

Unit - 9

Kinetic Theory

Of Gases

9.1 Kinetic Theory of Gases: Assumption

- (1) The molecules of a gas are identical, spherical and perfectly elastic point masses.
- (2) The volume of molecules is negligible in comparison to the volume of gas.
- (3) Molecules of a gas moves randomly in all direction.
- (4) The speed of gas molecules lie between zero and infinity.
- (5) Their collisions are perfectly elastic.
- (6) The number of collisions per unit volume in a gas remains constant.
- (7) No attractive or repulsive force acts between gas molecules.

9.2 Pressure of an ideal Gas

$$P = \frac{1}{3}\rho V_{\rm rms}^2 \text{ or } P = \frac{1}{3}\frac{mN}{V}V_{\rm rms}^2$$

ms velocity of the gas molecule
$$V_{ms} = \sqrt{\frac{V_1^2 + V_2^2 + V_3^2 + V_4^2 + \dots}{N}}$$

Relation between pressure and kinetic energy

$$\therefore \text{ K.E. per unit volume (E)} = \frac{1}{2} \left(\frac{M}{V} \right) V_{\text{rms}}^2 = \frac{1}{2} \rho V_{\text{rms}}^2 \quad P = \frac{2}{3} E$$

9.3 Ideal Gas Equation

The equation which relates the pressure (P), volume (V) and temperature (T) of the given state of an ideal gas is known as gas equation.

For 1 mole or N_A molecule or M gram or 22.4 littes of gas	PV = RT
For μ mole of gas	$PV = \mu RT$
For l molecule of gas	$PV = \left(\frac{R}{N_A}\right)T = kT$
For N molecules of gas	PV = NkT
For l gm of gas	$PV = \left(\frac{R}{M}\right)T = rT$
forn gm of gas	PV = ro T

(1) Universal gas constant (R): Dimension [ML²T⁻²θ⁻¹]

Thus universal gas constant signifies the work done by (or on) a gas per mole per kelvin.

S.T.P value: 8.31
$$\frac{\text{Joule}}{\text{Mole} \times \text{kelvin}} = 1.98 \frac{\text{cal}}{\text{mole} \times \text{kelvin}}$$

(2) Boltzman's constant (k): Dimension [ML²T⁻² θ ⁻¹]

$$k = 1/38 \times 10^{-23}$$
 Joule/kelvin

9.4 Various Speeds of Gas Molecules

(1) Root wean square speed
$$V_{rms} = \sqrt{\frac{3P}{\rho}} = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3kT}{m}}$$

(2) Most probable speed
$$V_{mp} = \sqrt{\frac{2P}{\rho}} = \sqrt{\frac{2RT}{M}} = \sqrt{\frac{2kT}{m}}$$

(3) Average speed
$$V_{av} = \sqrt{\frac{8P}{\pi \rho}} = \sqrt{\frac{8RT}{\pi M}} = \sqrt{\frac{8kT}{\pi m}}$$

•
$$V_{rms} > V_{av} > V_{mp}$$
 (remembering trick) (RAM)

9.5 Kinetic Energy of Ideal Gas

Molecules of ideal gases possess only translational motion. So they possess only translational kinetic energy.

Quantity of gas	Kinetic energy					
Kinetic energy of a gas molecule (Emolecule)	$= \frac{1}{2} m v_{\mathbf{ms}}^2 = \frac{1}{2} m \left(\frac{3kT}{m} \right) = \frac{3}{2} kT \left[\text{As } v_{\mathbf{ms}} = \sqrt{\frac{3kT}{m}} \right]$					
Kinetic energy of 1 mole (M gram) gas (Emole)	$= \frac{1}{2} M v_{\text{ms}}^2 = \frac{1}{2} M \frac{3RT}{m} = \frac{3}{2} RT \left[As \ v_{\text{ms}} = \sqrt{\frac{3RT}{M}} \right]$					
Kinetic energy of 1 gm gas (Egram)	$= \frac{3}{2} \frac{R}{M} T = \frac{3}{2} \frac{k N_A}{m N_A} T = \frac{3}{2} \frac{k}{m} T = \frac{3}{2} r T$					

Here m = mass of each molecule, M = Molecular weight of gas and $N_A - \text{Avogadro number} = 6.023 \times 10^{23}$.

