

# KINETIC THEORY

Q1) State the assumption of kinetic theory of gases

- a) A gas consists of a very large number of extremely small molecules.
- b) The molecules are rigid and perfectly elastic spheres of very small diameters.
- c) All the molecules of the same gas are identical.
- d) The actual volume occupied by the molecules is very small compared to the volume of the gas.
- e) The intermolecular forces of attraction between gas molecules are negligible.
- f) The molecules are always in a state of random motion.
- g) Due to random motion, the molecules constantly collide with each other and with the walls of the container. This exerts pressure on the walls of the container.
- h) The collisions are perfectly elastic, i.e. there is no loss of kinetic energy during collisions.
- i) Between two successive collisions, a molecule travels in a straight line with a constant velocity.
- j) The time of impact is very small compared to the time interval between the successive collisions.
- k) At constant temperature, the average kinetic energy of the gas molecules remains constant.

Q2) Define : (1) Mean free path (2) Root mean square velocity (3) Mean velocity

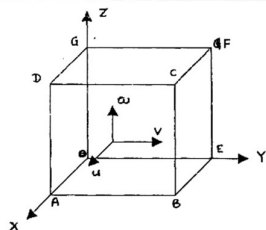
- (1) **Mean free path** : It is defined as the average distance covered by a molecule between two successive collisions.  
If  $S$  is the total distance covered by a molecule during which it has suffered  $N$  number of collisions, the mean free path =  $S/N$
- (2) **Root mean square velocity** : It is defined as the square root of the mean of the squares of the velocities of individual molecules.

$$\bar{C}_{rms} = \sqrt{\frac{C_1^2 + C_2^2 + \dots + C_N^2}{N}}$$

- (3) **Mean velocity** : It is the average of velocities of the gas molecules.

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

Q3) On the basis of kinetic theory of gases, obtain an expression for the pressure exerted by a gas



Consider an ideal gas, which is enclosed in a cubical container having each side of length  $L$ .

Let .....  
 $m$  = the mass of each molecule,  $N$  = the number of molecules of the gas  
 $M$  = the total mass of the gas =  $mN$

$A$  = the area of each face of the cube =  $L^2$ ,  $\rho$  = the density of the gas =  $\left(\frac{M}{V}\right)$

The molecules of the gas are moving in all possible directions with all possible velocities. Let  $C_1, C_2, C_3, \dots, C_N$  be the velocities of the molecules. Let  $(u_1, v_1, w_1), (u_2, v_2, w_2), (u_3, v_3, w_3), \dots, (u_N, v_N, w_N)$  respectively be the  $X, Y$  and  $Z$  components of their velocities.

Let us consider a molecule having velocity  $C_1$ . Then,  $C_1^2 = u_1^2 + v_1^2 + w_1^2$

Consider the motion of the above molecule along  $X$  axis.

Its momentum before collision with the wall  $ABCD = m u_1$ .

Its momentum after the collision is  $-m u_1$  (elastic collision)

So change in its momentum = (final momentum) - (initial momentum) =  $-2m u_1$

$\therefore$  Momentum imparted to the wall  $ABCD = +2m u_1$

The molecule now travels with velocity  $-u_1$  and collides with the wall  $EFGH$ .

Between two successive collisions with the same surface, the molecules cover a distance  $2L$ . Hence in 1 sec, the number of collisions of the molecule with the surface  $ABCD$  is

$$\frac{u_1}{2L}$$

$\therefore$  Total momentum imparted to the wall  $ABCD$  in one sec. = (Change in momentum)  $\times$  (Number of collisions) per second

$\therefore$  Rate of change of momentum of the wall  $ABCD = (2m u_1) \times \left(\frac{u_1}{2L}\right) = \frac{m u_1^2}{L}$

Total rate of change of the momentum =  $\left(\frac{m u_1^2}{L} + \frac{m u_2^2}{L} + \dots + \frac{m u_N^2}{L}\right)$

due to all the molecules along  $X$ -axis

According to Newton's second law of motion this is nothing but a force exerted by the molecules on the wall  $ABCD$  and  $EFGH$ .

$$\therefore F_x = \sum_{i=1}^N \frac{m u_i^2}{L}$$

$\therefore$  Pressure exerted by molecules on each wall perpendicular to  $X$ -axis is,

$$P_x = \frac{F_x}{L^2} = \sum_{i=1}^N \frac{m u_i^2}{L^3}$$

Similarly, pressure along  $Y$ -axis and  $Z$ -axis are,

$$P_y = \frac{F_y}{L^2} = \sum_{i=1}^N \frac{m v_i^2}{L^3} \quad \text{and} \quad P_z = \frac{F_z}{L^2} = \sum_{i=1}^N \frac{m w_i^2}{L^3}$$

