

## UNIT IX

---

## BEHAVIOUR OF PERFECT GAS AND KINETIC THEORY

---

### POINTS TO REMEMBER

---

- **Pressure exerted by a gas** : It is due to continuous collision of gas molecules against the walls of the container and is given by the relation

$$P = \frac{Mc^2}{3V} = \frac{1}{3} \rho c^2 \text{ where } c \text{ is the rms velocity of gas molecules.}$$

- **Average K.E. per molecule** of a gas  $\frac{1}{2} mC^2 = \frac{3}{2} k_B T$ . It is independent of the mass of the gas but depends upon the temperature of the gas.
- **Absolute zero** : It is that temperature at which the root mean square velocity of the gas molecules reduces to zero.
- **Different types of speed of gas molecules**

(i) Most probable speed  $v_{mp} = \sqrt{\frac{2k_B T}{m}}$

$k_B \rightarrow$  Boltzmann's Constant

- (ii) Mean speed

$$v_{\text{mean}} = \frac{v_1 + v_2 + \dots + v_n}{n} = \sqrt{\frac{8k_B T}{m\pi}}$$

$m$  = mass of one molecule of gas

$T$  = Temperature of gas

- (iii) Root mean square speed

$$v_{\text{rms}} = \sqrt{\frac{v_1^2 + v_2^2 + \dots + v_n^2}{n}} = \sqrt{\frac{3k_B T}{m}}$$

- (iv) The number of degrees of freedom = total number of independent co-ordinates required to describe completely the position and configuration of a system. For monoatomic gases,  $f = 3$

For diatomic gases,  $f = 5$

For linear triatomic gas molecules,  $f = 7$

For non-linear triatomic gas molecules,  $f = 6$

- According to the **law of equipartition of energy**, for any dynamical system in thermal equilibrium, the total energy is distributed equally amongst all the degrees of freedom. The average energy associated with each molecule per degree of freedom =  $\frac{1}{2} k_B T$ , where  $k_B$  is Boltzmann constant and  $T$  is temperature of the system.
- **Mean free path** of gas molecules is the average distance travelled by a molecule between two successive collisions. It is represented by  $\lambda$ .

$$\lambda = \frac{1}{\sqrt{2} \pi d^2 n}$$

where  $d$  = diameter of molecule and  $n$  = number of molecules per unit volume of the gas.

$$\text{also } \lambda = \frac{k_B T}{\sqrt{2} \pi d^2 p}$$

where  $k_B$  is Boltzmann constant;  $p$  is pressure and  $T$  is temperature of the gas.

### VERY SHORT ANSWER TYPE QUESTIONS (1 MARK)

1. Write two condition 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 prefect 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 STP?

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 Energy 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  $T$ ?
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)

1. When an automobile travels for a long distance the air pressure in the tyres increases. Why?
2. 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?
3. Why the land has a higher temperature than the ocean during the day but a lower temperature at night.
4. 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?
5. State Avogadro's law. Deduce it on the basis of Kinetic theory of gases.
6. Although the velocity of air molecules is nearly 0.5 km/s yet the smell of scent spreads at a much slower rate why.
7. 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?
8. 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

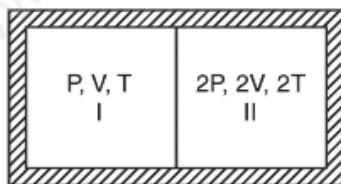
(i) The ratio of the rms speeds of the molecules

(ii) The ratio of the number of molecules.

9. Why gases at high pressure and low temperature show large deviation from ideal gas behaviour.
10. 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)

1. On what parameters does the  $\lambda$  (mean free path) depends.
2. Equal masses of oxygen and helium gases are supplied equal amount of heat. Which gas will undergo a greater temperature rise and why?
3. Why evaporation causes cooling?
4. 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 valve joining the two vessels is opened what is temperature of the vessel at equilibrium.
5. 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?



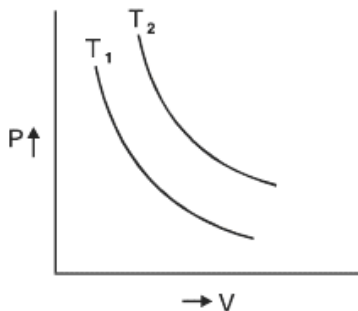
6. Prove that for a perfect gas having  $n$  degree of freedom

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

where  $C_p$  and  $C_v$  have their usual meaning.

7. 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.

8. 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.



9. 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?
10. State Graham's law of diffusion. How do you obtain this from Kinetic Theory of gases.

### LONG ANSWER TYPE QUESTIONS (5 MARKS)

1. Prove that the pressure exerted by a gas is given by

$$P = \frac{1}{3} \rho c^2$$

where  $\rho$  is density and  $c$  is root mean square velocity.

