

- 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 Å.
- Sol. For oxygen,

Molar volume (molecular volume per mole) =  $\left(\frac{4}{3}\pi r^3\right) N = \frac{4}{3}\pi (3 \times 10^{-10})^3 \times 6.023 \times 10^{23}$ One mole of every gas at STP occupies 224 litres i.e.,  $22.4 \times 10^{-3} m^3$ .  $\therefore \frac{\text{Molecular volume}}{\text{Actual volume}} = \frac{4}{3}\pi \frac{(3 \times 10^{-10})^3 \times 6.023 \times 10^{23}}{22.4 \times 10^{-3}} = 30.39 \times 10^{-4}$ 

**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 °C). Show that it is 22.4 litres.

Sol. Here, 
$$P = 1.01 \times 10^{3} \text{ Nm}^{-2}$$
,  $R = 8.3 \text{ J mol}^{-1} \text{ K}^{-1}$ ,  $T = 273.15 \text{ k}$   

$$\therefore V = \frac{\text{RT}}{P} = \frac{8.3 \times 273.15}{1.01 \times 10^{5}} = 22.4 \times 10^{-3} \text{ m}^{3} = 22.4 \text{ lt.}$$

- **13.3** Figure shows plot of PV/T versus P for  $1.00 \times 10^{-3}$  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<sub>2</sub> = 2.02 u, of O<sub>2</sub> = 32.0 u, R = 8.31 J mo1<sup>-1</sup> K<sup>-1</sup>)



- **Sol.** (a) Dotted plot corresponds to ideal gas behaviour.
  - (b)  $T_1 > T_2$
  - (c)  $0.26 \text{ JK}^{-1}$
  - (d) No,  $6.3 \times 10^{-5}$  kg of H<sub>2</sub> would yield the same value.
- **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cylinder of volume 30 litres has an initial gauge pressure of 15 atm and a temperature of 27°C. After some oxygen is withdrawn from the cylinder, the gauge pressure drops to 11 atm and its temperature drops to 17°C. Estimate the mass of oxygen taken out of the cylinder  $(R = 8.31 \text{ J mol}^{-1} \text{ K}^{-1}, \text{ molecular mass of } O_2 = 32 \text{ u}).$
- **Sol.** Given  $V_1 = 30$  litres  $= 30 \times 10^{-3} \text{ m}^3$ ,

 $P_1 = 15 \text{ atm} = 15 \times 1.01 \times 10^5 \text{ Pa}$ 

 $T_1 = 27 + 273 = 300 \text{ K}$ 

Let the cylinder contains  $n_1$  mole of  $O_2$  gas, then

 $P_1V_1 = n_1RT_1$  or  $n_1 = P_1V_1/RT_1$ 

$$n_1 = \frac{(15 \times 1.01 \times 10^5) (30 \times 10^{-3})}{8.3 \times 300} = 18.253$$

 $\therefore$  Initial mass of oxygen in cylinder =  $18.253 \times 32 = 584.1g$ 

When some oxygen is withdrawn, let number of moles of oxygen in cylinder be n<sub>2</sub>.

Now,  $V_2 = 30 \times 10^{-3} \text{ m}^3$ ,  $P_2 = 11 \times 1.01 \times 10^5 \text{ nm}^{-2}$ .  $T_2 = 17 + 273 = 290 \text{ K}$ 

$$\therefore \quad n_2 = \frac{P_2 V_2}{RT_2} = \frac{11 \times 1.01 \times 10^5 \times 30 \times 10^{-3}}{8.3 \times 290} = 13.847$$

- :. Mass of  $O_2$  gas in the cylinder = 13.847 × 32  $m_2 = 443.1$  g
- $\therefore$  Mass of O<sub>2</sub> gas withdrawn from the cylinder = m<sub>1</sub> m<sub>2</sub> = 584.1 443.1 = 141.0g
- **13.5** An air bubble of volume 1.0 cm<sup>3</sup> 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 ?

