Undergraduate Semester II

MJC-2(T): Physical Chemistry: States of Matter and Ionic Equilibrium

1. Gaseous State:

Derivation of Ideal Gas Equation from Kinetic Energy

Let's explore the derivation of ideal gas equation from kinetic energy using the principles of kinetic molecular theory.

Assumptions of the Kinetic Theory of Gases

- Gases are composed of countless tiny particles called molecules.
- These gas molecules are always moving in constant, random motions.
- The volume of individual gas molecules is negligible compared to the total volume.
- Intermolecular forces of attraction or repulsion between gas molecules are considered negligible (except when the molecules collide).
- Collisions between gas molecules & the container walls are assumed to be perfectly elastic.
- The motion of gas molecules follows Newton's laws of motion.

Pressure of an Ideal Gas:

From the above postulates, it is possible, by applying the laws of classical mechanics, to derive an expression for the pressure of a gas.

Let us consider N molecules of a gas, each having a mass m, enclosed in a cubical vessel of volume V, each side of the cube being l. The motion of molecules in the container, at any instant, is totally random.

Consider one molecule of the gas having a velocity c. This velocity can be resolved into components u, v and w, along the three axes x, y and z.

The velocity components are, evidently, perpendicular to the walls of the container. It can be easily shown that

$c^2 = u^2 + v^2 + w^2$ ……………………………………………(1)

Consider the motion of one molecule along the x - axis, striking the wall which is perpendicular to its motion. Since the collision is elastic and the wall remains stationary, on rebounding, only the sign of the velocity component changes. The resulting change of momentum in the

x-direction (Δp_x) is, therefore given by,

$\Delta p_x = m\ \{u-(-u)\} = 2mu$ ……………………….(2)

Immediately after the collision, the molecule takes time equal to l/u to collide with the opposite wall (and time equal to $2l/u$ to strike against the same wall again). Hence, the frequency of collisions on the two opposite walls is given by u/l and the change in momentum per unit time is given by,

$\Delta px/\Delta t = 2mu \times u/l = 2mu^2/l$ ………………………..(3)

The total change in momentum of the single molecule per unit time arising from collisions on all the six walls is given by,

$\Delta p/\Delta t = 2mu^2/l + 2mv^2/l + 2mw^2/l = (2m/l)\ (u^2 + v^2 + w^2) = 2mc^2/l$ …………….. (4)

The total change in momentum per unit time for all the N molecules in the container is obtained by summing the contributions of all the molecules. Thus,

$$\frac{\Delta P_{total}}{\Delta t} = \sum_{i=1}^{N} \frac{2mc_i^2}{l} = \frac{2m}{l} \sum_{i=1}^{N} c_i^2 \quad \text{— (5)}$$

Defining mean square velocity as

$$\langle c^2 \rangle = \sum c_i^2 / N \quad \text{— (6)}$$

$$\text{we get,} \quad \Delta P_{total}/\Delta t = \frac{2mN}{l} \langle c^2 \rangle \quad \text{— (7)}$$

According to Newton's second law of motion, the rate of change of momentum ($\Delta p_{total}/\Delta t$) is force ($f$) and force per unit area is pressure (P). Since the face area (A) of the cubical vessel is

$6l^2$ and its volume is V the pressure exerted by N molecules of the gas on the walls of the vessel is given by,

$$P = \frac{f}{A} = \frac{2mN\langle c^2\rangle}{l(6l^2)} = \frac{1}{3V}\, mN\langle c^2\rangle \quad \text{— (8)}$$

Evidently, $\langle c^2\rangle^{1/2}$ would be the root mean square velocity of the gaseous molecules, given by $(\Sigma c_i^2/N)^{1/2}$.

For the sake of convenience, the root mean square velocity is denoted by c. Therefore, eq. (8), giving the pressure of the gas, is written as,

$$P = (1/3V)\, mNc^2 \quad \text{— (9)}$$

Equation (9) is generally expressed as,

$$PV = (1/3)\, mNc^2 \quad \text{— (10)}$$

This is known as the kinetic gas equation.