2. What are the fundamental postulates of the Kinetic theory of gases?
3. Given that  $P = \frac{1}{3} \rho c^2$  where  $P$  is the pressure,  $\rho$  is the density and  $c$  is the rms. Velocity of gas molecules. Deduce Boyle's law and Charles law of gases from it.
4. 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

5. 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

1. An air bubble of volume  $1.0 \text{ cm}^3$  rises from the bottom of a lake 40 m deep at a temperature of  $12^\circ\text{C}$ . To what volume does it grow when it reaches the surface which is at a temperature of  $35^\circ\text{C}$ ?
2. An electric bulb of volume  $250 \text{ cm}^3$  was sealed off during manufacture at a pressure of  $10^{-3} \text{ mm of Hg}$  at  $27^\circ\text{C}$ . Find the number of air molecules in the bulb—

$$(R = 8.31 \text{ J mole}^{-1} \text{ K}^{-1}, N_A = 6.02 \times 10^{23} \text{ mole}^{-1})$$

$$(\text{density of mercury } \rho = 13.6 \times 10^3 \text{ kg m}^{-3})$$

3. An ideal gas has a specific heat at constant pressure ( $C_p = 5 R/2$ ). The gas is kept in a closed vessel of volume  $0.0083 \text{ m}^3$  at a temperature of  $300 \text{ K}$  and a pressure of  $1.6 \times 10^6 \text{ Nm}^{-2}$ . An amount of  $2.49 \times 10^4 \text{ J}$  of heat energy is supplied to the gas. Calculate the final temperature and pressure of the gas

$$(R = 8.3 \text{ J K}^{-1} \text{ mol}^{-1})$$

4. An oxygen cylinder of volume 30 litre has an initial gauge pressure of 15 atmosphere and a temperature of  $27^\circ\text{C}$ . After some oxygen is withdrawn from the cylinder, the gauge pressure drops to 11 atmosphere and its temperature drop to  $17^\circ\text{C}$ . Estimate the mass of oxygen taken out of the cylinder

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

$$(\text{molecular mass of } \text{O}_2 = 32)$$

5. At what temperature the rms speed of oxygen atom equal to r.m.s. speed of heliums gas atom at  $-10^\circ\text{C}$

$$\text{Atomic mass of helium} = 4$$

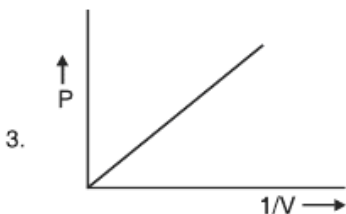
$$\text{Atomic mass of oxygen} = 32$$

6. The density of Carbon dioxide gas at  $0^\circ\text{C}$  and at a pressure of  $1.0 \times 10^6 \text{ newton/m}^2$  is  $1.98 \text{ kg/m}^3$ . Find the root mean square velocity of its molecules at  $0^\circ\text{C}$  and  $30^\circ\text{C}$ . Pressure is kept constant.

7. 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



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.  $P = \frac{1}{3} \frac{M}{V} K T$        $T \propto (PV)$

P and V are constant then T is also constant.

### ANSWERS (2 MARKS)

1. Work is done against friction. This work done is converted into heat.

- Rate of diffusion of a gas is inversely proportional to the square root of the density. So hydrogen leaked out more rapidly.
- Specific Heat of water is more than land (earth). Therefore for given heat change in temp. of land is more than ocean (water).
- The air molecules travel along a zigzag path due to frequent collision as a result their displacement per unit time is very small.

$$7. \quad C = \sqrt{\frac{3RT}{M}} = v \quad C' = \sqrt{\frac{3R(2T)}{M/2}} = \sqrt{\frac{3RT}{M}}$$

$$C' = 2V$$

$$8. \quad P = \frac{1}{3} \frac{m n c^2}{V} \quad P \propto n c^2 ; \quad c \propto \sqrt{T}$$

as the temperature is same rms speeds are same.

$$P \propto n \quad \text{i.e.} \quad \frac{P_1}{P_2} = \frac{n_1}{n_2} = \frac{1}{2}$$

- When temp is low and pressure is high the intermolecular forces become appreciable thus the volume occupied by the molecular is not negligibly small as compared to volume of gas.
- When piston is pulled out the volume of the gas increases, Now number of molecules colliding against the wall of container per unit area decreases. Hence pressure decreases.

### ANSWERS (3 MARKS)

- (i) diameter of molecule (iii)  $\lambda \propto \frac{1}{P}$
- (ii)  $\lambda \propto T$  (iv)  $\lambda \propto \frac{1}{\rho}$  (v)  $\lambda \propto \frac{1}{n}$  (iv)  $\lambda \propto m$
- 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.
- number of mole = Constant



$$\mu_1 + \mu_2 = \mu$$

$$\frac{P_1 V_1}{R T_1} + \frac{P_2 V_2}{R T_2} = \frac{P(V_1 + V_2)}{R T}$$

$$\text{from Boyles law } P(V_1 + V_2) = P_1 V_1 + P_2 V_2 \Rightarrow T = \frac{T_1 T_2 (P_1 V_1 + P_2 V_2)}{P_1 V_1 T_2 + P_2 V_2 T_1}$$

$$5. \quad n = \frac{pV}{kT} \quad h' = \frac{2p \cdot 2V}{2kT} = \frac{2pV}{kT}$$

