

KINETIC THEORY OF GASES

13.1 BOYLE'S LAW

1. State and explain Boyle's law.

Boyle's law. It is a fundamental gas law, discovered by Robert Boyle in 1662. It states that the volume of a given mass of a gas is inversely proportional to its pressure, provided the temperature remains constant. Mathematically

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

where K is a constant. Its value depends on (i) mass of the gas, (ii) its temperature and (iii) the units in which P and V are measured.

If P_1 and V_1 are the initial values of pressure and volume and P_2 and V_2 are their final values, then according to Boyle's law, $P_1V_1 = P_2V_2$

Fig. 13.1 shows graph between P and V and Fig. 13.2 shows the graph between P and $1/V$ for a given mass of a gas at a constant temperature T .

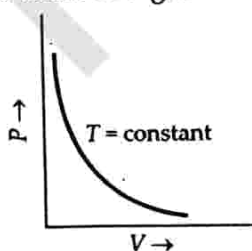


Fig. 13.1 P versus V graph

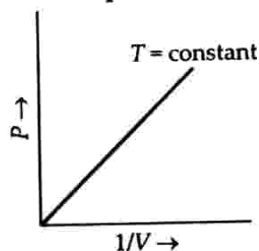


Fig. 13.2 P versus $1/V$ graph.

13.2 CHARLES' LAW

2. State and explain Charles' law.

Charles' law. This law gives relationship between volume and temperature of a gas at constant pressure. It was discovered by Alexander Charles in 1787. It states that if the pressure remains constant, then the volume of a given mass of a gas increases or decreases by $\frac{1}{273.15}$ of its volume at 0°C for each 1°C rise or fall of temperature.

Let V_0 be the volume of the given mass of a gas at 0°C . According to Charles' law, its volume at 1°C is

$$V_1 = V_0 + \frac{V_0}{273.15} = V_0 \left(1 + \frac{1}{273.15} \right)$$

Volume of the gas at 2°C ,

$$V_2 = V_0 \left(1 + \frac{2}{273.15} \right)$$

\therefore Volume of the gas at $t^\circ\text{C}$,

$$\begin{aligned} V_t &= V_0 \left(1 + \frac{t}{273.15} \right) \\ &= V_0 \left(\frac{273.15 + t}{273.15} \right) \end{aligned}$$

If T_0 and T are temperatures on Kelvin scale corresponding to 0°C and $t^\circ\text{C}$, then

$$T_0 = 273.15 + 0 = 273.15$$

and

$$T = 273.15 + t$$

$$\therefore V_t = V_0 \frac{T}{T_0} \quad \text{or} \quad \frac{V_t}{T} = \frac{V_0}{T_0}$$

$$\text{or} \quad \frac{V}{T} = \text{constant} \quad \text{i.e., } V \propto T$$

So Charles' law can be stated in another way. Pressure remaining constant, the volume of a given mass of a gas is directly proportional to its absolute temperature.

Fig. 13.3 shows the straight line graph between V and T for a given mass of a gas at constant pressure.

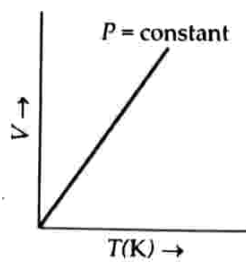


Fig. 13.3 V versus T graph

13.3 GAY LUSSAC'S LAW

3. State and explain Gay Lussac's law.

Gay Lussac's law. This law gives relationship between pressure and temperature of a gas. It was discovered by Joseph Gay Lussac. It states that if the volume remains constant, the pressure of a given mass of a gas increases or decreases by $\frac{1}{273.15}$ of its pressure at 0°C for each 1°C rise or fall of temperature.

If P_0 and P_t are the pressures of a given mass of gas at 0°C and $t^\circ\text{C}$ respectively, then according to Gay Lussac's law,

$$P_t = P_0 \left(1 + \frac{t}{273.15} \right) = P_0 \left(\frac{273.15 + t}{273.15} \right)$$

$$\text{or} \quad P_t = P_0 \frac{T}{T_0}$$

where T_0 (K) = 273.15 and T (K) = 273.15 + t

$$\therefore \frac{P_t}{P_0} = \frac{T}{T_0}$$

$$\text{or} \quad \frac{P}{T} = \text{constant} \quad \text{or} \quad P \propto T.$$

So Gay Lussac's law can be stated in another way. Volume remaining constant, the pressure of a given mass of a gas is directly proportional to its absolute temperature.

13.4 PERFECT GAS EQUATION

4. State and derive the perfect or ideal gas equation.

Ideal/perfect gas equation. This equation gives the relation between pressure P , volume V and absolute temperature T of a gas. The equation is

$$PV = nRT$$

where n is the number of moles of the gas and R is the universal gas constant.

Derivation. According to Boyle's law, for a given mass of a gas at constant temperature,

$$V \propto \frac{1}{P}$$

According to Charles' law, for a given mass of a gas at constant pressure,

$$V \propto T$$

Combining the above two laws,

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

For one mole of a gas, the constant has same value for all gases and is called *universal gas constant*, denoted by R . So the above equation becomes

$$PV = RT$$

For n moles of a gas,

$$PV = nRT$$

This is perfect or ideal gas equation.

If v is the volume of 1 gram mass of the gas and M_0 is the molecular mass, then the number of moles is

$$n = \frac{\text{Mass of the gas (in g)}}{\text{Molecular mass}} = \frac{1}{M_0}$$

$$\therefore Pv = \frac{1}{M_0} RT \quad \text{or} \quad Pv = rT$$

This is perfect gas equation for 1 gram of the gas. Here $r = R/M_0$ is the gas constant for one gram of the gas.

We define another fundamental constant of nature, called Boltzmann's constant (k_B). It is the gas constant per molecule.

$$\therefore k_B = \frac{R}{N_A} \quad \text{or} \quad R = k_B N_A$$

As number of moles,

$$n = \frac{\text{No. of molecules}}{\text{Avogadro's number}} = \frac{N}{N_A}$$

$$\therefore PV = nRT = \frac{N}{N_A} \cdot k_B N_A \cdot T$$

$$\text{or} \quad PV = k_B NT$$

13.5 UNIVERSAL GAS CONSTANT

5. Define universal gas constant. Give its SI and CGS units.

Universal gas constant. From ideal gas equation,

$$R = \frac{PV}{nT} = \frac{\text{pressure} \times \text{volume}}{\text{number of moles} \times \text{temperature}}$$

$$= \frac{\text{work done}}{\text{number of moles} \times \text{temperature}}$$

Clearly, the universal gas constant represents the work done by (or on) a gas per mole per kelvin.

$$\text{SI unit of } R = \frac{\text{J}}{\text{mole} \times \text{K}} = \text{J mole}^{-1} \text{K}^{-1}.$$

$$\text{CGS unit of } R = \text{cal mole}^{-1} \text{ } ^\circ\text{C}^{-1}.$$

6. Determine the numerical values of R and k_B .

Numerical value of R . Consider one mole of a gas at S.T.P. Then $R = \frac{P_0 V_0}{T_0}$

Standard pressure,

$$\begin{aligned} P_0 &= 0.76 \text{ m of Hg column} \\ &= 0.76 \times 13.6 \times 10^3 \times 9.8 \text{ Nm}^{-2} \end{aligned}$$

Standard temperature, $T_0 = 273.15 \text{ K}$

Volume of one mole of gas at S.T.P. is

$$V_0 = 22.4 \text{ litre} = 22.4 \times 10^{-3} \text{ m}^3$$

$$\therefore R = \frac{0.76 \times 13.6 \times 10^3 \times 9.8 \times 22.4 \times 10^{-3}}{273.15}$$

$$\text{or } R = 8.31 \text{ J mole}^{-1} \text{K}^{-1}.$$

In the CGS system,

$$R = \frac{8.31}{4.2} \text{ cal mole}^{-1} \text{ } ^\circ\text{C}^{-1} = 1.98 \text{ cal mole}^{-1} \text{ } ^\circ\text{C}^{-1}.$$

Numerical value of k_B . We know that

$$k_B = \frac{R}{N_A} = \frac{8.31 \text{ J mole}^{-1} \text{K}^{-1}}{6.02 \times 10^{23} \text{ mole}^{-1}} = 1.38 \times 10^{-23} \text{ JK}^{-1}.$$

13.6 IDEAL GASES

7. What is an ideal gas? Why do the real gases show deviations from ideal behaviour? Show these deviations graphically.

Ideal gas. A gas which obeys the ideal gas equation: $PV = nRT$, at all temperatures and pressures is called an ideal gas or perfect gas.

While deriving the ideal gas equation, the following two assumptions are used:

- (i) The size of the gas molecules is negligibly small.
- (ii) There is no force of attraction amongst the molecules of the gas.

However, no real or actual gas fulfills the above conditions. Hence the behaviour of a real gas differs from that of an ideal gas. At low pressures and high temperatures, the above assumptions are valid and some real gases like hydrogen, oxygen, nitrogen, helium, etc., almost behave like an ideal gas.

Deviations from ideal behaviour. (i) Fig. 13.4 shows the graph of PV/nT against pressure P for three different temperatures. For an ideal gas

$PV/nT = R = 8.314 \text{ J mole}^{-1} \text{K}^{-1}$. Clearly, departures from ideal gas behaviour become less at low pressures and high temperatures.

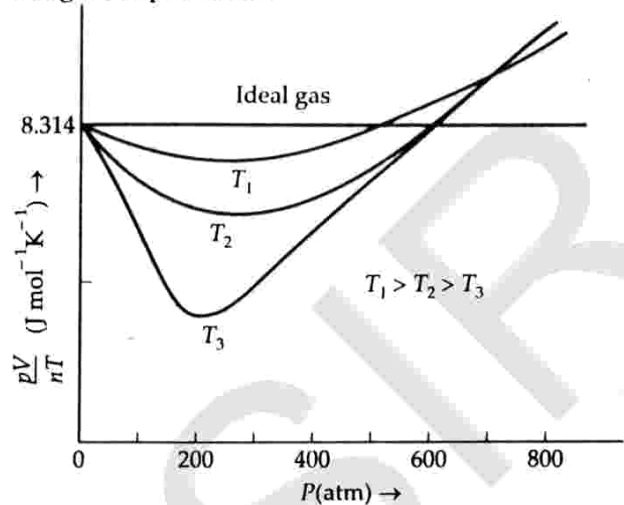


Fig. 13.4 Departures from ideal gas behaviour at three different temperatures

(ii) Fig. 13.5 shows the comparison between the experimental P - V curves and the theoretical curves predicted by Boyle's law.

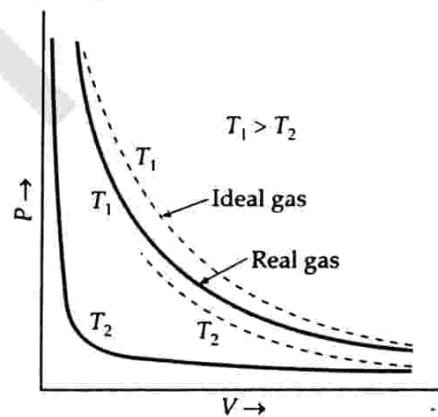


Fig. 13.5 Experimental P - V curves (solid lines) compared with Boyle's law (dotted lines)

(iii) Fig. 13.6 shows the comparison between experimental T - V curves and the theoretical curves predicted by Charles' law.

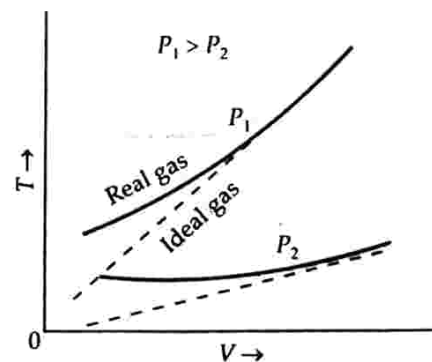


Fig. 13.6 Experimental T - V curves (solid lines) compared with Charles' law (dotted lines)

In the above cases, we note the behaviour of a real gas approaches the ideal gas behaviour for low pressures and high temperatures.

Examples based on

Gas Laws and Ideal Gas Equation

FORMULAE USED

1. Boyle's law : At constant temperature,

$$PV = \text{constant or } P_1 V_1 = P_2 V_2$$

2. Charles' law : At constant pressure,

$$V \propto T \quad \text{or} \quad \frac{V_2}{V_1} = \frac{T_2}{T_1}$$

3. Gay Lussac's law : At constant volume,

$$P \propto T \quad \text{or} \quad \frac{P_2}{P_1} = \frac{T_2}{T_1}$$

4. Perfect gas equation is $PV = nRT$

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

5. Boltzmann's constant, $k_B = \frac{R}{N}$

UNITS USED

Pressure P is in Nm^{-2} or Pa, Volume V in m^3 and temperature T in Kelvin (K).

CONSTANTS USED

$$R = 8.31 \text{ J mole}^{-1} \text{ K}^{-1}$$

$$k_B = 1.38 \times 10^{-23} \text{ J molecule}^{-1} \text{ K}^{-1}$$

EXAMPLE 1. A narrow uniform glass tube 80 cm long and open at both ends is half immersed in mercury. Then, the top of the tube is closed and it is taken out of mercury. A column of mercury 22 cm long then remains in the tube. What is the atmospheric pressure ?

Solution. Let $A \text{ cm}^2$ be the area of cross-section of the tube and P be the atmospheric pressure. When half of the tube is immersed in mercury [Fig. 13.7(a)],

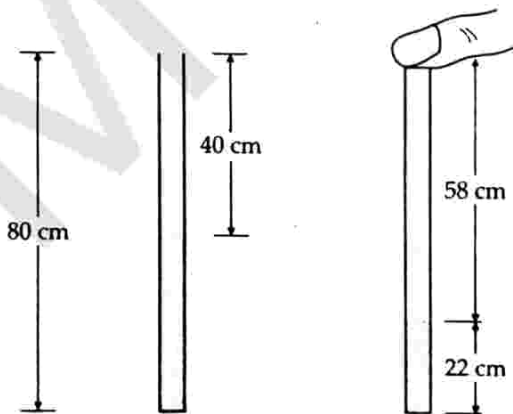


Fig. 13.7

Pressure of enclosed air, $P_1 = P$

Volume, $V_1 = A \times 40 \text{ cm}^3$

When the tube is taken out of mercury,

$P_2 = (P - 22) \text{ cm of Hg}$,

$V_2 = A \times 58 \text{ cm}^3$

If temperature remains constant, then from Boyle's law, we have

$$P_1 V_1 = P_2 V_2$$

$$P \times A \times 40 = (P - 22) \times A \times 58$$

$$\text{or} \quad 18P = 22 \times 58 \quad \text{or} \quad P = 70.9 \text{ cm.}$$

EXAMPLE 2. A gas at 27°C in a cylinder has a volume of 4 litre and pressure 100 Nm^{-2} . (i) Gas is first compressed at constant temperature so that the pressure is 150 Nm^{-2} . Calculate the change in volume (ii) It is then heated at constant volume so that temperature becomes 127°C . Calculate the new pressure.

Solution. (i) Here $V_1 = 4 \text{ litre}$, $P_1 = 100 \text{ Nm}^{-2}$,
 $P_2 = 150 \text{ Nm}^{-2}$, $V_2 = ?$

Using Boyle's law for constant temperature,

$$P_1 V_1 = P_2 V_2$$

$$\therefore V_2 = \frac{P_1 V_1}{P_2} = \frac{100 \times 4}{150} = 2.667 \text{ litre}$$

\therefore Change in Volume

$$= V_1 - V_2 = 4 - 2.667 = 1.333 \text{ litres.}$$

(ii) Here $T_1 = 27^\circ\text{C} = 127 + 273 = 400 \text{ K}$,

$P_1 = 100 \text{ Nm}^{-2}$, $T_2 = 127^\circ\text{C} = 127 + 273 = 400 \text{ K}$, $P_2 = ?$

Using Gay Lussac's law for constant volume,

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

$$\text{or} \quad P_2 = \frac{T_2}{T_1} \times P_1 = \frac{400 \times 100}{400} = 100 \text{ Nm}^{-2}$$

EXAMPLE 3. As an air bubble rises from the bottom of a lake to the surface, its volume is doubled. Find the depth of the lake. Take atmospheric pressure as to be 76 cm of Hg.

Solution. On reaching the surface of lake, volume of the air bubble becomes double. By Boyle's law (assuming $T = \text{constant}$), its pressure becomes half. As pressure on the lake is 1 atm, so pressure inside the bubble, at the depth of the lake = 2 atm. Here $2 \text{ atm} = 1 \text{ atm} + \text{Pressure due to water column of height } h$

\therefore Pressure due to water column of height h

$$= 1 \text{ atm} = 76 \text{ cm of Hg}$$

$$\text{or} \quad h \times 1 \times g = 76 \times 13.6 \times g$$

$$\therefore h = 76 \times 13.6 = 1033.6 \text{ cm} \approx 10.34 \text{ m.}$$

EXAMPLE 4. Using the ideal gas equation, determine the value of R . Given that one gram molecule of a gas at S.T.P. occupies 22.4 litres.

Solution. Here $P = 1 \text{ atm} = 1.013 \times 10^5 \text{ Pa}$,
 $T = 273 \text{ K}$, $V = 22.4 \text{ litre} = 22.4 \times 10^{-3} \text{ m}^3$
 For 1 mole of a gas, $PV = RT$
 $\therefore R = \frac{PV}{T} = \frac{1.013 \times 10^5 \times 22.4 \times 10^{-3}}{273}$
 $= 8.31 \text{ J mol}^{-1} \text{ K}^{-1}$.

EXAMPLE 5. A balloon partially filled with Helium has a volume of 30 m^3 , at the earth's surface, where pressure is 76 cm of Hg and temperature is 27°C , what will be the increase in volume of gas if balloon rises to a height, where pressure is 7.6 cm of Hg and temperature is (-54°C) ? [Chandigarh 08]

Solution. Here $V_1 = 30 \text{ m}^3$,
 $P_1 = 76 \text{ cm of Hg}$, $T_1 = 273 + 27 = 300 \text{ K}$
 $P_2 = 7.6 \text{ cm of Hg}$, $T_2 = 273 - 54 = 219 \text{ K}$
 As $\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$
 $\therefore V_2 = \frac{P_1 V_1 T_2}{T_1 P_2} = \frac{76 \times 30 \times 219}{300 \times 7.6} = 219 \text{ m}^3$

\therefore Increase in volume of gas
 $= V_2 - V_1 = 219 - 30 = 189 \text{ m}^3$

EXAMPLE 6. A vessel contains two non-reacting gases : neon (monoatomic) and oxygen (diatomic). The ratio of their partial pressures is 3 : 2. Estimate the ratio of (i) number of molecules and (ii) mass density of neon and oxygen in the vessel. Atomic number of Ne = 20.2, molecular mass of $\text{O}_2 = 32.0$. [NCERT]

Solution. As V and T are same for the two gases, we can write

$$P_1 V = n_1 RT \text{ and } P_2 V = n_2 RT$$

or $\frac{P_1}{P_2} = \frac{n_1}{n_2}$

But $\frac{P_1}{P_2} = \frac{3}{2} \therefore \frac{n_1}{n_2} = \frac{3}{2}$

If N_1 and N_2 are the number of molecules of the two gases and N is the Avogadro's number, then

$$\frac{n_1}{n_2} = \frac{N_1/N}{N_2/N} = \frac{3}{2} \therefore \frac{N_1}{N_2} = 1.5.$$

Now $n_1 = \frac{m_1}{M_1}$ and $n_2 = \frac{m_2}{M_2}$

$$\therefore \frac{\rho_1}{\rho_2} = \frac{m_1/V}{m_2/V} = \frac{m_1}{m_2} = \frac{n_1 M_1}{n_2 M_2}$$

$$= \frac{3}{2} \times \frac{20.2}{32} = 0.947.$$

EXAMPLE 7. A closed container of volume 0.02 m^3 contains a mixture of neon and argon gases at 27°C temperature and $1.0 \times 10^5 \text{ Nm}^{-2}$ pressure. If the gram-molecular weights of neon and argon are 20 and 40 respectively, find the masses of the individual gases in the container, assuming them to be ideal. ($R = 8.314 \text{ J mole}^{-1} \text{ K}^{-1}$). Total mass of the mixture = 28 g. [IIT 94]

Solution. Let mass of neon gas = $m \text{ g}$

Then mass of argon gas = $(28 - m) \text{ g}$

Number of moles of neon, $n_1 = \frac{m}{20}$

Number of moles of argon, $n_2 = \frac{(28 - m)}{40}$

Now $(P_1 + P_2) V = (n_1 + n_2) RT$

$$\therefore 1 \times 10^5 \times 0.02 = \left(\frac{m}{20} + \frac{28 - m}{40} \right) \times 8.314 \times (27 + 273)$$

$$\text{or } 2 \times 10^3 = 2494.2 \left(\frac{2m + 28 - m}{40} \right) = 62.355 (m + 28)$$

$$\text{or } m + 28 = 32.07 \text{ or } m = 4.07 \text{ g}$$

\therefore Mass of neon = 4.07 g

Mass of argon = $28 - 4.07 = 23.93 \text{ g}$.

PROBLEMS FOR PRACTICE

- Air is filled in a bottle and it is corked at 35°C . If the cork can come out at 3 atmospheric pressure, then upto what temperature should the bottle be heated in order to remove the cork? (Ans. 651°C)
- A narrow uniform glass tube contains air enclosed by 15 cm long thread of mercury. When the tube is vertical with the open end upper most, the air column is 30 cm long. When the tube is inverted, the length of the air column becomes 45 cm. Calculate the atmospheric pressure. (Ans. 75 cm of Hg)
- An open glass tube is immersed in mercury so that a length of 8 cm of the tube projects above the mercury. The tube is then closed and raised through 44 cm. What length of the tube will be occupied by the air after it has been raised? Given $1 \text{ atm} = 76 \text{ cm of Hg}$. (Ans. 15.4 cm)
- An empty barometer tube 1 m long is lowered vertically (mouth downwards) into a tank of water. What will be the depth above the water level in the tube, when the water has risen 20 cm inside the tube? Take $1 \text{ atm} = 10.4 \text{ m column of water}$. (Ans. 2.6 m)
- When a gas filled in a closed vessel is heated through 1°C , its pressure increases by 0.4%. What is the initial temperature of the gas? (Ans. 250 K)

- Molecular weight of oxygen is 32. At S.T.P., volume of 11 g of oxygen is 700 cm^3 . Find the value of gas constant R . (Ans. $8.31 \text{ J mol}^{-1} \text{ K}^{-1}$)
- A 3000 cm^3 tank contains O_2 gas at 20°C and a gauge pressure of $2.5 \times 10^6 \text{ Pa}$. Find the mass of oxygen in the tank. (Ans. 102.56 g)
- A vessel of volume $8.0 \times 10^{-3} \text{ m}^3$ contains an ideal gas at 300 K and 200 kPa . The gas is allowed to leak till the pressure falls to 125 kPa . Calculate the amount of gas leaked assuming that the temperature remains constant. (Ans. 0.24 mole)
- A vessel of volume of 2000 cm^3 contains 0.1 mole of O_2 and 0.2 mole of CO_2 . If temperature of the mixture is 300 K , find the pressure exerted by it. (Ans. $3.74 \times 10^5 \text{ Pa}$)
- A vessel of volume, $V = 5.0 \text{ litres}$ contains 1.4 g of nitrogen at temperature, $T = 1800 \text{ K}$. Find the pressure of the gas if 30% of its molecules are dissociated into atoms at this temperature. (Ans. $1.94 \times 10^5 \text{ Nm}^{-2}$)

HINTS

- Let P be the atmospheric pressure. When the open end of the tube is up, [Fig. 13.8(a)],

$$P_1 = P + 15$$

When the tube inverted [Fig. 13.8(b)],

$$P_2 = P - 15$$

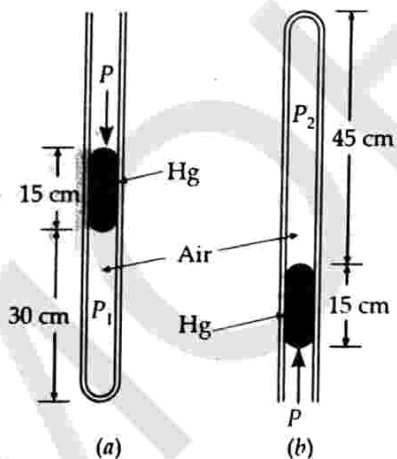


Fig. 13.8

Using Boyle's law for constant temperature,

$$P_1 V_1 = P_2 V_2$$

$$(P + 15) \times A \times 30 = (P - 15) \times A \times 45$$

or $P = 75 \text{ cm of Hg.}$

- When 8 cm of the tube projects out of mercury [Fig. 13.9(a)], for the air in the tube, we have

$$P_1 = P = 76 \text{ cm of Hg, } V_1 = A \times 8 \text{ cm}^3.$$

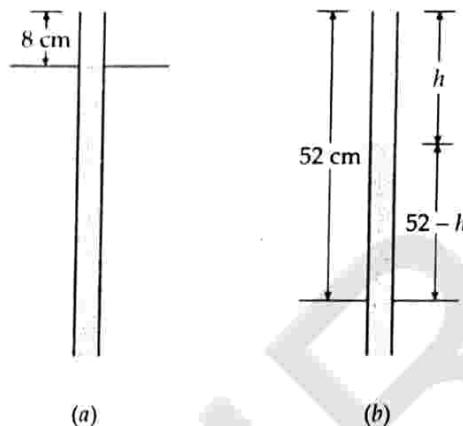


Fig. 13.9

When the tube is raised through 44 cm , total length of the tube outside the mercury becomes 52 cm . If h be the length of air column in the tube, then

$$P_2 = [P - (52 - h)] = (24 + h) \text{ cm of Hg}$$

$$V_2 = A \times h \text{ cm}^3$$

where A = area of cross-section of the tube.

Using Boyle's law for constant temperature,

$$P_1 V_1 = P_2 V_2$$

$$76 \times A \times 8 = (24 + h) \times A \times h$$

On solving, $h = 15.4 \text{ cm.}$

- Let $A \text{ cm}^2$ be the area of cross-section of the barometer tube. Then

$$P_1 = 10.4 \text{ m of water, } V_1 = 100 \times A \text{ cm}^3$$

$$P_2 = ? \quad V_2 = (100 - 20) A = 80 A \text{ cm}^3$$

At constant temperature,

$$P_1 V_1 = P_2 V_2$$

$$P_2 = \frac{P_1 V_1}{V_2} = \frac{10.4 \times 100 \times A}{80 A} = 13 \text{ m of water}$$

Depth of water level = $P_2 - P_1 = 13 - 10.4 = 2.6 \text{ m.}$

- $P_1 = P, P_2 = P + \frac{0.4}{100} P; T_1 = T, T_2 = T + 1$

At constant volume,

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

$$\therefore \frac{P(1 + 0.004)}{P} = \frac{T + 1}{T}$$

On solving, $T = 250 \text{ K.}$

- $P = 1 \text{ atm} = 1.013 \times 10^5 \text{ Pa, } T = 273 \text{ K, } M = 32$

Volume of 1 g of oxygen = 700 cm^3

Volume of 1 mole (32 g) of oxygen

$$= 700 \times 32 \text{ cm}^3 = 700 \times 32 \times 10^{-6} \text{ m}^3$$

For 1 mole of a gas, $PV = RT$

$$\therefore R = \frac{PV}{T} = \frac{1.013 \times 10^5 \times 700 \times 32 \times 10^{-6}}{273} = 8.31 \text{ mol}^{-1} \text{ K}^{-1}.$$

7. Here $P = 3000 \times 10^{-6} \text{ m}^3$, $T = 20 + 273 = 293 \text{ K}$,
 $R = 8.31 \text{ J mol}^{-1} \text{ K}^{-1}$.
 $P = 2.5 \times 10^6 \text{ Pa} + 1 \text{ atm} = 25 \times 10^5 + 1.013 \times 10^5$
 $= 26.013 \times 10^5 \text{ Pa}$.

As $PV = nRT$

$$\therefore n = \frac{PV}{RT} = \frac{26.013 \times 10^5 \times 3 \times 10^{-3}}{8.31 \times 293} = 3.205$$

Mass of oxygen $= 3.205 \times 32 = 102.5 \text{ g}$.