Sol. At bottom of lake  $V_1 = 1.0 \text{ cm}^3 = 10^{-6} \text{ m}^3$ .  $T_1 = 12^{\circ}\text{C} = 12 + 273 = 285 \text{ K},$ 

 $P_1 = P_{atm} + hdg = 1.01 \times 10^5 + 40 \times 10^3 \times 9.8 = 493000 \text{ Nm}^{-2}.$ 

At the surface of lake,  $T_2 = 35^{\circ}C = 35 + 273 = 308$  K,  $P_2 = P_{atm} = 1.01 \times 10^5$  Nm<sup>-2</sup>. Using gas equation,

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2} \Longrightarrow V_2 = \frac{P_1V_1T_2}{T_1 \cdot P_2} = \frac{493000 \times 1 \times 10^{-6} \times 308}{285 \times 1.01 \times 10^5} = 5.28 \times 10^{-6} \text{ m}^3.$$

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 m<sup>3</sup> at a temperature of 27 °C and 1atm pressure.

Sol. Here, V = 25.0 m<sup>3</sup>, T = 27.0 + 273 = 300 K P = 1.01 × 10<sup>5</sup> Nm<sup>-2</sup>, k = 1.38 × 10<sup>-23</sup> JK<sup>-1</sup>. From relation, PV = nKT n =  $\frac{PV}{VTT} = \frac{1.01 \times 10^5 \times 25.0}{22} = 6.09 \times 10^{26}.$ 

$$n = \frac{1.01 \times 10^{-2.23} \times 22.0}{1.38 \times 10^{-2.3} \times 300} = 6.09 \times 10^{-2.3} \times$$

13.7 Estimate the average thermal energy of a helium atom at (i) room temperature (27°C), (ii) the temperature on the surface of the Sun (6000 K), (iii) the temperature of 10 million kelvin (the typical core temperature in the case of a star).
Sol. (i) Here, T = 27 + 273 = 300 K

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∴ Average thermal energy = 
$$\frac{3}{2}$$
kT  
E =  $\frac{3}{2}$ ×1.38×10<sup>-23</sup>×300 = 6.21×10<sup>-21</sup> J  
(ii) T = 6000 K  
∴ E =  $\frac{3}{2}$ kT =  $\frac{3}{2}$ ×1.38×10<sup>-23</sup>×6000 = 1.24×10<sup>-19</sup> J  
(iii) T = 10×10<sup>16</sup> K

$$\therefore \quad \mathbf{E} = \frac{3}{2} \times 1.38 \times 10^{-23} \times 10^{6} = 2.1 \times 10^{-17} \,\mathrm{J}$$

- 13.8 Three vessels of equal capacity have gases at the same temperature and pressure. The first vessel contains neon (monatomic), the second contains chlorine (diatomic), and the third contains uranium hexafluoride (polyatomic). Do the vessels contain equal number of respective molecules? Is the root mean square speed of molecules the same in the three cases? If not, in which case is v<sub>rms</sub> the largest?
- (a) Yes, all the three vessels contain equal number of molecules. According to Avogadro's Sol. hypothesis, equal volume of all the gases under the same conditions of temperature and pressure equal volumes of all the gases contain equal number of molecules.
  - (b) Root mean square speed is given by  $v_{rms} = \sqrt{\frac{3kT}{M}}$  i.e.,  $v_{rms} \propto \frac{1}{\sqrt{M}}$

As v<sub>rms</sub> is inversely proportional to square root of mass it will not be same in the three cases. It will be largest for the highest gas is neon gas.