9.6 Degree of Freedom

The total number of independent modes (ways) in which a system can possess energy is called the degree of freedom (*f*).

The degree of freedom are of three types:

- (i) Translational degree of freedom
- (ii) Rotational degree of freedom
- (iii) Vibrational degree of freedom

General expression for degree of freedom

f = 3N - R, where N = Number of independent particles, R = Number of independent restriction

- (1) Monoatomic gas: It can have 3 degrees of freedom (all translational).
- (2) **Diatomic gas**: A diatomic molecule has 5 degree of freedom: 3 translational and 2 rotational.
- **(3) Triatomic gas (Non-linear) :** It has 6 degrees of freedom : 3 translational and 3 rotational.

(4) Tabular display of degree of freedom of different gases

Atomicity of gas	Example	N	R	f = 3N R	Figure
Monoatomic	He, Ne, Ar	Î	0	f=3	οÀ
Diatomic	H ₂ , O ₂	2	i	f = 5	A B A
Triatomic non linear	H ₂ O	3	:3:	f = 6	A B A
Triatomic linear	CO ₂ , BeCl ₂	3	2	f = 7	A A A A B B

The above degrees of freedom are shown at room temperature. Further
at high temperature the molecule will have an additional degrees of
freedom, due to vibrational motion.

9.7 Law of Equipartition of Energy

For any system in thermal equilibrium, the total energy is equally distributed among its various degree of freedom. And the energy associated with each

molecule of the system per degree of freedom of the system is $\frac{1}{2}kT$.

9.8 Mean Free Path

The average distance travelled by a gas molecule is known as mean free path.

Let λ_1 , λ_2 , λ_3 λ_n be the distance travelled by a gas molecule during n collisions respectively, then the mean free path of a gas molecule is given by

$$\lambda = \frac{\lambda_1 + \lambda_2 + \lambda_3 + \dots + \lambda_n}{n}$$

 $\lambda_1 = \frac{1}{\sqrt{2\pi n}d^2}$; where d = Diameter of the molecule, n = Number of molecules

per unit volume.

9.9 Specific heat or Specific Heat Capacity

- (1) Gram specific heat: It is defined as the amount of heat required to raise the temperature of unit mass of the substance by unit degree. Gram specific heat $c = \frac{\Delta Q}{m\Delta T}$.
- (2) Molar specific heat: It is defined as the amount of heat required to raise the temperature of one gram mole of the substance by a unit degree, it is represented by capital (C)

$$C = \frac{Q}{\mu \Delta T}$$

$$C = Mc = \frac{1}{\mu} \frac{\Delta Q}{\Delta T}$$

$$As \mu = \frac{m}{M}$$

9.10 Specific Heat of Gases

(i) In adiabatic process *i.e.*, $\Delta Q = 0$,

$$C = \frac{\Delta Q}{m(\Delta T)} = 0 \text{ i.e., } C = 0$$

(ii) In isothermal process *i.e.*, $\Delta T = 0$

$$\therefore \qquad C = \frac{\Delta Q}{m(\Delta T)} = \frac{\Delta Q}{0} = \infty \text{ i.e., } C = \infty$$

Specific heat of gas can have any positive value ranging from zero to infinity. Further it can even be negative. Out of many values of specific heat of a gas, two are of special significance.

- (1) Specific heat of a gas at constant volume (C_{ν}) : It is defined as the quantity of heat required to raise the temperature of unit mass of gas through 1 K when its volume is kept constant.
- (2) Specific heat of a gas at constant pressure (C_p) : It is defined as the quantity of heat required to raise the temperature of unit mass of gas through 1 K when its pressure is kept constant.

9.11 Mayer's Formula

$$C_p - C_v = R$$

This relation is called Mayer's formula and shows that $C_p > C_v$ *i.e.*, molar specific heat at constant pressure is greater than that at constant volume.