As molecules are free to move in all possible directions,  $P_x = P_y = P_z = P$

$$\therefore P = \frac{1}{3}(P_x + P_y + P_z)$$

or 
$$P = \frac{1}{3} \frac{m}{L^3} \sum_{i=1}^N (u_i^2 + v_i^2 + w_i^2)$$

But  $C_1^2 = u_1^2 + v_1^2 + w_1^2, C_2^2 = u_2^2 + v_2^2 + w_2^2, \dots, C_N^2 = u_N^2 + v_N^2 + w_N^2$

or 
$$P = \frac{1}{3} \frac{m}{L^3} \sum_{i=1}^N C_i^2 = \frac{1}{3} \frac{mN}{L^3} \sum_{i=1}^N \frac{C_i^2}{N}$$

But  $\sum_{i=1}^N \frac{C_i^2}{N} = \bar{C}^2 =$  mean square velocity of gas molecule and  $L^3$  is the volume  $V$ .

$$\therefore P = \frac{1}{3} \frac{mN}{V} \bar{C}^2 \quad \text{or} \quad P = \frac{1}{3} \frac{M}{V} \bar{C}^2 \quad \text{or} \quad P = \frac{2}{3} \rho \bar{C}^2$$

Where  $M$  = total mass and  $\rho$  = density of the gas.

Q4) Derive Boyle's law on the basis of kinetic theory of gases.

**Statement** : At constant temperature, the pressure exerted by a given mass of an enclosed ideal gas is inversely proportional to its volume.

$$P \propto \frac{1}{V} \quad \text{or} \quad PV = \text{constant}$$

According to kinetic theory of gases,

$$P = \frac{1}{3} \frac{Nm \bar{C}^2}{V}$$

$N$  = Number of molecules,  $m$  = mass of each molecule,

$\bar{C}^2$  = mean square velocity,  $V$  = volume

$$PV = \frac{1}{3} Nm \bar{C}^2 = \frac{2}{3} \frac{Nm \bar{C}^2}{2}$$

But  $\frac{m \bar{C}^2}{2}$  is the average kinetic energy per molecule of the gas.

$$PV = \frac{2}{3} N (\text{K.E. of a molecule})$$

According to the assumption of the kinetic theory of gases, at a constant temperature average kinetic energy of a gas molecule is constant.

Thus, for a given mass of a gas,  $PV = \text{constant}$ . Thus, Boyle's law is proved.

Q5) Obtain an expression for K.E. of a gas per unit volume.

Consider an ideal gas enclosed in a cylinder having volume  $V$ . Let  $M$  be its total mass and  $\bar{C}^2$  be the mean square velocity of its molecule. Then, the pressure exerted by the gas is

given by 
$$P = \frac{1}{3} \frac{M \bar{C}^2}{V}$$

$$\therefore M \bar{C}^2 = 3PV \quad \text{or} \quad \frac{M \bar{C}^2}{2} = \frac{3PV}{2}$$

But  $\frac{M \bar{C}^2}{2} =$  kinetic energy of the gas =  $\frac{3PV}{2}$

$$\text{Kinetic energy per unit volume} = \frac{3P}{2}$$

Q6) Obtain an expression for kinetic energy per unit mole.

Consider one mole of an ideal gas enclosed in a cylinder of volume  $V$ . Let  $M$  be its total mass and  $\bar{C}^2$  be the mean square velocity of its molecule. Then, the pressure exerted by the gas is given by

$$P = \frac{1}{3} \frac{M \bar{C}^2}{V}$$

$$M \bar{C}^2 = 3PV \quad \text{or} \quad \frac{M \bar{C}^2}{2} = \frac{3PV}{2}$$

But  $PV = RT$  for 1 mole of gas, and  $\frac{M \bar{C}^2}{2} =$  kinetic energy of the gas

$$\text{Kinetic energy per unit mole of gas} = \frac{3RT}{2}$$

$$\left( \text{Note : Kinetic energy per molecule} = \frac{3RT}{2N_A} = \frac{3KT}{2} \right)$$

where  $K = \text{Boltzmann's constant} = \frac{R}{N_A}$ ,  $N_A = \text{Avagadro's number}$

$$\text{kinetic energy per unit mass} = \frac{3RT}{2M_w}, \quad M_w = \text{molecular wt.}$$

Q7) Show that the R.M.S. velocity of the gas molecules is directly proportional to the square root of its absolute temperature.

