

# Kinetic Theory

- **Atomic hypothesis:** All things are made of atoms – little particles that move around in perpetual motion, attracting each other when they are at a little distance apart and repelling when squeezed into one another.
- **Atomic theory:** Proposed by John Dalton to explain the laws of definite and multiple proportions.
- First law states that any given compound has fixed proportion by mass of its constituents.
- Second law states that when two elements form more than one compound, for a fixed mass of one element, the masses of the other elements are in the ratio of small integers.
- **Gay-Lussac's law:** When gases combine chemically to yield another gas, their volumes are in the ratio of small integers.
- **Avogadro's law:** Equal volumes of all gases at equal temperature and pressure have the same number of molecules.
- **Boyle's Law**  $\rightarrow \rightarrow PV = \text{constant}$ , at constant temperature
- **Charles's Law**  $\rightarrow \rightarrow V \propto T$ , provided  $P$  is constant
- **Avogadro's Law**  $\rightarrow \rightarrow$  At the same temperature and pressure, equal volumes of all gases contain equal number of molecules.

- **Graham's Law of Diffusion** → → At same temperature and pressure, the rate of diffusion of each gas is inversely proportional to the square root of the density of the gas.

$$\frac{r_1}{r_2} = \sqrt{\frac{\rho_2}{\rho_1}}$$

- **Dalton's Law of Partial Pressure:** The pressure exerted by a mixture of several gases equals the sum of the pressures exerted by each gas occupying the same volume as that of the mixture.

$$P = P_1 + P_2 + P_3 + P_4 + \dots$$

- **Equation of state of a perfect gas** → →

$$\frac{PV}{T} = \text{Constant}$$

### Assumptions of Kinetic Theory of Gases:

- Gases are made up of a large number of tiny molecules.
- Molecules in a gas have much space between them, such that the actual volume occupied by the gas is very small compared to the total volume of the gas .
- Molecules are perfectly rigid and perfectly elastic spheres of very small diameters.
- All the molecules have same size, shape and mass.

### Random motion of gas molecules

- Gas molecules are in constant random motion. At any given time, molecules are moving in many different directions at many different speeds.
- Due to their random motion, the molecules constantly collide with each other and also with the walls of the container. Molecular collisions are perfectly elastic.
- Between two successive collisions, a molecule travels in a straight line with steady velocity. This is known as the mean free path.
- The time taken for the collision is very small compared to the time required to cover the free path between the two collisions.
- **Assumptions of kinetic theory of gases:**
  - The size of a molecule is much smaller than the average separation between the molecules. Also the volume of the gas is negligible compared to the volume of the container.
  - The molecules exert no force on each other or on the walls of the container except during collision. All collisions are perfectly elastic. And the molecules obey Newton's laws of motion.
  - The gas comes to a steady state after a sufficient time, and at the steady state the density and the distribution of molecules with different velocities are independent of position, direction and time.
  - All gases are made of molecules moving randomly in all directions.

- **Pressure of a gas**  $\rightarrow \rightarrow P = \frac{1}{3} \frac{nm}{V} C^2$ , where

$n \rightarrow \rightarrow$  Number of molecules

$m \rightarrow \rightarrow$  Mass of each molecule

$V \rightarrow \rightarrow$  Volume of the container

$C \rightarrow \rightarrow$  Root mean square speed of the molecules

- Internal energy ( $E$ ) of an ideal gas is purely kinetic.

$$E = N \times \frac{1}{2} m \bar{v}^2$$

- The average kinetic energy of a molecule is directly proportional to the absolute temperature of the gas.

$$\Rightarrow \frac{E}{N} = \frac{3}{2} K_B T$$

- Total number of co-ordinates or independent quantities required to describe the configuration of a system completely is called degree of freedom.
- **Law of Equipartition of Energy** – A dynamic system in thermal equilibrium has the energy system equally distributed amongst the various degrees of freedom and the energy associated with each degree of freedom per molecule is  $\frac{1}{2} k_B T$ .
- Monoatomic gas
  - It has three degrees of freedom for translational motion. Mean kinetic energy of translational motion of gas is

$$\frac{1}{2}mv^2 = \frac{3}{2}k_B T$$

- Translational and rotational degree of freedom of molecule contributes  $\frac{1}{2}k_B T$  to the energy.
- Vibrational mode has both kinetic and potential energy. Therefore, each vibrational frequency contributes  $2 \times \frac{1}{2}k_B T = k_B T$

### Specific heat capacity:

- Monatomic gases  $\rightarrow C_v = \frac{3}{2}R, C_p = \frac{5}{2}R, \gamma = \frac{5}{3}$
- Diatomic gases  $\rightarrow C_v = \frac{5}{2}R, C_p = \frac{7}{2}R, \gamma = \frac{7}{5}$
- Triatomic gases  $\rightarrow C_v = 3R, C_p = 4R, \gamma = \frac{4}{3}$
- Polyatomic Gases  $\rightarrow$   
 $C_v = (3 + f) R, C_p = (3 + f) R + R, \gamma = \frac{C_p}{C_v} = \frac{4+f}{3+f}$        $C_v=3+f R, C_p=3+f R+R, \gamma=C_p/C_v=4+f/3+f$   
 $f$  is number of vibrational modes.
- Specific heat capacity can be determined using the law of equipartition of energy.
- Specific heat capacity of solids,  $C = \frac{\Delta Q}{\Delta T} = 3R$ .  $C=\Delta Q/\Delta T=3R$ .
- The mean free path,  $l$ , is the average distance covered by a molecule between two successive collisions.

$$\bar{l} = \frac{1}{\sqrt{2n} d^2}$$

Here,  $n$  is the number density and  $d$  is the diameter of the molecule.

- We assumed that other molecules are at rest.
- For an ideal gas containing  $N$  molecules with velocities  $C_1, C_2, \dots, C_N$ .

$$\overline{C} = \frac{C_1 + C_2 + \dots + C_N}{N} \quad C = C_1 + C_2 + \dots + C_N$$

- Mean Velocity (Average velocity)  $\overline{C}$  of an ideal gas,

- Mean Square Velocity ( $\overline{C^2}$ ) of an ideal gas,

$$\overline{C^2} = \frac{C_1^2 + C_2^2 + \dots + C_N^2}{N} \quad C^2 = C_1^2 + C_2^2 + \dots + C_N^2$$

- Root Mean Square Velocity ( $\sqrt{\overline{C^2}}$ ) of an ideal gas,

$$C_{\text{RMS}} = \sqrt{\overline{C^2}}$$

- $C_{\text{RMS}} = \sqrt{\frac{C_1^2 + C_2^2 + \dots + C_N^2}{N}}$

- **Maxwell's Distribution :**

- In a given mass of gas, the velocities of all the molecules are different, even if the bulk parameters like pressure, volume and temperature are fixed.