

**Lesson at a Glance**

- The kinetic theory was developed in the nineteenth century by Maxwell, Boltzman and others. Kinetic theory explains the behaviour of gases based on the idea that the gas consists of rapidly moving atoms or molecules.

- **Ideal Gas**

An ideal gas or a perfect gas is that gas which strictly obeys gas laws such as Boyle's law, Charle's law, Gay Lussac's law etc.

An ideal gas has following characteristics:

- (i) Molecule of an ideal gas is a point mass with no geometrical dimensions.
- (ii) There is no force of attraction or repulsion amongst the molecules of the gas.

- **Kinetic Theory and Gas Pressure**

The pressure of a gas is the result of continuous bombardment of the gas molecules against the walls of the container. According to the kinetic theory, the pressure  $P$  exerted by an ideal gas is given by

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

where  $\rho$  is the density of the gas and  $\bar{c}^2$  is the mean square speed of the gas molecules.

If a container has  $n$  molecules each of mass  $m$ , then

$$P = \frac{1}{3} \frac{nm}{V} \bar{c}^2$$

where  $V$  is the volume of the container.

- **Boyle's Law**

According to this law, the volume ( $V$ ) of a fixed mass of a gas is inversely proportional to the pressure ( $P$ ) of the gas, provided temperature of the gas is kept constant.

*i.e.*  $V \propto \frac{1}{P}$  or  $PV = \text{constant}$

### • Charles's Law

According to this law, the volume ( $V$ ) of a given mass of a gas is directly proportional to the temperature of the gas, provided pressure of the gas remains constant.

$$\text{i.e.,} \quad V \propto T \text{ or } \frac{V}{T} = \text{a constant} \Rightarrow \frac{V_1}{T_1} = \frac{V_2}{T_2}$$

### • Gay Lussac's Law (or Pressure Law)

According to this law, the pressure  $P$  of a given mass of a gas is directly proportional to its absolute temperature  $T$ , provided the volume  $V$  of the gas remains constant.

$$\text{i.e.,} \quad P \propto T \text{ or } \frac{P}{T} = \text{a constant} \Rightarrow \frac{P_1}{T_1} = \frac{P_2}{T_2}$$

### • Equation of State of an Ideal Gas

The relationship between pressure  $P$ , volume  $V$  and absolute temperature  $T$  of a gas is called its equation of state. The equation of state of an ideal gas

$$PV = nRT$$

where  $n$  is the number of moles of the enclosed gas and  $R$  is the molar gas constant which is the same for all gases and its value is

$$R = 8.315 \text{ JK}^{-1} \text{ mol}^{-1}$$

### • Avagadro's Law

Equal volumes of all gases under S.T.P. contain the same number of molecules equalling  $6.023 \times 10^{23}$ .

### • Graham's Law of Diffusion of Gases

It states that rate of diffusion of a gas is inversely proportional to the square root of the density of the gas.

$$\text{i.e.,} \quad r \propto \frac{1}{\sqrt{\rho}}$$

Hence, denser the gas, the slower is the rate of diffusion.

### • Dalton's Law of Partial Pressures

According to this law, the resultant pressure exerted by a mixture of non-interacting gases is equal to the sum of their individual pressures.

$$\text{i.e.,} \quad P = P_1 + P_2 + \dots + P_n$$

### • Kinetic Interpretation of Temperature

The total average kinetic energy of all the molecules of a gas is proportional to its absolute temperature ( $T$ ). Thus, the temperature of a gas is a measure of the average kinetic energy ' $U$ ' of the molecules of the gas.

$$U = \frac{3}{2} RT$$

According to this interpretation of temperature, the average kinetic energy  $U$  is zero at  $T = 0$ , i.e., the motion of molecules ceases altogether at absolute zero.

### • Degrees of Freedom

The total number of independent co-ordinates required to specify the position of a molecule or the number of independent modes of motion possible with any molecule is called degree of freedom.

Mono-, di-, and polyatomic ( $N$ ) molecules have, 3, 5 or  $(3N - K)$  number of degrees of freedom where  $K$  is the number of constraints [restrictions associated with the structure].