8. $n_1 - n_2 = \frac{P_1 V}{RT} - \frac{P_2 V}{RT} = \frac{(P_1 - P_2) V}{RT}$
 $= \frac{(200 - 125) \times 10^3 \times 80 \times 10^{-3}}{8.31 \times 300} = 0.24 \text{ mole}$.

9. $P = P_1 + P_2 = \frac{n_1 RT}{V} + \frac{n_2 RT}{V} = \frac{(n_1 + n_2) RT}{V}$
 $= \frac{(0.1 + 0.2) \times 8.31 \times 300}{2000 \times 10^{-6}} = 3.74 \times 10^5 \text{ Pa}$.

10. Mass of molecular nitrogen $= 1.4 \times \frac{70}{100} = 0.98 \text{ g}$

Mass of atomic nitrogen $= 1.4 \times \frac{30}{100} = 0.42 \text{ g}$

No. of moles of molecular nitrogen,

$$n_1 = \frac{0.98}{28} = 0.035$$

No. of moles of atomic nitrogen,

$$n_2 = \frac{0.42}{14} = 0.03$$

$$P = P_1 + P_2 = \frac{n_1 RT}{V} + \frac{n_2 RT}{V}$$

$$= \frac{(n_1 + n_2) RT}{V}$$

$$= \frac{(0.035 + 0.03) \times 8.31 \times 1800}{5 \times 10^{-3}}$$

$$= 1.94 \times 10^5 \text{ Nm}^{-2}$$

2. The size of a molecule is negligible compared with the average distance between the molecules.

3. The molecules are in a state of continuous random motion, moving in all directions with all possible velocities.

4. During the random motion, the molecules collide with one another and with the walls of the vessel. During collision, their velocities are changed in magnitude and direction.

5. The collisions are perfectly elastic and there are no forces of attraction or repulsion between the molecules. Thus all internal energy of the gas is kinetic.

6. Between two collisions a molecule moves in a straight path with a uniform velocity. The average distance covered by a molecule between two successive collisions is called mean free path.

7. The collisions are almost instantaneous i.e., the time during which a collision lasts is negligible compared to the time of the free path between the molecules.

8. In spite of the molecular collisions, the density remains uniform throughout the gas.

13.8 HOW DOES A GAS EXERT PRESSURE ?

9. On the basis of kinetic theory of gases, explain how does a gas exert pressure.

Pressure exerted by a gas. According to kinetic theory, the molecules of a gas are in a state of continuous random motion. They collide with one another and also with the walls of the vessel. Whenever a molecule collides with the wall, it returns with a changed momentum and an equal momentum is transferred to the wall (conservation of momentum). According to Newton's second law of motion, the rate of transfer of momentum to the wall is equal to the force exerted on the wall. Since a large number of molecules collide with the wall, a steady force is exerted on the wall. The force exerted per unit area of the wall is the pressure of the gas. Hence a gas exerts pressure due to the continuous collisions of its molecules with the walls of the vessel.

13.7 KINETIC THEORY OF AN IDEAL GAS

8. State the assumptions on which kinetic theory of gas is based.

Kinetic theory of gases. All matter is made of molecules. The molecules of a gas are in state of rapid and continuous motion. Their velocity depends on temperature. Using this molecular motion, various properties of a gas like pressure, temperature, energy, etc. can be explained. Hence this theory is called kinetic theory of gases which was developed by Clausius and Maxwell.

Assumptions. 1. All gases consist of molecules. The molecules are rigid, elastic spheres identical in all respects for a given gas and different for different gases.

13.9 EXPRESSION FOR PRESSURE EXERTED BY A GAS

10. On the basis of kinetic theory, derive an expression for the pressure exerted by an ideal gas.

Expression for pressure exerted by a gas. Consider an ideal gas enclosed in a cubical vessel. Suppose the sides of the cube are parallel to the co-ordinate axes, as shown in Fig. 13.10. Let n be the number of gas molecules per unit volume and m be the mass of each molecule. A molecule moving with velocity (v_x, v_y, v_z) hits the planar wall (perpendicular to x-axis) of area A .

As the collision is elastic, the molecule rebounds with the same velocity. The y - and z -components of velocity do not change while the x -component reverses sign. So the velocity after the collision is $(-v_x, v_y, v_z)$.

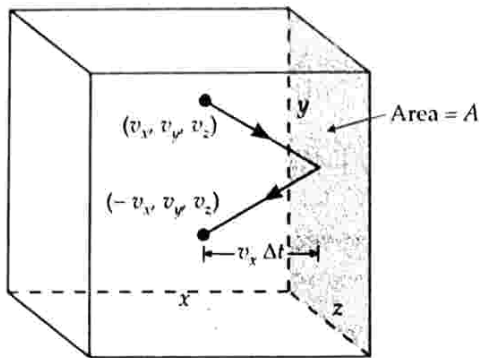


Fig. 13.10 Elastic collision of a gas molecule with the wall of the vessel.

The change in momentum of the molecule

$$= -mv_x - mv_x = -2mv_x$$

By the conservation of momentum, the momentum imparted to the wall in each collision = $2mv_x$.

In small time interval Δt , all those molecules which lie within distance $v_x \Delta t$ from the wall of area A will hit this wall. That is, the molecules which lie in the volume $Av_x \Delta t$ only will hit the wall in time Δt . On the average, half of such molecules are moving towards the wall and other half away from the wall.

\therefore Number of molecules hitting wall of area A in time Δt

$$\begin{aligned} &= \frac{1}{2} Av_x \Delta t \times \text{number of molecules per unit volume} \\ &= \frac{1}{2} Av_x \Delta t n \end{aligned}$$

Total momentum transferred to the wall in time Δt is

$$\Delta p = 2mv_x \times \frac{1}{2} Av_x \Delta t n = nmv_x^2 A \Delta t$$

Force exerted on the wall of area A

$$= \frac{\Delta p}{\Delta t} = nmv_x^2 A$$

$$\text{Pressure on the wall} = \frac{\text{Force}}{\text{Area}} = \frac{nmv_x^2 A}{A}$$

or
$$P = nmv_x^2$$

As the molecules move with different velocities, so we replace v_x^2 by its average value $\overline{v_x^2}$ in the above equation.

$$\therefore P = nm\overline{v_x^2}$$

Again, the gas is isotropic. So the molecular velocities are almost equally distributed in different directions. By symmetry,

$$\overline{v_x^2} = \overline{v_y^2} = \overline{v_z^2} = \frac{1}{3}(\overline{v_x^2} + \overline{v_y^2} + \overline{v_z^2}) = \frac{1}{3}\overline{v^2}$$

where $\overline{v^2}$ is the mean square velocity of the molecules.

$$\text{Hence } P = \frac{1}{3} nm\overline{v^2} \quad \dots(1)$$

$$\text{Density of gas, } \rho = \frac{\text{Mass}}{\text{Volume}} = \frac{nm}{1} = nm$$

$$\therefore P = \frac{1}{3} \rho \overline{v^2} \quad \dots(2)$$

According to Pascal's law, a gas transmits pressure equally in all directions. So equations (1) and (2) give the pressure exerted by the gas in any direction.

11. Show that the pressure exerted by a gas is two-thirds of the average kinetic energy per unit volume of the gas molecules.

Relation between pressure and K.E. per unit volume. According to the kinetic theory of gases, the pressure exerted by a gas of density ρ and r.m.s. velocity v is given by

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

$$\begin{aligned} \text{Mass per unit volume of the gas} &= \text{Volume} \times \text{density} \\ &= 1 \times \rho = \rho \end{aligned}$$

Average K.E. of translation per unit volume of the gas,

$$E' = \frac{1}{2} \rho v^2 \quad \therefore \frac{P}{E'} = \frac{\frac{1}{3} \rho v^2}{\frac{1}{2} \rho v^2} = \frac{2}{3}$$

or $P = \frac{2}{3} E' = \frac{2}{3} \times \text{Average K.E. per unit volume}$

Hence the pressure exerted by a gas is equal to two-thirds of average kinetic energy of translation per unit volume of the gas.

13.10 KINETIC INTERPRETATION OF TEMPERATURE

12. Show that the average K.E. of a gas molecule is directly proportional to the temperature of the gas. Hence give the kinetic interpretation of temperature.

Average K.E. per molecule of a gas : Kinetic interpretation of temperature. Consider one mole of a gas. Let P , V , T and M be the pressure, volume, temperature and molecular mass of the gas respectively.

$$\text{Density, } \rho = \frac{M}{V}$$

According to kinetic theory, the pressure exerted by the gas is

$$P = \frac{1}{3} \rho \overline{v^2} = \frac{1}{3} \frac{M}{V} \overline{v^2} \quad \text{or} \quad PV = \frac{1}{3} M \overline{v^2} = \frac{2}{3} \cdot \frac{1}{2} M \overline{v^2}$$

But $\frac{1}{2} M \overline{v^2}$ is the average kinetic energy E of one mole of the gas.

$$\therefore PV = \frac{2}{3} E$$

The ideal gas equation for one mole of a gas is

$$PV = RT$$

$$\therefore \frac{2}{3} E = RT \quad \text{or} \quad E = \frac{3}{2} RT$$

The above equation gives the mean kinetic energy of one mole of the gas. If N is the Avogadro's number, then the mean kinetic energy per molecule is given by

$$\bar{E} = \frac{E}{N} = \frac{3}{2} \frac{R}{N} T \quad \text{or} \quad \bar{E} = \frac{3}{2} k_B T$$

where $k_B = R/N$ is the gas constant per molecule and is called Boltzmann's constant. Thus the mean kinetic energy per molecule is proportional to the absolute temperature of the gas. It is independent of the pressure, volume and the nature of the ideal gas. Clearly,

$$E = \frac{1}{2} M \bar{v}^2 = \frac{3}{2} RT \quad \text{or} \quad \bar{v}^2 = \frac{3 RT}{M}$$

The square root of \bar{v}^2 is known as root mean square velocity and is given by

$$v_{rms} = \sqrt{\bar{v}^2} = \sqrt{\frac{3 RT}{M}} \quad \text{i.e.,} \quad v_{rms} \propto \sqrt{T}$$

Thus faster the motion of the molecules of a gas, higher will be their kinetic energy and hence higher will be the temperature of the gas. Hence the temperature of a gas is the measure of the average kinetic energy of its molecules. This is what we mean by the kinetic interpretation of temperature.

Also, at $T = 0$, $v_{rms} = 0$.

So we can define **absolute zero** as that temperature at which all molecular motion stops.

Examples based on

Kinetic Theory of Gases & Kinetic Interpretation of Temperature

FORMULAE USED

1. Pressure exerted by a gas, $P = \frac{1}{3} \frac{M}{V} v_{rms}^2 = \frac{1}{3} \rho v_{rms}^2$

2. $v_{rms} = \sqrt{\frac{3P}{\rho}}$

3. Mean K.E. per molecule of a gas,

$$\bar{E} = \frac{1}{2} m \bar{v}^2 = \frac{3}{2} k_B T$$

4. Mean K.E. per mole of a gas,

$$E = \frac{1}{2} M v_{rms}^2 = \frac{3}{2} RT = \frac{3}{2} k_B NT$$

3. K.E. of 1 g of a gas = $\frac{1}{2} v_{rms}^2 = \frac{3}{2} \frac{R}{M} T$

5. Avogadro's number = $\frac{\text{Molecular mass}}{\text{Mass of 1 molecule}}$

$$\text{or} \quad N = \frac{M}{m}$$

6. No. of moles, $n = \frac{\text{Mass of gas}}{\text{Molecular mass}}$

UNITS USED

Kinetic energies \bar{E} and E are in joule, pressure P in Nm^{-2} and density ρ in kg m^{-3} .

EXAMPLE 8. Calculate the r.m.s. velocity of air molecules at S.T.P. Given density of air at S.T.P. is 1.296 kg m^{-3} .

Solution. Here $P = 1 \text{ atm} = 1.013 \times 10^5 \text{ Nm}^{-2}$,

$$\rho = 1.296 \text{ kgm}^{-3}$$

\therefore Root mean square velocity of air molecules at S.T.P.,

$$v_{rms} = \sqrt{\frac{3P}{\rho}} = \sqrt{\frac{3 \times 1.013 \times 10^5}{1.296}} = 482.24 \text{ ms}^{-1}$$

EXAMPLE 9. 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.

Solution. According to kinetic theory of gases,

$$PV = \frac{1}{3} M v_{rms}^2$$

At constant temperature, v_{rms}^2 is constant. As V is also constant, so $P \propto M$

When the mass of the gas increases by 50%, pressure also increases by 50%,

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

EXAMPLE 10. Calculate the kinetic energy of one mole of argon at 127°C . Given, Boltzmann's constant, $k_B = 1.381 \times 10^{-23} \text{ J molecule}^{-1} \text{ K}^{-1}$. Avogadro's number, $N = 6.02 \times 10^{23} \text{ mol}^{-1}$.

Solution. Here $T = 127 + 273 = 400 \text{ K}$,

$$N = 6.02 \times 10^{23} \text{ mol}^{-1},$$

$$k_B = 1.381 \times 10^{-23} \text{ J mol}^{-1} \text{ K}^{-1}$$

Kinetic energy of one mole of gas,

$$E = \frac{3}{2} RT = \frac{3}{2} k_B NT$$

$$= \frac{3}{2} \times 1.381 \times 10^{-23} \times 6.02 \times 10^{23} \times 400$$

$$= 4988.2 \text{ J.}$$

EXAMPLE 11. Calculate the kinetic energy per molecule and also r.m.s. velocity of a gas at 127°C . Given $k_B = 1.38 \times 10^{-23} \text{ J molecule}^{-1} \text{ K}^{-1}$ and mass per molecule of the gas = $6.4 \times 10^{-27} \text{ kg}$.

Solution. Here $T = 127 + 273 = 400 \text{ K}$,

$$m = 6.4 \times 10^{-27} \text{ kg}$$

(i) K.E. per molecule

$$= \frac{1}{2} m v_{rms}^2 = \frac{3}{2} k_B T$$

$$= \frac{3}{2} \times 1.38 \times 10^{-23} \times 400$$

$$= 8.28 \times 10^{-21} \text{ J.}$$

$$(ii) \text{ Now } \frac{1}{2} m v_{rms}^2 = 8.28 \times 10^{-21} \text{ J}$$

$$\begin{aligned} \therefore v_{rms} &= \sqrt{\frac{2 \times 8.28 \times 10^{-21}}{m}} \\ &= \sqrt{\frac{2 \times 8.28 \times 10^{-21}}{6.4 \times 10^{-27}}} = 1.608 \times 10^3 \text{ ms}^{-1}. \end{aligned}$$

EXAMPLE 12. Calculate the number of molecules in $2 \times 10^{-6} \text{ m}^3$ of a perfect gas at 27°C and at a pressure of 0.01 m of mercury. Mean kinetic-energy of a molecule at 27°C is $4 \times 10^{-11} \text{ J}$ and $g = 98 \text{ ms}^{-2}$. [Chandigarh 07]

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

$$P = hpg = 0.01 \times 13.6 \times 10^3 \times 98 = 13.6 \times 98 \text{ Nm}^{-2}$$

Total K.E. of the gas molecules,

$$\frac{1}{2} M v_{rms}^2 = \frac{3}{2} PV = \frac{3}{2} \times 13.6 \times 98 \times 2 \times 10^{-6} \text{ J}$$

\therefore No. of molecules in the given volume

$$\begin{aligned} &= \frac{\text{Total K.E. of the gas molecules}}{\text{K.E. per molecule}} \\ &= \frac{3 \times 13.6 \times 98 \times 10^{-6}}{4 \times 10^{-11}} = 9996 \times 10^4 \approx 10^8. \end{aligned}$$

EXAMPLE 13. (a) Calculate (i) the root mean square speed and (ii) the mean kinetic energy of one gram molecule of hydrogen at S.T.P. Given that the density of hydrogen at S.T.P. is 0.09 kg m^{-3} and $R = 8.31 \text{ J mole}^{-1} \text{ K}^{-1}$.

(b) Given that the mass of a molecule of hydrogen is $334 \times 10^{-27} \text{ kg}$, calculate Avogadro's number.

(c) Calculate Boltzmann's constant.

Solution. (a) (i) Here $\rho = 0.09 \text{ kgm}^{-3}$,

$$P = 1 \text{ atm} = 1.013 \times 10^5 \text{ Nm}^{-2}$$

$$\text{As } P = \frac{1}{3} \rho v_{rms}^2$$

$$\therefore v_{rms} = \sqrt{\frac{3P}{\rho}} = \sqrt{\frac{3 \times 1.013 \times 10^5}{0.09}} = 1837.5 \text{ ms}^{-1}.$$

(ii) At S.T.P., volume of one gram molecule of hydrogen = 22.4 litre

$$= 22.4 \times 10^{-3} \text{ m}^3$$

Mass of one gram molecule of hydrogen,

$$M = \text{Volume} \times \text{density} = 22.4 \times 10^{-3} \text{ m}^3$$

Mass of one gram molecule of hydrogen,

$$\begin{aligned} M &= \text{Volume} \times \text{density} \\ &= 22.4 \times 10^{-3} \times 0.09 = 2.016 \times 10^{-3} \text{ kg} \end{aligned}$$

Mean K.E. of one gram molecule of hydrogen at S.T.P.

$$\begin{aligned} &= \frac{1}{2} M v_{rms}^2 = \frac{1}{2} \times 2.016 \times 10^{-3} \times (1837.5)^2 \\ &= 3.4 \times 10^3 \text{ J}. \end{aligned}$$

(b) Avogadro's number,

$$\begin{aligned} N &= \frac{\text{Molecular mass of hydrogen}}{\text{Mass of 1 molecule of hydrogen}} \\ &= \frac{M}{m} = \frac{2.016 \times 10^{-3}}{3.34 \times 10^{-27}} = 6.03 \times 10^{23}. \end{aligned}$$

(c) Boltzmann's constant,

$$k_B = \frac{R}{N} = \frac{8.31}{6.03 \times 10^{23}} = 1.38 \times 10^{-23} \text{ JK}^{-1}.$$

EXAMPLE 14. At what temperature will the average velocity of oxygen molecules be sufficient so as to escape from the earth? Escape velocity of earth is 11.0 kms^{-1} and mass of one molecule of oxygen is $5.34 \times 10^{-26} \text{ kg}$. Boltzmann constant = $1.38 \times 10^{-23} \text{ J molecule}^{-1} \text{ K}^{-1}$.

Solution. For the molecule to just escape from the earth,

Average K.E. of the molecule at temperature T
= Escape energy of the molecule

$$\text{or } \frac{3}{2} k_B T = \frac{1}{2} m v_e^2$$

$$\begin{aligned} \therefore T &= \frac{m v_e^2}{3 k_B} = \frac{5.34 \times 10^{-26} \times (11.0 \times 10^3)^2}{3 \times 1.38 \times 10^{-23}} \\ &= 1.56 \times 10^5 \text{ K}. \end{aligned}$$

EXAMPLE 15. A vessel A contains hydrogen and another vessel B whose volume is twice of A contains same mass of oxygen at the same temperature. Compare (i) average kinetic energies of hydrogen and oxygen molecules (ii) root mean square speeds of the molecules and (iii) pressures of gases in A and B. Molecular weights of hydrogen and oxygen are 2 and 32 respectively.

Solution. (i) For all gases at the same temperature, average K.E. per molecule is same and is

$$\bar{E} = \frac{3}{2} k_B T$$

As the gases in both vessels are at the same temperature, so the ratio of their average K.E. per molecule = 1 : 1.

$$(ii) \text{ As } v_{rms}^2 = \frac{3RT}{M}$$

$$\therefore \frac{v_H}{v_O} = \sqrt{\frac{M_O}{M_H}} = \sqrt{\frac{32}{2}} = 4 : 1.$$

(iii) According to kinetic theory, $P = \frac{1}{3} \frac{M}{V} v_{rms}^2$

where M is the mass and V is the volume of the gas. Masses of both gases are equal. So the ratio of their pressures is

$$\frac{P_H}{P_O} = \left[\frac{v_H}{v_O} \right]^2 \times \frac{V_O}{V_H} = \frac{16}{1} \times \frac{2}{1} = 32 : 1.$$

EXAMPLE 16. A flask contains argon and chlorine in the ratio of 2 : 1 by mass. The temperature of the mixture is 27°C. Obtain the ratio of

- average kinetic energy per molecule, and
- root mean square speed (v_{rms}) of the molecules of the two gases. Atomic mass of argon = 39.9 u; Molecular mass of chlorine = 70.9 u. [NCERT]

Solution. (i) The average kinetic energy per molecule of any gas is $\frac{3}{2} k_B T$. It depends only on temperature and not on the nature of the gas.

As both argon and chlorine have the same temperature in the flask, the ratio of average K.E. per molecule of the two gases is 1 : 1.

(ii) If m is mass of single molecule and M the molecular mass, then

$$\frac{1}{2} m v_{rms}^2 = \frac{3}{2} k_B T$$

$$= \text{constant at a given temperature}$$

$$\therefore \frac{(v_{rms})_{Ar}}{(v_{rms})_{Cl_2}} = \frac{(m)_{Cl_2}}{(m)_{Ar}} = \frac{M_{Cl_2}}{M_{Ar}} = \frac{70.9}{39.9} = 1.777$$

$$\text{or } \frac{(v_{rms})_{Ar}}{(v_{rms})_{Cl_2}} = \sqrt{1.777} = 1.333.$$

EXAMPLE 17. Two perfect gases at absolute temperatures T_1 and T_2 are mixed. There is no loss of energy. Find the temperature of the mixture if the masses of the molecules are m_1 and m_2 and the number of molecules in the gases are n_1 and n_2 respectively. [Roorkee 89]

Solution. According to the kinetic theory, the average kinetic energy of a gas molecule = $\frac{3}{2} k_B T$. Before mixing the two gases, the average kinetic energy of all the molecules of the gas

$$= \frac{3}{2} k_B n_1 T_1 + \frac{3}{2} k_B n_2 T_2$$

After mixing, the mean kinetic energy of both the gases

$$= \frac{3}{2} k_B (n_1 + n_2) T$$

where T is the temperature of the mixture. If there is no energy loss, then

$$\frac{3}{2} k_B (n_1 + n_2) T = \frac{3}{2} k_B n_1 T_1 + \frac{3}{2} k_B n_2 T_2.$$

$$\therefore T = \frac{n_1 T_1 + n_2 T_2}{n_1 + n_2}.$$

PROBLEMS FOR PRACTICE

- Calculate the root mean square velocity of a gas of density 1.5 g litre⁻¹ at a pressure of 2×10^6 Nm⁻². (Ans. 2×10^3 ms⁻¹)

- The r.m.s. velocity of the molecules of a gas at S.T.P. is 485.6 ms⁻¹. Calculate the density of the gas. (Ans. 1.289 kg m⁻³)

- Calculate the value of Boltzmann constant k_B , given $R = 8.3 \times 10^3$ J/kg-mol-K and Avogadro's number, $N = 6.03 \times 10^{26}$ /kg-mol. (Ans. 1.376×10^{-23} J molecule⁻¹ K⁻¹)

- Kinetic energy of oxygen molecule at 0°C is 5.64×10^{-21} J. Calculate the value of Avogadro's number. Given $R = 8.31$ J mole⁻¹ K⁻¹. (Ans. 6.06×10^{23})

- Calculate the total K.E. of 1 g of nitrogen at 300 K. Molecule weight of nitrogen = 28. (Ans. 133.4 J)

- Calculate for hydrogen at 27°C (i) kinetic energy of one gram-molecule of the gas (ii) kinetic energy of one gram gas and (iii) root mean square velocity of the molecules. Molecular weight of hydrogen = 2. [Ans. (i) 3.74×10^3 J (ii) 1.87×10^3 J (iii) 1.93×10^3 ms⁻¹]

- At what temperature the average value of the kinetic energy of the molecule of a gas will be 1/3 of the average value of kinetic energy at 27°C? (Ans. -173°C)

- If the temperature of air is increased from 27°C to 227°C, in what ratio will the average kinetic energies of its molecules be increased? (Ans. It increases 5/3 times)

HINTS

- $\rho = 1.5$ g litre⁻¹ = 1.5 kg m⁻³, $P = 2 \times 10^6$ Nm⁻²

$$v_{rms} = \sqrt{\frac{3P}{\rho}} = \sqrt{\frac{3 \times 2 \times 10^6}{1.5}} = 2 \times 10^3 \text{ ms}^{-1}.$$

- $\rho = \frac{3P}{v_{rms}^2} = \frac{3 \times 1.013 \times 10^5}{485.6 \times 485.6} = 1.289 \text{ kgm}^{-3}.$

$$6. (i) \frac{3}{2} RT = 3.74 \times 10^3 \text{ J.}$$

$$(ii) \frac{3}{2} \frac{RT}{M} = 1.87 \times 10^3 \text{ J.}$$

$$(iii) v_{rms} = \sqrt{\frac{3RT}{M}} = 1.93 \times 10^3 \text{ ms}^{-1}.$$

13.11 DERIVATION OF THE GAS LAWS

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

Boyle's law. It states that the volume (V) of a given mass of a gas is inversely proportional to its pressure (P) provided the temperature (T) remains unchanged, i.e.,

$$V \propto 1/P \text{ or } PV = \text{constant} \quad (\text{At constant } T)$$

Derivation. According to kinetic theory, pressure exerted by a gas is

$$P = \frac{1}{3} \rho \overline{v^2} = \frac{1}{3} \frac{M}{V} \overline{v^2} \quad \therefore PV = \frac{1}{3} M \overline{v^2}$$

But at constant temperature, total kinetic energy of gas $\frac{1}{2} M \overline{v^2}$ or $\overline{v^2}$ will be constant.

\therefore At a constant temperature, $PV = \text{constant}$

This proves the Boyle's law.

14. Derive Charles' law on the basis of kinetic theory of gases.

Charles' law. It states that at constant pressure, the volume of a given mass of a gas is directly proportional to its absolute temperature, i.e.,

$$V \propto T \quad (\text{At constant } P)$$

Derivation. According to kinetic theory of gases,

$$\text{Pressure of a gas, } P = \frac{1}{3} \rho \overline{v^2} = \frac{1}{3} \frac{M}{V} \overline{v^2}.$$

$$\text{or } V = \frac{1}{3} \cdot \frac{M}{P} \overline{v^2}$$

For a given mass of a gas and at constant pressure P , we have

$$V \propto \overline{v^2}$$

According to kinetic theory, $\overline{v^2} \propto T$

$$\therefore V \propto T$$

This proves the Charles' law.

15. Derive Gay Lussac's law on the basis of kinetic theory of gases.

Gay Lussac's law. It states that at constant volume, the pressure exerted by a given mass of a gas is directly proportional to its absolute temperature, i.e.,

$$P \propto T \quad (\text{At constant } V)$$

Derivation. According to kinetic theory of gases,

$$P = \frac{1}{3} \frac{M}{V} \overline{v^2}$$

For a given mass and at constant volume V , we have

$$P \propto \overline{v^2}$$

$$\text{But } \overline{v^2} \propto T \quad \therefore P \propto T$$

This proves Gay Lussac's law, also called Regnault's law.

16. Derive perfect gas equation on the basis of kinetic theory of gases.

Derivation of perfect gas equation. The pressure exerted by a gas is given by

$$P = \frac{1}{3} \frac{M}{V} \overline{v^2} \quad \therefore PV = \frac{1}{3} M \overline{v^2}$$

$$\text{But } \overline{v^2} \propto T$$

$$\therefore PV \propto T \quad \text{or } PV = RT.$$

where R is called the gas constant for one mole of gas. The above equation is called the perfect gas equation.

17. Derive Avogadro's law on the basis of kinetic theory of gases.

Avogadro's law. It states that equal volumes of all gases under similar conditions of temperature and pressure, contain equal number of molecules.

Derivation. Consider equal volume (say V each) of two gases A and B at the same temperature T and pressure P .