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

$$8. \quad T = \frac{PV}{\mu R} \quad T \propto P V \text{ (}\mu \text{ is constant)} (\mu \text{ is constant)}$$

since  $PV$  is greater for the curve at  $T_2$  than for the curve  $T_1$  therefore  $T_2 > T_1$

Three vessels at the same pressure and temperature have same volume and contain equal number of molecules

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

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

## ANSWERS NUMERICALS

$$1. \quad V_1 = 10^{-6} \text{ m}^3$$

Pressure on bubble  $P_1$  = water pressure + Atmospheric pressure

$$= \rho gh + P_{atm}$$

$$= 4.93 \times 10^5 \text{ Pa}$$

$$T_1 = 285 \text{ K}, T_2 = 308 \text{ K}$$

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

$$V_2 = \frac{4.93 \times 10^{-5} \times 1 \times 10^{-6} \times 308}{285 \times 1.01 \times 10^5} = 5.3 \times 10^{-6} \text{ m}^3$$

2.  $V = 250 \text{ cc} = 250 \times 10^{-6} \text{ m}^3$

$$P = 10^{-6} \text{ m } \rho = 13.6 \times 10^3 \text{ kg/m}^3$$

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

$$\mu = \frac{PV}{RT} = \frac{h\rho gV}{RT} = 1.3 \times 10^{-8} \text{ mole}$$

$$\text{number of molecule} = \mu N_A = 8 \times 10^{15}$$

3.  $PV = nRT \Rightarrow n = \frac{PV}{RT}$

$$n \rightarrow \text{number of mole of gas} = \frac{1.6 \times 10^{-6} \times .0083}{8.314 \times 300}$$

$$\approx 4$$

Heat has been supplied at constant volume

$$\therefore \Delta Q_v = nC_v \Delta T \text{ When } C_v = C_p - R$$

$$= \frac{5}{2}R - R = \frac{3}{2}R$$

$$2.49 \times 10^6 = 4 \times \frac{3}{2} \times 8.3 (T' - 300) \Delta T = T' - 300$$

$$\Rightarrow T' = 800 \text{ K } T' \rightarrow \text{final temperature}$$

If  $P'$  be the final pressure then

$$P'V = nRT'$$

$$P' = \frac{nRT'}{V} = \frac{4 \times 8.3 \times 800}{.0083}$$

$$= 4 \times 8 \times 10^5 = 3.2 \times 10^6 \text{ N/m}^2$$

$$4. \quad V_1 = 30 \text{ litre} = 30 \times 10^3 \text{ cm}^3 = 3 \times 10^{-2} \text{ m}^3$$

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

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

$$\mu_1 = \frac{P_1 V_1}{RT_1} = 18.3$$

$$\mu_2 = \frac{P_2 V_2}{RT_2}$$

$$P_2 = 11 \times 1.013 \times 10^5 \text{ N/m}^2$$

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

$$T_2 = 290 \text{ K}$$

$$\mu_2 = 13.9$$

$$= 18.3 - 13.9 = 4.4$$

$$\text{Mass of gas taken out of cylinder} = 4.4 \times 32 \text{ g}$$

$$= 140.8 \text{ g}$$

$$= 0.140 \text{ kg.}$$

$$5. \quad V_{\text{rms}} = \left[ \frac{3PV}{M} \right]^{1/2} = \left[ \frac{3RT}{M} \right]^{1/2}$$

Let r.m.s speed of oxygen is  $(V_{\text{rms}})_1$  and of helium is  $(V_{\text{rms}})_2$  is equal at temperature  $T_1$  and  $T_2$  respectively.

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

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

$$T_1 = \frac{32 \times 263}{4} = 2104 \text{ K}$$

$$6. \quad P = \frac{1}{3} \rho v^2$$

$$V_{rms} = \sqrt{\langle v^2 \rangle} = \sqrt{\frac{3P}{\rho}}$$

$$V_{rms} = \sqrt{\frac{3 \times 1 \times 10^5}{1.98}} = 389 \text{ m/sec}$$

$$V_{rms} \propto \sqrt{T}$$

$$\frac{(V_{rms})_{30}}{(V_{rms})_0} = \sqrt{\frac{273 + 30}{273}} = \sqrt{\frac{303}{273}} = 1.053$$

$$(V_{rms})_{30} = 389 \times 1.053 = 410 \text{ m/s}$$

7. Number of mole in 0.014 kg of Nitrogen.

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

$$C_V = \frac{5}{2} R = \frac{5}{2} \times 2 = 5 \text{ cal / mole K}$$

$$\frac{v_2}{v_1} = \sqrt{\frac{T_2}{T_1}} \quad T_2 = 4T_1$$

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

$$= 3 \times 300 = 900 \text{ K}$$

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