### • Law of Equipartition of Energy

For a dynamic system in thermal equilibrium, the energy of the system is equally distributed amongst the various degrees of freedom and the energy associated with each degree of freedom per molecule is  $\frac{1}{2} kT$ , where  $k$  is Boltzman constant.

### • Mean Free Path

Mean free path of a molecule in a gas is the average distance travelled by the molecule between two successive collisions.

If  $\lambda_1, \lambda_2, \lambda_3, \dots, \lambda_N$  be the free paths travelled by the molecule in  $N$  successive collisions. Then, mean free path is given by

$$\lambda = \frac{\lambda_1 + \lambda_2 + \lambda_3 + \dots + \lambda_N}{N} = \left| \frac{1}{\sqrt{2}nd^2n} = \frac{kT}{\sqrt{2}nd^2p} \right|$$

where,  $d \rightarrow$  molecular diameter

$n \rightarrow$  number of molecules per unit volume

$T \rightarrow$  absolute temperature

$P \rightarrow$  pressure

### TEXTBOOK QUESTIONS SOLVED

13.1. Estimate the fraction of molecular volume to the actual volume occupied by oxygen gas at STP. Take the diameter of an oxygen molecule to be  $3 \text{ \AA}$ .

Ans. Diameter of an oxygen molecule,  $d = 3 \text{ \AA} = 3 \times 10^{-10} \text{ m}$ . Consider one mole of oxygen gas at STP, which contain total  $N_A = 6.023 \times 10^{23}$  molecules.

Actual molecular volume of  $6.023 \times 10^{23}$  oxygen molecules

$$\begin{aligned} V_{\text{actual}} &= \frac{4}{3} \pi r^3 \cdot N_A \\ &= \frac{4}{3} \times 3.14 \times (1.5)^3 \times 10^{-3} \times 6.02 \times 10^{23} \text{ m}^3 \\ &= 8.51 \times 10^{-6} \text{ m}^3 \\ &= 8.51 \times 10^{-3} \text{ litre} \quad [\because 1 \text{ m}^3 = 10^3 \text{ litre}] \end{aligned}$$

$\therefore$  Molecular volume of one mole of oxygen

$$V_{\text{actual}} = 8.51 \times 10^{-3} \text{ litre}$$

At STP, the volume of one mole of oxygen

$$V_{\text{molar}} = 22.4 \text{ litre}$$

$$\frac{V_{\text{actual}}}{V_{\text{molar}}} = \frac{8.51 \times 10^{-3}}{22.4} = 3.8 \times 10^{-4} \approx 4 \times 10^{-4}$$

13.2. Molar volume is the volume occupied by 1 mol of any (ideal) gas at standard temperature and pressure (STP : 1 atmospheric pressure,  $0^\circ \text{C}$ ). Show that it is 22.4 litres.

Ans. For one mole of an ideal gas, we have

$$PV = RT \Rightarrow V = \frac{RT}{P}$$

Putting  $R = 8.31 \text{ J mol}^{-1} \text{ K}^{-1}$ ,  $T = 273 \text{ K}$

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

$$\therefore V = \frac{8.31 \times 273}{1.013 \times 10^5} = 0.0224 \text{ m}^3$$

$$= 0.0224 \times 10^6 \text{ cm}^3 = 22400 \text{ ml} \quad [1 \text{ cm}^3 = 1 \text{ ml}]$$

13.3. Following figure shows plot of  $PV/T$  versus  $P$  for  $1.00 \times 10^{-3} \text{ kg}$  of oxygen gas at two different temperatures.

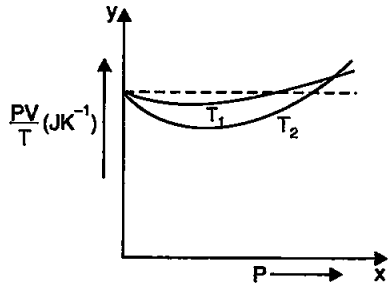
(a) What does the dotted plot signify?

(b) Which is true :  $T_1 > T_2$  or  $T_1 < T_2$ ?