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  $-20^{\circ}$ C? (Atomic mass of Ar = 39.9 u, of He = 4.0 u).

$$v_{rms} \propto \sqrt{1}$$
  
 $\frac{(v_{rms})_2}{(v_{rms})_1} = \frac{\sqrt{T_2}}{\sqrt{T_1}}$   
Given  $(v_{rms})_2 = \frac{(v_{rms})_1}{2}$  and  $T_1 = 0 + 273 = 273$  K  
 $\therefore \frac{1}{2} = \sqrt{\frac{T_2}{273}}$  or  $\frac{1}{4} = \frac{T_2}{273}$   
 $T_2 = \frac{273}{4} = 68.25$  K =  $-204.75^{\circ}$ C

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Sol.

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13.10 Estimate the mean free path and collision frequency of a nitrogen molecule in a cylinder containing nitrogen at 2.0atm and temperature 17°C. Take the radius of a nitrogen molecule to be roughly 1.0 Å. Compare the collision time with the time the molecule moves freely between two successive collisions (Molecular mass of  $N_2 = 28.0 \text{ u}$ ). Here, P = 2.0 atm,  $T = 17^{\circ}\text{C} = 17 + 273 = 290 \text{ K}$ ,  $r = 1.0 \text{ Å} = 10^{-10} \text{ m}$ 

Sol. Molecular mass of nitrogen = 28.0 u

Mean free path 
$$\lambda = \frac{KT}{\sqrt{2\pi}d^2P}$$
  
 $d = 2 \times 1.01 \times 10^5 \text{ Nm}^{-2}.$   
 $P = 2 \text{ atm} = 2 \times 1.01 \times 10^{-10} \text{ m}$   
 $\lambda = \frac{1.38 \times 10^{-23} \times 290}{\sqrt{2} \times \frac{22}{7} \times 4 \times 10^{-20} \times 2.02 \times 10^5} = 1.1 \times 10^{-7} \text{ m}$   
Now,  $\frac{N_1}{V_1} = \frac{\text{no. of molecules per mole}}{\text{no. of litres per mole}} = \frac{6.02 \times 10^{23}}{22.4}$  molecules per litre  
 $= \frac{6.02 \times 10^{23}}{22.4 \times 10^{-3}}$  molecules per m<sup>3</sup> = 2.7 × 10^{25} m^{-3} .....(1)

For calculation of number of molecules at 2 atm pressure and 17°C we follow as -

$$\begin{split} & P_1 V_1 = n_1 R T_1 \\ & P_2 V_2 = n_2 R T_2 \end{split}$$

$$\therefore \quad \frac{n_2}{n_1} = \frac{P_2 V_2 T_1}{P_1 V_1 T_2} = \frac{(2 \text{ atm}) (V_1) (273)}{(1 \text{ atm}) (V_1) (273 + 17)} = \frac{2 \times 273}{290} = 1.883 \quad \dots \dots \dots (2)$$

 $n_1$  and  $n_2$  are number of moles of the gas under two different condition's of pressure and temperature.

$$\frac{n_2}{n_1} = \frac{N_2 / V_2}{N_1 / V_1} \text{ or } \frac{N_2}{V_2} = \frac{n_2}{n_1} \times \frac{N_1}{V_1} = 1.883 \times 2.7 \times 10^{25} \text{ [using eq. (1) & (2)]}$$

$$= 5.1 \times 10^{25}$$
Now,  $v_{rms} = \sqrt{\frac{3KT}{M}} = \sqrt{\frac{3 \times 1.38 \times 10^{-23} \times 290}{28.0 \times 1.66 \times 10^{-27}}} = 5.1 \times 10^2 \text{ ms}^{-1}$ 
Collision frequency  $= \frac{v_{rms}}{\lambda} = \frac{5.1 \times 10^2}{1.0 \times 10^{-7}} = 5.1 \times 10^9 \text{ Hz}$ 
Time taken for collision  $= \frac{d}{v_{rms}} = \frac{2 \times 10^{-10}}{5.1 \times 10^2} = 4.0 \times 10^{-13} \text{s}$ 
Time taken between successive collisions
$$\frac{\lambda}{v_{rms}} = \frac{1.1 \times 10^{-7}}{5.1 \times 10^2} = 2 \times 10^{-10} \text{s}$$

$$\therefore \text{ Required ratio} = \frac{\text{Time taken between successive collisions}}{\text{Time taken for collision}} = \frac{2.0 \times 10^{-10}}{4 \times 10^{-13}} = 5000$$

