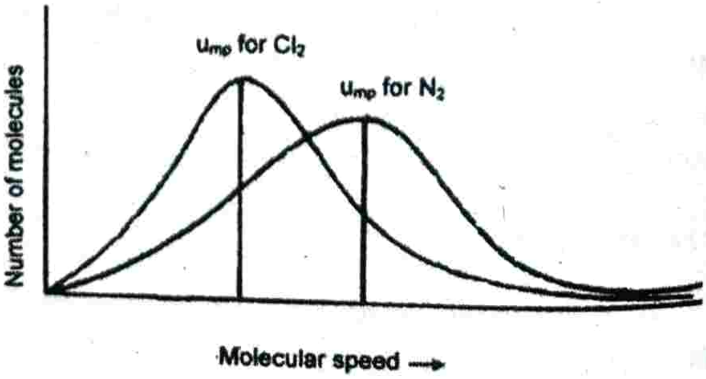

Fig. 5.6

Root mean square speed (u_{rms})

It is the square root of the mean of the squares of the speeds of the molecules. It is given by the expression,

$$u_{rms} = \sqrt{\frac{u_1^2 + u_2^2 + \ldots\ldots\ldots\ldots u_n^2}{n}}$$

It is generally calculated using the relation

$$\boxed{U_{rms} = \sqrt{\frac{3RT}{M}}}$$

Relationship among the different types of speeds

The ratio among the three speeds for a gas at a particular temperature is given below:

$$\boxed{u_{mp} : u_{av} : u_{rms} = 1 : 1.128 : 1.224}$$

or $U_{rms} : U_{av} : U_{mp} = 1 : 0.921 : 0.817$.

Thus, it can be seent hat

$$u_{rms} > u_{av} > u_{mp}$$

Example 5.12. Calculate the RMS speed of oxygen molecule at 27°C

Solution: $U_{rms} = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3 \times 8.314 \times 10^7 \times 300}{32}} = 4.835 \times 10^4 \ cm\ s^{-1}$

Deviation from Ideal Behaviour: Behaviour of Real Gases

A gas which obeys the general gas equation $PV = nRT$ at all temperatures and pressures is called an ideal gas. However, there is no gas which obeys the gas equation under all conditions of temperature and pressure. Hence the concept of ideal gas is only theoretical or hypothetical. *Actual gases or real gases show ideal behaviour (or approach ideal behaviour) only at low pressures and high temperatures.* As the pressure becomes high and temperature becomes low, more and more deviations are observed from general gas equation and other gas laws.

The deviation from ideal behaviour can be understood by studying the deviation of real gases from Boyle's law. According to Boyle's law, a plot of *PV* against *P* should be a straight line parallel to the pressure (*P*) axis. The plots obtained for some real gases at 273 K are shown in Fig. 5.7.

From the plots, we observe that for H_2 and *He*, *PV* increases continuously with increase of pressure. For other gases such as *CO*, CH_4, etc. *PV* first decreases, reaches a minimum value and then increases with increase of pressure.

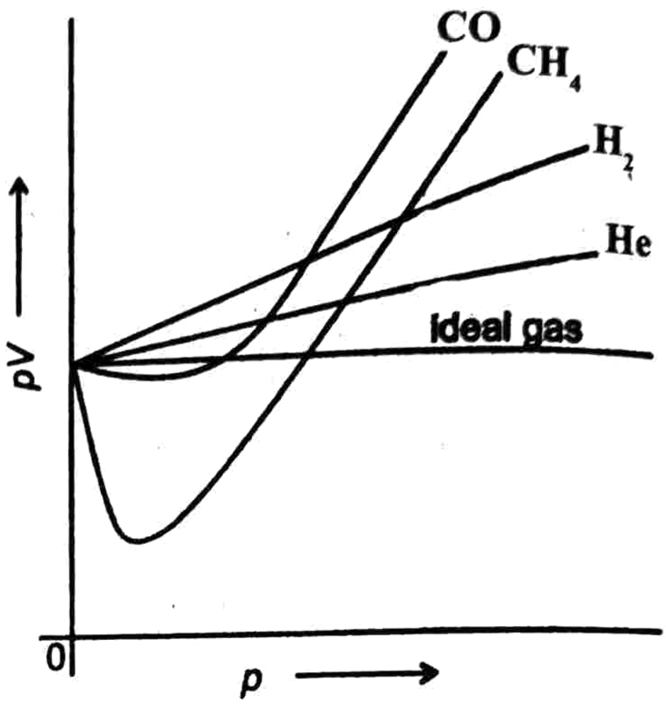

Fig. 5.7

Compressibility Factor

The extent to which a real gas deviates from ideal behaviour can also be conveniently studied in terms of a quantity Z called the compressibility factor, which is defined as $Z = \frac{PV}{nRT}$

For ideal gases, $Z = 1$ at all temperatures and pressures. Thus, a convenient way to study the deviation of a real gas from ideal behaviour is to plot the compressibility factor ($PV/\ nRT$) against *P*. The plot of *Z* versus *P* for a few real gases are shown in Fig 5.8