(c) What is the value of  $PV/T$  where the curves meet on the  $y$ -axis?

(d) If we obtained similar plots for  $1.00 \times 10^{-3}$  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  $H_2 = 2.02$  u, of  $O_2 = 32.0$  u,  $R = 8.31$  J mol $^{-1}$  K $^{-1}$ .)

Ans. (a) The dotted plot corresponds to 'ideal' gas behaviour as it is parallel to  $P$ -axis and it tells that value of  $PV/T$  remains same even when  $P$  is changed.



(b) The upper position of  $PV/T$  shows that its value is lesser for  $T_1$ , thus  $T_1 > T_2$ . This is because the curve at  $T_1$  is more close to dotted plot than the curve at  $T_2$ . Since the behaviour of a real gas approaches the perfect gas behaviour, as the temperature is increased.

(c) Where the two curves meet, the value of  $PV/T$  on  $y$ -axis is equal to  $\mu R$ . Since ideal gas equation for  $\mu$  moles is  $PV = \mu RT$

$$\text{where, } \mu = \frac{1.00 \times 10^{-3} \text{ kg}}{32 \times 10^{-3} \text{ kg}} = \frac{1}{32}$$

$$\therefore \text{ Value of } \frac{PV}{T} = \mu R = \frac{1}{32} \times 8.31 \text{ JK}^{-1} = 0.26 \text{ JK}^{-1}$$

(d) If we obtained similar plots for  $1.00 \times 10^{-3}$  kg of hydrogen,

we will not get the same value of  $\frac{PV}{T}$  at the point, where

the curves meet on the  $y$ -axis. This is because molecular mass of hydrogen is different from that of oxygen.

For the same value of  $\frac{PV}{T}$ , mass of hydrogen required is

obtained from

$$\frac{PV}{T} = nR = \frac{m}{2.02} \times 8.31 = 0.26$$

$$m = \frac{2.02 \times 0.26}{8.31} \text{ gram} = 6.32 \times 10^{-2} \text{ gram.}$$

- 13.4. An oxygen cylinder of volume 30 litre has an initial gauge pressure of 15 atmosphere and a temperature of 27 °C. After some oxygen is withdrawn from the cylinder, the gauge pressure drops to 11 atmosphere and its temperature drops to 17 °C. Estimate the mass of oxygen taken out of the cylinder. ( $R = 8.31 \text{ J mol}^{-1} \text{ K}^{-1}$ , molecular mass of  $\text{O}_2 = 32 \text{ u.}$ )

Ans. Initial volume,  $V_1 = 30 \text{ litre} = 30 \times 10^3 \text{ cm}^3$   
 $= 30 \times 10^3 \times 10^{-6} \text{ m}^3 = 30 \times 10^{-3} \text{ m}^3$

Initial pressure,  $P_1 = 15 \text{ atm}$   
 $= 15 \times 1.013 \times 10^5 \text{ N m}^{-2}$

Initial temperature,  $T_1 = (27 + 273) \text{ K} = 300 \text{ K}$

Initial number of moles,

$$\mu_1 = \frac{P_1 V_1}{RT_1} = \frac{15 \times 1.013 \times 10^5 \times 30 \times 10^{-3}}{8.31 \times 300} = 18.3$$

Final pressure,  $P_2 = 11 \text{ atm}$   
 $= 11 \times 1.013 \times 10^5 \text{ N m}^{-2}$

Final volume,  $V_2 = 30 \text{ litre} = 30 \times 10^{-3} \text{ m}^3$

Final temperature,  $T_2 = 17 + 273 = 290 \text{ K}$

Final number of moles,

$$\mu_2 = \frac{P_2 V_2}{RT_2} = \frac{11 \times 1.013 \times 10^5 \times 30 \times 10^{-3}}{8.31 \times 290} = 13.9$$

Number of moles taken out of cylinder

$$= 18.3 - 13.9 = 4.4$$

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  $1.0 \text{ cm}^3$  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.

