Chapter -13

Kinetic Theory

Gases have negligible force of molecular interaction. They have no shape and size and can be contained in vessels of any shape and size. So. gases expands indefinitely and uniformly to fill the available space by considering that gases are made up of atomic particles, many scientists like Boyle and Newton tried to explain the behaviour of gases.

But the real theory was developed in the nineteenth century by Maxwell and Boltzmann. In this chapter we shall study some of the features of Kinetic theory.

Molecular Theory of Matter

According to the law of definite proportions, a given compound always contains same element in the same proportion. irrespective of the source. According to the laws of multiple proportions if two elements can combine to form more than one compound, the masses of one element that combine with a fixed mass of other element, are in the same ratio.

John Datlon, about 200 years ago, proposed the atomic theory. Accoding to this theory

1. The smallest constituents of an element are atoms.

2. Atoms of one element are identical but differ form those of other elements.

3. A small number of atoms of each element combine to form a molecule of a compound.

Behaviour of Gases

In gases molecules are far from each other and due to this the interatomic forces between the molecules is negligible except, when two molecules collide. Hence, the properties of gases are easier to understand then those of solids and liquids.

Gases satisfy a simple relation between pressure, temperature and volume at low pressure and high temperature, this relation is given by equation

$$\boxed{PV = nRT}$$

Where all symbols have their usual meaning.

(i). Avogadro's Hypothesis

According to this hypothesis, "At a

fixed temperature and pressure the number of molecules per unit volume is same for all gases".

The number of molecules in 22.4 litres of any gas is 6.02×10^{23}. This is known as Avogadro number and is denoted by N_A. The mass of 22.4 litres of any gas at S.T.P. (standard temperature 273 K and pressure 1 atm) is equal to its molecular weight which is equal to one mole.

(ii) Boyle's law

According to this law. keeping temperature constant, the pressure of a give mass of a gas varies inversely with volume. If n and T are fixed in ideal gas equation then. PV is constant.

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

$$\boxed{PV = \text{constant}}$$

(iii). Charles' law

According to this law, the volume (V) of a given mass of a gas is directly proportional to the temperature of the gas, provided pressure of the gas remains constant.

$$V \propto T$$

$$\boxed{\frac{V}{T} = \text{constant}}$$

(iv). Gay Lussac's Law

According to this law, the pressure P of a given mass of a gas is directly proportional to its absolute temperature T. provided the volume V of the gas remains constant.

$$P \propto T$$

$$\boxed{\frac{P}{T} = \text{constant}}$$

(v). Dalton's law of partial pressure

According to this law, the total pressure of a mixture of non-interacting ideal gases is the sum of partial pressures.

$$P = P_1 + P_2 + P_3 + \ldots\ldots$$

(vi). Graham's Law of Diffusion

It states that rate of diffusion of a gas is inversely proportional to the square root of the density of the gas.

$$r \propto \sqrt{\frac{1}{\rho}}$$

Hence, denser the gas, the slower is the rate of diffusion.

Kinetic Theory of an Ideal Gas

Kinetic theory of gases is based on the

molecules picture of matter. According to which

1. A given amount of gas is a mixture of very large number of identical molecules of the order of Avogadro's number.

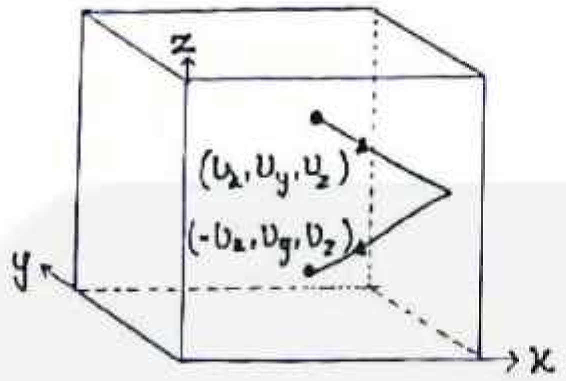
2. The molecules are moving randomly in all directions.

3. At ordinary temperature and pressure the size of the molecules is very small as compared to the distances between them. Thus, the interaction between them is negligible.