According to kinetic theory, pressure exerted by a gas is

$$P = \frac{1}{3} \frac{M}{V} \overline{v^2} = \frac{1}{3} \frac{mn}{V} \overline{v^2}$$

As pressures exerted by two gases are equal

$$\text{i.e., } P_1 = P_2$$

$$\therefore \frac{1}{3} \frac{m_1 n_1 \overline{v_1^2}}{V} = \frac{1}{3} \frac{m_2 n_2 \overline{v_2^2}}{V}$$

$$\text{or } m_1 n_1 \overline{v_1^2} = m_2 n_2 \overline{v_2^2} \quad \dots(1)$$

Again, at a given temperature the kinetic energy per molecule of each and every gas is constant and is independent of the nature of gas or the mass of gas molecule. Therefore, for the given gases, we have

$$\frac{1}{2} m_1 \overline{v_1^2} = \frac{1}{2} m_2 \overline{v_2^2}$$

$$\text{or } m_1 \overline{v_1^2} = m_2 \overline{v_2^2} \quad \dots(2)$$

Dividing (1) by (2), we get : $n_1 = n_2$

\therefore Number of molecules in gas A
= Number of molecules in gas B .

This proves Avogadro's law.

18. Deduce Graham's law of diffusion from kinetic theory of gases using expression for pressure.

Graham's law of Diffusion. It states that rate of diffusion of a gas is inversely proportional to the square root of its density.

Derivation. Let us consider two gases A and B diffusing into one another. Let ρ_1 and ρ_2 be their densities and v_1 and v_2 be their respective r.m.s. velocities.

$$\text{Pressure exerted by gas } A, P_1 = \frac{1}{3} \rho_1 v_1^2$$

$$\text{and Pressure exerted by gas } B, P_2 = \frac{1}{3} \rho_2 v_2^2$$

When steady state of diffusion is reached,

$$P_1 = P_2$$

$$\therefore \frac{1}{3} \rho_1 v_1^2 = \frac{1}{3} \rho_2 v_2^2$$

$$\text{or} \quad \frac{v_1^2}{v_2^2} = \frac{\rho_2}{\rho_1}$$

$$\text{or} \quad \frac{v_1}{v_2} = \sqrt{\frac{\rho_2}{\rho_1}}$$

We know that diffusion is a direct consequence of molecular motion and rate of diffusion of a gas is directly proportional to its r.m.s. velocity. Thus if r_1 and r_2 be the rates of diffusion of gases A and B respectively, then

$$\frac{r_1}{r_2} = \frac{v_1}{v_2} = \sqrt{\frac{\rho_2}{\rho_1}}$$

19. Derive Dalton's law of partial pressures on the basis of kinetic theory of gases.

Dalton's law of partial pressure. It states that the total pressure exerted by a mixture of non-reacting gases occupying a given volume is equal to the sum of the partial pressures which each gas would exert if it alone occupied the same volume at the given temperature.

Derivation. Consider a mixture of gases occupying a volume V . Let m_1, m_2, m_3, \dots be the molecular masses of the gases; n_1, n_2, n_3, \dots the number of their molecules; P_1, P_2, P_3, \dots the pressures exerted by individual gases and v_1, v_2, v_3, \dots be the r.m.s. velocities of the molecules of various gases. According to kinetic theory

$$P_1 = \frac{1}{3} \frac{m_1 n_1}{V} v_1^2, \quad P_2 = \frac{1}{3} \frac{m_2 n_2}{V} v_2^2, \quad P_3 = \frac{1}{3} \frac{m_3 n_3}{V} v_3^2, \dots$$

Adding, we get

$$P_1 + P_2 + P_3 + \dots = \frac{1}{3} \frac{m_1 n_1}{V} v_1^2 + \frac{1}{3} \frac{m_2 n_2}{V} v_2^2 + \frac{1}{3} \frac{m_3 n_3}{V} v_3^2 + \dots$$

As the temperature of all the gases in the mixture is the same, therefore

$$\frac{1}{2} m_1 v_1^2 = \frac{1}{2} m_2 v_2^2 = \frac{1}{2} m_3 v_3^2 = \dots = \frac{1}{2} m v^2 \text{ (say)}$$

$$\text{or} \quad m_1 v_1^2 = m_2 v_2^2 = m_3 v_3^2 = \dots = m v^2$$

$$\therefore P_1 + P_2 + P_3 + \dots = \frac{1}{3V} (n_1 + n_2 + n_3 + \dots) m v^2$$

$$= \frac{1}{3} \frac{m n}{V} v^2$$

where $n = n_1 + n_2 + n_3 + \dots$, is the total number of molecules in the mixture.

But $\frac{1}{3} \frac{m n}{V} v^2 = P$, the total pressure exerted by the mixture

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

This proves the Dalton's law of partial pressures.

13.12 ▽ MAXWELL'S SPEED DISTRIBUTION*

20. Discuss Maxwell's distribution of molecular speeds for a gas. Also define the most probable speed.

Maxwell's distribution of molecular speeds. In any gas, the molecules randomly collide against each other. So the velocity of any individual gas molecule changes continuously. At any instant, the speeds of the molecules vary over a wide range. However, the velocities distribution remains fixed in a steady state. James Clerk Maxwell was the first to derive a mathematical relation for the most probable distribution of speeds among the molecules of a gas.

Maxwell's law of speed distribution in a gas at temperature T is

$$dN_v = 4\pi N a^3 e^{-bv^2} v^2 dv = n_v dv$$

$$\text{where } a = \sqrt{\frac{m}{2\pi k_B T}}, \quad b = \frac{m}{2k_B T}$$

N = the total number of gas molecules

dN_v = the number of molecules having speeds between v and $v + dv$

The graph of n_v versus v is known as Maxwellian speed distribution and is shown in Fig. 13.11.

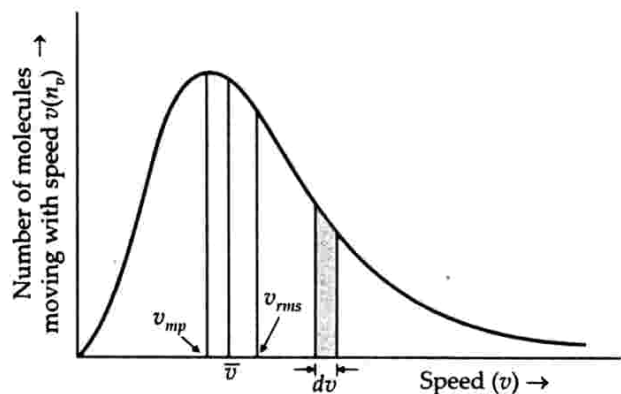


Fig. 13.11 Maxwell's distribution of molecular speeds.

The important features of the speed distribution curve are as follows :

- (i) At any temperature, the speed of molecules varies from zero to infinity.
- (ii) The area of the shaded region gives the number of molecules whose velocities lie in between v and $v + dv$.

- (iii) The speed possessed by the largest fraction of molecules at a given temperature is called most probable speed (v_{mp}). It corresponds to the maximum of the curve.
- (iv) The distribution is not symmetric about the most probable speed. Instead, it is skewed. The area under the curve to the right of the maximum is greater than that to the left. This is because the lowest speed is zero whereas there is no limit to the upper speed that a molecule can have.
- (v) The total area under the speed distribution curve gives the total number of molecules in the given sample of the gas.

13.13 AVERAGE, ROOT MEAN SQUARE AND MOST PROBABLE SPEEDS

22. Define average, root mean square and most probable speeds. Express these speeds in terms of temperature of the gas.

Average speed. It is defined as the arithmetic mean of the speeds of the molecules of a gas at a given temperature. If $v_1, v_2, v_3, \dots, v_n$ are the speeds of the n gas molecules, then the average speed \bar{v} is given by

$$\bar{v} = \frac{v_1 + v_2 + v_3 + \dots + v_n}{n}$$

By using Maxwell speed distribution law, it can be shown that

$$\bar{v} = \sqrt{\frac{8 k_B T}{\pi m}} = \sqrt{\frac{8 RT}{\pi M}} = \sqrt{\frac{8 PV}{\pi M}}$$

$$[k_B = R/N, mN = M, RT = PV]$$

where m is the mass of a single molecule and M is the molecular mass of the gas.

Root mean square speed. It is defined as the square root of the mean of the squares of the speeds of the individual molecules of a gas. If $v_1, v_2, v_3, \dots, v_n$ are the speeds of the n gas molecules, then the root mean square speed for the gas is given by

$$v_{rms} = \sqrt{\frac{v_1^2 + v_2^2 + v_3^2 + \dots + v_n^2}{n}}$$

From Maxwell's speed distribution law, it can be seen that

$$v_{rms} = \sqrt{\frac{3 k_B T}{m}} = \sqrt{\frac{3 RT}{M}} = \sqrt{\frac{3 PV}{M}}$$

Clearly, $v_{rms} \propto \sqrt{T}$

Thus, the root mean square speed of the gas molecules is directly proportional to the square root of the temperature of the gas.

At a given temperature, $v_{rms} \propto \frac{1}{\sqrt{M}}$

Hence for lighter gases, the r.m.s. speed is comparatively high, as it depends inversely upon the square root of its molecular mass. The r.m.s. speed of hydrogen molecules is four times that of oxygen molecules at the same temperature.

Most probable speed. It is defined as the speed possessed by the maximum number of molecules in a gas sample at a given temperature.

From Maxwell's speed distribution law, it can be seen that

$$v_{mp} = \sqrt{\frac{2 k_B T}{m}} = \sqrt{\frac{2 RT}{M}} = \sqrt{\frac{2 PV}{M}}$$

Relations between \bar{v} , v_{rms} and v_{mp} . As the Maxwell's speed distribution curve is not symmetric, so \bar{v} , v_{rms} and v_{mp} are not same. Clearly,

$$\bar{v} = \sqrt{\frac{8 k_B T}{\pi m}} = \sqrt{\frac{8}{3\pi}} v_{rms} = 0.92 v_{rms}$$

$$v_{mp} = \sqrt{\frac{2 k_B T}{m}} = \sqrt{\frac{2}{3}} v_{rms} = 0.816 v_{rms}$$

$$\text{Also, } v_{rms} = \sqrt{3} \sqrt{\frac{k_B T}{m}} = 1.73 \sqrt{\frac{k_B T}{m}}$$

$$\bar{v} = \sqrt{\frac{8}{\pi}} \sqrt{\frac{k_B T}{m}} = 1.60 \sqrt{\frac{k_B T}{m}}$$

$$v_{mp} = \sqrt{2} \sqrt{\frac{k_B T}{m}} = 1.41 \sqrt{\frac{k_B T}{m}}$$

$$\text{Ratio } v_{rms} : \bar{v} : v_{mp} = 1.73 : 1.60 : 1.41$$

Clearly, $v_{rms} > \bar{v} > v_{mp}$.

Examples based on

Average, R.M.S. & Most Probable Speeds

FORMULAE USED

1. Average speed, $\bar{v} = \frac{v_1 + v_2 + v_3 + \dots + v_n}{n}$
2. $\bar{v} = \sqrt{\frac{8 k_B T}{\pi m}} = \sqrt{\frac{8 RT}{\pi M}} = \sqrt{\frac{8 PV}{\pi M}}$
3. R.M.S. speed, $v_{rms} = \sqrt{\frac{v_1^2 + v_2^2 + v_3^2 + \dots + v_n^2}{n}}$
4. $v_{rms} = \sqrt{\frac{3 k_B T}{m}} = \sqrt{\frac{3 RT}{M}} = \sqrt{\frac{3 PV}{M}}$
5. Most probable speed,

$$v_{mp} = \sqrt{\frac{2 k_B T}{m}} = \sqrt{\frac{2 RT}{M}} = \sqrt{\frac{2 PV}{M}}$$

UNITS USED

All speeds \bar{v} , v_{rms} and v_{mp} are in ms^{-1} .

EXAMPLE 18. Four molecules of a gas have speeds 2, 4, 6 and 8 kms^{-1} respectively. Calculate their average speed and root mean square speed. [Central Schools 12]

Solution. Average speed,

$$\bar{v} = \frac{v_1 + v_2 + v_3 + v_4}{4} = \frac{2 + 4 + 6 + 8}{4} = 5 \text{ kms}^{-1}.$$

Root mean square speed,

$$v_{rms} = \sqrt{\frac{v_1^2 + v_2^2 + v_3^2 + v_4^2}{4}} = \sqrt{\frac{2^2 + 4^2 + 6^2 + 8^2}{4}} \\ = \sqrt{\frac{120}{4}} = \sqrt{30} = 5.48 \text{ kms}^{-1}.$$

EXAMPLE 19. If three gas molecules have velocities of 0.5, 1 and 2 kms^{-1} respectively, calculate the ratio of their root mean square speed and the average speed.

Solution. Root mean square speed,

$$v_{rms} = \sqrt{\frac{(0.5)^2 + 1^2 + 2^2}{3}} = \sqrt{\frac{5.25}{3}} = \sqrt{1.75} \\ = 1.3229 \text{ kms}^{-1}$$

Average speed,

$$\bar{v} = \frac{0.5 + 1 + 2}{3} = \frac{3.5}{3} = 1.1666 \text{ kms}^{-1}$$

$$\text{Ratio, } \frac{v_{rms}}{\bar{v}} = \frac{1.3229}{1.1666} = 1.13.$$

EXAMPLE 20. Calculate the r.m.s. velocity of oxygen molecules at S.T.P. The molecular weight of oxygen is 32. [Himachal 05C]

Solution. Here $P = 1 \text{ atm} = 1.013 \times 10^5 \text{ Nm}^{-2}$,

$$M = 32 \text{ g} = 32 \times 10^{-3} \text{ kg},$$

$V =$ Molar volume at S.T.P.

$$= 22.4 \text{ litre} = 22.4 \times 10^{-3} \text{ m}^3$$

Root mean square velocity of oxygen molecules at S.T.P.,

$$v_{rms} = \sqrt{\frac{3PV}{M}} = \sqrt{\frac{3 \times 1.013 \times 10^5 \times 22.4 \times 10^{-3}}{32 \times 10^{-3}}} \\ = 461.23 \text{ ms}^{-1}.$$

EXAMPLE 21. The r.m.s. velocity of hydrogen at S.T.P. is $u \text{ ms}^{-1}$. If the gas is heated at constant pressure till its volume is three fold, what will be its final temperature and the r.m.s. velocity?

Solution. Here $v_1 = u \text{ ms}^{-1}$, $T_1 = 273 \text{ K}$,

$$V_1 = V \text{ (say)}, V_2 = 3V$$

Using Charles' law for constant pressure,

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

$$\text{or } T_2 = \frac{V_2}{V_1} \times T_1 = \frac{3V}{V} \times 273 = 819 \text{ K}.$$

$$\text{As } \frac{v_2}{v_1} = \sqrt{\frac{T_2}{T_1}} \quad \therefore \frac{v_2}{u} = \sqrt{\frac{819}{273}} = \sqrt{3}$$

$$\text{or } v_2 = \sqrt{3} u \text{ ms}^{-1}.$$

EXAMPLE 22. The r.m.s. speed of oxygen molecules at a certain temperature T is v . If the temperature is doubled and the oxygen gas dissociates into atomic oxygen, what is the changed r.m.s. speed?

Solution. The r.m.s. speed of molecular oxygen at temperature T is

$$v = \sqrt{\frac{3RT}{M}}$$

The r.m.s. speed of atomic oxygen at temperature $2T$ will be

$$v' = \sqrt{\frac{3R \times 2T}{M/2}} = 2 \sqrt{\frac{3RT}{M}} = 2v.$$

Thus the changed r.m.s. speed is $2v$.

EXAMPLE 23. At what temperature is the r.m.s. velocity of hydrogen molecule equal to that of an oxygen molecule at 47°C ? [AIEEE 02]

$$\text{Solution. } v_{rms} = \sqrt{\frac{3RT}{M}}$$

Now r.m.s. velocity of H_2 molecule
= r.m.s. velocity of O_2 molecule

$$\text{or } \sqrt{\frac{3R \times T}{2}} = \sqrt{\frac{3R \times (47 + 273)}{32}}$$

$$\text{or } T = \frac{2 \times 320}{32} = 20 \text{ K}.$$

EXAMPLE 24. Calculate the temperature at which r.m.s. velocity of gas molecules is double its value at 27°C , pressure of the gas remaining the same. [Central Schools 07]

Solution. Let $t^\circ\text{C}$, be the temperature at which the r.m.s. velocity (v_t) of the gas molecules is double its value at 27°C (v_{27}).

$$\text{As } v \propto \sqrt{T} \quad \therefore \frac{v_t}{v_{27}} = \sqrt{\frac{273 + t}{273 + 27}}$$

$$\text{But } v_t = 2v_{27} \quad \text{or } \frac{v_t}{v_{27}} = 2$$

$$\therefore \sqrt{\frac{273 + t}{300}} = 2 \quad \text{or } \frac{273 + t}{300} = 4$$

$$\text{or } t = 927^\circ\text{C}.$$

EXAMPLE 25. Calculate the temperature at which r.m.s. velocity of a gas is half its value at 0°C , pressure remaining constant. [Chandigarh 04]

Solution. Let v be the r.m.s. velocity at 0°C . Let t be the temperature at which r.m.s. velocity becomes $v/2$.

Then $v_1 = v$, $T_1 = 273 + 0 = 273$ K

$$v_2 = v/2, T_2 = (273 + t) \text{ K}$$

As $\frac{v_2}{v_1} = \sqrt{\frac{T_2}{T_1}}$

$$\therefore \frac{v/2}{v} = \sqrt{\frac{273+t}{273}} \quad \text{or} \quad \frac{1}{2} = \sqrt{1 + \frac{t}{273}}$$

or $\frac{t}{273} = \frac{1}{4} - 1 = -\frac{3}{4}$

or $t = -\frac{3}{4} \times 273 = -204.75^\circ\text{C}$

EXAMPLE 26. Uranium has two isotopes of masses 235 and 238 units. If both are present in Uranium hexafluoride gas, which would have the larger average speed? If atomic mass of fluorine is 19 units, estimate the percentage difference in speeds at any temperature.

How is the above concept of difference in speeds utilised in the enrichment of uranium needed for nuclear fission?

[NCERT]

Solution. At a fixed temperature, the average energy $= \frac{1}{2} m v_{rms}^2$ is constant. So smaller the mass of a molecule, faster will be its speed. Clearly,

$$\text{Speed of molecule} \propto \frac{1}{\sqrt{\text{Molecular mass}}}$$

Molecular mass of ^{235}U hexafluoride
 $= 235 + 6 \times 19 = 349$

Molecular mass of ^{238}U hexafluoride
 $= 238 + 6 \times 19 = 352$

$$\therefore \frac{v_{349}}{v_{352}} = \left(\frac{352}{349}\right)^{1/2} = 1.0044$$

Percentage difference in speeds,

$$\frac{\Delta v}{v} \times 100 = 0.0044 \times 100 = 0.44 \%$$

^{235}U is the isotope needed for nuclear fission. To separate it from the more abundant isotope ^{238}U , the mixture is surrounded by a porous cylinder. The porous cylinder must be thick and narrow, so that the molecule wanders through individually, colliding with the walls of the long pore, as shown in Fig. 13.12. The faster molecule will leak out more than the slower one and so there is more of the lighter molecule (enrichment) outside the porous cylinder. The method is not very efficient and has to be repeated several times for sufficient enrichment.

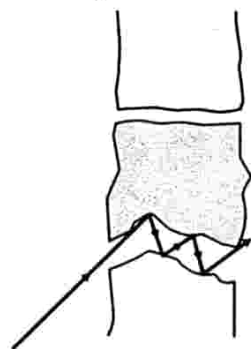


Fig. 13.12 A molecule going through a porous wall.

PROBLEMS FOR PRACTICE

- The velocities of 10 particles in ms^{-1} are 0, 2, 3, 4, 4, 4, 5, 5, 6, 9. Calculate their (i) average speed and (ii) r.m.s. speed. [Ans. (i) 4.2 ms^{-1} (ii) 4.77 ms^{-1}]
- The velocities of ten molecules of any gas are given $v, 0, 2v, 4v, 3v, 2v, v, 3v, 5v, v$. Calculate their root mean square velocity. (Ans. $2.64 v$)
- Calculate the rms velocity of the molecules of ammonia at S.T.P. Given molecular weight of ammonia = 17. (Ans. 632.8 ms^{-1})
- Show that the rms velocity of O_2 is $\sqrt{2}$ times that of SO_2 . Atomic weight of sulphur is 32 and that of oxygen is 16.
- Calculate the temperature at which rms velocity of SO_2 is the same as that of oxygen at 27°C . (Ans. 327°C)
- Estimate the temperature at which the oxygen molecules will have the same rms velocity as the hydrogen molecules at 150°C . Molecular weight of oxygen is 32 and that of hydrogen is 2. (Ans. 6495°C)
- If the root mean square velocity of the molecules of hydrogen at S.T.P. is 1.84 kms^{-1} , calculate the rms velocity of oxygen molecules at S.T.P. Molecular weights of hydrogen and oxygen are 2 and 32 respectively. (Ans. 0.46 kms^{-1})
- The density of CO_2 gas at 0°C and at a pressure of $1.0 \times 10^5 \text{ Nm}^{-2}$ is 1.98 kg m^{-3} . Find the root mean square velocity of its molecules at 0°C and 30°C assuming pressure to be constant. (Ans. $389 \text{ ms}^{-1}, 410 \text{ ms}^{-1}$)

HINTS

$$3. \quad v_{rms} = \sqrt{\frac{3PV}{M}} = \sqrt{\frac{3 \times 1.013 \times 10^5 \times 22.4 \times 10^{-3}}{17 \times 10^{-3}}} = 632.8 \text{ ms}^{-1}$$

4. Molecular weight of $\text{O}_2 = 32$

Molecular weight of $\text{SO}_2 = 64$

As $v \propto \frac{1}{\sqrt{M}}$

$$\frac{v_{\text{O}_2}}{v_{\text{SO}_2}} = \sqrt{\frac{64}{32}} = \sqrt{2} \quad \text{or} \quad v_{\text{O}_2} = \sqrt{2} v_{\text{SO}_2}$$

5. For O_2 , $v_{rms} = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3R \times 300}{32}}$

For SO_2 , $v'_{rms} = \sqrt{\frac{3RT'}{M'}} = \sqrt{\frac{3RT'}{64}}$

As $v' = v \therefore \sqrt{\frac{3RT'}{64}} = \sqrt{\frac{3R \times 300}{32}}$

or $T' = 600 \text{ K} = 600 - 273 = 327^\circ\text{C}$

$$7. \frac{v_{O_2}}{v_{H_2}} = \sqrt{\frac{M_{H_2}}{M_{O_2}}} = \sqrt{\frac{2}{32}} = \frac{1}{4}$$

$$\therefore v_{O_2} = \frac{1}{4} v_{H_2} = \frac{1}{4} \times 1.84 = 0.46 \text{ kms}^{-1}.$$

8. Root mean square velocity at 0°C is

$$v_0 = \sqrt{\frac{3P}{\rho}} = \sqrt{\frac{3 \times 1.0 \times 10^5}{1.98}} = 389 \text{ ms}^{-1}.$$

As $v \propto \sqrt{T}$

$$\therefore \frac{v_{30}}{v_0} = \sqrt{\frac{273 + 30}{273 + 0}} = \sqrt{\frac{303}{273}} = 1.053$$

$$\text{or } v_{30} = v_0 \times 1.053 = 389 \times 1.053 = 410 \text{ ms}^{-1}.$$

13.14 DEGREES OF FREEDOM

23. What do you mean by degrees of freedom? Show that the number of degrees of freedom of a system consisting of N particles and having k independent relations between them is $(3N - k)$.

✓ **Degrees of freedom.** The degrees of freedom of a dynamical system are defined as the total number of co-ordinates or independent quantities required to describe completely the position and configuration (arrangement of constituent atoms in space) of the system.

The degrees of freedom of a system may also be defined as the total number of independent ways in which the particles of the system can absorb energy.

Consider a system with just one particle.

- (i) If the particle moves along a straight line, we need just one (x -) coordinate to specify its position. So it has one translational degree of freedom.
- (ii) If the particle moves along a plane, we need two (x -, y -) co-ordinates to specify its position. So it has two translational degrees of freedom.
- (iii) If the particle moves in space, we need three (x -, y -, z -) coordinates to specify its position. So it has three translational degrees of freedom.

Consider now a system of two particles. Each particle has three degrees of freedom, so that the system has six degrees of freedom. If the two particles remain at fixed distance from each other, then there is one definite relation between them. As a result, the number of coordinates required to describe the configuration of the system reduces by one. So the system has $(6 - 1) = 5$ degrees of freedom.

In general, we can say that the number of degrees of freedom of a system is equal to the total number of coordinates required to specify the positions of the constituent particles of the system minus the number of independent relations existing between the particles.

If N = number of particles in the system,
 k = number of independent relations between the particles,

then the number of degrees of freedom of the system is

$$f = 3N - k$$

Degrees of freedom of a rigid body. A rigid body of finite size can have both translatory and rotatory motions. Just like translatory motion, the rotatory motion can be resolved into mutually perpendicular components. Hence a rigid body has six degrees of freedom, three for translatory motion and three for rotatory motion.

✓ **24.** Find the degrees of freedom of monoatomic, diatomic and triatomic gas molecules.

(a) **Degrees of freedom of a monoatomic gas.** The molecule of a monoatomic gas like He, Ne, Ar, etc. consists of a single atom (a point-mass). It is capable of translatory motion only. So it has three degrees of freedom.

Here $N = 1, k = 0$, so $f = 3 \times 1 - 0 = 3$.

(b) **Degrees of freedom of a diatomic gas.** The molecule of a diatomic gas like N_2, O_2, H_2, CO , etc. consists of two atoms A and B , a fixed distance apart. Corresponding to the translatory motion, the molecule has 3 degrees of freedom. The molecule has two additional degrees of freedom due to rotational motion, about two mutually perpendicular axes passing through its centre of mass. As the atoms are point-masses, so rotation is not possible about the line AB . The rotatory motion contributes 2 degrees of freedom, so that the total degrees of freedom is 5.

Here $N = 2, k = 1$, so $f = 3 \times 2 - 1 = 5$.

At high temperature ($\approx 5000 \text{ K}$), a diatomic molecule has two additional degrees of freedom due to vibrational motion. Each vibrational motion has both kinetic and potential energies. So one degree of freedom of vibrational motion is taken as two.

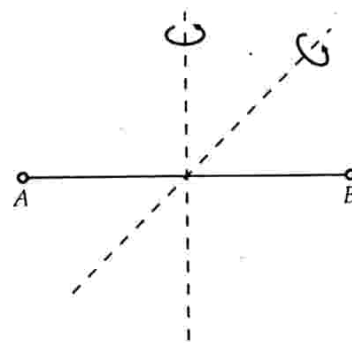


Fig. 13.13 Rotational motion of a diatomic molecule about two independent axes.

Degrees of freedom of a triatomic gas. Triatomic gas molecules are of two types :

(a) In a *non-linear molecule* like H_2O , SO_2 , etc., the three atoms are located at the vertices of a triangle [Fig. 13.14(a)]. The molecule has 3 degrees of freedom due to translatory motion and 3 degrees of freedom due to rotational motion about three mutually perpendicular axes through its centre of mass. At ordinary temperature, vibrational motion may be ignored.

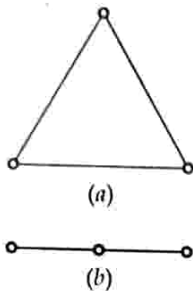


Fig. 13.14 Two types of triatomic molecules.

Here $N=3$, $k=3$,
so $f=3 \times 3 - 3 = 6$.

(b) In a *linear molecule* such as CO_2 , CS_2 , HCN , etc., the three atoms are arranged along a straight line [Fig. 13.14(b)]. The number of independent relations between them is only 2.

$$\therefore f = 3N - k = 3 \times 3 - 2 = 7.$$

13.15 LAW OF EQUIPARTITION OF ENERGY

25. State and prove the law of equipartition of energy.

Law of equipartition of energy. It states that in any dynamical system in thermal equilibrium, the energy is equally distributed amongst its various degrees of freedom and the energy associated with each degree of freedom per molecule is $\frac{1}{2} k_B T$, where k_B is Boltzmann's constant and T is the absolute temperature of the system.