9.12 Specific Heat in Terms of Degree of Freedom

Specific heat and kinetic energy for different gases

		Monoatomic	Diatomic	Triatomic non-linear	
Atomicity	A	1	2	3	3
Restriction	В	0	1	3	2
Degree of freedom	f = 3A - B	3	5	6	7
Molar specific heat at constant volume	$C_v = \frac{f}{2}R = \frac{R}{\gamma - 1}$	$\frac{3}{2}$ R	$\frac{5}{2}$ R	3R	$\frac{7}{2}$ R
Molar specific heat at constant pressure	$C_p = \left(\frac{f}{2} + 1\right) R = \left(\frac{\gamma}{\gamma - 1}\right) R$	$\frac{5}{2}$ R	$\frac{7}{2}$ R	4R	$\frac{9}{2}$ R
Ratio of C_p and C_v	$y = \frac{C_p}{C_v} = 1 + \frac{2}{f}$	$\frac{5}{3} = 1.66$	$\frac{7}{5} = 1.4$	$\frac{4}{3}$ = 1.33	$\frac{9}{7} = 1.28$
Kinetic energy of 1 mole	$E_{\text{mole}} = \frac{f}{2}RT$	$\frac{3}{2}$ RT	$\frac{5}{2}$ RT	3RT	$\frac{7}{2}$ RT
Kinetic energy of 1 molecule	$E_{\text{molecule}} = \frac{f}{2}kT$	$\frac{3}{2}kT$	$\frac{5}{2}kT$	3 <i>k</i> T	$\frac{7}{2}kT$
Kinetic energy of 1 gm	$E_{gram} = \frac{f}{2}rT$	$\frac{3}{2}rT$	$\frac{5}{2}rT$	3rT	$\frac{7}{2}rT$

QUESTIONS

VERY SHORT ANSWER TYPE QUESTIONS (1 MARK)

1. Write two conditions when real gases obey the ideal gas equation (PV = nRT). $n \rightarrow$ number of mole.

- **2.** If the number of molecule in a container is doubled. What will be the effect on the rms speed of the molecules ?
- **3.** Draw the graph between P and 1/V (reciprocal of volume) for a perfect gas at constant temperature.
- **4.** Name the factors on which the degree of freedom of gas depends.
- **5.** What is the volume of a gas at absolute zero of temperature?
- **6.** How much volume does one mole of a gas occupy at NTP?
- 7. What is an ideal gas?
- **8.** The absolute temperature of a gas is increased 3 times what is the effect on the root mean square velocity of the molecules?
- **9.** What is the Kinetic per unit volume of a gas whose pressure is P?
- **10.** A container has equal number of molecules of hydrogen and carbon dioxide. If a fine hole is made in the container, then which of the two gases shall leak out rapidly?
- 11. What is the mean translational Kinetic energy of a perfect gas molecule at temperature?
- **12.** Why it is not possible to increase the temperature of a gas while keeping its volume and pressure constant.

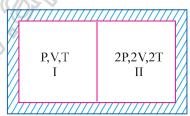
SHORT ANSWER TYPE QUESTIONS (2 MARKS)

- **13.** When an automobile travels for a long distance the air pressure in the tyres increases. Why?
- **14.** A gas storage tank has a small leak. The pressure in the tank drop more quickly if the gas is hydrogen than if it is oxygen. Why?
- **15.** Why the land has a higher temperature than the ocean during the day but a lower temperature at night.
- **16.** Helium is a mixture of two isotopes having atomic masses 3g/mol and 4g/mol. In a sample of helium gas, which atoms move faster on average?
- 17. State Avogadro's law. Deduce it on the basis of Kinetic theory of gases.
- **18.** Although the velocity of air molecules is nearly 0.5 km/s yet the smell of scent spreads at a much slower rate why.
- 19. The root mean square (rms) speed of oxygen molecule at certain temperature 'T' is 'V'. If temperature is doubled and oxygen gas dissociates into atomic oxygen what is the speed of atomic oxygen?

- **20.** Two vessels of the same volume are filled with the same gas at the same temperature. If the pressure of the gas in these vessels be in the ratio 1 : 2 then state
 - (i) The ratio of the rms speeds of the molecules.
 - (ii) The ratio of the number of molecules.
- **21.** Why gases at high pressure and low temperature show large deviation from ideal gas behaviour?
- **22.** A gas is filled in a cylinder fitted with a piston at a definite temperature and pressure. Why the pressure of the gas decreases when the piston is pulled out.

