

5) Graham's law of diffusion :-

Since

$$PV = \frac{1}{3} mNc^2 \quad \text{--- (1)}$$

$$c = \sqrt{\frac{3PV}{mN}} = \sqrt{\frac{3P}{\rho}} \quad \text{--- (2)}$$

Since $\frac{mN}{V} = \rho$ (density of the gas)

The rate of diffusion (r) of a gas depends upon the mean velocity of its molecules.

$$\text{i.e. } r \propto c \propto \left(\frac{3P}{\rho}\right)^{\frac{1}{2}} \text{ or } \left(\frac{1}{2}\rho\right)^{\frac{1}{2}} \text{ at constant } P$$

The rate of diffusion of gas is inversely proportional to the square root of the density of gas at constant pressure. This is known as Graham's law of diffusion.

<6> Dalton's law of Partial Pressure :-

Suppose N_1 molecules, each of mass m_1 , of a gas A, are contained in a vessel of volume V .

According to eq.

$$P = \left(\frac{1}{3}V\right) mNc^2 \quad \text{--- (1)}$$

The pressure P_a of the gas will be given by

$$P_a = \frac{m_1 N_1 c_1^2}{3V} \quad \text{--- (2)}$$

where c_1 is the root mean square velocity of molecules of gas A.

For N_2 molecules, each of mass m_2 , of another gas B in the same vessel and at the same temperature

$$P_b = m_2 N_2 C_2^2 / 3V \quad \text{--- (3)}$$

C_2 is the root mean square velocity of the molecules of gas B.

If both the gases are present in the same vessel at the same time, then the total pressure P will be given by

$$\begin{aligned} P &= m_1 N_1 C_1^2 / 3V + m_2 N_2 C_2^2 / 3V \\ &= p_a + p_b \quad \text{--- (4)} \end{aligned}$$

For more gases the equation is

$$P = p_a + p_b + p_c + \dots + \dots \quad \text{--- (5)}$$

The equation is known as Dalton's law of Partial Pressure.

Kinetic Energy and temperature:-

suppose one mole of gas is under consideration. The number of molecules involved will be then N_A (the Avogadro's number). The kinetic gas equation may be written as

$$PV = \frac{1}{3} m N_A C^2 = \frac{2}{3} \times \frac{1}{2} m N_A C^2 = \frac{2}{3} E \quad \text{--- (1)}$$

Here E is the translational energy of one mole of gas

For ideal gas

$$PV = RT \quad (n=1) \quad \text{--- (2)}$$

Therefore

$$E = \frac{3}{2} RT \quad \text{--- (3)}$$

Thus, the translational kinetic energy of an ideal gas is directly proportional to the absolute temperature.

Since, Translational kinetic energy $\propto c^2$

Therefore

$$c^2 \propto T \quad \text{or} \quad c \propto \sqrt{T}$$

It can, therefore, be said that molecular velocity of any gas is proportional to the square root of absolute temperature.

That is why molecular motion is also referred as thermal motion of the molecules.

At absolute zero ($T=0$), $K.E = 0$.

Thus, the thermal motion also completely ceases at absolute zero.

The translational K.E. is independent of volume or pressure, molar mass and nature of the gas. But it depends only upon the temperature.

* This is the reason why H_2 molecule has velocity same average translational K.E. as a molecule of N_2 , NH_3 or CH_4 . However, the molecular velocities are much different.

One molecule of ideal gas has average translational K.E. given as

$$E = \frac{E}{N_A} = \frac{3}{2} RT/N_A = \frac{3}{2} kT$$

Here ($k = R/N_A$) is the Boltzmann constant.

and its numerical value is $1.38 \times 10^{-23} \text{ JK}^{-1}$.

Q Calculate the average translational K.E. of an ideal gas per molecule (E) and per mole (E) at 25°C .

Maxwell distribution of molecular velocities:-

$$p(u) du = \left(\frac{m}{2kT\pi} \right)^{1/2} e^{-mu^2/2kT} du \quad \text{--- (1)}$$

Maxwell distribution of molecular velocities in one direction

where $p(u)$ is the probability of a molecule having velocity component between u and $u+du$, for a gas having mass (m) and velocity component u .

For probability of molecular velocity distribution in three directions can be given by,

$$p(u, v, w) = p(u) \cdot p(v) \cdot p(w) \quad \text{--- (2)}$$

$$\text{or } p(u, v, w) du dv dw = p(u) du \cdot p(v) dv \cdot p(w) dw \quad \text{--- (3)}$$

The fraction of molecules with velocity between c and $c+dc$ ($c^2 = u^2 + v^2 + w^2$) regardless of the direction can be given as.

$$p(u, v, w) du dv dw = \left(\frac{m}{2\pi kT} \right)^{3/2} \exp \left[-\frac{m(u^2 + v^2 + w^2)}{2kT} \right] du dv dw \quad \text{--- (4)}$$

Consider the molecules having velocity points lying within a spherical shell of thickness dc at a distance c . This shell has volume $4\pi c^2 dc$.

$$\text{Also } \int du \cdot dv \cdot dw = 4\pi c^2 dc \quad \text{--- (5)}$$

Hence

$$p(c) dc = 4\pi \left(\frac{m}{2\pi kT} \right)^{3/2} c^2 \exp(-mc^2/2kT) dc \quad \text{--- (6)}$$

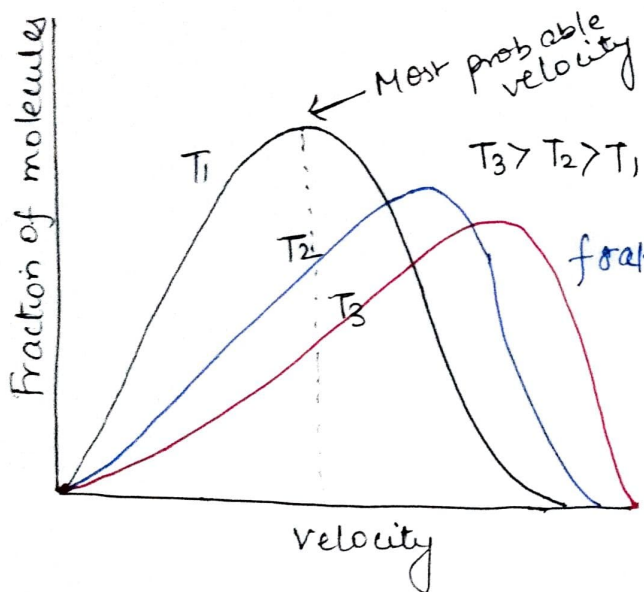
↑

Maxwell's distribution of molecular velocity.

$p(c) dc = dN/N$ where $p(c) dc$ is the fraction of molecules with velocity between c and $c+dc$.

The molecular mass $m = \frac{M}{N_A}$ where M is the molar mass and N_A is the Avogadro's number. Hence equation (6) can be rewritten as

$$p(c)dc = \frac{dN}{N} = 4\pi \left[\left(\frac{M}{2\pi RT} \right)^{3/2} c^2 \exp\left(-\frac{Mc^2}{2RT}\right) \right] dc$$



← Plot of molecular velocity distribution

It can be seen clearly that fraction of molecules having velocity greater than zero increases with an increase in velocity, rises to a maximum and then falls at higher velocity.

The curve has two salient features:-

- i) There is small fraction of molecules with very high velocity or low velocity.
- ii) There is a certain velocity at which the fraction of molecules is maximum. This is called most probable velocity.

Most probable velocity is defined as velocity possessed by maximum number of molecules of gas at a given temperature. It is directly dependent on the volume of gas.

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