Ans. Volume of the bubble inside,  $V_1 = 1.0 \text{ cm}^3 = 1 \times 10^{-6} \text{ m}^3$

Pressure on the bubble,  $P_1 =$  Pressure of water

+ Atmospheric pressure

$$= pgh + 1.01 \times 10^5$$

$$= 1000 \times 9.8 \times 40 + 1.01 \times 10^5$$

$$= 3.92 \times 10^5 + 1.01 \times 10^5 = 4.93 \times 10^5 \text{ Pa}$$

Temperature,  $T_1 = 12 \text{ °C} = 273 + 12 = 285 \text{ K}$

Also, pressure outside the lake,  $P_2 = 1.01 \times 10^5 \text{ N m}^{-2}$

Temperature,  $T_2 = 35 \text{ °C} = 273 + 35 = 308 \text{ K}$ , volume  $V_2 = ?$

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

$$\therefore V_2 = \frac{P_1 V_1}{T_1} \cdot \frac{T_2}{P_2} = \frac{4.93 \times 10^5 \times 1 \times 10^{-6} \times 308}{285 \times 1.01 \times 10^5} \\ = 5.3 \times 10^{-6} \text{ m}^3$$

13.6. Estimate the total number of air molecules (inclusive of oxygen, nitrogen, water vapour and other constituents) in a room of capacity  $25.0 \text{ m}^3$  at a temperature of  $27^\circ\text{C}$  and  $1 \text{ atm}$  pressure.

Ans. Here, volume of room,  $V = 25.0 \text{ m}^3$ , temperature,

$$T = 27^\circ\text{C} = 300 \text{ K and}$$

Pressure,

$$P = 1 \text{ atm} = 1.01 \times 10^5 \text{ Pa}$$

According to gas equation,

$$PV = \mu RT = \mu N_A \cdot k_B T$$

Hence, total number of air molecules in the volume of given gas,

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

$$\therefore N = \frac{1.01 \times 10^5 \times 25.0}{(1.38 \times 10^{-23}) \times 300} = 6.1 \times 10^{26}$$

13.7. Estimate the average thermal energy of a helium atom at (i) room temperature ( $27^\circ\text{C}$ ), (ii) the temperature on the surface of the Sun ( $6000 \text{ K}$ ), (iii) the temperature of  $10$  million kelvin (the typical core temperature in the case of a star).

Ans. (i) Here,

$$T = 27^\circ\text{C} = 27 + 273 = 300 \text{ K}$$

$$\text{Average thermal energy} = \frac{3}{2} kT$$

$$= \frac{3}{2} \times 1.38 \times 10^{-23} \times 300 = 6.2 \times 10^{-21} \text{ J.}$$

(ii) At  $T = 6000 \text{ K}$ ,

$$\text{Average thermal energy} = \frac{3}{2} kT$$

$$= \frac{3}{2} \times 1.38 \times 10^{-23} \times 6000 = 1.24 \times 10^{-19} \text{ J.}$$

(iii) At  $T = 10$  million  $\text{K} = 10^7 \text{ K}$

$$\text{Average thermal energy} = \frac{3}{2} kT$$

$$\begin{aligned}
 &= \frac{3}{2} \times 1.38 \times 10^{-23} \times 10^7 \\
 &= 2.1 \times 10^{-16} \text{ J}
 \end{aligned}$$

- 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). Do the vessels contain equal number of respective molecules? Is the root mean square speed of molecules the same in the three cases? If not, in which case is  $v_{rms}$  the largest?

Ans. Equal volumes of all the gases under similar conditions of pressure and temperature contains equal number of molecules (according to Avogadro's hypothesis). Therefore, the number of molecules in each case is same.

The rms velocity of molecules is given by

$$v_{rms} = \sqrt{\frac{3kT}{m}}$$

Clearly

$$v_{rms} \propto \frac{1}{\sqrt{m}}$$

Since neon has minimum atomic mass  $m$ , its rms velocity is maximum.

- 13.9. At what temperature is the root mean square speed of an atom in an argon gas cylinder equal to the rms speed of a helium gas atom at  $-20^\circ\text{C}$ ? (atomic mass of Ar = 39.9 u, of He = 4.0 u).