Proof. Consider one mole of a monoatomic gas in thermal equilibrium at temperature T . A monoatomic gas molecule can be taken as a point mass. So each such molecule has 3 degrees of freedom due to translatory motion. According to the kinetic theory of gases, the average translational kinetic energy of a gas molecule is given by

$$\frac{1}{2} m \overline{v^2} = \frac{3}{2} k_B T$$

where $\overline{v^2}$ is the mean square velocity of a gas molecule of mass m .

If $\overline{v_x^2}$, $\overline{v_y^2}$ and $\overline{v_z^2}$ are the components of mean square velocity of the gas molecules along the three coordinate axes, then

$$\overline{v^2} = \overline{v_x^2} + \overline{v_y^2} + \overline{v_z^2}$$

$$\therefore \frac{1}{2} m \overline{v_x^2} + \frac{1}{2} m \overline{v_y^2} + \frac{1}{2} m \overline{v_z^2} = \frac{3}{2} k_B T$$

As the molecular motion is random, there is no preferred direction of motion. So the average kinetic

energy of each molecule along each of the three axes is the same.

$$\therefore \frac{1}{2} m \overline{v_x^2} = \frac{1}{2} m \overline{v_y^2} = \frac{1}{2} m \overline{v_z^2}$$

Combining the above two equations, we get

$$\frac{1}{2} m \overline{v_x^2} = \frac{1}{2} m \overline{v_y^2} = \frac{1}{2} m \overline{v_z^2} = \frac{1}{2} k_B T$$

Thus the average kinetic energy per molecule per degree of freedom is $\frac{1}{2} k_B T$. This result was first deduced by Boltzmann and is called the law of equipartition of energy.



For Your Knowledge

- ▲ The law of equipartition of energy holds good for all degrees of freedom whether translational, rotational or vibrational.
- ▲ Each square term in the total energy expression of a molecule contributes towards one degree of freedom.
- ▲ A monoatomic gas molecule has only translational kinetic energy,

$$\epsilon_t = \frac{1}{2} m v_x^2 + \frac{1}{2} m v_y^2 + \frac{1}{2} m v_z^2$$

So a monoatomic gas molecule has only three (translational) degrees of freedom.

- ▲ In addition to translational kinetic energy, a diatomic molecule has two rotational kinetic energies.

$$\epsilon_t + \epsilon_r = \frac{1}{2} m v_x^2 + \frac{1}{2} m v_y^2 + \frac{1}{2} m v_z^2 + \frac{1}{2} I_y \omega_y^2 + \frac{1}{2} I_z \omega_z^2$$

Here the line joining the two atoms has been taken as X -axis about which there is no rotation. So the degree of freedom of a diatomic molecule is 5, it does not vibrate.

- ▲ Diatomic molecule like CO has a mode of vibration even at moderate temperatures. Its atoms vibrate along the interatomic axis and contribute a vibrational energy term ϵ_v to the total energy.

$$\begin{aligned} \epsilon &= \epsilon_t + \epsilon_r + \epsilon_v \\ &= \frac{1}{2} m v_x^2 + \frac{1}{2} m v_y^2 + \frac{1}{2} m v_z^2 \\ &\quad + \frac{1}{2} I_y \omega_y^2 + \frac{1}{2} I_z \omega_z^2 + \frac{1}{2} m \dot{\eta}^2 + \frac{1}{2} k \eta^2 \end{aligned}$$

where k is the force constant of the oscillator, η the vibrational coordinate and $\dot{\eta} = \frac{dx}{dt}$.

So a diatomic molecule has 7 degree of freedom if it vibrates.

- ▲ Each translational and rotational degree of freedom corresponds to one mode of absorption of energy and has energy $\frac{1}{2} k_B T$. Each vibrational frequency has two modes of energy (kinetic and potential) with corresponding energy equal to $2 \times \frac{1}{2} k_B T = k_B T$.

13.16 ▽ SPECIFIC HEATS OF MONOATOMIC, DIATOMIC AND POLYATOMIC GASES

26. Using the law of equipartition of energy, determine the values of C_p , C_v and γ for (i) monoatomic, (ii) diatomic and (iii) triatomic gases.

(i) **Specific heats of monoatomic gas.** In case of a monoatomic gases, like He, Ar, etc., a molecule has three translational degree of freedom. According to the law of equipartition of energy, average energy associated with each degree of freedom per molecule = $\frac{1}{2} k_B T$.

\therefore Average energy associated with three degrees of freedom per molecule = $\frac{3}{2} k_B T$

Let R = gas constant per mole of a gas

N_A = Avogadro's number i.e., the number of atoms in one mole of the gas.

Then the total internal energy of one mole of a monoatomic gas,

$$U = \frac{3}{2} k_B T \times N_A = \frac{3}{2} RT \quad [\because k_B N_A = R]$$

The molar specific heat at constant volume will be

$$C_v \text{ (monoatomic)} = \frac{dU}{dT} = \frac{d}{dT} \left(\frac{3}{2} RT \right) = \frac{3}{2} R$$

The molar specific heat at constant pressure,

$$C_p \text{ (monoatomic)} = C_v + R = \frac{3}{2} R + R = \frac{5}{2} R$$

$$\text{Specific heat ratio, } \gamma = \frac{C_p}{C_v} = \frac{(5/2) R}{(3/2) R} = \frac{5}{3} = 1.67.$$

(ii) **Specific heats of diatomic gas.** (a) Diatomic molecules such as N_2 , O_2 , etc., behave as *rigid rotator* at moderate temperatures. Such molecules have 5 degrees of freedom : 3 translational and 2 rotational. According to the law of equipartition of energy, the total energy of a mole of such a gas is

$$U = \frac{5}{2} k_B T \times N_A = \frac{5}{2} RT$$

$$\therefore C_v \text{ (rigid diatomic)} = \frac{dU}{dT} = \frac{5}{2} R$$

$$C_p \text{ (rigid diatomic)} = C_v + R = \frac{7}{2} R$$

$$\gamma \text{ (rigid diatomic)} = \frac{(7/2) R}{(5/2) R} = \frac{7}{5} = 1.4.$$

(b) If the diatomic molecule is not rigid but has also a vibrational mode, then each molecule has an additional energy equal to $2 \times (\frac{1}{2}) k_B T = k_B T$, because a vibrational frequency has both kinetic and potential energy modes.

$$\therefore U = \left(\frac{5}{2} k_B T + k_B T \right) N_A = \frac{7}{2} k_B N_A T = \frac{7}{2} RT$$

$$C_v \text{ (diatomic with vibrational mode)} = \frac{dU}{dT} = \frac{7}{2} R$$

$$C_p \text{ (diatomic with vibrational mode)} = C_v + R = \frac{9}{2} R$$

$$\gamma \text{ (diatomic with vibrational mode)} = \frac{(9/2) R}{(7/2) R} = \frac{9}{7} = 1.28.$$

(iii) **Specific heats of triatomic gas.** (a) A non-linear triatomic gas molecule has six degrees of freedom.

$$\therefore U = \frac{6}{2} k_B T \times N_A = 3RT$$

$$C_v = \frac{dU}{dT} = 3R$$

$$C_p = C_v + R = 4R$$

$$\gamma = \frac{C_p}{C_v} = \frac{4}{3} = 1.33.$$

(b) A linear triatomic molecule has seven degrees of freedom.

$$\therefore U = \frac{7}{2} k_B T \times N_A = \frac{7}{2} RT$$

$$C_v = \frac{dU}{dT} = \frac{7}{2} R$$

$$C_p = C_v + R = \frac{9}{2} R$$

$$\gamma = \frac{C_p}{C_v} = \frac{(9/2) R}{(7/2) R} = \frac{9}{7} = 1.28.$$

27. Using the law of equipartition of energy, obtain a relation between the degrees of freedom f and the specific heat ratio γ of a polyatomic gas.

Specific heats of a polyatomic gas. Consider one mole of a perfect polyatomic gas at absolute temperature T . Suppose the total degrees of freedom of each molecule be f . According to the law of equipartition of energy,

$$\text{average energy of each molecule} = \frac{f}{2} k_B T$$

\therefore Internal energy of one mole of the gas,

$$U = \frac{f}{2} k_B T \times N_A = \frac{f}{2} RT$$

$$C_v = \frac{dU}{dT} = \frac{f}{2} R$$

$$C_p = C_v + R$$

$$= \frac{f}{2} R + R = \left(\frac{f}{2} + 1 \right) R$$

$$\gamma = \frac{C_p}{C_v} = \frac{\left(\frac{f}{2} + 1 \right) R}{\frac{f}{2} R} \quad \text{or} \quad \gamma = 1 + \frac{2}{f}$$

 **For Your Knowledge**

▲ Generally, a polyatomic atomic gas has 3 translational, 3 rotational degrees of freedom and a certain number (f') of vibrational modes. Therefore, the internal energy of one mole of such a gas is

$$U = \left(\frac{3}{2} k_B T + \frac{3}{2} k_B T + f' k_B T \right) N_A$$

$$= (3 + f') k_B N_A T = (3 + f') RT$$

$$\therefore C_V = \frac{dU}{dT} = (3 + f') R$$

$$C_P = C_V + R = (4 + f') R \text{ and } \gamma = \frac{C_P}{C_V} = \frac{4 + f'}{3 + f'}$$

Examples based on

Degrees of Freedom, Specific Heats of Monoatomic Diatomic and Polyatomic Gases

FORMULAE USED

1. Energy associated with each degree of freedom per molecule = $\frac{1}{2} k_B T$

2. For a gas of polyatomic molecules having f degrees of freedom,

$$\text{Energy associated with 1 mole of gas, } U = \frac{f}{2} RT$$

$$C_V = \frac{f}{2} R, \quad C_P = \left(1 + \frac{f}{2} \right) R, \quad \gamma = \frac{C_P}{C_V} = 1 + \frac{2}{f}$$

3. For monoatomic gas $f = 3$, so

$$U = \frac{3}{2} RT, \quad C_V = \frac{3}{2} R, \quad C_P = \frac{5}{2} R, \quad \gamma = 1.66$$

4. For a diatomic gas, $f = 5$

$$U = \frac{5}{2} RT, \quad C_V = \frac{5}{2} R, \quad C_P = \frac{7}{2} R, \quad \gamma = 1.4$$

5. For a triatomic gas of non-linear molecules $f = 6$, so

$$U = 3 RT, \quad C_V = 3R, \quad C_P = 4R, \quad \gamma = 1.33$$

6. For a triatomic gas of linear molecules $f = 7$, so

$$U = \frac{7}{2} RT, \quad C_V = \frac{7}{2} R, \quad C_P = \frac{9}{2} R, \quad \gamma = 1.28$$

UNITS USED

C_V, C_P are in $\text{J mol}^{-1} \text{K}^{-1}$ and c_V, c_P are in $\text{J kg}^{-1} \text{K}^{-1}$.

EXAMPLE 27. Calculate the total number of degrees of freedom possessed by the molecules in 1 cm^3 of H_2 gas at N.T.P.

Solution. Number of H_2 molecules in 22.4 litres or 22400 cm^3 at N.T.P.

$$= 6.02 \times 10^{23}$$

\therefore Number of H_2 molecules in 1 cm^3 at N.T.P.

$$= \frac{6.02 \times 10^{23}}{22400} = 2.6875 \times 10^{19}$$

Number of degrees of freedom associated with each H_2 (a diatomic) molecule

$$= 5$$

\therefore Total number of degrees of freedom associated with 1 cm^3 of gas

$$= 2.6875 \times 10^{19} \times 5 = 1.34375 \times 10^{20}$$

EXAMPLE 28. Calculate the internal energy of 1 g of oxygen at N.T.P.

Solution. Oxygen is a diatomic gas.

\therefore Energy associated with 1 mole of oxygen,

$$U = \frac{5}{2} RT$$

Hence internal energy of 1 g of oxygen,

$$u = \frac{U}{M} = \frac{1}{32} \times \frac{5}{2} RT$$

$$= \frac{5}{64} \times 8.31 \times 273 = 177.2 \text{ J}$$

EXAMPLE 29. Hydrogen is heated in a vessel to a temperature of 10,000 K. Let each molecule possess an average energy E_1 . A few molecules escape into the atmosphere at 300 K. Due to collisions, their energy changes to E_2 . Calculate ratio E_1 / E_2 .

Solution. Number of degrees of freedom of H_2 at 10,000 K = 7

Number of degrees of freedom of H_2 at 300 K = 5

$$\therefore \frac{E_1}{E_2} = \frac{\frac{7}{2} k_B T_1}{\frac{5}{2} k_B T_2} = \frac{7}{5} \times \frac{T_1}{T_2} = \frac{7}{5} \times \frac{10,000}{300} = \frac{140}{3}$$

EXAMPLE 30. Calculate the molecular K.E. of 1 gram of Helium (Molecular weight 4) at 127°C .

Given $R = 8.31 \text{ J mol}^{-1} \text{K}^{-1}$.

[Delhi 05]

Solution. Here $T = 127 + 273 = 400 \text{ K}$

Helium is a monoatomic gas.

$$\therefore \text{Average K.E. per mole of helium} = \frac{3}{2} RT$$

$$\text{Average K.E. of 1 gram of helium} = \frac{3}{2} \frac{RT}{M}$$

$$= \frac{3 \times 8.31 \times 400}{2 \times 4} = 12.465 \text{ J}$$

EXAMPLE 31. How many degrees of freedom are associated with 2 g of He at N.T.P. ? Calculate the amount of heat energy required to raise the temperature of this amount from 27°C to 127°C . Given Boltzmann's constant = $1.38 \times 10^{-16} \text{ erg molecule}^{-1} \text{K}^{-1}$ and Avogadro's number = 6.02×10^{23} .

Solution. Molecular weight of helium = 4

∴ Number of molecules in 4 g of helium
 $= 6.02 \times 10^{23}$

Number of molecules in 2 g of helium
 $= \frac{1}{2} \times 6.02 \times 10^{23} = 3.01 \times 10^{23}$

As helium is a monoatomic gas, it has 3 degrees of freedom

Total degrees of freedom of 3.01×10^{23} molecules
 $= 3 \times 3.01 \times 10^{23} = 9.03 \times 10^{23}$

Boltzmann's constant,

$$k_B = 1.38 \times 10^{-16} \text{ erg molecule}^{-1} \text{ K}^{-1} \\ = 1.38 \times 10^{-23} \text{ J molecule}^{-1} \text{ K}^{-1}$$

Energy associated with 1 degree of freedom per molecule = $\frac{1}{2} k_B T$

∴ Energy associated with 2 g of He at 300 K,

$$E_1 = 9.03 \times 10^{23} \times \frac{1}{2} \times 1.38 \times 10^{-23} \times 300 = 1869.2 \text{ J}$$

Energy associated with 2 g of He at 400 K,

$$E_2 = 9.03 \times 10^{23} \times \frac{1}{2} \times 1.38 \times 10^{-23} \times 400 = 2492.3 \text{ J}$$

Here energy required to raise the temperature from 27°C to 127°C

$$= E_2 - E_1 = 2492.3 - 1869.2 = 623.1 \text{ J.}$$

EXAMPLE 32. Calculate the limiting ratio of the internal energy possessed by helium and hydrogen gases at 10,000 K.

Solution. For helium gas: As helium is monoatomic gas, the number of degrees of freedom of helium molecule = 3

∴ The internal energy of helium molecule at 10,000 K,

$$U_{\text{He}} = 3 \times \frac{1}{2} k_B T \\ = 3 \times \frac{1}{2} \times k_B \times 10000 = 1.5 \times 10^4 k_B$$

For hydrogen gas: At 10,000 K, no. of degrees of freedom of a H_2 molecule = 7

∴ The internal energy of hydrogen molecule at 10,000 K,

$$U_{\text{H}} = 7 \times \frac{1}{2} k_B T \\ = 7 \times \frac{1}{2} k_B \times 10000 = 3.5 \times 10^4 k_B$$

Hence $\frac{U_{\text{He}}}{U_{\text{H}}} = \frac{1.5 \times 10^4 k_B}{3.5 \times 10^4 k_B} = 3 : 7.$

EXAMPLE 33. A cylinder of fixed capacity 44.8 litres contains helium gas at standard pressure and temperature. What is the amount of heat needed to raise the temperature of the gas by 15.0°C ? $R = 8.31 \text{ J mol}^{-1} \text{ K}^{-1}$. [NCERT]

Solution. Volume of 1 mole of He at S.T.P.
 $= 22.4 \text{ litres}$

Total volume of He at S.T.P. = 44.8 litres

∴ No. of moles of He, $n = \frac{44.8}{22.4} = 2$

Molar specific heat of He (monoatomic gas) at constant volume,

$$C_V = \frac{3}{2} R = \frac{3}{2} \times 8.31 \text{ J mol}^{-1} \text{ K}^{-1}$$

$$\Delta T = 15^\circ\text{C} = 15 \text{ K}$$

Heat required

$$Q = n C_V \Delta T = 2 \times \frac{3}{2} \times 8.31 \times 15 = 373.95 \text{ J.}$$

EXAMPLE 34. 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 $R = 8.31 \text{ J mol}^{-1} \text{ K}^{-1}$. [Roorkee 93; Delhi 06]

Solution. 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

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

or $C_V'' = \frac{9}{4} \times 8.31 = 18.7 \text{ J mole}^{-1} \text{ K}^{-1}.$

EXAMPLE 35. One mole of ideal monoatomic gas ($\gamma = 5/3$) is mixed with one mole of diatomic gas ($\gamma = 7/5$). What is γ for the mixture? Here γ denotes the ratio of specific heat at constant pressure to that at constant volume. [AIIEE 02, 04]

Solution. $\gamma = \frac{C_P}{C_V} = \frac{C_V + R}{C_V} = 1 + \frac{R}{C_V}$ or $C_V = \frac{R}{\gamma - 1}$

For monoatomic gas, $C_V = \frac{R}{5/3 - 1} = \frac{3}{2} R$

For diatomic gas $C_V = \frac{R}{7/5 - 1} = \frac{5}{2} R$

$$C_V (\text{mixture}) = \frac{n C_V + n' C_V'}{n + n'} = \frac{1 \times \frac{3}{2} R + 1 \times \frac{5}{2} R}{1 + 1} = 2 R$$

$$\gamma (\text{mixture}) = 1 + \frac{R}{C_V (\text{mixture})} = 1 + \frac{R}{2 R} = 1.5.$$

EXAMPLE 36. A gaseous mixture consists of 16 g of helium and 16 g of oxygen. Find the ratio C_p / C_v of the mixture.

[AIEEE 05]

Solution. Number of moles of helium = $\frac{16}{4} = 4$

Number of moles of oxygen = $\frac{16}{32} = \frac{1}{2}$

For the monoatomic helium gas, degrees of freedom $f = 3$, so

$$C_v = \frac{f}{2} R = \frac{3}{2} R$$

For the diatomic oxygen gas, $f = 5$, so

$$C_v = \frac{f}{2} R = \frac{5}{2} R$$

$$\begin{aligned} \therefore C_v (\text{mixture}) &= \frac{nC_v + n' C_v'}{n + n'} \\ &= \frac{4 \times \frac{3}{2} R + \frac{1}{2} \times \frac{5}{2} R}{4 + \frac{1}{2}} = \frac{29}{18} R \end{aligned}$$

$$\begin{aligned} \gamma (\text{mixture}) &= \frac{C_p}{C_v} = 1 + \frac{R}{C_v (\text{mixture})} \\ &= 1 + \frac{R}{\frac{29}{18} R} = 1 + \frac{18}{29} = \frac{47}{29} = 1.62. \end{aligned}$$

EXAMPLE 37. A gaseous mixture enclosed in a vessel contains 1 gram mole of a gas A (with $\gamma = 5/3$) and another gas B (with $\gamma = 7/5$) at a temperature T . The gases A and B do not react with each other and assumed to be ideal. Find the number of gram moles of B if γ for the gaseous mixture is 19/13.

[IIT 95]

Solution. Let the mixture contain n moles of gas B.

$$\text{As } C_p - C_v = R \quad \text{and} \quad \gamma = \frac{C_p}{C_v}$$

$$\therefore C_v = \frac{R}{\gamma - 1}$$

$$\text{For gas A, } C_v = \frac{R}{5/3 - 1} = \frac{3}{2} R$$

$$\text{For gas B, } C_v = \frac{R}{7/2 - 1} = \frac{5}{2} R$$

$$\text{For the mixture, } C_v = \frac{R}{19/13 - 1} = \frac{13}{6} R$$

By conservation of energy, molar sp. heat of the mixture is

$$C_v = \frac{n_A (C_v)_A + n_B (C_v)_B}{n_A + n_B}$$

$$\therefore \frac{13}{6} R = \frac{1 \times \frac{3}{2} R + n \times \frac{5}{2} R}{1 + n} = \frac{(3 + 5n) R}{2(1 + n)}$$

$$\text{or } n = 2.$$

✱ PROBLEMS FOR PRACTICE

- Calculate the total number of degrees of freedom for a mole of diatomic gas at N.T.P. (Ans. 30.1×10^{23})
- Calculate the number of degrees of freedom in 10 cm^3 of O_2 at N.T.P. (Ans. 1.344×10^{21})
- Calculate the number of degrees of freedom in 15 cm^3 of nitrogen at N.T.P. (Ans. 2.015×10^{21})
- The specific heat of argon at constant volume is $0.075 \text{ kcal kg}^{-1} \text{ K}^{-1}$. Calculate its atomic weight. Given $R = 2 \text{ cal mol}^{-1} \text{ K}^{-1}$ (Ans. 40)
- A certain gas possesses 3 degrees of freedom corresponding to the translational motion and 2 degrees of freedom corresponding to rotational motion. (i) What is the kinetic energy of translational motion of one such molecule of gas at 300 K? (ii) If the temperature is raised by 1°C , what energy must be supplied to the one molecule of the gas? Given Avogadro's number, $N = 6.023 \times 10^{23} \text{ mol}^{-1}$ and Boltzmann's constant, $k_B = 1.38 \times 10^{-23} \text{ J molecule}^{-1} \text{ K}^{-1}$. (Ans. (i) $6.21 \times 10^{-21} \text{ J}$ (ii) 20.78 J)

✱ HINTS

- No. of degrees of freedom of a diatomic molecule at 273 K = 5
 \therefore No. of degrees of freedom of 1 mole or 6.02×10^{23} molecules at N.T.P.
 $= 5 \times 6.02 \times 10^{23} = 30.1 \times 10^{23}$.
- No. of nitrogen molecules in 22400 cm^3 of gas at N.T.P. = 6.02×10^{23}
 \therefore No. of nitrogen molecules in 15 cm^3 of gas at N.T.P.
 $= \frac{6.02 \times 10^{23} \times 15}{22400} = 4.2 \times 10^{20}$
 No. of degrees of freedom of nitrogen (diatomic) molecule at 273 K = 5
 \therefore Total degrees of freedom of 15 cm^3 of gas
 $= 4.03 \times 10^{20} \times 5 = 2.015 \times 10^{21}$.
- Argon is a monoatomic gas, so its molar specific heat at constant volume is

$$C_v = \frac{3}{2} R = \frac{3}{2} \times 2 = \text{cal mol}^{-1} \text{ K}^{-1}$$

$$\text{Given } c_v = 0.075 \text{ kcal kg}^{-1} \text{ K}^{-1} = 0.075 \text{ cal g}^{-1} \text{ K}^{-1}$$

$$\text{As } C_v = M c_v$$

$$\therefore M = \frac{C_v}{c_v} = \frac{3}{0.075} = 40.$$

5. Translational K.E. of a gas molecule at 300 K

$$= 3 \times \frac{1}{2} k_B T = \frac{3}{2} \times 1.38 \times 10^{-23} \times 300$$

$$= 6.21 \times 10^{-21} \text{ J.}$$

(ii) Energy required to raise the temperature of one mole of gas by 1°C or 1 K

$$= 5 \times \frac{1}{2} k_B \Delta T \times N$$

$$= 5 \times \frac{1}{2} \times 1.38 \times 10^{-23} \times 1 \times 6.023 \times 10^{23}$$

$$= 20.78 \text{ J.}$$

13.17 SPECIFIC HEAT OF SOLIDS

28. State and prove Dulong and Petit's law. What does it signify ?

Specific heat of solids : Dulong and Petit's law.

Near the room temperature the molar specific heat of most of the solids at constant volume is equal to $3R$ or $6 \text{ cal mol}^{-1} \text{ K}^{-1}$ or $25 \text{ J mol}^{-1} \text{ K}^{-1}$. This statement is known as Dulong and Petit's law.

Proof. In a solid, the atoms vibrate about their mean positions. During vibration, the kinetic energy (E_k) of an atom changes continuously into potential energy (E_p) and vice-versa. So the average values of E_k and E_p are equal in a solid. Since an atom can vibrate along three mutually perpendicular directions, it has three degrees of freedom. Applying the law of equipartition of energy, we get

$$E_k = 3 \times \frac{1}{2} k_B T = \frac{3}{2} k_B T$$

$$E_p = 3 \times \frac{1}{2} k_B T = \frac{3}{2} k_B T$$

∴ Average vibrational energy per atom

$$= E_k + E_p = 3k_B T$$

The total vibrational energy or the internal energy of one mole of atoms of the solid is given by

$$U = N_A \times 3k_B T = 3RT \quad [\because R = k_B N_A]$$

Since for a solid ΔV is negligible, so

$$\Delta Q = \Delta U + P \Delta V = \Delta U$$

Therefore, $C_V = \frac{\Delta Q}{\Delta T} = \frac{\Delta U}{\Delta T} = 3R$

This proves the Dulong and Petit's law.

Significance of Dulong and Petit's law. This law signifies the fact that the heat energy required to raise the temperature of a sample of metal depends on the total number of atoms present in the sample and not on the masses of individual atoms of the metal. Since one mole of every metal contains an Avogadro's number of atoms, so the molar specific heat of all metals is same near the room temperature.

29. How does the specific heat of a solid vary with temperature ? What is Debye temperature ?

Variation of specific heat of a solid with temperature. Fig. 13.15 shows the variation of molar specific heat (C_V) of a solid as a function of temperature. Clearly, at higher temperatures the molar specific heat (C_V) of all solids is close to the Dulong and Petit's value $3R$. At lower temperatures, the molar specific heat decreases rapidly with temperature, tending to become zero at 0 K. Physically, this is related to the fact that the number of degrees of freedom of a molecule decreases as we go to low temperatures. In fact, some of the modes of motion get frozen.

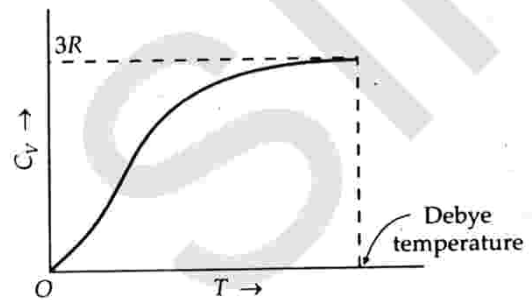


Fig. 13.15 Variation of C_V of a solid with temperature

The behaviour of specific heats at low temperatures could not be explained on the basis of classical physics according to which the modes of motion remain unchanged and only the amplitude of motion decreases at low temperatures. This behaviour was first explained by Einstein in 1905 by using quantum theory. It was explained more satisfactorily by Debye in 1915.

Quantum mechanics requires a minimum, non-zero amount of energy before a degree of freedom comes into play. That is why vibrational degrees of freedom become active only under some situations.

The temperature at which the molar specific heat of a solid at constant volume becomes equal to $3R$ is called **Debye temperature**.

Table 13.1 Specific heats and molar specific heats of some solids at room temperature and atmospheric pressure

Substance	Specific heat ($\text{J kg}^{-1} \text{ K}^{-1}$)	Molar specific heat ($\text{J mol}^{-1} \text{ K}^{-1}$)
Aluminium	900.0	24.4
Carbon	506.5	6.1
Copper	386.4	24.5
Lead	127.7	26.5
Silver	236.1	25.5
Tungsten	134.4	24.9

The experimental values of molar specific heat agree well with the predicted value $25 \text{ J mol}^{-1} \text{ K}^{-1}$. Here carbon is an exception. The deviation from the predicted value is more at lower temperatures.