**13.11** A metre long narrow bore held horizontally (and closed at one end) contains a 76 cm long mercury thread, which traps a 15cm column of air. What happens if the tube is held vertically with the open end at the bottom?



h = 23.8 cm. i.e., 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 cm<sup>3</sup> s<sup>-1</sup>. The diffusion of another gas under the same conditions is measured to have an average rate of 7.2cm<sup>3</sup>s<sup>-1</sup>. Identify the gas.
- **Sol.** Here,  $r_1 = 28.7 \text{ cm}^3 \text{ s}^{-1}$  and  $r_2 = 7.2 \text{ cm}^3 \text{ s}^{-1}$ .

According to Grahm's law of diffusion,  $\frac{r_1}{r_2} = \sqrt{\frac{M_2}{M_1}}$ 

where M<sub>1</sub> and M<sub>2</sub> are molecular weights of hydrogen and unknown gas.

$$\therefore \quad M_2 = M_1 \times \left(\frac{r_1}{r_2}\right)^2 = M_1 \left(\frac{28.7}{7.2}\right)^2 = 16M_1, \text{ which is true for Oxygen gas.}$$

**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  $n_2 = n_1 \exp \left[ - mg (h_2 - h_1) / \text{kBT} \right]$ 

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  $\rho$  is the density of the suspended particle, and  $\rho'$  that of surrounding medium. [N<sub>A</sub> is Avogadro's number, and R the universal gas constant.]

Sol. Law of atmospheres states,

$$\mathbf{n}_2 = \mathbf{n}_1 \exp\left[-\frac{\mathbf{mg}}{\mathbf{K}_{\mathrm{B}} \mathbf{T}} (\mathbf{h}_2 - \mathbf{h}_1)\right] \qquad \dots \dots \dots$$

If we consider the sedimentation equilibrium of suspended particles in a liquid, then in place of mg, we will have to take effective weight of the suspended particle.

.. (1)

 $\rho$  = density of particle,  $\rho'$  = density of liquid, m = mass of one suspended particle, m' = mass of equal volume of liquid, V = average volume of a suspended particle. Effective weight of a particle = mg - m'g = mg - V\rho' g

$$= mg - \frac{m}{\rho}\rho'g = mg\left(1 - \frac{\rho'}{\rho}\right) \qquad \dots \dots (2)$$
  
Boltzmann constant, K = R/N .....(3)  
Using eq. (2) and (3) eq. (1) becomes,  
$$n_2 = n_1 \exp\left[-\frac{mgN}{RT}\left(1 - \frac{\rho'}{\rho}\right)(h_2 - h_1)\right]$$

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 $(10^3 \text{ Kg m}^{-3})$
	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
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**Sol.** Density,  $\rho = \frac{m}{\frac{4}{3}\pi r^3}$  or  $r = \left(\frac{3m}{4\pi\rho}\right)^{1/3}$ 

For carbon, m = 12.01 amu =  $12.01 \times 1 \times 1.66 \times 10^{-27}$  kg,  $\rho = 2.22 \times 10^3$  kg m<sup>-3</sup>.

$$\therefore \quad \mathbf{r} = \left[ \frac{3 \times 12.01 \times 1.66 \times 10^{-27}}{4\pi \times 2.22 \times 10^3} \right] = (2145 \times 10^{-30} \text{ m}^3)^{1/3}$$

 $r = 1.29 \times 10^{-10} = 1.29 \text{ Å}, \text{ Similarly for Gold, } r = 1.59 \text{ Å}$ Nitrogen r = 1.77 Å, Lithium r = 1.73 Å, Fluorine r = 1.88 Å