SHORT ANSWER TYPE QUESTIONS (3 MARKS)

- 23. On what parameters does the λ (mean free path) depends.
- **24.** Equal masses of oxygen and helium gases are supplied equal amount of heat. Which gas will undergo a greater temperature rise and why?
- **25.** Why evaporation causes cooling?
- **26.** Two thermally insulated vessels 1 and 2 are filled, with air at temperatures (T_1, T_2) , volume (V_1, V_2) at pressure (P_1, P_2) respectively. If the value joining the two vessels is opened what is temperature of the vessel at equilibrium?
- **27.** A partition divides a container having insulated walls into two compartments I and II. The same gas fills the two compartment. What is the ratio of the number of molecules in compartments I and II ?



28. Prove that for a perfect gas having n degree of freedom

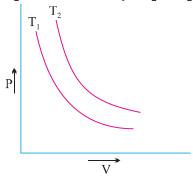
$$\frac{C_p}{C_v} = 1 + \frac{2}{n}$$

where C_p and C_v have their usual meaning.

29. The ratio of specific heat capacity at constant pressure to the specific heat capacity at constant volume of a diatomic gas decreases with increase in

temperature. Explain.

30. Isothermal curves for a given mass of gas are shown at two different temperatures T_1 and T_2 state whether $T_1 > T_2$ or $T_2 > T_1$ justify your answer.



- 31. Three vessels of equal capacity have gases at the same temperature and pressure. The first vessel contains neon (monatomic) the second contains chlorine (diatomic) and the third contains uranium hexafluoride (polyatomic). Do the vessels contain equal number of respective molecules? Is the root mean square speed of molecules the same in the three cases? If not in which case is V_{rms} the largest?
- **32.** State Grahm's law of diffusion. How do you obtain this form Kinetic Theory of gases.

LONG ANSWER TYPE QUESTIONS (5 MARKS)

- **33.** What are the basic assumptions of kinetic theory of gases ? On their basis derive an expression for the pressure exerted by an ideal gas.
- **34.** What is meant by mean free path of a gas molecule? Derive an expression for it.
- **35.** Given that $P = \frac{1}{3}\rho c^2$ where P is the pressure, ρ is the density and c is the rms. Velocity of gas molecules. Deduce Boyle's law and Charles law of gases from it.
- **36.** What do you understand by mean speed, root mean square speed and most probable speed of a gas. The velocities of ten particles in m/s are 0, 2, 3, 4, 4, 4, 5, 5, 6, 9 calculate.
 - (i) Average speed
 - (ii) r.m.s. speed
- **37.** What is law of equipartition of energy? Find the value of $\gamma = C_p/C_v$ for diatomic and monatomic gas. Where symbol have usual meaning.

NUMERICALS

- **38.** An air bubble of volume 1.0 cm³ rises from the bottom of a lake 40 m deep at a temperature of 12°C. To what volume does it grow when it reaches the surface which is at a temperature of 35°C?
- **39.** A vessel is filled with a gas at a pressure of 76 cm of mercury at a certain temperature. The mass of the gas is increased by 50% by introducing more gas in the vessel at the same temperature. Find out the resultant pressure of the gas.
- **40.** One mole of a monoatomic gas is mixed with three moles of a diatomic gas. What is the molecular specific heat of the mixture at constant volume?

Take $R = 8.31/\text{mol}^{-1} \text{ K}^{-1}$.

41. An oxygen cylinder of volume 30 litre has an initial gauge pressure of 15 atmosphere and a temperature of 27°C. After some oxygen is withdrawn from the cylinder, the gauge pressure drops to 11 atmosphere and its temperature drop to 17°C. Estimate the mass of oxygen taken out of the cylinder.

 $(R = 8.31/\text{mol}^{-1} \text{ K}^{-1})$

(molecular mass of $O_2 = 32$)

42. At what temperature the rms speed of oxygen atom equal to r.m.s. speed of helium gas atom at -10° C?

Atomic mass of helium = 4

Atomic mass of oxygen = 32

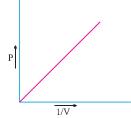
- **43.** Estimate the total number of molecules inclusive of oxygen, nitrogen, water vapour and other constituents in a room of capacity 25.0 m³ at a temperature of 27°C and 1 atmospheric pressure.
- **44.** 0.014 kg of nitrogen is enclosed in a vessel at a temperature of 27°C. How much heat has to be transferred to the gas to double the rms speed of its molecules.