13.18 ▽ SPECIFIC HEAT OF WATER

30. Using the law of equipartition of energy, predict the specific heat of water. How does the specific heat of water vary with temperature? Define one calorie.

Specific heat of water. We may treat water like a solid. By the law of equipartition of energy, the average vibrational energy per atom is $3 k_B T$. Now a water molecule has three atoms : two hydrogen and one oxygen.

∴ Average vibrational energy per water molecule
 $= 3 \times 3k_B T = 9 k_B T$

The total vibrational or the internal energy of one mole of water molecules,

$$U = N_A \times 9 k_B T = 9RT \quad [\because R = k_B N_A]$$

Neglecting ΔV , like for a solid, we get

$$\Delta Q = \Delta U + P\Delta V = \Delta U$$

∴ $C_V = \frac{\Delta Q}{\Delta T} = \frac{\Delta U}{\Delta T} = 9R$

This predicted value is found to be in good agreement with the observed value. The specific heat of water is nearly $75 \text{ J mol}^{-1} \text{ K}^{-1} \approx 9R$.

Variation of specific heat of water with temperature. Fig. 13.16 shows the variation of specific heat of water with temperature in the temperature range 0°C to 100°C . Water shows peculiar behaviour, its specific heat first decreases and then increases with temperature. For this reason, we have to specify the unit temperature interval for defining calorie.

One calorie is defined as the amount of heat required to raise the temperature of 1 g of water from 14.5°C to 15.5°C .

$$1 \text{ calorie} = 4.186 \text{ J.}$$

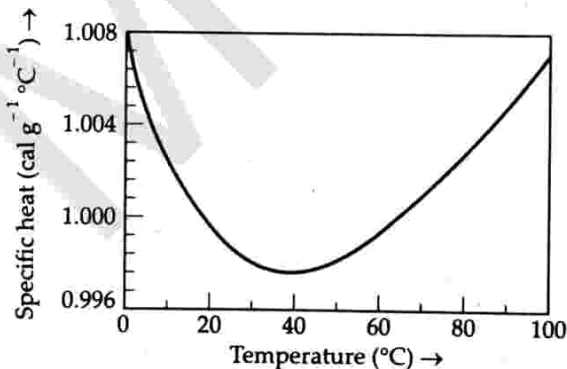


Fig. 13.16 Variation of specific heat of water with temperature

13.19 ▽ MEAN FREE PATH

31. What is meant by the mean free path of a gas molecule? Derive an expression for it. On which factors does the mean free path depend?

Mean free path. The molecules of a gas are in state of continuous, rapid and random motion. As these molecules have a finite though small size, so they collide against one another frequently. Between two successive collisions, a molecule moves along a straight line path with uniform velocity. This path is called **free path**. But after every collision, velocity of each molecule changes both in magnitude and direction. Hence each molecule follows a series of straight line zig-zag paths, as shown in Fig. 13.17.

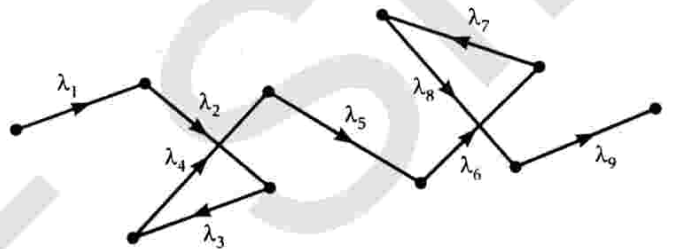


Fig. 13.17 Zig-zag path of a gas molecule.

The **mean free path** of a gas molecule may be defined as the average distance travelled by the molecule between two successive collisions.

As shown in Fig. 13.17, if a molecule covers free paths $\lambda_1, \lambda_2, \lambda_3, \dots$, after successive collisions, then its mean free path is given by

$$\bar{\lambda} = \frac{\lambda_1 + \lambda_2 + \lambda_3 + \dots}{\text{Total number of collisions}}$$

Expression for mean free path. In order to derive the expression for the mean free path, we make use of the following assumptions :

- (i) Each molecule of the gas is a sphere of diameter d .
- (ii) All molecules of the gas except the molecule A under consideration are at rest.

As shown in Fig. 13.18, suppose the molecule A has average speed \bar{v} . It will collide with all those molecules whose centres lie within a distance d from its path. In

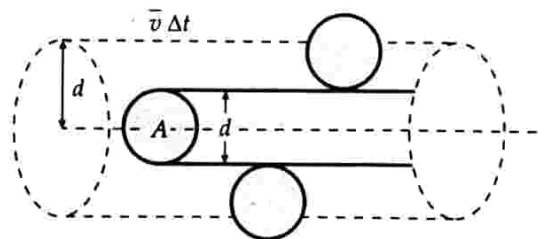


Fig. 13.18 Volume swept by molecule A in time Δt in which any molecule can collide with it.

time Δt , it will obviously collide with all those molecules in the cylinder of volume $\pi d^2 \bar{v} \Delta t$. Let n be the number of molecules per unit volume.

Number of collisions suffered by the molecule A in time Δt

$$\begin{aligned} &= \text{Volume of the cylinder swept by molecule } A \text{ in} \\ &\quad \text{time } \Delta t \times \text{number of molecules per unit volume} \\ &= \pi d^2 \bar{v} \Delta t \times n \end{aligned}$$

Mean free path of a gas molecule,

$$\begin{aligned} \bar{\lambda} &= \frac{\text{Distance covered in time } \Delta t}{\text{Number of collisions suffered in time } \Delta t} \\ &= \frac{\bar{v} \Delta t}{\pi d^2 \bar{v} \Delta t n} = \frac{1}{n \pi d^2} \end{aligned}$$

In the above derivation, we have assumed the other molecules to be at rest. Taking into consideration the motion of all the gas molecules, the mean free path comes out to be

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

If m is the mass of each gas molecule, then the density of the gas is

$$\rho = mn \quad \text{or} \quad n = \frac{\rho}{m}$$

$$\therefore \bar{\lambda} = \frac{m}{\sqrt{2} \pi d^2 \rho}$$

For one mole of a gas,

$$PV = RT \quad \text{or} \quad P = \frac{RT}{V} = \frac{N}{V} \times \frac{R}{N} \times T = nk_B T$$

$$\text{or} \quad n = \frac{P}{k_B T} \quad \therefore \bar{\lambda} = \frac{k_B T}{\sqrt{2} \pi d^2 P}$$

Factors on which the mean free path depends. It is obvious from the above expressions for $\bar{\lambda}$ that

- (i) $\bar{\lambda} \propto m$, i.e., the mean free path is directly proportional to the mass of the gas molecule.
- (ii) $\bar{\lambda} \propto \frac{1}{\rho}$, i.e., the mean free path is inversely proportional to the density of the gas.
- (iii) $\bar{\lambda} \propto \frac{1}{d^2}$, i.e., the mean free path is inversely proportional to the square of the molecular diameter.
- (iv) $\bar{\lambda} \propto T$, i.e., the mean free path is directly proportional to the absolute temperature of the gas.
- (v) $\bar{\lambda} \propto \frac{1}{P}$, i.e., the mean free path is inversely proportional to the pressure of the gas.

13.20 AVOGADRO'S NUMBER

32. What is Avogadro's number? Give its significance.

Avogadro's number. It is the number of atoms present in one gram atom of an element or the number of molecules present in one gram molecule of the substance. In general, it is the number of particles present in one mole of the substance. Its most accepted value is

$$N_A = 6.0225 \times 10^{23} \text{ mole}^{-1}$$

Importance of Avogadro's number.

- (i) To calculate the actual weight of one atom of an element.

$$\begin{aligned} &\text{Weight of one atom of an element} \\ &= \frac{\text{Atomic weight (in gram)}}{\text{Avogadro's number}} \end{aligned}$$

- (ii) To calculate the actual weight of one molecule of a substance.

$$\begin{aligned} &\text{Weight of one molecule of a substance} \\ &= \frac{\text{Molecular weight (in gram)}}{\text{Avogadro's number}} \end{aligned}$$

- (iii) To calculate the number of atoms present in given amount of an element.

$$\begin{aligned} &\text{Number of atoms present in } m \text{ gram of an} \\ &\text{element} = \frac{\text{Avogadro's number}}{\text{Atomic weight}} \times m \end{aligned}$$

- (iv) To calculate the number of molecules present in given amount of a substance.

$$\begin{aligned} &\text{Number of molecules present in } m \text{ gram of a} \\ &\text{substance} = \frac{\text{Avogadro's number}}{\text{Molecular weight}} \times m \end{aligned}$$

- (v) To calculate the number of molecules present in given volume of the gas. At S.T.P., the 22.4 litres of every gas contain an Avogadro's number of molecules.

$$\therefore \text{Number of molecules present in } V \text{ litres of a gas at S.T.P.} = \frac{\text{Avogadro's number}}{22.4} \times V$$

EXAMPLE 38. The density of water is 1000 kg m^{-3} . The density of water vapour at 100°C and 1 atm pressure is 0.6 kg m^{-3} . The volume of a molecule multiplied by the total number gives, what is called molecular volume. Estimate the ratio (or fraction) of the molecular volume to the total volume occupied by the water vapour under the above conditions of temperature and pressure. [NCERT]

Solution. For a given mass of water molecules,

$$\text{Volume} \propto \frac{1}{\text{Density}}$$

Therefore, the ratio (or fraction) of the molecular volume to the total volume of water vapour

$$\begin{aligned} &= \frac{\text{Density of water vapour}}{\text{Density of water}} = \frac{0.6 \text{ kg m}^{-3}}{1000 \text{ kg m}^{-3}} \\ &= 6 \times 10^{-4}. \end{aligned}$$

EXAMPLE 39. Estimate the volume of a water molecule. Given density of water is 1000 kg m^{-3} and Avogadro's number $= 6 \times 10^{23} \text{ mole}^{-1}$. [NCERT]

Solution. Molecular mass of water = 18

$$\therefore \text{Number of molecules in 18 g or 0.018 kg of water} = 6 \times 10^{23}$$

$$\begin{aligned} \text{Mass of 1 molecule of water} \\ &= \frac{0.018}{6 \times 10^{23}} = 3 \times 10^{-26} \end{aligned}$$

In the liquid phase, the molecules of water are closely packed. The density of water molecules may be taken equal to the density of bulk water $= 1000 \text{ kg m}^{-3}$.

$$\begin{aligned} \therefore \text{Volume of a water molecule} \\ &= \frac{\text{Mass}}{\text{Density}} = \frac{3 \times 10^{-26}}{1000} = 3 \times 10^{-29} \text{ m}^3 \end{aligned}$$

EXAMPLE 40. What is the average distance between atoms (interatomic distance) in water? Use the data given in Examples 38 and 39. [NCERT]

$$\begin{aligned} \text{Solution. Volume of water in vapour state} \\ &= \frac{1}{6 \times 10^{-4}} \times \text{Volume of water in liquid state} \\ &= 1.67 \times 10^3 \times \text{Volume of water in liquid state.} \end{aligned}$$

This is also the increase in amount of volume available for each molecule of water. When volume V increases by 10^3 times, the radius increases by $V^{1/3}$ or 10 times.

But volume of a water molecule,

$$\frac{4}{3} \pi r^3 = 3 \times 10^{-29} \text{ m}^3$$

$$\therefore r = \left(\frac{9}{4\pi} \times 10^{-29} \right)^{1/3} \approx 2 \times 10^{-10} \text{ m} = 2 \text{ \AA}$$

$$\text{Increased radius} = 10 \times 2 = 20 \text{ \AA}$$

$$\text{Average distance} = 2 \times \text{Increased radius} = 40 \text{ \AA}.$$

13.21 BROWNIAN MOTION*

33. What is Brownian motion? How can it be accounted for? What are the factors which affect Brownian motion?

Brownian motion. In 1827, a Scottish botanist Robert Brown, while examining pollen grains of a flower suspended in water under a microscope, noticed that they continuously moved about in a zig-zag, random motion. This irregular motion of the suspended particles is called Brownian motion. It provided a direct evidence for the existence of molecules and their motion.

Cause of Brownian motion. Any object suspended in a fluid is continuously bombarded by the fluid molecules from all directions. If the object is sufficiently small but still visible under a microscope (such as pollen grains which are about 10^{-5} m in diameter), the impact of molecules from all sides gives rise to an unbalanced force in a certain direction. As soon as the particle moves a little, the magnitude and direction of the unbalanced force change making the particle move in a new direction. The suspended object thus moves about in a zig-zag manner and tumbles about randomly.

Factors affecting the Brownian motion. The Brownian motion increases

- (i) with the decrease in size of the suspended particles.
- (ii) with the increase in temperature of the fluid.
- (iii) with the decrease in density of the fluid.
- (iv) with the decrease in viscosity of the fluid.

Very Short Answer Conceptual Problems

Problem 1. Mention the different ways of increasing the number of molecular collisions per unit time in a gas.

Solution. The number of collisions per unit time can be increased by

- (i) increasing the temperature of the gas,
- (ii) increasing the number of molecules, and
- (iii) decreasing the volume of the gas.

Problem 2. What is an ideal gas? Give its main characteristics.

Solution. An ideal gas is one which obeys the gas laws at all values of temperature and pressure. Its main characteristics are

- (i) The size of the molecules is negligibly small.
- (ii) There is no force of attraction or repulsion amongst its molecules.

Problem 3. Fig. 13.19 shows the variation of the product PV with respect to the pressure (P) of given masses of three gases, A , B and C . The temperature is kept constant. State with proper arguments which of these gases is ideal.

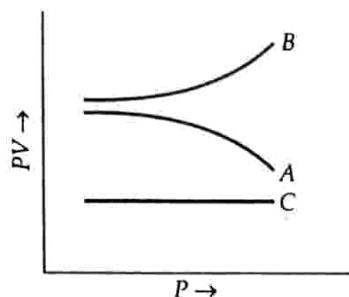


Fig. 13.19

Solution. Gas C is ideal, because PV is constant for it. That is, gas C obeys Boyle's law at all pressures.

Problem 4. Why do the gases at low temperature and high pressure show large deviations from ideal behaviour?

Solution. At low temperature and high pressure, the intermolecular attractions become appreciable. Moreover, the volume occupied by the gas molecules cannot be neglected in comparison to the volume of the gas. Hence the real gases show large deviations from ideal gas behaviour.

Problem 5. On reducing the volume of a gas at constant temperature, the pressure of the gas increases. Explain it on the basis of kinetic theory.

Solution. On reducing the volume, the number of molecules per unit volume increases. Hence a large number of molecules collide with the walls of the vessel per second and a larger momentum is transferred to the wall per second. This increases the pressure of the gas.

Problem 6. When an automobile travels for a long distance, the air pressure in the tyres increases slightly. Why?

Solution. Due to the friction between the tyres and the road, the tyres get heated. The temperature of air inside the tyres increases. Consequently, the air pressure in the tyres increases slightly.

Problem 7. When a gas is heated, its temperature increases. Explain it on the basis of kinetic theory of gases.

Solution. When a gas is heated, the root mean square velocity of its molecules increases. As $v_{rms} \propto \sqrt{T}$, so the temperature of the gas increases.

Problem 8. In the upper part of the atmosphere the kinetic temperature of air is of the order of 1000 K, even then one feels severe cold there. Why?

Solution. As we go up in the atmosphere, the number of air molecules per unit volume decreases. The quantity of heat per unit volume or the heat density is low. But the

translational kinetic energy per molecule is quite large. As the kinetic temperature is the measure of translational kinetic energy, so the kinetic temperature is quite high in the upper atmosphere but one feels severe cold there due to low heat density.

Problem 9. In the kinetic theory of gases, why do we not take into account the changes in gravitational potential energy of the molecule?

Solution. The changes in gravitational potential energy are negligibly small as compared to the mean kinetic energy of molecules.

Problem 10. What type of motion is associated with the molecules of a gas?

Solution. Brownian motion. In this motion any particular molecule will follow a zig-zag path due to the collisions with the other molecules or with the walls of the container.

Problem 11. Although the root-mean-square speed of gas molecules is of the order of the speed of sound in that gas, yet on opening a bottle of ammonia in one corner of a room its smell takes time in reaching the other corner. Why?

Solution. The molecules of ammonia have random motion. They frequently collide with one another. Consequently, their net speed in any particular direction is low. So gas takes several seconds to go from one corner to the other corner of the room.

Problem 12. On which factors does the average kinetic energy of gas molecules depend: Nature of the gas, temperature, volume?

Solution. The average K.E. of a gas molecule depends only on the absolute temperature of the gas and is directly proportional to it.

Problem 13. What do you mean by the r.m.s. speed of the molecules of a gas? Is r.m.s. speed same as the average speed?

Solution. The r.m.s. speed of the molecules of a gas is defined as the square root of the mean of the squared velocities of the molecules of a gas. No, r.m.s. speed is different from the average speed. For example,

$$v_{rms} = \sqrt{\frac{v_1^2 + v_2^2 + v_3^2}{3}}$$

and
$$\bar{v} = \frac{v_1 + v_2 + v_3}{3}$$

Problem 14. The ratio of vapour densities of two gases at the same temperature is 8 : 9. Compare the r.m.s. velocities of their molecules.

Solution.

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

$$= \sqrt{\frac{\rho_2}{\rho_1}} = \sqrt{\frac{9}{8}} = 3 : 2\sqrt{2}$$

Problem 15. What is the average velocity of the molecules of an ideal gas ?

Solution. The average velocity of the molecules of an ideal gas is zero, because the molecules possess all sorts of velocities in all possible directions so their vector sum and hence average is zero.

Problem 16. Given a sample of 1 cm^3 of hydrogen and 1 cm^3 of oxygen both at S.T.P. Which sample has a larger number of molecules ?

Solution. Both the samples contain the same number of molecules in accordance with Avogadro's law.

Problem 17. At what temperature does all molecular motion cease ? Explain. [Himachal 06, 07C]

Or

Molecular motion ceases at zero kelvin. Explain.

[Himachal 09]

Solution. All molecular motion ceases at absolute zero or at 0 K. According to the kinetic interpretation of temperature,

$$\bar{E} = \frac{3}{2} k_B T \quad \text{or} \quad T = \frac{2}{3} \frac{\bar{E}}{k_B}$$

or absolute temperature \propto average K.E. of molecules
 \therefore The temperature = 0 K, average K.E. = 0.

Thus at 0 K, the velocity of molecules becomes zero.

Problem 18. Why temperature less than absolute zero is not possible ?

Solution. According to the kinetic interpretation of temperature,

Absolute temperature \propto average K.E. of molecules

As the heat is removed, the temperature falls and velocity of molecules decreases. At absolute zero, the molecular motion ceases *i.e.*, the kinetic energy becomes zero. As kinetic energy cannot be negative, so no further decrease in kinetic energy is possible. Hence temperature cannot be decreased below 0 K.

Problem 19. For an ideal gas, the internal energy can only be translational kinetic energy. Explain.

Solution. In an ideal gas, the molecules can be considered as point masses with no intermolecular forces between them. So there can neither be internal potential energy nor the internal energy due to rotation or vibration. The molecules can have only translational kinetic energy.

Problem 20. At a given temperature, equal masses of monoatomic and diatomic gases are supplied equal quantities of heat. Which of the two gases will suffer a larger temperature rise ?

Solution. The temperature of the monoatomic gas will rise by a large value. In case of the monoatomic gas, the heat supplied is used entirely to increase the translational K.E. of the molecules. In case of the diatomic gas, the heat supplied is used to increase the translational, rotational

and sometimes even the vibrational kinetic energy of the molecules. It is only the translational K.E. which increases the temperature.

Problem 21. Deduce the dimensional formula for R used in the ideal gas equation $PV = nRT$.

$$\begin{aligned} \text{Solution. } R &= \frac{PV}{nT} = \frac{FV}{nAT} \\ [R] &= \frac{\text{MLT}^{-2} \cdot \text{L}^3}{\text{mol} \cdot \text{L}^2 \cdot \text{K}} = [\text{ML}^2 \text{T}^{-2} \text{K}^{-1} \text{mol}^{-1}]. \end{aligned}$$

Problem 22. A box contains equal number of molecules of hydrogen and oxygen. If there is a fine hole in the box, which gas will leak rapidly ? Why ?

$$\text{Solution. As } v_{rms} \propto \frac{1}{\sqrt{M}}$$

Hence hydrogen gas will leak more rapidly because of its smaller molecular mass.

Problem 23. The mass of a molecule of krypton is 2.25 times the mass of a hydrogen molecule. A mixture of equal masses of these gases is enclosed in a vessel. Calculate at any temperature the ratio of the root mean square velocities of krypton and hydrogen gases.

$$\text{Solution. } \frac{(v_{rms})_{Kr}}{(v_{rms})_{H_2}} = \sqrt{\frac{M_{H_2}}{M_{Kr}}} = \sqrt{\frac{1}{2.25}} = \frac{10}{15} = 2:3.$$

Problem 24. A sample of an ideal gas occupies a volume V at a pressure P and absolute temperature T . The mass of each molecule is m . If k_B is the Boltzmann's constant, then write the expression for the density of the gas.

Solution. According to kinetic theory of gases,

$$P = \frac{1}{3} \rho \bar{v}^2 = \frac{2}{3} \rho \cdot \frac{1}{2} m \bar{v}^2 = \frac{2}{3} \cdot \frac{\rho}{m} \cdot \frac{3}{2} k_B T$$

$$\therefore \text{Density, } \rho = \frac{Pm}{k_B T}$$

Problem 25. The volume of vessel A is twice the volume of another vessel B , and both of them are filled with the same gas. If the gas in A is at twice the temperature and twice the pressure in comparison to the gas in B , what is the ratio of the gas molecules in A and B ?

Solution. As $PV = nRT$

$$\therefore n_B = \frac{PV}{RT} \quad \text{and} \quad n_A = \frac{2P \cdot 2V}{R \cdot 2T} = 2 \frac{PV}{RT} \quad \text{and} \quad n_A : n_B = 2:1$$

Problem 26. Two gases, each at temperature T , volume V and pressure P are mixed such that the temperature and volume of the mixture are T and V respectively. What would be the pressure of the mixture ? Justify your answer on the basis of kinetic theory.

$$\text{Solution. From kinetic theory, } P = \frac{1}{3} \frac{M}{V} \bar{v}^2$$

$$\text{But } \bar{v}^2 \propto T \quad \therefore \quad P \propto \frac{MT}{V}$$

As both T and V remain unchanged but mass M is doubled, so the pressure of mixture gets doubled *i.e.*, it is equal to $2P$.

Problem 27. The total translational kinetic energy of the molecules of a gas having volume V and pressure P is 500 J. What will be the total translational kinetic energy of the molecules of the same gas occupying the same volume V but exerting a pressure $2P$?

Solution. If E is the translational K.E. per unit volume, then

$$P = \frac{2}{3} E \quad \text{or} \quad E = \frac{3P}{2}$$

Total translational K.E. of volume V is

$$EV = \frac{3PV}{2} = 500 \text{ J}$$

When pressure becomes $2P$, total translational K.E.
 $= 2 \times 500 = 1000 \text{ J}$.

Problem 28. Write the equation of state for 16 g of O_2 .

Solution. Number of moles in 32 g of $O_2 = 1$

$$\therefore \text{Number of moles in 16 g of } O_2 = \frac{1}{32} \times 16 = \frac{1}{2}$$

$$\text{As } PV = nRT \text{ and } n = 1/2, \text{ so } PV = \frac{1}{2} RT.$$

Problem 29. When a gas filled in a closed vessel is heated through 1°C , its pressure increases by 0.4%. What is the initial temperature of the gas?

$$\text{Solution. } P' = P + \frac{0.4}{100} P, \quad T' = T + 1$$

$$\text{By Gay Lussac's law, } \frac{P}{T} = \frac{\left(P + \frac{0.4}{100} P\right)}{T + 1}$$

On solving, $T = 250 \text{ K}$.

Problem 30. A gas in a closed vessel is at the pressure P_0 . If the masses of all the molecules be made half and their speeds be made double, then find the resultant pressure.

$$\text{Solution. } P_0 = \frac{1}{3} \frac{mN}{V} v^2$$

$$\therefore P' = \frac{1}{3} \frac{(m/2)}{V} (2v)^2 = \frac{2}{3} \frac{mN}{V} v^2 = 2P_0.$$

Problem 31. What is evaporation?

Solution. All the molecules do not have the same velocity. The molecules which possess large velocities are able to overcome the molecular attraction and escape the liquid surface, which is known as evaporation.

Short Answer Conceptual Problems

Problem 1. A gas is filled in a cylinder fitted with a piston at a constant temperature. Explain on the basis of kinetic theory:

(i) The pressure of the gas increases by raising the temperature.

Problem 32. Why does evaporation cause cooling?

[Himachal 05C]

Solution. The evaporation of a liquid from its surface occurs because some molecules acquire velocities sufficient enough to escape from the attractive force at the surface. Because escaping molecules have higher kinetic energy, hence the average kinetic energy of the molecules left behind decreases. As average kinetic energy is directly related with temperature, hence evaporation causes cooling.

Problem 33. Cooking gas containers are kept in a lorry moving with uniform speed. What will be the effect on temperature of the gas molecules? [AIEEE 02]

Solution. As the lorry is moving with a uniform speed, there will be no change in the translational motion or K.E. of the gas molecules. Hence the temperature of the gas will remain same.

Problem 34. Should the specific heat of monoatomic gas be less than, equal to or greater than that of a diatomic gas at room temperature? Justify your answer.

Solution. The specific heat of a gas at constant volume is equal to $\frac{f}{2} R$.

$$\text{For monoatomic gases, } f = 3, \text{ so } C_V = \frac{3}{2} R.$$

$$\text{For diatomic gases, } f = 5, \text{ so } C_V = \frac{5}{2} R.$$

Hence the specific heat for monoatomic gas is less than that for a diatomic gas.

Problem 35. What is Debye temperature?

Solution. The temperature above which the molar specific heat of a solid becomes equal to $6 \text{ cal mol}^{-1} \text{ K}^{-1}$ is called Debye temperature.

Problem 36. Equal masses of helium and oxygen gases are given equal quantities of heat. Which gas will undergo a greater temperature rise?

Solution. Helium is a monoatomic gas, while oxygen is diatomic. Therefore the heat given to helium will be totally used up in increasing the translational kinetic energy of its molecules; whereas the heat given to oxygen will be used up in increasing the translational kinetic energy of its molecules and also in increasing the kinetic energy of rotation and vibration. Hence, there will be a greater rise in the temperature of helium.

(ii) On pulling the piston out, the pressure of the gas decreases.

Solution. (i) On raising the temperature, the average speed of the gas molecules increases. As a result, the molecules collide more frequently with the walls of the

vessel and also greater momentum is transferred to the wall in each collision. Both of these factors increase the pressure of the gas.

(ii) When the piston is pulled out, the volume of the gas increases. The molecules have to traverse a large distance to collide with the walls of the cylinder. So a lesser number of molecules collides with the walls per second. Moreover, the collisions now occur on a larger area of the walls. Both of these factors decrease the pressure of the gas.

Problem 2. There are N molecules of a gas in a container. If the number of molecules is increased to $2N$, what will be (i) pressure of the gas, (ii) total energy of the gas and (iii) r.m.s. speed of the gas ?

$$\text{Solution. } P = \frac{1}{3} mn \overline{v^2} = \frac{1}{3} \frac{mN}{V} \overline{v^2} \quad \left[n = \frac{N}{V} \right]$$

(i) As $P \propto N$, so the pressure of the gas is *doubled* when the number of molecules is increased from N to $2N$.

$$(ii) \text{ Average K.E. per molecule, } \frac{1}{2} m \overline{v^2} = \frac{3}{2} k_B T.$$

$$\text{Total energy of } N \text{ molecules} = \frac{1}{2} mN \overline{v^2} = \frac{3}{2} k_B NT.$$

When the number of molecules is increased from N to $2N$, total energy of the gas is **doubled**, though the average K.E. per molecule remains same.

(iii) The r.m.s. speed remains same because it depends only upon temperature.

Problem 3. Although the velocity of air molecules is nearly 0.5 km s^{-1} , yet the smell of scent spreads at a much slower rate. Why ?

Solution. The air molecules travel along a zig-zag path due to frequent collisions. As a result, their displacement per unit time is very small. Hence the smell of scent spreads very slowly.