Ans. Let  $C$  and  $C'$  be the rms velocity of argon and a helium gas atoms at temperature  $T$  K and  $T'$  K respectively.

Here,  $M = 39.9$ ;  $M' = 4.0$ ;  $T = ?$ ;  $T' = -20 + 273 = 253$  K

$$\text{Now, } C = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3RT}{39.9}} \text{ and } C' = \sqrt{\frac{3RT'}{M'}} = \sqrt{\frac{3R \times 253}{4}}$$

Since  $C = C'$

$$\text{Therefore, } \sqrt{\frac{3RT}{39.9}} = \sqrt{\frac{3R \times 253}{4}}$$

$$\text{or } T = \frac{39.9 \times 253}{4} = 2523.7 \text{ K.}$$

- 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  $17^\circ\text{C}$ . Take the radius of a nitrogen molecule to be roughly  $1.0 \text{ \AA}$ . Compare the collision time with the time the molecule moves freely between two successive collisions (Molecular mass of  $\text{N}_2 = 28.0$  u).



Ans. Here,

$$P = 2.0 \text{ atm} = 2 \times 1.013 \times 10^5 \text{ Pa} \\ = 2.026 \times 10^5 \text{ Pa}$$

$$T = 17^\circ\text{C} = 17 + 273 = 290$$

Radius,  $R = 1.0 \text{ \AA} = 1 \times 10^{-10} \text{ m}$ , Molecular mass = 28 u

$$\therefore m = 28 \times 1.66 \times 10^{-27} = 4.65 \times 10^{-26} \text{ kg}$$

Also,  $R = 8.31 \text{ J mol}^{-1} \text{ K}^{-1}$ ,  $k = 1.38 \times 10^{-23} \text{ JK}^{-1}$

Now for one mole of a gas,

$$PV = RT \Rightarrow V = \frac{RT}{P} = \frac{8.31 \times 290}{2.026 \times 10^5}$$

$$\Rightarrow V = 1.189 \times 10^{-2} \text{ m}^3$$

$\therefore$  Number of molecules per unit volume,  $n = \frac{N}{V}$

$$\therefore n = \frac{6.023 \times 10^{23}}{1.189 \times 10^{-2}} = 5.06 \times 10^{25} \text{ m}^{-3}$$

Now, mean free path,

$$\lambda = \frac{1}{\sqrt{2} \pi n d^2} = \frac{1}{\sqrt{2} \pi n (2r)^2} \\ = \frac{1}{1.414 \times 3.14 \times 5.06 \times 10^{25} \times (2 \times 1 \times 10^{-10})^2} \\ = 1.1 \times 10^{-7} \text{ m.}$$

$$\text{Also, } v_{rms} = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3 \times 8.31 \times 290}{28 \times 10^{-3}}} = 5.08 \times 10^2 \text{ ms}^{-1}$$

$\therefore$  Collision frequency,

$$v = \frac{v_{rms}}{\lambda} = \frac{5.08 \times 10^2}{1.1 \times 10^{-7}} = 4.62 \times 10^9 \text{ s}^{-1}$$

Time between successive collisions

$$= \frac{1}{v} = \frac{1}{4.62 \times 10^9} = 2.17 \times 10^{-10} \text{ s}$$

Also the collision time

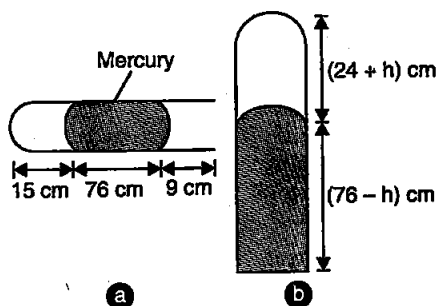
$$= \frac{d}{v_{rms}} = \frac{2 \times 1 \times 10^{-10}}{5.08 \times 10^2} \text{ s} = 3.92 \times 10^{-13} \text{ s.}$$

**13.11.** A meter 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.** When the tube is held horizontally, the mercury thread of length 76 cm traps a length of air = 15 cm. A length of 9 cm of the tube will be left at the open end. The pressure of air enclosed in tube will be atmospheric pressure. Let area of cross-section of the tube be 1 sq. cm.

$$\therefore P_1 = 76 \text{ cm} \quad \text{and} \quad V_1 = 15 \text{ cm}^3$$

When the tube is held vertically, 15 cm air gets another 9 cm of air (filled in the right hand side in the horizontal position) and let  $h$  cm of mercury flows out to balance the atmospheric pressure. Then the heights of air column and mercury column are  $(24 + h)$  cm and  $(76 - h)$  cm respectively.