ANSWERS (1 MARK)

- 1. (i) Low pressure
- (ii) High temperature.

2. No effect

3.



- 4. Atomicity and temperature.
- **5.** 0
- **6.** 22.4 litre
- 7. Gas in which intermolecular forces are absent.
- 8. increases $\sqrt{3}$ times
- 9. 3P/2
- **10.** Hydrogen (rms speed is greater)
- 11. $\frac{3}{2}$ RT
- 12. $P = \frac{1}{3} \frac{M}{V} KT$, $T \propto (PV)$

P and V are constant then T is also constant.

ANSWERS (2 MARKS)

- 13. Work is done against friction. This work done is converted into heat. Temperature rises. PV = nRT, As volume of tyre is const. $P \propto T$.
- 14. Rate of diffusion of a gas is inversely proportional to the square root of the density. So hydrogen leaked out more rapidly.
- 15. Specific Heat of water is more than land (earth). Therefore for given heat change in temp. of land is more than ocean (water).

19.
$$c = \sqrt{\frac{3RT}{M}} = v, c' = \sqrt{\frac{3R(2T)}{M/2}} = 2\sqrt{\frac{3RT}{M}}$$

 $c' = 2v$
20. (i) $C \propto \sqrt{T}$

$$c' = 21$$

20. (i)
$$C \propto \sqrt{T}$$

as the temperature is same rms speeds are same.

(ii)
$$P = \frac{1}{3} \frac{mnc^2}{V} \Rightarrow P_1 = \frac{1}{3} \frac{mn_1c^2}{V}, P_2 = \frac{1}{3} \frac{mn_2c^2}{V}$$

i.e.,
$$\frac{P_1}{P_2} = \frac{n_1}{n_2} = \frac{1}{2}$$

21. When temperature is low and pressure is high the intermolecular forces become appreciable thus the volume occupied by the molecular is not negligibly small as composed to volume of gas.

22. When piston is pulled out the volume of the gas increases, Now losses number of molecules colliding against the wall of container per unit area decreases. Hence pressure decreases.

ANSWERS (3 MARKS)

- 23. (i) diameter of molecule as $\lambda \propto \frac{1}{J^2}$
 - (ii) Pressure of gas as $\lambda \propto \frac{1}{R}$
- **24.** Heat supplied to oxygen = Heat supplied to Helium

$$mc_{1}\Delta T_{1} = mc_{2}\Delta T_{2}$$

$$\frac{\Delta T_{1}}{\Delta T_{2}} = \frac{c_{2}}{c_{1}}, \text{ As } c \times \frac{1}{m}, m = \text{molecular mass}$$

$$\frac{\Delta T_{1}}{\Delta T_{2}} = \frac{c_{2}}{c_{1}} = \frac{m_{1}}{m_{2}}, \text{ As } m_{1} > m_{2}$$

$$\Delta T_{1} > \Delta T_{2}$$

- 25. During evaporation fast moving molecules escape a liquid surface so the average kinetic energy of the molecules left behind is decreased thus the temperature of the liquid is lowered.
- **26.** number of mole = Constant

$$\begin{split} \mu_1 + \mu_2 &= \mu \\ \frac{P_1 V_1}{R T_1} + \frac{P_2 V_2}{R T_2} &= \frac{P(V_1 + V_2)}{R T} \end{split}$$

From Boyle's law,
$$P(V_1 + V_2) = P_1V_1 + P_2V_2$$

$$n = \frac{pV}{kT}, n' = \frac{2p2V}{kT}$$

$$n/n' = \frac{1}{2}$$

30. $T = \frac{PV}{\mu R}$, $T \propto P V [\mu R = constant]$

Since PV is greater for the curve at T2 than for the curve T1 therefore

31. Three vessels at the same pressure and temperature have same volume and

contain equal number of molecules.

$$V_{\rm rms} = \sqrt{\frac{3{\rm RT}}{m}}, \ V_{\rm rms} \propto \frac{1}{\sqrt{m}}$$

rms speed will not same, neon has smallest mass therefore rms speed will be largest for neon.