Consider one mole of an ideal gas enclosed in a cylinder of volume  $V$ . Let  $M$  be its total mass and  $\bar{C}^2$  be the mean square velocity of its molecule. Then, the pressure exerted by the gas is given by

$$P = \frac{1}{3} \frac{MC^2}{V}$$

$$\bar{C}^2 = \frac{3PV}{M}$$

But  $PV = nRT$  for  $n$  mole of a gas,

$$C_{\text{rms}} = \sqrt{\frac{3nRT}{M}}$$

But  $n = \frac{M}{M_w} = \frac{\text{total mass of a gas}}{\text{molecular weight of that gas}}$

$$\therefore C_{\text{rms}} = \sqrt{\frac{3RT}{M_w}}$$

**First law of thermodynamics:** If a thermodynamic system absorbs a quantity of heat  $dQ$  as a result of which its internal energy is increased by  $dU$  and it does an amount of external work  $dW$ , then  $dQ = dU + dW$  ..... (1)  
But  $dQ$  is in heat unit while  $dU$  and  $dW$  are in work unit, then equation (1) can be written as  $dQ = \frac{dU + dW}{J}$ , where  $J = \text{mechanical equivalent of heat} = 4185.5 \frac{\text{J}}{\text{Kcal}}$

Q10) Define principal and molar specific heat of a gas at constant pressure and at constant volume.

**Principle specific heat at constant volume** is defined as the quantity of heat required to raise the temperature of unit mass of a gas through  $1^\circ\text{C}$  or  $1^\circ\text{K}$  at constant volume. It is denoted by  $c_v$  and its unit is  $\text{kcal / kg / }^\circ\text{K}$

**Principle specific heat at constant pressure** is defined as the quantity of heat required to raise the temperature of unit mass of a gas through  $1^\circ\text{C}$  or  $1^\circ\text{K}$  at constant pressure. It is denoted by  $c_p$  and its unit  $\text{kcal / kg / }^\circ\text{K}$ .

**Molar specific heat at constant volume** is defined as the quantity of heat required to raise the temperature of one mole (express in kg) of a gas through  $1^\circ\text{C}$  or  $1^\circ\text{K}$  at constant volume. It is denoted by  $C_v$  and its unit is  $\text{kcal / kmole / }^\circ\text{K}$ .

**Molar specific heat at constant pressure** is defined as the quantity of heat required to raise the temperature of one mole (express in kg) of a gas through  $1^\circ\text{C}$  or  $1^\circ\text{K}$  at constant pressure. It is denoted by  $C_p$  and its unit  $\text{kcal / kmole / }^\circ\text{K}$

Q11) Why is  $c_p > c_v$ ? (2)

When a given mass of heated at a constant volume then the entire heat supplied is used to raise the kinetic energy of the gas molecules which also called internal energy of a gas  $dU$ . As a result its temperature also rises by  $dT$ .

$$dQ_v = dU = mc_v dT \dots (1)$$

When the same gas is heated at constant pressure so that its temperature rises by same amount  $dT$  then the heat supplied is used for

- 1) to increase its heated energy ( $dU$ ) which is same as ( $dQ$ ) and
- 2) to do work against external pressure while pushing the piston up ( $dW$ )

$$dQ_p = dU + dW \dots (2)$$

$$\text{But } dQ_p = mc_p dT$$

$$mc_p dT = dU + mc_v dT$$

$$\text{Thus } c_p > c_v$$

$$\begin{aligned} dQ &= dU + dW \\ nC_p dT &= nC_v dT + P \cdot dV \\ nC_p dT &= nC_v dT + nRdT \\ C_p &= C_v + R \\ C_p - C_v &= R \text{ (Mayer's Relation)} \\ \text{Thus, } C_p &> C_v \end{aligned}$$

Let  $\rightarrow L = \text{Total latent heat}$ ,  $L_i = \text{internal latent heat}$ ,  $L_e = \text{external latent heat}$

$$L = L_i + L_e$$

But  $L_e = P \cdot dV$ , where  $P = \text{external pressure}$  and  $dV = \text{increase in the volume}$

$$L = L_i + P \cdot dV \text{ or } L = L_i + \frac{PdV}{J}$$

**Definition:**

- (a) **Internal latent heat:** It is the amount of heat absorbed by unit mass of the substance to do work against intermolecular forces of attraction during the change of state without change in temperature.
- (b) **External latent heat:** It is the amount of heat absorbed by the unit mass of the substance to do work against the external pressure during the change of state without change in temperature.