The pressure of air =  $76 - (76 - h) = h$  cm of mercury.

$$\therefore V_2 = (24 + h) \text{ cm}^3 \quad \text{and} \quad P_2 = h \text{ cm}$$

If we assume that temperature remains constant, then

$$\begin{aligned} P_1 V_1 &= P_2 V_2 \quad \text{or} \quad 76 \times 15 \\ &= h \times (24 + h) \quad \text{or} \quad h^2 + 24h - 1140 = 0 \end{aligned}$$

$$\begin{aligned} \text{or} \quad h &= \frac{-24 \pm \sqrt{(24)^2 + 4 \times 1140}}{2} \\ &= 23.8 \text{ cm} \quad \text{or} \quad -47.8 \text{ cm} \end{aligned}$$

Since  $h$  cannot be negative (because more mercury cannot flow into the tube), therefore  $h = 23.8$  cm.

Thus in the vertical position of the tube, 23.8 cm of mercury flows out.

- 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 of gases, the rate of diffusion of a gas is inversely proportional to the square root of its molecular mass.

If  $R_1$  and  $R_2$  be the rates of diffusion of two gases having molecular masses  $M_1$  and  $M_2$  respectively, then

$$\frac{R_1}{R_2} = \sqrt{\frac{M_2}{M_1}}$$

Now,  $R_1 = 28.7 \text{ cm}^3 \text{ s}^{-1}$ ,  $R_2 = 7.2 \text{ cm}^3 \text{ s}^{-1}$ ,  $M_1 = 2$ ,  $M_2 = ?$

$$\therefore \frac{28.7}{7.2} = \sqrt{\frac{M_2}{2}} \quad \text{or} \quad \frac{M_2}{2} = \frac{28.7 \times 28.7}{7.2 \times 7.2}$$

$$\text{or} \quad M_2 = \frac{2 \times 28.7 \times 28.7}{7.2 \times 7.2} = 31.78 \approx 32$$

This is molecular mass of oxygen. Therefore, the second 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 :

$$n_2 = n_1 \exp [-mg N_A (\rho - \rho') (h_2 - h_1)/(RT)]$$

where  $\rho$  is the density of the suspended particle, and  $\rho'$  that of surrounding medium. [ $N_A$  is Avogadro's number, and  $R$  the universal gas constant.]

[Hint : Use Archimedes principle to find the apparent weight of the suspended particle.]

- Ans.** Considering the particles and molecules to be spherical, the weight of the particle is

$$W = mg = \frac{4}{3} \pi r^3 \rho g \quad \dots(i)$$

where  $r$  = radius of the particle and  $\rho$  = density of the particle. Its motion under gravity causes buoyant force to act upward which is equal to

$$\begin{aligned} B &= \text{Volume of particle} \\ &\times \text{density of the surrounding medium} \times g \\ &= \frac{4}{3} \pi r^3 \rho' g \quad \dots(ii) \end{aligned}$$

If  $F$  be the downward force acting on the particle, then

$$F = W - B = \frac{4}{3} \pi r^3 (\rho - \rho') g \quad \dots(iii)$$

Also 
$$n_2 = n_1 \exp \left[ \frac{-mg}{k_B T} (h_2 - h_1) \right] \quad \dots(iv)$$

where  $k_B$  = Boltzman constant

$n_1$  and  $n_2$  are number densities at heights  $h_1$  and  $h_2$  respectively.

Here  $mg$  can be replaced by effective force  $F$  given by equation (iii).