38.
$$V_1 = 10^{-6} \text{ m}^3$$

Pressure on bubble
$$P_1$$
 = Water pressure + Atmospheric pressure
= pgh + Patm
= 4.93×10^5 Pa
 T_1 = $285 k$, T_2 = $308 k$
 $\frac{P_1V_1}{T_1}$ = $\frac{P_2V_2}{T_2}$
 V_2 = $\frac{4.93 \times 10^5 \times 1 \times 10^{-6} \times 308}{285 \times 1.01 \times 10^5}$ = $5.3 \times 10^{-6} m^3$.

39. According to kinetic theory of gases,

$$PV = \frac{1}{3}mv_{\rm rms}^2$$

At constant temperature, $v_{\rm rms}^2$ is constant. As v is also constant, so $P \propto m$. When the mass of the gas increase by 50% pressure also increases by 50%,

$$\therefore \qquad \text{Final pressure} = 76 + \frac{50}{100} \times 76 = 114 \text{ cm of Hg.}$$

40. For monoatomic gas, $C_v = \frac{3}{2} R$, n = 1 mole

For diatomic gas,
$$C_{v}' = \frac{5}{2} R$$
, $n' = 3$ mole

From conservation of energy, the molecular specific heat of the mixture is

$$C_{v}' = \frac{n(C_{v}) + n'(C_{v}')}{(n+n')}$$
$$= \frac{1 \times \frac{3}{2} R + 3 \times \frac{5}{2} R}{(1+3)} = \frac{9}{4} R$$

 $C'v = \frac{9}{4} \times 8.31 = 18.7 \text{ J mol}^{-1} \text{ K}^{-1}.$ or $V_1 = 30 \text{ litre} = 30 \times 10^3 \text{ cm}^3 = 3 \times 10^{-2} \text{ m}^3$

$$P_1 = 15 \times 1.013 \times 10^5 \text{ N/m}^2$$

$$T_1 = 300 \text{ K}$$

$$\mu_1 = \frac{P_1 V_1}{R T_1} = 18.3$$

$$P_2 = 11 \times 1.013 \times 10^5 \text{ N/m}^2$$
 $V_2 = 3 \times 10^{-2} m^3$
 $T_2 = 290 k$

$$V_2 = 3 \times 10^{-2} \, m^3$$

$$\Gamma_2 = 290 k$$

$$T_2 = 290 k$$

$$\mu_2 = \frac{P_2 V_2}{R T_2} = 13.9$$

$$\mu_2 - \mu_1 = 18.3 - 13.9 = 4.4$$

Mass of gas taken out of cylinder

42.

41.

$$v_{\rm rms} = \left[\frac{3\rm PV}{\rm M}\right]^{1/2} = \left[\frac{3\rm RT}{\rm M}\right]^{1/2}$$

Let r.m.s. speed of oxygen is $(v_{rms})_1$ and of helium is $(v_{rms})_2$ is equal at temperature T₁ and T₂ respectively.

$$\frac{(v_{\text{rms}})_1}{(v_{\text{rms}})_2} = \sqrt{\frac{M_2 T_1}{M_1 T_2}}$$

$$\left[\frac{4T_1}{32 \times 263}\right]^{1/2} = 1$$

$$\left[\frac{4T_1}{32\times263}\right]^{1/2} = 1$$

$$T_1 = \frac{32 \times 263}{4} = 2104k.$$

43. As Boltzmann's constant,

$$k_{\rm B}$$

$$=\frac{R}{N}$$
, $\therefore R = k_B N$

Now

$$PV = nRT = nk_B NT$$

.. The number of molecules in the room

$$= nN = \frac{PV}{Tk_B}$$
$$= \frac{1.013 \times 10^5 \times 25.0}{300 \times 1.38 \times 10^{-23}}$$

$$=6.117 \times 10^{26}$$
.

44. Number of mole in 0.014 kg of Nitrogen

$$n = \frac{0.014 \times 10^3}{28} = \frac{1}{2} \text{ mole}$$

$$C_v = \frac{5}{2}R = \frac{5}{2} \times 2 = 5 \text{ cal/mole } k$$

$$\frac{V_2}{V_1} = \sqrt{\frac{T_2}{T_1}}, \quad T_2 = 4T_1$$

$$\Delta T = T_2 - T_1 = 4T_1 - T_1 = 3T_1$$

= 3 × 300 = 900 K

$$\Delta Q = n c_v \Delta T = \frac{1}{2} \times 5 \times 900 = 2250 \text{ cal.}$$