### Degree of Freedom

The total number of independent ways in which the particle of a system can take up energy.

$$d.f. = 3N - k$$

**Monoatomic:**  $N = 1$ ;  $k = 0$ ;  $d.f. = 3$

**Diatomic:**  $N = 2$ ;  $k = 1$ ;  $d.f. = 5$

**Triatomic:**  $N = 3$ ;  $k = 3$ ;  $d.f. = 6$  (triangular)  
 $N = 3$ ;  $k = 2$ ;  $d.f. = 7$  (linear)

### Law of Equipartition of Energy

Any dynamical system in thermal equilibrium, the energy is equally distributed among its various d.f.s and energy associated with each d.f. is  $\frac{1}{2} k \cdot T$

**Proof:** K.E./molecule =  $\frac{1}{2} m c^2 = \frac{3}{2} k \cdot T$

$$\frac{1}{2} m (c_x^2 + c_y^2 + c_z^2) = \frac{3}{2} k \cdot T$$

$$\frac{1}{2} m c_x^2 + \frac{1}{2} m c_y^2 + \frac{1}{2} m c_z^2 = \frac{3}{2} k \cdot T$$

$$KEx/\text{molecule} + KEy/\text{molecule} + KEz/\text{molecule} = \frac{3}{2} k \cdot T$$

But,  $KEx = KEy = KEz$  (due to random motion)

$$K.E.x / \text{molecule} + K.E.y / \text{molecule} + K.E.z / \text{molecule} = \frac{1}{2} k \cdot T$$

### Cp, Cv, γ for Mono, Di, Tri, Poly atomic

**Monoatomic:**  $d.f. = 3$

$$\begin{aligned} \text{Total Internal Energy per mole (U)} &= d.f. (KE/\text{molecule}) \times N_A \\ &= 3 \left( \frac{1}{2} k T \right) N_A \\ &= \frac{3}{2} RT \end{aligned}$$

$$C_v = dU/dT = \frac{3}{2} R ; C_p = C_v + R = \frac{5}{2} R ; \gamma = C_p/C_v = 5/3 = 1.67$$

**Diatomic:**  $d.f. = 5$

$$\begin{aligned} \text{Total Internal Energy per mole (U)} &= d.f. (KE/\text{molecule}) \times N_A \\ &= 5 \left( \frac{1}{2} k T \right) N_A \\ &= \frac{5}{2} RT \end{aligned}$$

$$C_v = dU/dT = \frac{5}{2} R ; C_p = C_v + R = \frac{7}{2} R ; \gamma = C_p/C_v = 7/5 = 1.4$$

**Triatomic:**  $d.f. = 6$  (triangular)

$$\begin{aligned} \text{Total Internal Energy per mole (U)} &= d.f. (KE/\text{molecule}) \times N_A \\ &= 6 \left( \frac{1}{2} k T \right) N_A \\ &= 3 RT \end{aligned}$$

$$C_v = dU/dT = 3R ; C_p = C_v + R = 4R ; \gamma = C_p/C_v = 4/3 = 1.33$$

**Triatomic:**  $d.f. = 7$  (Linear)

$$\begin{aligned} \text{Total Internal Energy per mole (U)} &= d.f. (KE/\text{molecule}) \times N_A \\ &= 7 \left( \frac{1}{2} k T \right) N_A \\ &= \frac{7}{2} RT \end{aligned}$$

$$C_v = dU/dT = \frac{7}{2} R ; C_p = C_v + R = \frac{9}{2} R ; \gamma = C_p/C_v = 9/7 = 1.28$$

**Polyatomic:**  $d.f. = f$

$$\begin{aligned} \text{Total Internal Energy per mole (U)} &= d.f. (KE/\text{molecule}) \times N_A \\ &= f \left( \frac{1}{2} k T \right) N_A \\ &= \frac{f}{2} RT \end{aligned}$$

$$C_v = dU/dT = \frac{f}{2} R ; C_p = C_v + R = \left( \frac{f}{2} + 1 \right) R ; \gamma = C_p/C_v = 1 + \frac{2}{f}$$

### Dalton's Law of Partial Pressures

The resultant pressure exerted by a mixture of gasses or vapours which do not interact in any way is equal to sum of their individual pressures.

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

$$P = \frac{1}{3} \rho_1 c_1^2 + \frac{1}{3} \rho_2 c_2^2 + \dots$$

REFER TEXTBOOK FOR MAXWELL DISTRIBUTION, zeroth law, second law of Thermodynamics, heat engine, refrigerator

**Navlakhi**