Problem 4. When do the real gases obey more correctly the gas equation : $PV = nRT$?

Solution. An ideal gas is one whose molecules have zero volume and no mutual force between them. At low pressure, the volume of a gas is large and so the volume occupied by the molecules is negligible in comparison to the volume of the gas. At high temperature, the molecules have large velocities and so the intermolecular force has no influence on their motion. Hence at low pressure and high temperature, the behaviour of real gases approach the ideal gas behaviour.

Problem 5. Explain qualitatively how the extent of Brownian motion is affected by the

- size of the Brownian particle,
- density of the medium,
- temperature of the medium,
- viscosity of the medium ?

[NCERT]

Solution. The effect of the various factors on the Brownian motion is as follows :

Factors	Effects
(a) Decrease in the size of the Brownian particle.	Increase of Brownian motion.
(b) Decrease in the density of the medium.	Increase of Brownian motion.
(c) Increase in temperature of the medium.	Increase of Brownian motion.
(d) Increase in viscosity of the medium.	Decrease of Brownian motion.

Problem 6. For Brownian motion of particles of suspensions in liquids, what should be the typical size of suspended particles ? Why should not the size of the particles be too small (say of atomic dimensions 10^{-10} m) or too large (say of the order of 1 m) ? [NCERT]

Solution. The typical size of the suspended particles should be 10^{-6} m . If the size of the suspended particles is too small ($\approx 10^{-10} \text{ m}$), the net momentum imparted to the suspended particle due to bombardment of neighbouring fluid particles would be zero and hence no Brownian motion is possible. If the size of the suspended particle is too large ($\approx 1 \text{ m}$), the particle will not move due to its large inertia, even when an unbalanced force is acting on it.

Problem 7. What is the simplest evidence in nature that you can think of to suggest that atoms are not point particles ? [NCERT]

Solution. Brownian motion is the simplest evidence in nature to suggest that atoms are not point particles but have finite size. The particles suspended in a fluid move in the direction of the unbalanced force due to the unequal bombardment caused by the atoms or molecules of the fluid in which they are suspended. This shows that the atoms have finite size.

Problem 8. In an experiment, the specific heats of some inert gases (at ordinary temperatures) are measured to be as follows :

Gas	Atomic mass (u)	Specific heat ($\text{cal g}^{-1} \text{K}^{-1}$)
Helium	4.00	0.748
Neon	20.18	0.147
Argon	39.94	0.0760
Krypton	83.80	0.0358
Xenon	131.3	0.0226

Try to discover a regularity in the data and explain it on the basis of kinetic energy. [NCERT]

Solution. Molar specific heat
= Atomic mass \times specific heat

Gas	Molar specific heat
Helium	$4.00 \times 0.748 = 2.992 \text{ cal mol}^{-1} \text{ K}^{-1}$
Neon	$20.18 \times 0.147 = 2.966 \text{ cal mol}^{-1} \text{ K}^{-1}$
Argon	$39.94 \times 0.0760 = 3.035 \text{ cal mol}^{-1} \text{ K}^{-1}$
Krypton	$83.80 \times 0.0358 = 3.000 \text{ cal mol}^{-1} \text{ K}^{-1}$
Xenon	$131.3 \times 0.0226 = 2.967 \text{ cal mol}^{-1} \text{ K}^{-1}$

Thus the molar specific heat of each gas is nearly $3 \text{ cal mol}^{-1} \text{ K}^{-1}$. It should be so on the basis of kinetic theory of gases according to which for a monoatomic gas,

$$C_V = \frac{3}{2} R = \frac{3}{2} \times 2 \text{ cal mol}^{-1} \text{ K}^{-1} \\ = 3 \text{ cal mol}^{-1} \text{ K}^{-1}.$$

Problem 9. What is meant by molar specific heat of a gas? The molar specific heat of hydrogen H_2 is about $\frac{5}{2} R$ in the temperature range of about 250 K to 750 K. At lower temperatures, molar specific heat of hydrogen decreases to the value typical of monoatomic gases: $\frac{3}{2} R$. At higher temperatures, it tends to the value $\frac{7}{2} R$. What do you think is happening? [NCERT; Delhi 03]

Solution. The molar specific heat of a gas is defined as the amount of heat required to raise the temperature of 1 mole of a gas through 1°C .

The molar specific heat of a gas at constant volume is given by $C_V = \frac{f}{2} R$, where f is degrees of freedom of the gas. In the range of about 250 to 750 K, a diatomic gas such as H_2 gas possesses 5 degrees of freedom (3 corresponding to translational and 2 corresponding to rotational modes of motion of the gas). Hence

$$C_V = \frac{5}{2} R \quad (\text{between } 250 \text{ to } 750 \text{ K})$$

But at lower temperatures, the rotational motion is not excited and hydrogen gas molecule possesses only 3 degrees of freedom corresponding to translational motion.

HOTS

Problem 1. Two rigid boxes containing different ideal gases are placed on a table. Box A contains one mole of nitrogen at temperature T_0 while box B contains one mole of helium at temperature $(7/3) T_0$. The boxes are then put into thermal contact with each other and heat flows between them until the gases reach a common final temperature. Ignore the heat capacity of the boxes. Find the final temperature T_f of the gases in terms of T_0 . [AIEEE 06]

Hence at lower temperatures,

$$C_V = \frac{3}{2} R$$

At higher temperatures, hydrogen gas molecule has 2 additional degrees of freedom corresponding to vibrational mode of the motion, so that total degrees of freedom become $f = 5 + 2 = 7$.

Hence at higher temperatures,

$$C_V = \frac{7}{2} R.$$

Problem 10. (a) When a molecule (or an elastic ball) hits a (massive) wall, it rebounds with the same speed. When a ball hits a massive bat held firmly, the same thing happens. However, when the bat is moving towards the ball, the ball rebounds with a different speed. Does the ball move faster or slower?

(b) When gas in a cylinder is compressed by pushing in a piston, its temperature rises. Guess at an explanation of this in terms of kinetic theory using (a) above.

(c) What happens when a compressed gas pushes a piston out and expands? What would you observe?

(d) Sachin Tendulkar uses a heavy cricket bat while playing. Does it help him in any way? [NCERT]

Solution. (a) Let the speed of the ball be u relative to the wicket behind the bat. If the bat is moving towards the ball with a speed V relative to the wicket, then the relative speed of the ball to bat is $V + u$ towards the bat. When the ball rebounds (after hitting the massive bat) its speed, relative to bat, $V + (V + u) = 2V + u$, moving away from the wicket. So the ball speeds up after the collision with the bat. For a molecule this would imply an increase in temperature.

(b) When a gas in cylinder is compressed by pushing in a piston, the speed of the molecules or their kinetic energy increases. This increases the temperature of the gas.

(c) When a compressed gas pushes a piston out, the speed of the molecules or their kinetic energy decreases. This decreases the temperature of the gas.

(d) When the ball is hit with a heavy bat, the rebound speed of the ball further increases. It helps to score better.

Problems on Higher Order Thinking Skills

Solution. Nitrogen is a diatomic gas while helium is a monoatomic gas. There is no net change in internal energy of the system.

$$\Delta U = 0$$

$$\text{or } 1 \times \frac{5}{2} R (T_0 - T_f) + 1 \times \frac{3}{2} R \left(\frac{7}{3} T_0 - T_f \right) = 0$$

$$\text{or } 12T_0 - 8T_f = 0 \quad \text{or } T_f = \frac{3}{2} T_0$$

Problem 2. A vessel is filled with a mixture of two different gases. However, the number of molecules per unit volume of the two gases in the mixture are the same. (i) Will the mean K.E. per molecule of both the gases be equal? (ii) Will the root mean square velocities of the molecules be equal. (iii) Will the pressure be equal? Give reasons.

Solution. (i) Yes. Mean K.E. per molecule,

$$\frac{1}{2} m \overline{v^2} = \frac{3}{2} k_B T$$

As the temperature of both the gases in the mixture is the same, so mean K.E. per molecule of both the gases will be equal.

(ii) No. As $v_{rms} = \sqrt{\frac{3 k_B T}{m}}$

Due to different masses of the molecules, the r.m.s. velocities for the two gases will not be equal.

(iii) No. As $P = \frac{1}{3} mn \overline{v^2}$

Due to different masses of the molecules, the pressures exerted by the two gases will not be equal.

Problem 3. Two vessels of the same size are at the same temperature. One of them contains 1 g of H₂ gas, and the other contains 1 g of N₂ gas. (i) Which of the vessels contains more molecules? (ii) Which of the vessels is under greater pressure and why? (iii) In which vessel is the average molecular speed greater? How many times greater?

Solution. (i) According to Avogadro's hypothesis,

Number of molecules in 2 g of H₂ = N_A

∴ Number of molecules in 1 g of H₂ = N_A / 2

Number of molecules in 28 g of N₂ = N_A

∴ Number of molecules in 1 g of N₂ = N_A / 28

$$\frac{\text{Number of molecules of H}_2}{\text{Number of molecules of N}_2} = \frac{N_A / 2}{N_A / 28} = 14$$

So hydrogen containing vessel contains more molecules.

(ii) The average K.E. per molecule at a given temperature is independent of the molecular mass.

$$P = \frac{2}{3} \times n \times \overline{\text{K.E.}} = \frac{2}{3} \times \frac{N}{V} \times \overline{\text{K.E.}}$$

$$\frac{\text{Pressure exerted by H}_2}{\text{Pressure exerted by N}_2} = \frac{\text{No. of molecules of H}_2}{\text{No. of molecules of N}_2} = \frac{N_A / 2}{N_A / 28} = 14$$

∴ Pressure exerted by hydrogen is 14 times the pressure exerted by N₂.

$$(iii) \frac{(v_{rms})_{H_2}}{(v_{rms})_{N_2}} = \sqrt{\frac{M_{N_2}}{M_{H_2}}} = \sqrt{\frac{28}{2}} = \sqrt{14} = 3.74$$

The r.m.s. speed of H₂ is 3.74 times the r.m.s. speed of N₂.

Problem 4. Two thermally insulated vessels 1 and 2 are filled with air at temperatures (T₁, T₂), volumes (V₁, V₂) and pressures (P₁, P₂) respectively. If the valve joining the two vessels is opened, what will be the temperature inside the vessel at equilibrium? [AIIEE 04]

Solution. As PV = nRT ∴ $n = \frac{PV}{RT}$

For first vessel, $n_1 = \frac{P_1 V_1}{RT_1}$

For second vessel, $n_2 = \frac{P_2 V_2}{RT_2}$

For the combined vessel, $n = \frac{P(V_1 + V_2)}{RT}$

But $n = n_1 + n_2$

$$\therefore \frac{P(V_1 + V_2)}{RT} = \frac{P_1 V_1}{RT_1} + \frac{P_2 V_2}{RT_2}$$

or

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

Using Boyle's law,

$$P(V_1 + V_2) = P_1 V_1 + P_2 V_2$$

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

Problem 5. An insulated container containing monoatomic gas of molar mass m is moving with a velocity v₀. If the container is suddenly stopped, find the change in temperature. [IIT 03]

Solution. Suppose the container has n moles of the monoatomic gas. Then the loss in kinetic energy of the gas

$$\Delta E = \frac{1}{2} (mn) v_0^2$$

If the temperature of the gas changes by ΔT, then heat gained by the gas,

$$\Delta Q = \frac{3}{2} nR \Delta T$$

Now $\Delta Q = \Delta E$

or $\frac{3}{2} nR \Delta T = \frac{1}{2} (mn) v_0^2$ or $\Delta T = \frac{m v_0^2}{3R}$

Problem 6. A cubical box of side 1 metre contains helium gas (atomic weight 4) at a pressure of 100 N / m². During an observation time of 1 second, an atom travelling

with the root-mean-square speed parallel to one of the edges of the cube, was found to make 500 hits with a particular wall, without any collision with other atoms.

Take $R = \frac{25}{3} \text{ J/mol-K}$ and $k = 1.38 \times 10^{-23} \text{ J/K}$.

- (a) Evaluate the temperature of the gas.
 (b) Evaluate the average kinetic energy per atom.
 (c) Evaluate the total mass of helium gas in the box.

[IIT Mains 02]

Solution. (a) Time interval between two successive collisions,

$$t = \frac{2l}{v_{rms}}$$

or $\frac{1}{500} = \frac{2 \times 1}{v_{rms}} \quad \left[\because t = \frac{1}{500} \text{ s}, l = 1 \text{ m} \right]$

$$\therefore v_{rms} = 1000 \text{ ms}^{-1}.$$

$$\text{But } v_{rms} = \sqrt{\frac{3RT}{M}}$$

$$\therefore 1000 = \sqrt{\frac{3 \times (25/3) T}{4}}$$

On solving, we get $T = 160 \text{ K}$.

(b) The average kinetic energy per atom of the monoatomic gas,

$$\begin{aligned} \overline{\text{K.E.}} &= \frac{3}{2} k_B T = \frac{3}{2} \times 1.38 \times 10^{-23} \times 160 \\ &= 3.312 \times 10^{-21} \text{ J.} \end{aligned}$$

(c) From kinetic gas equation,

$$P = \frac{1}{3} \frac{m}{V} v_{rms}^2$$

where m is the mass of the gas.

$$\therefore 100 = \frac{1}{3} \times \frac{m}{1} \times (1000)^2 \text{ or } m = 3 \times 10^{-4} \text{ kg.}$$

Problem 7. The temperature of an ideal gas is increased from 120 K to 480 K. If at 120 K, the root mean square velocity of the gas molecules is V , then what will be the root mean square velocity at 480 K? [IIT 96]

Solution. Here $T_1 = 120 \text{ K}$, $T_2 = 480 \text{ K}$, $C_1 = V$, $C_2 = ?$

$$\text{As } C \propto \sqrt{T}$$

$$\therefore \frac{C_2}{C_1} = \sqrt{\frac{T_2}{T_1}} \text{ or } \frac{C_2}{V} = \sqrt{\frac{480}{120}} = 2$$

$$\text{or } C_2 = 2V.$$

Problem 8. You have the following group of particles, n_i represents the number of molecules with speed v_i :

n_i	2	4	8	6	3
$v_i \text{ (ms}^{-1}\text{)}$	1.0	2.0	3.0	4.0	5.0

Calculate (i) the average speed (ii) the r.m.s. speed and (iii) the most probable speed. [IIT]

Solution. (i)

$$\begin{aligned} v_{av} &= \frac{n_1 v_1 + n_2 v_2 + n_3 v_3 + n_4 v_4 + n_5 v_5}{n_1 + n_2 + n_3 + n_4 + n_5} \\ &= \frac{2 \times 1 + 4 \times 2 + 8 \times 3 + 6 \times 4 + 3 \times 5}{2 + 4 + 8 + 6 + 3} \\ &= 3.17 \text{ ms}^{-1}. \end{aligned}$$

$$\begin{aligned} \text{(ii) } v_{rms} &= \sqrt{\frac{n_1 v_1^2 + n_2 v_2^2 + n_3 v_3^2 + n_4 v_4^2 + n_5 v_5^2}{n_1 + n_2 + n_3 + n_4 + n_5}} \\ &= \sqrt{\frac{2 \times 1^2 + 4 \times 2^2 + 8 \times 3^2 + 6 \times 4^2 + 3 \times 5^2}{2 + 4 + 8 + 6 + 3}} \\ &= \sqrt{\frac{261}{23}} = 3.37 \text{ ms}^{-1}. \end{aligned}$$

(iii) Most probable speed = Speed possessed by maximum number of particles
 $= 3.0 \text{ ms}^{-1}$.

Problem 9. In a certain region of space there are only 5 molecules per cm^3 on an average. The temperature there is 3 K. What is the pressure of this gas? ($k_B = 1.38 \times 10^{-23} \text{ J molecule}^{-1} \text{ K}^{-1}$). [Roorkee 88]

Solution. Let μ be the number of molecules in the gas. Then

$$PV = \mu k_B T \text{ or } P = \frac{\mu k_B T}{V}$$

$$\text{But } \frac{\mu}{V} = 5 \text{ cm}^{-3} = 5 \times 10^{-6} \text{ m}^{-3}$$

$$\therefore P = 5 \times 10^{-6} \times 1.38 \times 10^{-23} \times 3 = 20.7 \times 10^{-17} \text{ Nm}^{-2}.$$

Problem 10. Two glass bulbs of equal volumes are connected by a narrow tube and are filled with a gas at 0°C and a pressure of 76 cm of mercury. One of the bulbs is then placed in melting ice and the other in a water-bath maintained at 62°C . What is the new value of the pressure inside the bulbs? The volume of the connecting tube is negligible. [IIT 85]

Solution. According to the gas equation, $PV = nRT$, so long as the mass of a system remains constant, the sum of the terms pV/T for different parts of the system remains unchanged.

$$\Sigma \frac{PV}{T} = \text{constant}$$

Let V be the volume of each bulb. Initially for the two bulbs, we have

$$\Sigma \frac{PV}{T} = \frac{76V}{273} + \frac{76V}{273} = \frac{2 \times 76 \times V}{273} \quad \dots(i)$$

When one bulb is placed at melting ice and another maintained at 62°C we have

$$\Sigma \frac{PV}{T} = \frac{P \times V}{273} + \frac{P \times V}{335} \quad \dots(ii)$$

From (i) and (ii), we get

$$\frac{2 \times 76 \times V}{273} = \frac{PV}{273} + \frac{PV}{335}$$

or
$$P = \frac{2 \times 76}{273} \times \frac{273 \times 335}{608} = 83.75 \text{ cm of Hg.}$$

Problem 11. A vessel of volume $2 \times 10^{-2} \text{ m}^3$ contains a mixture of hydrogen and helium at 47°C temperature and $4.15 \times 10^5 \text{ Nm}^{-2}$ pressure. The mass of the mixture is 10^{-2} kg . Calculate the masses of hydrogen and helium in the given mixture. [Roorkee 94]

Solution. Mass of mixture = $10^{-2} \text{ kg} = 10 \text{ g}$

Let mass of hydrogen in the mixture = $m \text{ g}$

Then mass of helium in the mixture = $(10 - m) \text{ g}$

Number of moles of hydrogen, $n_1 = \frac{m}{2}$

Number of moles of helium, $n_2 = \frac{(10 - m)}{4}$

Also, $V = 2 \times 10^{-2} \text{ m}^3$, $T = 47 + 273 = 320 \text{ K}$,

$$R = 8.3 \text{ J mole}^{-1} \text{ K}^{-1}$$

Let P_1 and P_2 be the pressures exerted by hydrogen and helium respectively.

Then $P_1 + P_2 = 4.15 \times 10^5 \text{ Nm}^{-2}$

Now $P_1 V = n_1 RT$ and $P_2 V = n_2 RT$

$\therefore (P_1 + P_2) V = (n_1 + n_2) RT$

or $(4.15 \times 10^5) \times 2 \times 10^{-2} = \left(\frac{m}{2} + \frac{10 - m}{4}\right) \times 8.3 \times 320$

or $83 \times 10^3 = 2656 \left[\frac{2m + 10 - m}{4}\right] = 664(m + 10)$

$\therefore (m + 10) = 12.5$ or $m = 2.5 \text{ g}$

Mass of hydrogen = $2.5 \text{ g} = 2.5 \times 10^{-3} \text{ kg}$.

Mass of helium = $10 - 2.5 = 7.5 \text{ g} = 7.5 \times 10^{-3} \text{ kg}$.

Problem 12. A thin tube, sealed at both ends, is 100 cm long. It lies horizontally, the middle 10 cm containing mercury and the two equal ends containing air at standard atmospheric pressure. If the tube is now turned to a vertical position, by what amount will the mercury be displaced ?

[Roorkee 89, IIT]

Solution. When the tube is horizontal, the length of the air column on the either side of the mercury thread will be 45 cm [Fig. 13.20(a)]. Initially for each half, we have

$$P = 76 \text{ cm of mercury, } V = 45 \text{ cm}$$

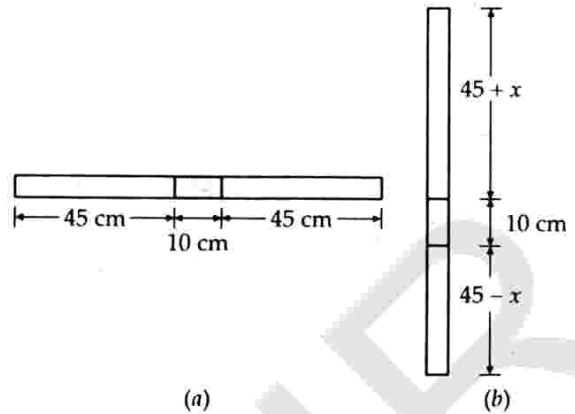


Fig. 13.20

When the tube is held vertically [Fig. 13.20(b)], suppose that mercury thread moves through a distance x . Let P_1 and P_2 be pressure of the air in the upper half and lower half respectively. The volume of air in the two halves will be

$$V_1 = 45 + x \quad \text{and} \quad V_2 = 45 - x$$

Using Boyle's law for upper half,

$$PV = P_1 V_1 \quad \text{or} \quad 76 \times 45 = P_1 \times (45 + x)$$

and for lower half,

$$PV = P_2 V_2 \quad \text{or} \quad 76 \times 45 = P_2 \times (45 - x)$$

Now $P_2 = P_1 + 10 \text{ cm of Hg}$

or
$$\frac{76 \times 45}{45 - x} = \frac{76 \times 45}{45 + x} + 10$$

or
$$76 \times 45 \left[\frac{1}{45 - x} - \frac{1}{45 + x} \right] = 10$$

or
$$\frac{76 \times 45 \times 2x}{45^2 - x^2} = 10 \quad \text{or} \quad \frac{6840x}{2025 - x^2} = 10$$

$$x^2 + 684x - 2025 = 0$$

$$\therefore x = \frac{-684 \pm \sqrt{(684)^2 + 8100}}{2} = \frac{-684 \pm 689.9}{2}$$

$$x = -686.95 \text{ cm or } 2.95 \text{ cm}$$

As x cannot be negative, so $x = 2.95 \text{ cm}$.

Problem 13. A thin tube of uniform cross-section is sealed at both ends. When it lies horizontally, the middle 5 cm length contains mercury and the two equal ends contain air

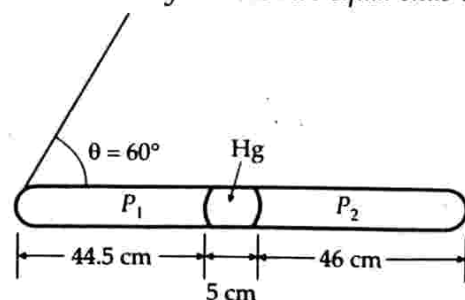


Fig. 13.21

at the same pressure P . When the tube is held at an angle of 60° with the vertical, then the lengths of the air columns above and below the mercury column are 46 cm and 44.5 cm respectively. Calculate the pressure P in cm of mercury. The temperature of the system is kept at 30°C . [IIT 86]

Solution. Let A be the area of cross-section of the tube. When the tube is horizontal, the 5 cm column of Hg is in the middle, so length of air column on either side at pressure P

$$= \frac{46 + 44.5}{2} = 45.25 \text{ cm}$$

When the tube is held at 60° with the vertical, the lengths of air columns at the bottom and the top are 44.5 cm and 46 cm respectively. If P_1 and P_2 are their pressures, then

$$P_1 - P_2 = 5 \cos 60^\circ = 5 \times \frac{1}{2} = \frac{5}{2} \text{ cm of Hg}$$

Using Boyle's law for constant temperature,

$$PV = P_1V_1 = P_2V_2$$

$$P \times A \times 45.25 = P_1 \times A \times 44.5 = P_2 \times A \times 46$$

$$\frac{P \times 45.25}{44.5} = \frac{P \times 45.25}{46} = \frac{5}{2}$$

or
$$P = \frac{5 \times 44.5 \times 46}{2 \times 45.25 \times 15} = 75.4 \text{ cm.}$$

Problem 14. Calculate the root mean square speed of smoke particles each of mass 5×10^{-17} kg in their Brownian motion in air at N.T.P.

Given $k_B = 1.38 \times 10^{-23}$ J molecule $^{-1}$ K $^{-1}$. [Roorkee 82]

Solution. According to kinetic theory, average K.E. of a gas molecule,

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

$$\therefore v_{rms} = \sqrt{\frac{3k_B T}{m}} = \sqrt{\frac{3 \times 1.38 \times 10^{-23} \times 273}{5 \times 10^{-17}}}$$

$$= 1.5 \times 10^{-2} \text{ ms}^{-1}.$$

Problem 15. N molecules each of mass m of gas A and $2N$ molecules each of mass $2m$ of gas B are contained in the same vessel which is maintained at a temperature T . If the mean square velocity of the molecules of B type is denoted by v^2 and the mean square of the x component of the velocity of A is denoted by ω^2 , then what is the value of ω^2 / v^2 ?

[PMT 1990]

Solution. The mean square velocity of the gas molecules is given by

$$C^2 = 3kT / m$$

For gas A : $C_A^2 = 3kT / m$ and

For gas B : $C_B^2 = 3kT / 2m = v^2$... (i)

The molecule A has equal probability of motion in all directions, therefore

$$C_x^2 = C_y^2 = C_z^2 = \omega^2 \text{ (given)}$$

$$\therefore C_A^2 = C_x^2 + C_y^2 + C_z^2 = 3C_x^2 = 3\omega^2$$

$$\text{or } \omega^2 = \frac{C_A^2}{3} = \frac{1}{3} \left(\frac{3kT}{m} \right) = \frac{kT}{m} \text{ ... (ii)}$$

Dividing (ii) by (i), we get :
$$\frac{\omega^2}{v^2} = \frac{kT/m}{3kT/2m} = \frac{2}{3}$$

Guidelines to NCERT Exercises

13.1. Estimate the fraction of the molecular volume to the actual volume occupied by oxygen gas at STP. Take the radius of an oxygen molecule to be roughly 3 Å.

Ans. Radius of oxygen molecule
 $= 3 \text{ \AA} = 3 \times 10^{-10} \text{ m}$

Volume of an oxygen molecule
 $= \frac{4}{3} \pi (3 \times 10^{-10})^3 \text{ m}^3$

Number of molecules in 1 mole of oxygen
 $= 6 \times 10^{23}$

Volume of 6×10^{23} molecules
 $= \frac{4}{3} \pi (3 \times 10^{-10})^3 \times 6 \times 10^{23}$
 $= 0.78 \times 10^{-5} \text{ m}^3$

Actual volume occupied by 1 mole of oxygen gas at STP

$$= 22.4 \text{ litre} = 22.4 \times 10^{-3} \text{ m}^3$$

Hence fraction of the molecular volume to the actual volume

$$= \frac{0.78 \times 10^{-5}}{22.4 \times 10^{-3}}$$

$$\approx 3 \times 10^{-3}.$$

13.2. Molar volume is the volume occupied by 1 mole of any (ideal) gas at standard temperature and pressure (0°C , 1 atmospheric pressure). Show that it is 22.4 litres.

Ans. $T = 273 \text{ K}$, $n = 1 \text{ mol}$

$$P = 1 \text{ atm} = 1.013 \times 10^5 \text{ Pa}$$

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

As $PV = nRT$
 $\therefore V = \frac{nRT}{P} = \frac{1 \times 8.31 \times 273}{1.013 \times 10^5}$
 $= 22.4 \times 10^{-3} \text{ m}^3$
 $= 22.4 \text{ litres.}$

13.3. Fig. 13.22 shows plot of PV/T versus P for $1.00 \times 10^{-3} \text{ kg}$ of oxygen gas at two different temperatures.

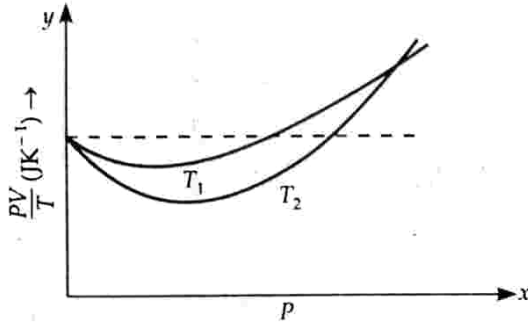


Fig. 13.22

- (a) What does the dotted plot signify?
 (b) Which is true: $T_1 > T_2$ or $T_1 < T_2$? [Delhi 12]
 (c) What is the value of PV/T where the curves meet on the y-axis?
 (d) If we obtained similar plots for $1.00 \times 10^{-3} \text{ kg}$ of hydrogen, would we get the same value of PV/T at the point where the curves meet on the y-axis? If not, what mass of hydrogen yields the same value of PV/T (for low pressure high temperature region of the plot)?