4. The molecules do not exert any force of attration or repulsion on each other, except during collisions.

5. The collisions of molecules against each other or with the wells of the container are perfectly elastic. Such that the momentum and the kinetic energy of the molecules are conserved during

collisions, though their velocities change.



Kinetic Interpretation of Temperature

The total average kinetic energy of all the molecules of a gas is proportional to its absolute temperature (T). Thus, the temperature of a gas is a measure of the average kinetic energy 'U' of the molecules of the gas.

$$\boxed{U = \frac{3}{2} RT}$$

According to this interpretation of temperature, the average kinetic energy U is zero at T = 0, i.e., the motion of molecules ceases altogether at absolute zero.

Law of Equipartition of Energy

For a dynamic system in thermal equilibrium, the energy of the system is equally distributed amongst the various degrees of freedom and the energy associated with each degree of freedom per molecule is 1/2 kT, where k is Baltzman constant.

$$\boxed{\left\langle \frac{1}{2} mv^2 \right\rangle = \frac{1}{2} kT}$$

Degrees of Freedom

Degrees of freedom of a system is defined as the total number of co-ordinates or independent quantities required to describe the position and configuration of the system completely.

Mono-, di-, and polyatomic (N) molecules have 3, 5 or (3N-K) number of freedom where k is the number of constraints.

Specific Heat Capacity

Specific heat capacity is defined as the amount of heat energy required to raise the temperature of a gas by one degree celsius.

(i). Monoatomic Gas

The molecule of a monatomic gas has only three translational degress of freedom. Thus. the average energy of a molecule at temperture T is (3/2) K B T. The total internal energy of a mole of such a gas is

$$\boxed{U = \frac{3}{2} k \times T \times N_A = \frac{3}{2} RT}$$

The molar specific heat at constant

volume, C_v, is

$$C_v = \frac{dU}{dT} = \frac{3}{2} RT$$

Malar specific heat for ideal gas at constant pressure C_p is given by.

$$C_p = R + C_v$$

$$C_p = R + \frac{3}{2} RT$$

$$C_p = \frac{5}{2} RT$$

$$\boxed{\gamma = \frac{C_p}{C_v} = \frac{5}{3}}$$

(ii). Diatomic Gas

A diatomic molecule treated as a rigid rotator, like a dumbbell, has 5 degrees of freedom: 3 translational and 2 rotational. Using the law of equipartition of energy, the total internal energy of a male of such a gas is

$$U = \frac{5}{2} k \times T \times N_A = \frac{5}{2} RT$$

The malar specific heats are then given by

$$C_v = \frac{dU}{dT} = \frac{5}{2} R$$

Malar specific heat for ideal gas at constant pressure Cp is given by.

$$C_p = R + C_v$$

$$C_p = R + \frac{7}{2} RT$$

$$C_p = \frac{9}{2} RT$$

$$\boxed{\gamma = \frac{C_p}{C_v} = \frac{9}{7}}$$

(iii). Polyatomic Gas

In general, a polyatomic molecule has 3 translational, 3 rotational degrees of freedom and f vibrational modes. According to the law of equipartition of energy, the total internal energy for one mole of polyatomic gas can be calculated as

$$U = \left(\frac{3}{2}KT + \frac{3}{2}KT + fKT\right)N_A$$

$$U = (3+f)RT$$

$$\boxed{C_v = \frac{dU}{dT} = (3+f)R}$$

Molar specific heat for ideal gas at constant pressure C_p is given by.

$$C_p = R + C_v$$

$$C_p = R + (3+f)R$$

$$C_p = (4+f)R$$

$$\gamma = \frac{C_p}{C_v} = \frac{(4+f)}{(3+f)}$$

Mean Free Path

Mean free path of a molecule in a gas is the averge distance travelled by the molecule between two successive collisions.

If $\lambda_1, \lambda_2, \lambda_3, \ldots \lambda_N$ be the free paths tavelled by the molecule in N successiv collision, then mean free path is given by

$$\lambda = \frac{\lambda_1 + \lambda_2 + \lambda_3 + \ldots + \lambda_N}{N}$$

$$\boxed{\lambda = \frac{1}{\sqrt{2}\, n \pi d^2}}$$