$\therefore$  From (iii) and (iv), we get

$$\begin{aligned} n_2 &= n_1 \exp \left[ \frac{-\frac{4\pi}{3} r^3 (\rho - \rho')}{k_B T} g (h_2 - h_1) \right] \\ &= n_1 \exp \left[ \frac{-\frac{4\pi}{3} r^3 \rho g \left(1 - \frac{\rho'}{\rho}\right) (h_2 - h_1)}{\left(\frac{RT}{N_A}\right)} \right] \quad \left[ \because k_B = \frac{R}{N_A} \right] \\ n_2 &= n_1 \exp \left[ \frac{-mg N_A \left(1 - \frac{\rho'}{\rho}\right) (h_2 - h_1)}{RT} \right] \end{aligned}$$

which is required relation

where,  $\frac{4}{3} \pi r^3 \rho g$  = mass of the particle  $\times g$  =  $mg$ .

**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 ( $10^3 \text{ Kg m}^{-3}$ )
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

[Hint : Assume the atoms to be 'tightly packed' in a solid or liquid phase, and use the known value of Avogadro's number. You should, however, not take the actual numbers you obtain for various atomic sizes too literally. Because of the crudeness of the tight packing

approximation, the results only indicate that atomic sizes are in the range of a few Å].

**Ans.** In one mole of a substance, there are  $6.023 \times 10^{23}$  atoms

$$\therefore \left(\frac{4}{3}\pi R^3\right) \times 6.023 \times 10^{23} = \frac{M}{\rho}$$

$$\text{or } R = \left[\frac{3M}{4\pi\rho \times 6.023 \times 10^{23}}\right]^{1/3}$$

For carbon,  $M = 12.01 \times 10^{-3}$  kg and  $\rho = 2.22 \times 10^3$  kg m<sup>-3</sup>

$$\begin{aligned} \therefore R &= \left[\frac{3 \times 12.01 \times 10^{-3}}{4 \times 3.14 \times 2.22 \times 10^3 \times 6.023 \times 10^{23}}\right]^{1/3} \\ &= 1.29 \times 10^{-10} \text{ m} = 1.29 \text{ \AA} \end{aligned}$$

For gold,  $M = 197 \times 10^{-3}$  kg and  $\rho = 19.32 \times 10^3$  kg m<sup>-3</sup>

$$\begin{aligned} \therefore R &= \left[\frac{3 \times 197 \times 10^{-3}}{4 \times 3.14 \times 19.32 \times 10^3 \times 6.023 \times 10^{23}}\right]^{1/3} \\ &= 1.59 \times 10^{-10} \text{ m} = 1.59 \text{ \AA} \end{aligned}$$

For nitrogen (liquid)

$M = 14.01 \times 10^{-3}$  kg and  $\rho = 1.00 \times 10^3$  kg m<sup>-3</sup>

$$\begin{aligned} \therefore R &= \left[\frac{3 \times 14.01 \times 10^{-3}}{4 \times 3.14 \times 1.00 \times 10^3 \times 6.023 \times 10^{23}}\right]^{1/3} \\ &= 1.77 \times 10^{-10} \text{ m} = 1.77 \text{ \AA} \end{aligned}$$

For lithium,  $M = 6.94 \times 10^{-3}$  kg,  $\rho = 0.53 \times 10^3$  kg m<sup>-3</sup>

$$\begin{aligned} \therefore R &= \left[\frac{3 \times 6.94 \times 10^{-3}}{4 \times 3.14 \times 0.53 \times 10^3 \times 6.023 \times 10^{23}}\right]^{1/3} \\ &= 1.73 \times 10^{-10} \text{ m} = 1.73 \text{ \AA} \end{aligned}$$

For fluorine (liquid)

$M = 19.00 \times 10^{-3}$  kg,  $\rho = 1.14 \times 10^3$  kg m<sup>-3</sup>

$$\begin{aligned} \therefore R &= \left[\frac{3 \times 19.00 \times 10^{-3}}{4 \times 3.14 \times 1.14 \times 10^3 \times 6.023 \times 10^{23}}\right]^{1/3} \\ &= 1.88 \times 10^{-10} \text{ m} = 1.88 \text{ \AA} \end{aligned}$$