(Molecular mass of $H_2 = 2.02 \text{ u}$ of $O_2 = 32.0 \text{ u}$, $R = 8.31 \text{ J mol}^{-1} \text{ K}^{-1}$).

Ans. (a) As the dotted line is parallel to P -axis, it shows that PV/T remains same when the pressure is increased. It thus indicates the ideal behaviour of the gas.

(b) The curve at temperature T_1 is more close to the dotted line than the curve at temperature T_2 . Since the behaviour of a real gas approaches the ideal gas behaviour at high temperature, so $T_1 > T_2$.

(c) Number of moles in $1.00 \times 10^{-3} \text{ kg}$ or 1 g of oxygen,

$$n = \frac{\text{Mass of oxygen in grams}}{\text{Molecular mass}}$$

$$= \frac{1}{32} \text{ mole}$$

As $PV = nRT$
 $\therefore \frac{PV}{T} = nR = \frac{1}{32} \times 8.31$
 $= 0.26 \text{ JK}^{-1}$.

(d) No. This is because PV/T depends upon the volume of the gas and volumes of equal masses of different gases are different.

If we wish to have the curve of hydrogen gas to start from the same point, the PV/T of hydrogen should be equal to PV/T of oxygen.

From part (c),

$$\frac{PV}{T} = nR = 0.26$$

$$\therefore n = \frac{0.26}{R} = \frac{0.26}{8.31} = \frac{1}{32} \text{ mole}$$

Mass of 1 mole of $H_2 = 2.02 \text{ g}$

$$\therefore \text{Mass of } 1/32 \text{ mole of } H_2 = 2.02 \times \frac{1}{32} = 0.063 \text{ g}$$

$$= 6.3 \times 10^{-5} \text{ kg}$$

13.4. An oxygen cylinder of volume 30 litres has an initial gauge pressure of 15 atm and a temperature of 27°C . After some oxygen is withdrawn from the cylinder, the gauge pressure drops to 11 atm and its temperature drops to 17°C . Estimate the mass of oxygen taken out of the cylinder, $R = 8.3 \text{ J mol}^{-1} \text{ K}^{-1}$, molecule weight of oxygen = 32

Ans. Initial volume,

$$V_1 = 30 \text{ litres} = 30 \times 10^{-3} \text{ m}^3$$

Initial pressure,

$$P_1 = 15 \text{ atm} = 15 \times 1.013 \times 10^5 \text{ Nm}^{-2}$$

Initial temperature,

$$T_1 = 27 + 273 = 300 \text{ K}$$

Initial number of moles,

$$n_1 = \frac{P_1 V_1}{RT_1} = \frac{15 \times 1.013 \times 10^5 \times 30 \times 10^{-3}}{8.31 \times 300} = 18.3$$

Final pressure,

$$P_2 = 11 \text{ atm} = 11 \times 1.013 \times 10^5 \text{ Nm}^{-2}$$

Final volume,

$$V_2 = 30 \text{ litres} = 30 \times 10^{-3} \text{ m}^3$$

Final temperature,

$$T_2 = 17 + 273 = 290 \text{ K}$$

Final number of moles,

$$n_2 = \frac{P_2 V_2}{RT_2} = \frac{11 \times 1.013 \times 10^5 \times 30 \times 10^{-3}}{8.31 \times 290} = 13.8$$

Number of moles of oxygen taken out

$$= 18.3 - 13.9 = 4.4$$

Mass of gas taken out of cylinder

$$= 4.4 \times 32 \text{ g} = 140.8 \text{ g} = 0.141 \text{ kg.}$$

13.5. An air bubble of volume 1.0 cm^3 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 ?

Given $1 \text{ atm} = 1.01 \times 10^5 \text{ Pa}$.

Ans. Temperature at 40 m depth,

$$T_1 = 12 + 273 = 285 \text{ K}$$

Volume of the air bubble at 40 m depth,

$$V_1 = 1.0 \text{ cm}^3 = 1.0 \times 10^{-6} \text{ m}^3$$

Pressure at 40 m depth, $P_1 = 1 \text{ atm} + h\rho g$

$$= 1.01 \times 10^5 + 40 \times 10^3 \times 9.8 = 4.93 \times 10^5 \text{ Pa}$$

Temperature at the surface of water,

$$T_2 = 35 + 273 = 308 \text{ K}$$

Pressure at the surface of the lake,

$$P_2 = 1 \text{ atm} = 1.01 \times 10^5 \text{ Pa}$$

Let V_2 be volume of air bubble at the surface of the lake.

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

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

$$= \frac{4.93 \times 10^5 \times 1.0 \times 10^{-6} \times 308}{285 \times 1.01 \times 10^5}$$

$$= 5.275 \times 10^{-6} \text{ m}^3.$$

13.6. Estimate the total number of molecules inclusive of oxygen, nitrogen, water vapour and other constituents in a room of capacity 25.0 m^3 at a temperature of 27°C and 1 atmospheric pressure.

$$\text{Given } k_B = 1.38 \times 10^{-23} \text{ JK}^{-1}.$$

Ans. As Boltzmann's constant,

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

$$\text{Now } PV = nRT = nk_B NT$$

\therefore The number of molecules in the room

$$= nN = \frac{PV}{Tk_B}$$

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

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

13.7. Estimate the average energy of a helium atom at (i) room temperature (27°C) (ii) the temperature on the surface of the sun (6000 K) and (iii) the temperature of 10^7 K .

$$\text{Given } k_B = 1.38 \times 10^{-23} \text{ J molecule}^{-1} \text{ K}^{-1}.$$

Ans. Here $k_B = 1.38 \times 10^{-23} \text{ J mol}^{-1} \text{ K}^{-1}$

Average kinetic energy per molecule is given by

$$\bar{E} = \frac{3}{2} k_B T$$

$$(i) \quad T = 27 + 273 = 300 \text{ K}$$

$$\therefore \bar{E} = \frac{3}{2} \times 1.38 \times 10^{-23} \times 300 = 6.21 \times 10^{-21} \text{ J}.$$

$$(ii) \quad T = 6000 \text{ K}$$

$$\bar{E} = \frac{3}{2} \times 1.3 \times 10^{-23} \times 6000 = 1.242 \times 10^{-19} \text{ J}.$$

$$(iii) \quad T = 10^7 \text{ K}$$

$$\begin{aligned} \bar{E} &= \frac{3}{2} k_B T = \frac{3}{2} \times 1.38 \times 10^{-23} \times 10^7 \\ &= 2.07 \times 10^{-16} \text{ J}. \end{aligned}$$

13.8. Three vessels of equal capacity have gases at the same temperature and pressure. The first vessel contains neon (monoatomic), the second contains chlorine (diatomic), and the third contains uranium hexafluoride (polyatomic). (i) Do the vessels contain equal number of respective molecules? (ii) Is the root mean squared speed of molecules same in the three cases? If not, in which case is v_{rms} the largest? [Delhi 2010]

Ans. (i) Yes, the vessels contain equal number of respective molecules. This is in accordance with Avogadro's hypothesis that equal volumes of all gases under similar conditions of temperature and pressure contain equal number of molecules.

$$(ii) \quad v_{rms} = \sqrt{\frac{3RT}{M}} \quad \text{i.e., } v_{rms} \propto \frac{1}{\sqrt{M}}$$

As the molecular masses of the three gases are different, so the r.m.s. speeds of the molecules will be different in the three cases. Moreover as the value of M is smallest for neon, so v_{rms} is largest for neon.

13.9. At what temperature is the root mean square speed of an atom in an argon gas cylinder equal to the r.m.s. speed of a helium gas atom at -20°C ? Atomic mass of argon = 39.9 u and that of helium = 4.0 u .

Ans. Root mean square speed for argon at temperature T ,

$$v = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3RT}{39.9}}$$

Root mean square speed for helium at temperature -20 is

$$v' = \sqrt{\frac{3R \times 253}{4.0}}$$

As $v = v'$, so we have

$$\sqrt{\frac{3RT}{39.9}} = \sqrt{\frac{3R \times 253}{4.0}}$$

$$\frac{T}{39.9} = \frac{253}{4.0} \quad \text{or} \quad T = \frac{253 \times 39.9}{4.0} = 2523.7 \text{ K}.$$

13.10. Estimate the mean free path and collision frequency of a nitrogen molecule in a cylinder containing nitrogen at 2.0 atm and temperature 17°C . Take the radius of a nitrogen molecule to be roughly 1.0 \AA . Compare the collision time with the time the molecule moves freely between two successive collisions (Molecular mass of $\text{N}_2 = 28.0 \text{ u}$).

Ans. Here $T = 273 + 17 = 290 \text{ K}$,

$$d = 2 \times 1.0 \times 10^{-10} \text{ m}$$

$$P = 2.0 \text{ atm} = 2 \times 1.013 \times 10^5 \text{ Pa}$$

$$k_B = 1.37 \times 10^{-23} \text{ JK}^{-1}$$

Mean free path,

$$\bar{\lambda} = \frac{k_B T}{\sqrt{2} \pi d^2 P}$$

$$= \frac{1.37 \times 10^{-23} \times 290}{1.414 \times 3.14 \times (2 \times 10^{-10})^2 \times 2 \times 1.013 \times 10^5}$$

$$\approx 1.1 \times 10^{-7} \text{ m.}$$

$$v_{rms} = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3 \times 8.31 \times 290}{0.028}} \approx 5.1 \times 10^2 \text{ ms}^{-1}.$$

Collision frequency

$$f = \frac{v_{rms}}{\bar{\lambda}} = \frac{5.1 \times 10^2}{1.1 \times 10^{-7}} = 4.6 \times 10^9 \text{ s}^{-1}$$

Time taken for the collision

$$t = \frac{d}{v_{rms}} = \frac{2.0 \times 10^{-10}}{5.1 \times 10^2} \approx 4 \times 10^{-13} \text{ s}$$

Time taken between two successive collisions

$$T = \frac{1}{f} = \frac{1}{4.6 \times 10^9 \text{ s}^{-1}} \approx 2 \times 10^{-10} \text{ s}$$

$$\therefore \frac{T}{t} = \frac{2 \times 10^{-10} \text{ s}}{4 \times 10^{-13} \text{ s}} = 500$$

Obviously, the time taken between two successive collisions is 500 times the time taken for a collision. Hence a molecule in a gas moves essentially free for most of the time.

13.11. A metre long narrow bore held horizontally (and closed at one end) contains a 76 cm long mercury thread, which traps a 15 cm column of air. What happens if the tube is held vertically with the open end at the bottom?

Ans. As shown in Fig. 13.23(a), when the tube is held horizontally, 76 cm of Hg thread traps 15 cm of air and a length of 9 cm is left at the open end.

Area of cross-section of tube = $A \text{ cm}^2$

Pressure of air enclosed, $P_1 = 1 \text{ atm} = 76 \text{ cm of Hg}$

Volume, $V_1 = A \times l = A \times 15 \text{ cm}^3$.

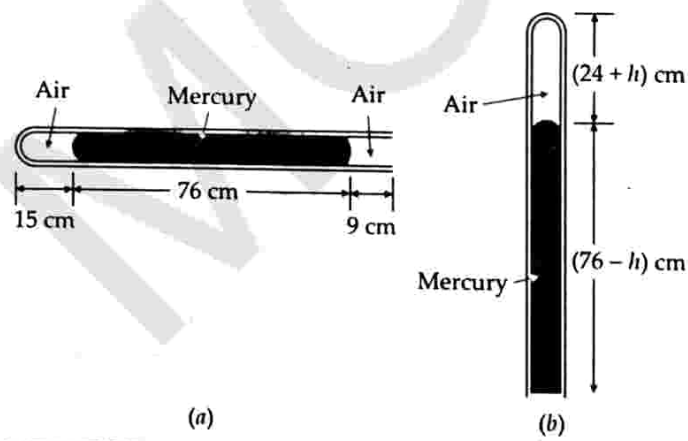


Fig. 13.23

As shown in Fig. 13.23(b), when the tube is held vertically, mercury thread reaches the open end and length of air column becomes $15 + 9 = 24 \text{ cm}$. Let $h \text{ cm}$

of Hg flow out to balance the atmospheric pressure. Length of mercury thread decreases to $(76 - h) \text{ cm}$ and that air column increases to $(24 + h) \text{ cm}$. Let P_2 be the pressure exerted by air column. Then

$$P_2 + (76 - h) = 1 \text{ atm} = 76 \text{ cm of Hg}$$

$$P_2 = 76 - 76 + h = h \text{ cm of Hg}$$

$$V_2 = A \times (24 + h) \text{ cm}^3.$$

If temperature remains constant, then from Boyle's law,

$$P_1 V_1 = P_2 V_2$$

$$76 \times A \times 15 = h \times A \times (24 + h)$$

$$\text{or } h^2 + 24h - 1140 = 0$$

$$\text{or } h = \frac{-24 \pm \sqrt{576 + 4560}}{2}$$

$$= \frac{-24 \pm \sqrt{5126}}{2} = \frac{-24 \pm 71.6}{2}$$

$$= 23.8 \text{ cm or } -47.8 \text{ cm}$$

Since, h cannot be negative (more mercury cannot flow into the tube), $h = 23.8 \text{ cm}$. Therefore, when the tube is held vertically, the mercury thread will **decrease in length by 23.8 cm**.

13.12. From a certain apparatus, the diffusion rate of hydrogen has an average value of $28.7 \text{ cm}^3 \text{ s}^{-1}$. The diffusion of another gas under the same conditions is measured to have an average rate of $7.2 \text{ cm}^3 \text{ s}^{-1}$. Identify the gas.

Ans. According to Graham's law of diffusion,

$$\frac{r_1}{r_2} = \sqrt{\frac{M_2}{M_1}}$$

Here

r_1 = diffusion rate of hydrogen = $28.7 \text{ cm}^3 \text{ s}^{-1}$

r_2 = diffusion rate of unknown gas = $7.2 \text{ cm}^3 \text{ s}^{-1}$

M_1 = molecular mass of hydrogen = 2

M_2 = molecular mass of unknown gas = ?

$$\text{Now } M_2 = \left(\frac{r_1}{r_2}\right)^2 M_1 = \left(\frac{28.7}{7.2}\right)^2 \times 2 = 3178 \approx 32$$

Obviously, the unknown gas is oxygen.

13.13. A gas in equilibrium has uniform density and pressure throughout its volume. This is strictly true only if there are no external influences. A gas column under gravity, for example, does not have uniform density (and pressure). As you might expect, its density decreases with height. The precise dependence is given by the so-called law of atmospheres,

$$n_2 = n_1 \exp[-mg(h_2 - h_1) / k_B T]$$

where n_2, n_1 refer to number density at heights h_2 and h_1 respectively. Use this relation to derive the equation for sedimentation equilibrium of a suspension in a liquid column:

$$n_2 = n_1 \exp[-mg N_A (\rho - \rho')(h_2 - h_1) / \rho RT]$$

where ρ is the density of the suspended particle, and ρ' that of surrounding medium. [N_A is Avogadro's number, and R the universal gas constant]

Ans. According to the law of atmospheres,

$$n_2 = n_1 \exp\left[-\frac{mg(h_2 - h_1)}{k_B T}\right] \quad \dots(i)$$

When the suspension is in sedimentation equilibrium in a liquid column, the weight mg of the suspended particle needs to be replaced by its apparent weight.

Now the apparent weight of the suspended particle

$$\begin{aligned} mg' &= \text{Actual weight} - \text{Upthrust} \\ &= mg - V\rho'g \\ &= mg - \frac{m}{\rho} \cdot \rho'g = mg\left(\frac{\rho - \rho'}{\rho}\right) \end{aligned}$$

Also, $k_B = \frac{R}{N_A}$

Replacing mg by mg' and putting the value of k_B in equation (i), we get

$$n_2 = n_1 \exp\left[-\frac{mg'(h_2 - h_1)}{k_B T}\right]$$

or $n_2 = n_1 \exp\left[-\frac{mgN_A(\rho - \rho')(h_2 - h_1)}{\rho RT}\right]$

13.14. Given below are densities of some solids and liquids. Give rough estimates of the size of their atoms :

Substance	Atomic Mass (u)	Density (10^3 kg m^{-3})
Carbon (diamond)	12.01	2.22
Gold	197.00	19.32
Nitrogen (liquid)	14.01	1.00
Lithium	6.94	0.53
Fluorine (liquid)	19.00	1.14

Ans. If r is the atomic radius, then

$$\text{volume of each atom, } v = \frac{4}{3}\pi r^3$$

Volume of one mole of atoms,

$$V = N_A v = N_A \times \frac{4}{3}\pi r^3$$

If M is the atomic mass and ρ the density of the substance, then

$$V = \frac{M}{\rho}$$

$$\therefore N_A \times \frac{4}{3}\pi r^3 = \frac{M}{\rho} \quad \text{or} \quad r = \left(\frac{3M}{4\pi\rho N_A}\right)^{1/3}$$

For carbon: $M = 12.01 \times 10^{-3} \text{ kg}$, $\rho = 2.22 \times 10^3 \text{ kg m}^{-3}$

$$\begin{aligned} \therefore r &= \left(\frac{3 \times 12.01 \times 10^{-3}}{4\pi \times 2.22 \times 10^3 \times 6.023 \times 10^{23}}\right)^{1/3} \\ &= 1.29 \times 10^{-10} \text{ m} = 1.29 \text{ \AA} \end{aligned}$$

For gold: $M = 197 \times 10^{-3} \text{ kg}$, $\rho = 19.32 \times 10^3 \text{ kg m}^{-3}$

$$\begin{aligned} \therefore r &= \left(\frac{3 \times 197 \times 10^{-3}}{4\pi \times 19.32 \times 10^3 \times 6.023 \times 10^{23}}\right)^{1/3} \\ &= 1.59 \times 10^{-10} \text{ m} = 1.59 \text{ \AA} \end{aligned}$$

For lithium: $M = 6.94 \times 10^{-3} \text{ kg}$, $\rho = 0.53 \times 10^3 \text{ kg m}^{-3}$

$$\begin{aligned} \therefore r &= \left(\frac{3 \times 6.94 \times 10^{-3}}{4\pi \times 0.53 \times 10^3 \times 6.023 \times 10^{23}}\right)^{1/3} \\ &= 1.73 \times 10^{-10} \text{ m} = 1.73 \text{ \AA} \end{aligned}$$

For fluorine: $M = 19 \times 10^{-3} \text{ kg}$, $\rho = 1.14 \times 10^3 \text{ kg m}^{-3}$

$$\begin{aligned} \therefore r &= \left(\frac{3 \times 19 \times 10^{-3}}{4\pi \times 1.14 \times 10^3 \times 6.023 \times 10^{23}}\right)^{1/3} \\ &= 1.88 \times 10^{-10} \text{ m} = 1.88 \text{ \AA} \end{aligned}$$

Text Based Exercises

Type A : Very Short Answer Questions

1 Mark Each

- Name the phenomena which give direct experimental evidence in support of the molecular motion.
- What is an equation of state ?
- At which temperature does all molecular motion cease ?
- What is the nature of graph between pressure (P) and volume (V) for a given mass of a gas at a fixed temperature ?

5. What is the nature of graph of P versus $(1/V)$ for a given mass of gas at constant temperature ?
6. What is the nature of graph of PV versus P for a given mass of gas at constant temperature ?
7. What is the lowest temperature attainable according to Charles' law ?
8. Who proposed a model for a gas for the kinetic theory of gases ?
9. What do you mean by mean free path of a gas molecule ?
10. Write the equation of state for an ideal gas.
11. What does the universal gas constant R signify ?
12. What is the value of R in SI units ?
13. Does the average K.E. per molecule of the gas depend upon the mass of the molecule ?
14. On which factor, does the average K.E. of translation per molecule of a gas depend ?
15. Define absolute zero, according to kinetic interpretation of temperature. [Delhi 08]
16. What is Boltzmann's constant ? Give its value.
17. How is the average K.E. of a gas molecule related to the temperature of the gas ?
18. The absolute temperature of a gas is increased four times its original value. What will be the change in r.m.s. velocity of its molecules ? [Delhi 12]
19. A molecule of mass m normally strikes a wall with velocity u and retraces its path after striking the wall. What is the change of momentum of the molecule ?
20. At a constant temperature, what is the relation between the pressure P and density ρ of a gas ?
21. A gas enclosed in a vessel has pressure P , volume V and absolute temperature T . Write the formula for the number of molecules N of the gas.
22. Write the value of gas constant in CGS system for 1 g of helium.
23. The velocities of three molecules are $3v$, $4v$ and $5v$. Determine the root mean square velocity.
24. What will be the ratio of the root mean square speeds of the molecules of an ideal gas at 270 K and 30 K ?
25. A mixture of helium and hydrogen gases is filled in a vessel at 30°C. Compare the root mean square velocities of the molecules of these gases at this temperature. Atomic weight of hydrogen = 4.
26. A container with porous walls is filled with a mixture of two gases. It is placed in evacuated space. The lighter of the two gases will escape out soon. Write the relevant relation which we use for explanation.
27. How much volume does one mole of a gas occupy at normal temperature and pressure ? [Himachal 02]
28. Write the relation between the pressure and kinetic energy per unit volume of a gas.
29. What is the mean translational kinetic energy of a perfect gas molecule at temperature T ?
30. Two vessels A and B of the same volume are filled with the same gas at the same temperature. The pressure of the gas in vessel B is twice the pressure of the gas in A . What is the ratio of the number of molecules in B and A ?
31. Two cylinders contain helium at 2 atmosphere and argon at 1 atmosphere respectively. If both the gases are filled in one of the cylinders, then what would be the pressure ?
32. What is the translational K.E. per unit volume of a gas whose pressure is P ?
33. A liquid is frozen at absolute zero of temperature. What happens to its molecular motion ?
34. Water solidifies into ice at 273 K. What happens to the kinetic energy of water molecules ?
35. Two gases having same volume V , temperature T and pressure P are mixed. If the mixture is also at the temperature T , and has volume V , what will be the final pressure ? [Delhi 96]
36. Define Avogadro's number and give its value. [Himachal 02]
37. Write the relation between the ratio of the specific heats of a gas and degrees of freedom.
38. Is molar specific heat of a solid a constant quantity ?
39. What is the mean translational kinetic energy of a perfect gas molecule at temperature T ? [Central Schools 08]
40. Name two factors on which the degrees of freedom of a gas depend. [Central Schools 08]

Answers

1. The phenomena of diffusion of gases and Brownian motion provide direct experimental evidence in support of molecular motion.
2. An equation which relates the pressure, volume and temperature of a system is called an equation of state.

3. At zero kelvin.
4. It is a rectangular hyperbola.
5. It is a straight line passing through the origin.
6. It is a straight line parallel to the pressure axis.
7. -273.15°C .
8. R. Clausius and J.C. Maxwell.
9. The mean free path of a gas molecule is the average distance traversed by the molecule between its two successive collisions with other molecules.
10. $PV = nRT$.
11. The universal gas constant R signifies the work done by (or on) a gas per mole per kelvin.
12. $R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$.
13. No.
14. Temperature.
15. Absolute zero is the temperature at which all molecular motion ceases.
16. Boltzmann's constant is defined as the gas constant per molecule.

$$k_B = \frac{R}{N_A} = 1.38 \times 10^{-23} \text{ JK}^{-1}.$$

17. Average K.E. of a gas molecule,

$$\frac{1}{2} m \overline{v^2} = \frac{3}{2} k_B T.$$

$$18. \quad v_{rms} \propto \sqrt{T}$$

$$\therefore v'_{rms} \propto \sqrt{4T}$$

$$\frac{v'_{rms}}{v_{rms}} = 2$$

$$\text{or } v'_{rms} = 2 v_{rms}$$

Change in r.m.s. velocity of molecules

$$= v'_{rms} - v_{rms} = v_{rms}$$

Thus the change in r.m.s. velocity will be equal to its initial value.

19. $2 mu$
20. At constant temperature,
 $\frac{P}{\rho} = \text{constant}.$
21. $N = \frac{PV}{k_B T}.$
22. $r = 2078 \times 10^7 \text{ erg g}^{-1} \text{ }^\circ\text{C}^{-1}.$

$$23. \quad v_{rms} = \sqrt{\frac{(3v)^2 + (4v)^2 + (5v)^2}{3}}$$

$$= \sqrt{\frac{50}{3}} v = 4.08 v.$$

$$24. \quad \frac{v_{rms}}{v'_{rms}} = \sqrt{\frac{T}{T'}} = \sqrt{\frac{270}{30}} = 3 : 1.$$

$$25. \quad \frac{(v_{rms})_{\text{He}}}{(v_{rms})_{\text{H}_2}} = \sqrt{\frac{M_{\text{H}_2}}{M_{\text{He}}}}$$

$$= \sqrt{\frac{2}{4}} = 1 : \sqrt{2}.$$

26. The ratio of the rates of diffusion of two gases

$$\frac{r_1}{r_2} = \frac{(v_{rms})_1}{(v_{rms})_2} = \sqrt{\frac{M_2}{M_1}}.$$

Hence lighter gas diffuses more rapidly.

27. 22.4 litre or $22.4 \times 10^{-3} \text{ m}^3.$

$$28. \quad P = \frac{2}{3} E.$$

$$29. \quad \overline{\text{K.E.}} = \frac{3}{2} k_B T.$$

$$30. \quad P = \frac{1}{3} \frac{mN}{V} \overline{v^2}$$

For constant m, V and $T, P \propto n$

$$\therefore \frac{n_B}{n_A} = \frac{P_B}{P_A} = \frac{2P}{P} = 2 : 1$$

31. According to Dalton's law of partial pressures,

$$P = P_1 + P_2 = 2 + 1 = 3 \text{ atmosphere.}$$

$$32. \quad E = \frac{3}{2} P.$$

33. The molecular motion ceases at absolute zero.

34. The kinetic energy of the water molecules gets partly converted into the binding energy of the ice.

35. $2P$. Refer to solution of Problem 26 on page 13.28.

36. It is the number of particles present in one mole of a substance.

$$N_A = 6.0225 \times 10^{23} \text{ mole}^{-1}.$$

$$37. \quad \gamma = \frac{C_p}{C_v} = 1 + \frac{2}{f}.$$

38. Yes. Near the room temperature, its value is $3 \text{ cal mol}^{-1} \text{ K}^{-1}.$

39. A perfect gas molecules has only translational K.E.

$$\therefore E = \frac{3}{2} k_B T$$

40. Degrees of freedom of a gas depend on

- (i) Atomicity of the gas molecules.
- (ii) Shape of the molecules.
- (iii) Temperature of the gas.

Type B : Short Answer Questions

2 or 3 Marks Each

1. Write any four fundamental postulates of the kinetic theory of an ideal gas.

[Himachal 08, 09 ; Delhi 03]

2. What is an ideal gas ? Why do the real gases show deviation from ideal behaviour.
3. Draw P - V curves showing deviations from ideal behaviour for a given mass of a gas for two different temperatures.
4. On the basis of kinetic theory of gases, explain how does a gas exert pressure.
5. Show that the pressure exerted by a gas is two-thirds of the average kinetic energy per unit volume of the gas molecules.

Or

Derive the relation between pressure and mean kinetic energy of a gas. [Himachal 05]

6. Calculate the total random kinetic energy for one mole of a gas at constant volume. [Delhi 97]
7. Discuss the kinetic interpretation of temperature. Hence define absolute zero of temperature [Himachal 05, 07C, 09C]
8. Show that the average kinetic energy of a gas molecule is directly proportional to the absolute temperature of the gas. Hence give the kinetic interpretation of temperature. [Himachal 09 ; Delhi 08]
9. Explain the concept of absolute zero of temperature on the basis of kinetic theory of gases. [Delhi 09]
10. Derive Boyle's law on the basis of kinetic theory of gases.
11. Derive Charles' law on the basis of kinetic theory of gases.
12. Deduce Gay Lussac's law on the basis of kinetic theory of gases.
13. Derive perfect gas equation from kinetic theory of gases.
14. State Avogadro's law. Deduce it on the basis of kinetic theory of gases.
15. Deduce Graham's law of diffusion from kinetic theory of gases using expression for pressure.
16. State Dalton's law of partial pressures. Deduce it from the kinetic theory of gases.
17. Draw a curve showing Maxwell's distribution of molecular speeds of a gas at a given temperature. Indicate on this curve

(i) most probable velocity,

(ii) average velocity and

(iii) root mean square velocity.