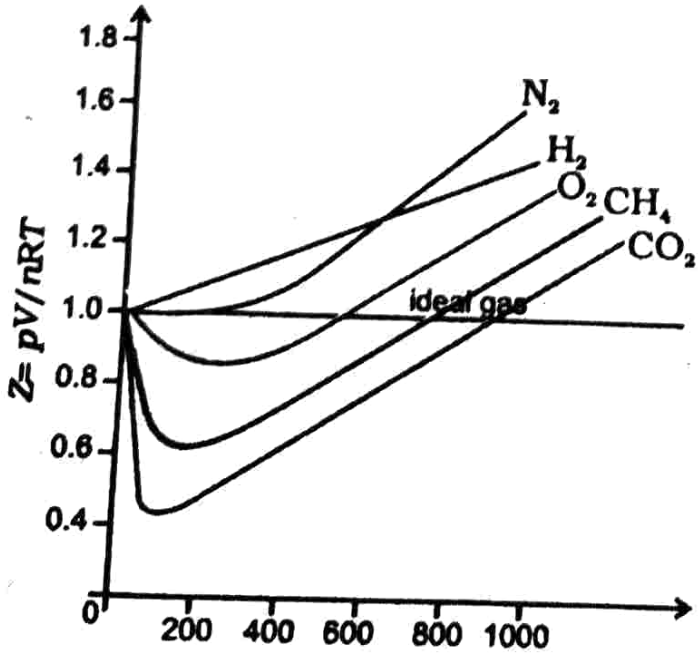

Fig. 5.8

It is clear from the figure that the deviations from ideal behaviour are most pronounced at high pressures. The quantity Z often shows both positive ($Z > 1$) and negative ($Z < 1$) deviations from unity. The extent of deviation at any given temperature and pressure depends upon the nature of the gas. Moreover, Z approaches unity as pressure approaches zero. This means that the equation $PV = nRT$ is valid at low pressures for almost all gases.

Significance of compressibility factor (Z)

We have seen that $Z = \frac{PV_{\text{real}}}{nRT}$

If the gas behaves ideally, $PV_{\text{ideal}} = nRT$ or $V_{\text{ideal}} = \frac{nRT}{P}$

Substituting this value of V_{ideal} in the above equation for Z, we get

$$Z = \frac{V_{\text{real}}}{V_{\text{ideal}}}$$

Thus compressibility factor is the ratio of the actual molar volume of a gas to the calculated ideal molar volume of it at the same temperature and pressure.

Boyle temperature

The temperature at which a real gas behaves like an ideal gas over an appreciable pressure range is called Boyle temperature or Boyle point.

Boyle point of a gas depends upon its nature. For example, Boyle temperature of N_2 is $323K$ and that of H_2 is $108K$. Below Boyle temperature, the value of compressibility factor (z) at first decreases, approaches a minimum and then increases as the pressure is increased. Above the Boyle temperature, the value of the compressibility factor (z) shows a continuous increase with increase in pressure.

Causes of deviation from ideal behaviour

The cause of the deviation of real gases from ideal behaviour may be attributed to the two faulty assumptions of the kinetic theory of gases. These faulty assumptions are

(i) The volume occupied by the gas molecules is negligible as compared to the total volume of the gas.

(ii) The forces of attraction among the molecules are negligible

Let us discuss these two assumptions of the kinetic theory.

(i) We know that a gas can be condensed into a liquid or solid with finite volume by cooling under pressure. This implies that the molecules in the gas must also occupy some volume. Under ordinary conditions of temperature and pressure, the actual volume of molecules may be negligible in comparison with the total volume. However, at high pressures or at low temperatures, the total volume of the gas decreases appreciably. Under these conditions the volume of the molecules is not negligible as compared to the total volume.

(ii) The assumption that there are no intermolecular forces between gas molecules is not strictly true. The very fact that gases can be condensed to liquids and solids indicates that there are weak attractive forces present between molecules. The attractive forces become large when molecules are crowded together at high pressure or low temperature. Thus this assumption is also invalid at high pressure and low temperature.

van der Waal's Equation

By taking into account, the volume of individual molecules and the intermolecular force of attraction in a gas, van der Waals modified the ideal gas equation to make it applicable to real gases.

At high pressures, molecules of a gas are close together and there is considerable intermolecular interaction. So the molecules of the gas do not strike the walls of the container with full impact because they are dragged back by other molecules present in the bulk. Thus the pressure exerted by the gas is lower than the pressure expected for ideal gas. The ideal pressure is obtained by adding a correction tem for the observed (or real) pressure. The correction term is given by

$\frac{an^2}{V^2}$, where '*a*' is a constant and '*n*' is the number of moles

i.e., $P_{ideal} = P_{real} + \frac{an^2}{V^2}$

Again, at high pressure the volume occupied by the molecules becomes significant. Instead of moving through the whole volume *V*, the molecules are restricted to move through a volume $(V - nb)$ where *nb* is approximately the total volume occupied by the molecules of *n* moles of the gas

The modified equation, known as van der Waals equation, for *n* moles of a gas is

$$\left(P + \frac{an^2}{v^2}\right)(v - nb) = nRT$$

For 1 mole of a real gas, the equation become $\left(P + \frac{a}{V^2}\right)(V - b) = RT$

where '*a*' and ''*b*' are the van der Waals constants, the values of which depend on the nature of the gas.