18. Define average, root mean square and most probable speeds. Arrange them in the decreasing order of their values.
19. What do you mean by degrees of freedom ? Show that the number of degrees of freedom of a system consisting of N -particles and having k independent relation between them is $(3N - k)$.
20. Define degrees of freedom. Calculate the degrees of freedom of monoatomic, diatomic and triatomic gas molecules. [Himachal 07C]
21. State the law of equipartition of energy. Determine the values of γ for diatomic gas N_2 at moderate temperature. [Delhi 11]
22. State the law of equipartition of energy and prove that for a diatomic gas at high temperature, the ratio of the two specific heats is $9/7$.
23. Using the law of equipartition of energy, show that for an ideal gas having f degrees of freedom,

$$\gamma = 1 + \frac{2}{f}$$

24. State the law of equipartition of energy and using this find the relation for the total internal energy of a mole of monoatomic gases. [Delhi 08]
25. What is Dulong and Petit's law ? Illustrate it graphically also. [Delhi 95]
26. What is Brownian motion ? How can it be accounted for ?
27. State four factors on which Brownian motion depends.
28. Derive the expression for pressure exerted by an ideal gas using kinetic theory of gases. Hence define root mean square velocity. [Himachal 07C ; Central Schools 09 ; Delhi 12]
29. Using the expression for pressure exerted by a gas, deduce Avogadro's law and Graham's law of diffusion. [Chandigarh 08]
30. (i) Define Absolute zero.
- (ii) Deduce the dimensional formula for R , using ideal gas equation
- $$PV = nRT.$$
- (iii) Find the degree of freedom of a monoatomic gas. [Central Schools 07 ; Delhi 10]

31. State the number of degrees of freedom possessed by a monoatomic molecule in space. Also give the expression for total energy possessed by it at a given temperature. Hence give the total energy of the atom at 300 K. [Centrl Schools 08]
32. Drive the relation between the ratio of two specific heats of gas and degree of freedom. [Central Schools 09]
33. State and explain the law of equipartition of energy. [Himachal 09]
34. State the law of equipartition of energy of a dynamic system and use it to find the value of the ratio of two specific heats of monoatomic and diatomic gas molecules. [Himachal 09C]

Answers

1. Refer answer to Q. 8 on page 13.7.
2. Refer answer to Q. 7 on page 13.3
3. See Fig. 13.5 on page 13.3
4. Refer answer to Q. 9 on page 13.7.
5. Refer answer to Q. 11 on page 13.8.
6. Refer answer to Q. 12 on page 13.8.
7. Refer answer to Q. 12 on page 13.8.
8. Refer answer to Q. 12 on page 13.8.
9. Refer answer to Q. 12 on page 13.8.
10. Refer answer to Q. 13 on page 13.11.
11. Refer answer to Q. 14 on page 13.12.
12. Refer answer to Q. 15 on page 13.12.
13. Refer answer to Q. 16 on page 13.12.
14. Refer answer to Q. 17 on page 13.12.
15. Refer answer to Q.18 on page 13.12.
16. Refer answer to Q. 19 on page 13.13.
17. See Fig. 13.11 on page 13.13.
18. Refer answer to Q.22 on page 13.14.
19. Refer answer to Q.23 on page 13.17.
20. Refer answer to Q. 24 on page 13.17.
21. Refer answer to Q. 26(ii)(a) on page 13.19.
22. Refer answer to Q. 26(ii)(b) on page 13.19.
23. Refer answer to Q. 27 on page 13.19.
24. Refer answer to Q. 25 on page 13.18 and Q. 26(i) on page 13.19.
25. Refer answer to Q. 28 on page 13.23 and see Fig. 13.15.
26. Refer answer to Q. 33 on page 13.26.
27. Refer answer to Q. 33 on page 13.26.
28. Refer answer to Q. 10 on page 13.17.
29. Refer answer to Q. 17 and Q. 18 on page 13.12.
30. (i) Absolute zero is defined as that temperature at which all molecular motion stops.
(ii) Refer to the solution of Problem 22 on page 13.28.
(iii) Refer answer to Q. 24(a) on page 13.17.
31. No. of degrees of freedom of a monoatomic molecule = 3
Total energy possessed by a monoatomic molecule
$$\bar{E} = \frac{3}{2} k_B T$$
At temperature $T = 300$ K,
$$\bar{E} = \frac{3}{2} \times 1.38 \times 10^{23} \times 300$$
$$= 621 \times 10^{23} \text{ J.}$$
32. Refer answer to Q. 27 on page 13.19.
33. Refer answer to Q. 25 on page 13.18.
34. Refer answer to Q. 26(i) and (ii) on page 13.19.

Type C : Long Answer Questions

5 Marks Each

1. What are the basic assumptions of kinetic theory of gases ? On their basis derive an expression for the pressure exerted by an ideal gas. [Himachal 05, 08C ; Delhi 99]
2. State the postulates of kinetic theory of gases. Derive an expression for the pressure exerted by an ideal gas. Molar volume is the volume occupied by 1 mole of any (ideal) gas at standard temperature and pressure (STP = 1 atm pressure, 0°C). Show that it is 22.4 litres. [Delhi 06]

3. Prove that the pressure exerted by a gas is $P = \frac{1}{3} \rho c^2$, where ρ is the density and c is the root mean square velocity.
[Himachal 04 ; Central Schools 09, 12]
4. What is meant by degrees of freedom ? State the law of equipartition of energy. Hence calculate the values of molar specific heats at constant volume and pressure for monoatomic, diatomic and triatomic gases. [Himachal 02]
5. State and prove the law of equipartition of energy. On its basis find the value of the two molar specific heats of a gas and the ratio of the two specific heats. What will be the values of C_p , C_v and γ , when the gas under consideration is (i) a monoatomic gas (ii) a diatomic gas ? [Himachal 01]
6. What is meant by mean free path of a gas molecule ? Derive an expression for it. On which factors does it depend ? [Himachal 07]

Answers

1. Refer answer to Q. 8 and Q. 10 on page 13.7.
2. Refer answer to Q. 8 and Q. 10 on page 13.7 and see answer of NCERT Exercise 13.2 on page 13.35.
3. Refer answer to Q. 10 on page 13.7.
4. Refer to points 19, 20 and 21 of Glimpses
5. Refer answer to Q. 25 on page 13.18 and refer to point 21 of Glimpses.
6. Refer answer to Q. 31 on page 13.24.

Kinetic Theory of Gases

GLIMPSES

1. Boyle's law. It states that at constant temperature, the volume of a given mass of a gas is inversely proportional to its pressure.

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

$$\text{or } P_1 V_1 = P_2 V_2 \quad (\text{For constant } m \text{ and } T)$$

2. Charles' law. It states that if the pressure remains constant, then the volume of a given mass of a gas increases or decreases by $1/273.15$ of its volume at 0°C for each 1°C rise or fall of temperature. Mathematically,

$$V_t = V_0 \left(1 + \frac{t}{273.15} \right) = V_0 \left(\frac{273.15 + t}{273.15} \right)$$

If we put $273.15 + t = T$ and $273.15 = T_0$, then

$$\frac{V_t}{T} = \frac{V_0}{T_0} \text{ or } \frac{V}{T} = \text{constant}$$

So Charles' law can also be stated as follows :

At constant pressure, the volume of a given mass of a gas is directly proportional to its absolute temperature.

3. Gay Lussac's law. It states that if the volume remains constant, then the pressure of the given mass of a gas increases or decreases by $1/273.15$ of its pressure at 0°C for each 1°C rise or fall of temperature. Mathematically,

$$P_t = P_0 \left(1 + \frac{t}{273.15} \right) = P_0 \left(\frac{273.15 + t}{273.15} \right)$$

$$\text{or } \frac{P_t}{P_0} = \frac{T}{T_0}$$

$$\text{or } \frac{P}{T} = \text{constant}$$

So Gay Lussac's law can also be stated as follows :

At constant volume, the pressure of a given mass of a gas is directly proportional to its absolute temperature.

4. Ideal gas equation. For n moles of a gas,

$$PV = nRT \quad \text{or} \quad \frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

For 1 mole of a gas,

$$PV = RT$$

5. Universal gas constant. It signifies the work done by the gas per mole per kelvin.

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

6. Boltzmann's constant. It is the gas constant per molecule of a gas. If N is Avogadro's number, then

$$k_B = \frac{R}{N} = 1.38 \times 10^{-23} \text{ J molecule}^{-1} \text{ K}^{-1}$$

7. Ideal or perfect gas. A gas which obeys gas laws strictly is an ideal or perfect gas. The molecules of such a gas are of point size and there is no force of attraction between them.

The actual real gases obey the ideal gas equation only approximately at low pressures and high temperatures.

8. Assumptions of kinetic theory of gases :

(i) All gases consist of molecules. The molecules are rigid, elastic spheres identical in all respects for a given gas and different for different gases.

(ii) The size of a molecule is negligible compared with the average distance between two molecules.

(iii) The molecules are in a state of continuous random motion, moving in all directions with all possible velocities.

(iv) During the random motion, the molecules collide with one another and with the walls of the vessel.

- (v) The collisions are perfectly elastic and there are no forces of attraction or repulsion between them.
- (vi) Between two collisions, a molecule moves in a straight path with a uniform velocity.
- (vii) The collisions are almost instantaneous.
- (viii) The molecular density remains uniform throughout the gas.

9. **Pressure exerted by a gas.** According to kinetic theory of gases, the pressure exerted by a gas of mass M and volume V or density ρ is given by

$$P = \frac{1}{3} \frac{M}{V} \overline{v^2} = \frac{1}{3} \rho \overline{v^2} = \frac{1}{3} mn \overline{v^2}$$

Here n is the number of molecules per unit volume, m the mass of each molecule and $\overline{v^2}$ is the mean of square speed.

10. **Average kinetic energy of a gas.** Let M be the molecular mass and V the molar volume of a gas. Let m be the mass of each molecule. Then

(i) Mean K.E. per mole of a gas,

$$E = \frac{1}{2} M \overline{v^2} = \frac{3}{2} PV = \frac{3}{2} RT = \frac{3}{2} k_B N_A T$$

(ii) Mean K.E. per molecule of a gas,

$$\overline{E} = \frac{1}{2} m \overline{v^2} = \frac{3}{2} k_B T$$

This is the *kinetic interpretation of temperature*. That is, the temperature of a gas is a measure of the average kinetic energy of a molecule.

(iii) K.E. of 1 gram of gas $= \frac{1}{2} \overline{v^2} = \frac{3}{2} \frac{RT}{M}$.

11. **Avogadro's law.** It states that equal volume of all gases under similar conditions of temperature and pressure contain equal number of molecules.

12. **Avogadro's number.** It is the number of particles present in one mole of a substance. Its most accepted value is

$$N_A = 6.0225 \times 10^{23} \text{ mole}^{-1}$$

13. **Graham's law of diffusion.** It states that the rate of diffusion of a gas is inversely proportional to the square root of its density.

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

14. **Dalton's law of partial pressures.** It states that the total pressure exerted by a mixture of non-reacting gases occupying a given volume is equal to the sum of the partial pressures which gas would exert if it alone occupied the same volume at the given temperature.

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

15. **Average speed.** It is defined as the arithmetic mean of the speeds of the molecules of a gas at a given temperature.

$$\overline{v} = \frac{v_1 + v_2 + v_3 + \dots + v_n}{n}$$

$$\overline{v} = \sqrt{\frac{8k_B T}{\pi m}} = \sqrt{\frac{8RT}{\pi M}} = \sqrt{\frac{8PV}{\pi M}}$$

16. **Root mean square speed.** It is defined as the square root of the mean of the squares of the speeds of the individual molecules of a gas.

$$v_{rms} = \sqrt{\frac{v_1^2 + v_2^2 + v_3^2 + \dots + v_n^2}{n}}$$

$$v_{rms} = \sqrt{\frac{3k_B T}{m}} = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3PV}{M}}$$

17. **Most probable speed.** It is defined as the speed possessed by the maximum number of molecules in a gas sample at a given temperature.

$$v_{mp} = \sqrt{\frac{2k_B T}{m}} = \sqrt{\frac{2RT}{M}} = \sqrt{\frac{2PV}{M}}$$

18. **Relations between \overline{v} , v_{rms} and v_{mp} .**

$$\overline{v} = 0.92 v_{rms}$$

$$v_{mp} = 0.816 v_{rms}$$

$$v_{rms} : \overline{v} : v_{mp} = 1.73 : 1.60 : 1.41$$

Clearly, $v_{rms} > \overline{v} > v_{mp}$.

19. **Degrees of freedom.** The degrees of freedom of a dynamical system are defined as the total number of coordinates or independent quantities required to describe completely the position and configuration of the system.

If N = number of particles in the system,
 k = number of independent relations between the particles

then the number of degrees of freedom of the system is

$$f = 2N - k$$

A monoatomic molecule gas has 3 degrees of freedom, a diatomic gas molecule has 5 degrees of freedom. At high temperature, a diatomic molecule has 7 degrees of freedom.

20. **Law of equipartition of energy.** It states that in any dynamical system in thermal equilibrium, the energy of the system is equally divided amongst its various degrees of freedom and the energy associated with each degree of freedom is $\frac{1}{2} k_B T$,

where k_B is Boltzmann's constant and T is the absolute temperature of the system.

21. Internal energies and specific heats of monoatomic, diatomic and polyatomic gases. The law of equipartition of energy leads to the following results :

(i) For a gas of polyatomic molecules having f degrees of freedom,

Energy associated with 1 mole of gas,

$$U = \frac{f}{2} RT \quad C_v = \frac{f}{2} R,$$

$$C_p = \left(1 + \frac{f}{2}\right) R \quad \gamma = \frac{C_p}{C_v} = 1 + \frac{2}{f}$$

(ii) For a monoatomic gas, $f = 3$, so

$$U = \frac{3}{2} RT, \quad C_v = \frac{3}{2} R,$$

$$C_p = \frac{5}{2} R, \quad \gamma = 1.66.$$

(iii) For a diatomic gas with no vibrational mode, $f = 5$, so

$$U = \frac{5}{2} RT, \quad C_v = \frac{5}{2} R,$$

$$C_p = \frac{7}{2} R, \quad \gamma = 1.4.$$

(iv) For a diatomic gas with vibrational mode, $f = 7$, so

$$U = \frac{7}{2} RT, \quad C_v = \frac{7}{2} R,$$

$$C_p = \frac{9}{2} R, \quad \gamma = \frac{9}{7} = 1.28.$$

(v) For a triatomic gas of non-linear molecules, $f = 6$, so

$$U = 3RT, \quad C_v = 3R,$$

$$C_p = 4R, \quad \gamma = 1.33$$

(vi) For a triatomic gas of linear molecules, $f = 7$, so

$$U = \frac{7}{2} RT, \quad C_v = \frac{7}{2} R,$$

$$C_p = \frac{9}{2} R, \quad \gamma = 1.28.$$

22. Mean free path. It is the average distance covered by a molecule between two successive collisions. It is given by

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

where n is the number density and d is the diameter of the molecule.

23. Brownian motion. It provides a direct evidence for the existence of molecules and their motion. The zig-zag motion of gas molecules is Brownian motion because it occurs due to random collision of molecules. But this motion cannot be seen. However, the zig-zag motion of pollen grains ($\approx 10^{-5}$ m) can be seen under a microscope.

IIT Entrance Exam

MULTIPLE CHOICE QUESTIONS WITH ONE CORRECT ANSWER

1. A vessel contains 1 mole of O_2 gas (relative molar mass 32) at a temperature T . The pressure of the gas is P . An identical vessel containing one mole of He gas (relative molar mass 4) at a temperature $2T$ has a pressure of

- (a) $P/8$ (b) P
(c) $2P$ (d) $8P$ [IIT 97]

2. The average translational kinetic energy of O_2 molecules (relative molar mass 32) at a particular temperature is 0.048 eV. The translational kinetic energy of N_2 molecules (relative molar mass 28) in eV at the same temperature is

- (a) 0.0015 (b) 0.003
(c) 0.048 (d) 0.768 [IIT 97]

3. The average translational energy and the r.m.s. speed of molecules in a sample of oxygen gas at 300 K

are 6.21×10^{-21} J and 484 ms^{-1} respectively. The corresponding values at 600 K are nearly (assuming ideal gas behaviour)

- (a) 12.42×10^{-21} J, 968 ms^{-1}
(b) 8.78×10^{-21} J, 684 ms^{-1}
(c) 6.21×10^{-21} J, 968 ms^{-1}
(d) 12.42×10^{-21} J, 684 ms^{-1} [IIT 97]

4. A gas mixture consists of 2 moles of oxygen and 4 moles of argon at temperature T . Neglecting all vibrational modes, the total internal energy of the system is

- (a) $4RT$ (b) $9RT$
(c) $11RT$ (d) $15RT$ [IIT 99]

5. The ratio of the speed of sound in nitrogen gas to that in helium gas, at 300 K is

- (a) $\sqrt{2/7}$ (b) $\sqrt{1/7}$
(c) $(\sqrt{3})/5$ (d) $(\sqrt{6})/5$ [IIT 99]

6. From the following statements, concerning ideal gas at any given temperature T , select the correct one(s) :

- (a) The co-efficient of volume expansion at constant pressure is the same for all ideal gases
- (b) The average translational kinetic energy per molecule of oxygen gas is $3kT$, k being Boltzmann constant
- (c) The mean-free path of molecules increases with increases in the pressure
- (d) In a gaseous mixture, the average translational kinetic energy of the molecules of each component is different. [IIT 95]

7. An ideal gas is expanding such that $PT^2 = \text{constant}$. The coefficient of volume expansion of the gas is

- (a) $\frac{1}{T}$
- (b) $\frac{2}{T}$
- (c) $\frac{3}{T}$
- (d) $\frac{4}{T}$ [IIT 08]

8. A real gas behaves like an ideal gas if its

- (a) Pressure and temperature are both high
- (b) Pressure is high and temperature is low
- (c) Pressure and temperature are both low
- (d) Pressure is low and temperature is high [IIT 2010]

MULTIPLE CHOICE QUESTIONS WITH ONE OR MORE THAN ONE CORRECT ANSWER

9. At room temperature, the r.m.s. speed of the molecules of a certain diatomic gas is found to be $1,920 \text{ ms}^{-1}$. The gas is

- (a) H_2
- (b) F_2
- (c) O_2
- (d) Cl_2 [IIT 84]

10. The temperature of an ideal gas is increased from 120 K to 480 K. If at 120 K, the r.m.s. velocity of the gas molecules is v ; at 480 K, it becomes

- (a) $4v$
- (b) $2v$
- (c) $v/2$
- (d) $v/4$ [IIT 96]

11. Let \bar{v} , v_{rms} and v_p respectively denote the mean speed, root mean square speed and most probable speed of the molecules in an ideal monoatomic gas at absolute temperature T . The mass of the molecule is m . Then

- (a) no molecule can have a speed greater than $\sqrt{2}v_{rms}$

- (b) no molecule can have a speed less than $v_p / \sqrt{2}$
- (c) $v_p < \bar{v} < v_{rms}$
- (d) the average kinetic energy of a molecule is $\frac{3}{4}mv_p^2$. [IIT 98]

12. A vessel contains a mixture of 1 mole of oxygen and 2 moles of nitrogen at 300 K. The ratio of the average rotational kinetic energy per O_2 molecule to that per N_2 molecule is

- (a) 1 : 1
- (b) 1 : 2
- (c) 2 : 1
- (d) depends on the moment of inertia of the two molecules. [IIT 80]

13. When an ideal diatomic gas is heated at constant pressure, the fraction of the heat energy supplied, which increases the internal energy of the gas is

- (a) 2/5
- (b) 3/5
- (c) 3/7
- (d) 5/7. [IIT 90]

14. If one mole of monoatomic gas ($\gamma = 5/3$) is mixed with one mole of a diatomic gas ($\gamma = 7/5$), the value of adiabatic exponent γ for mixture is

- (a) 1.35
- (b) 1.40
- (c) 1.50
- (d) 1.75. [IIT 88]

15. A given quantity of an ideal gas is at pressure P and absolute temperature T . The isothermal bulk modulus of the gas is

- (a) $\frac{2}{3}P$
- (b) P
- (c) $\frac{3}{2}P$
- (d) $2P$. [IIT 98]

16. Three closed vessels A, B and C are at the same temperature T and contain gases which obey the Maxwellian distribution of velocities. Vessel A contains only O_2 , B only N_2 and C a mixture of equal quantities of O_2 and N_2 . If the average speed of the O_2 molecules in vessel A is v_1 that of the N_2 molecules in vessel B is v_2 , the average speed of the O_2 molecules in vessel C is

- (a) $\frac{v_1 + v_2}{2}$
- (b) v_1
- (c) $(v_1 \cdot v_2)^{1/2}$
- (d) $\sqrt{\frac{3kT}{M}}$

where M is the mass of an oxygen molecule. [IIT 92]

17. C_v and C_p denote the molar specific heat capacities of a gas at constant volume and constant pressure, respectively.

Then

- (a) $C_p - C_v$ is larger for a diatomic ideal gas than for a monoatomic ideal gas
 (b) $C_p + C_v$ is larger for a diatomic ideal gas than for a monoatomic ideal gas

- (c) C_p / C_v is larger for a diatomic ideal gas than for a monoatomic ideal gas
 (d) $C_p \cdot C_v$ is larger for a diatomic ideal gas than for a monoatomic ideal gas [IIT 09]

Answers and Explanations

1. (c) $PV = nRT$ or $P = \frac{nRT}{V}$

For same n , R and V , $P \propto T$

$$\frac{P_2}{P_1} = \frac{T_2}{T_1} \quad \text{or} \quad \frac{P_2}{P} = \frac{2T}{T} \quad \text{or} \quad P_2 = 2P.$$

2. (c) Average translational K.E. of a molecule

$$= \frac{3}{2} kT$$

It depends on temperature and not on molecular mass. Hence average translational K.E. for N_2 will also be 0.048 eV.

3. (d) Average translational K.E. $= \frac{3}{2} kT \propto T$

$$\text{r.m.s. speed} = \sqrt{\frac{3RT}{M}} \propto \sqrt{T}$$

When temperature increases from 300 K to 600 K, average translational K.E. increases 2 times and r.m.s. speed increases $\sqrt{2}$ or 1.414 times.

\therefore Average translational K.E.
 $= 2 \times 6.21 \times 10^{-21} = 12.42 \times 10^{-21} \text{ J}$
 r.m.s. speed $= 1.414 \times 484 = 684 \text{ ms}^{-1}$.

4. (c) For two moles of diatomic nitrogen with no vibrational mode,

$$U_1 = 2 \times \frac{5}{2} RT = 5RT$$

For four moles of monoatomic argon,

$$U_2 = 4 \times \frac{3}{2} RT = 6RT \quad \therefore U = U_1 + U_2 = 11RT.$$

5. (c) $v = \sqrt{\frac{\gamma RT}{M}}$

$$\frac{v(N_2)}{v(He)} = \sqrt{\frac{\gamma_{N_2}}{\gamma_{He}} \cdot \frac{M_{He}}{M_{N_2}}} = \sqrt{\frac{7/5}{5/3} \times \frac{4}{28}} = \frac{\sqrt{3}}{5}$$

6. (a) Coefficient of cubical expansion of an ideal gas, $\gamma = \frac{1}{T}$.

At a given T , γ is same for all ideal gases.

(b) The average translational K.E. per molecule is $(3/2) kT$ and not $3kT$.

(c) With increase of pressure, volume decreases. The collisions become more frequent. The mean free path decreases.

(d) The average K.E. does not depend on the nature of the gas, so each component of the gaseous mixture has the same average translational kinetic energy.

Hence only option (a) is correct.

7. (c) Given $PT^2 = C$

But $PV = nRT$ or $P = \frac{nRT}{V}$

$$\therefore \frac{nRT^3}{V} = C \quad \text{or} \quad V = \frac{nRT^3}{C}$$

Hence $\frac{dV}{dT} = \frac{3nRT^2}{C} = \frac{3V}{T}$ [Put $T^3 = \frac{CV}{nR}$]

or $\gamma = \frac{dV/dT}{V} = \frac{3}{T}$

8. (d) Real gas behaves like an ideal gas if its pressure is low and temperature is high. This ensures large intermolecular separation and no interaction.

9. (a) $v_{rms} = \sqrt{\frac{3RT}{M}}$

$$\therefore M = \frac{3RT}{(v_{rms})^2} = \frac{3 \times 8.3 \times 300}{(1920)^2} = 2$$

Hence the gas is H_2 .

10. (b) $\frac{v_{rms(2)}}{v_{rms(1)}} = \sqrt{\frac{T_2}{T_1}} = \sqrt{\frac{480}{120}} = 2.$

$$v_{rms(2)} = 2v_{rms(1)} = 2v.$$

11. (c), (d) $v_{rms} = \sqrt{\frac{3RT}{M}}$

$$\bar{v} = \sqrt{\frac{8RT}{\pi M}} = \sqrt{\frac{2.5RT}{M}}$$

$$v_p = \sqrt{\frac{2RT}{M}}$$

Clearly, $v_p < \bar{v} < v_{rms}$

$$v_{rms} = \sqrt{\frac{3}{2}} v_p$$

∴ Average K.E. of a gas molecule

$$= \frac{1}{2} m v_{rms}^2 = \frac{1}{2} m \left(\sqrt{\frac{3}{2}} v_p \right)^2 = \frac{3}{4} m v_p^2$$

Hence options (c) and (d) are correct.

12. (a) Both gases are diatomic. Both have two rotational degrees of freedom at 300 K.

Average rotational K.E. per molecule of each gas will be same

$$= 2 \times \frac{1}{2} kT = 1 kT.$$

Hence the required ratio is 1 : 1.

13. (d) Required fraction,

$$\frac{\Delta U}{\Delta Q} = \frac{n C_V dT}{n C_P dT} = \frac{C_V}{C_P} = \frac{1}{\gamma}$$

For a diatomic gas, $\gamma = 7/5$

$$\therefore \frac{\Delta U}{\Delta Q} = \frac{5}{7}.$$

14. (c) Refer to the solution of Example 36 on page 13.21.

15. (a) At a given temperature, $PV = \text{constant}$

$$\therefore P \Delta V + V \Delta P = 0$$

or $P = -\frac{V \Delta P}{\Delta V} = -\frac{\Delta P}{\Delta V / V} = \text{Isothermal bulk modulus}$

16. (b) $\bar{v} = \sqrt{\frac{8RT}{\pi M}} \propto \sqrt{T}$ (for a given gas)

As vessels A and C have the same temperature,

Average speed of O_2 in C

$$= \text{Average speed of } O_2 \text{ in } A = v_1.$$

17. (b), (d) $C_p - C_V = R$ for all ideal gases.

Hence option (a) is incorrect.

$$(C_p + C_V)_{\text{Diatomic}} = \frac{7R}{2} + \frac{5R}{2} = 6R$$

$$(C_p + C_V)_{\text{Monoatomic}} = \frac{5R}{2} + \frac{3R}{2} = 4R$$

∴ $(C_p + C_V)$ is larger for a diatomic gas.

Hence option (b) is correct.

$$\left(\frac{C_p}{C_V} \right)_{\text{Diatomic}} = \frac{7}{5} = 1.4$$

$$\left(\frac{C_p}{C_V} \right)_{\text{Monoatomic}} = \frac{5}{3} = 1.67$$

∴ C_p / C_V is smaller for a diatomic gas.

Hence option (c) is incorrect.

$$(C_p C_V)_{\text{Diatomic}} = \frac{35}{4} R^2$$

$$(C_p C_V)_{\text{Monoatomic}} = \frac{15}{2} R^2$$

∴ Product $C_p C_V$ is larger for a diatomic gas.

Hence option (d) is correct.