Question 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 3Å.

Answer

Diameter of an oxygen molecule, d = 3Å

Radius, $r = \frac{d}{2} = \frac{3}{2}$ = 1.5 Å = 1.5×10^{-8} cm

Actual volume occupied by 1 mole of oxygen gas at STP = 22400 cm^3

Molecular volume of oxygen gas, $V = \frac{4}{3}\pi r^3 \cdot N$

Where, N is Avogadro's number = 6.023×10^{23} molecules/mole

$$\therefore V = \frac{4}{3} \times 3.14 \times \left(1.5 \times 10^{-8}\right)^3 \times 6.023 \times 10^{23} = 8.51 \text{ cm}^3$$

Ratio of the molecular volume to the actual volume of oxygen $= \frac{8.51}{22400}$

$= 3.8 \times 10^{-4}$

Question 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.

Answer

The ideal gas equation relating pressure (P), volume (V), and absolute temperature (T) is given as:

$PV = nRT$

Where,

R is the universal gas constant = 8.314 J mol^{-1} K^{-1}

n = Number of moles = 1

T = Standard temperature = 273 K

P = Standard pressure = 1 atm = 1.013×10^5 Nm^{-2}

$$\therefore V = \frac{nRT}{P}$$

$$= \frac{1 \times 8.314 \times 273}{1.013 \times 10^5}$$

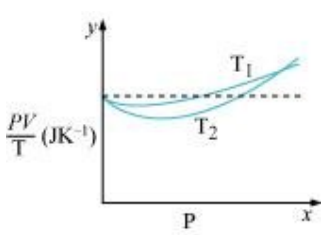
= 0.0224 m^3

= 22.4 litres

Hence, the molar volume of a gas at STP is 22.4 litres.

Question 13.3:

Figure 13.8 shows plot of PV/T versus Pfor 1.00×10^{-3} kg of oxygen gas at two different temperatures.



What does the dotted plot signify?

Which is true: $T_1 > T_2$ or $T_1 < T_2$?

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

If we obtained similar plots for 1.00×10^{-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 mo1^{-1} K^{-1}.)

Answer

The dotted plot in the graph signifies the ideal behaviour of the gas, i.e., the ratio $\frac{PV}{T}$ is equal. μR (μ is the number of moles and R is the universal gas constant) is a constant quality. It is not dependent on the pressure of the gas.

The dotted plot in the given graph represents an ideal gas. The curve of the gas at temperature T_1 is closer to the dotted plot than the curve of the gas at temperature T_2. A real gas approaches the behaviour of an ideal gas when its temperature increases. Therefore, $T_1 > T_2$ is true for the given plot.

The value of the ratio PV/T, where the two curves meet, is μR. This is because the ideal gas equation is given as:

$PV = \mu RT$

$$\frac{PV}{T} = \mu R$$

Where,

P is the pressure

T is the temperature

V is the volume

μ is the number of moles

R is the universal constant

Molecular mass of oxygen = 32.0 g

Mass of oxygen = 1×10^{-3} kg = 1 g

R = 8.314 J mole^{-1} K^{-1}

$$\therefore \frac{PV}{T} = \frac{1}{32} \times 8.314$$

$= 0.26 \text{ J K}^{-1}$

Therefore, the value of the ratio PV/T, where the curves meet on the y-axis, is

0.26 J K^{-1}.

If we obtain similar plots for 1.00×10^{-3} kg of hydrogen, then we will not get the same value of PV/T at the point where the curves meet the y-axis. This is because the molecular mass of hydrogen (2.02 u) is different from that of oxygen (32.0 u).

We have:

$$\frac{PV}{T} = 0.26 \text{ J K}^{-1}$$

$R = 8.314 \text{ J mole}^{-1} \text{ K}^{-1}$

Molecular mass (M) of H_2 = 2.02 u

$$\frac{PV}{T} = \mu R \text{ at constant temperature}$$

$$\text{Where, } \mu = \frac{m}{M}$$

m = Mass of H_2

$$\therefore \quad m = \frac{PV}{T} \times \frac{M}{R}$$

$$= \frac{0.26 \times 2.02}{8.31}$$

$= 6.3 \times 10^{-2}$ g $= 6.3 \times 10^{-5}$ kg

Hence, 6.3×10^{-5} kg of H_2 will yield the same value of PV/T.

Question 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 ($R = 8.31 \text{ J mol}^{-1} \text{ K}^{-1}$, molecular mass of O_2 = 32 u).

Answer

Volume of oxygen, V_1 = 30 litres = 30×10^{-3} m^3

Gauge pressure, P_1 = 15 atm = $15 \times 1.013 \times 10^5$ Pa

Temperature, T_1 = 27°C = 300 K

Universal gas constant, R = 8.314 J $mole^{-1}$ K^{-1}

Let the initial number of moles of oxygen gas in the cylinder be n_1.

The gas equation is given as:

$P_1V_1 = n_1RT_1$

$$\therefore n_1 = \frac{P_1V_1}{RT_1}$$

$$= \frac{15.195 \times 10^5 \times 30 \times 10^{-3}}{(8.314) \times 300} = 18.276$$

But, $n_1 = \frac{m_1}{M}$

Where,

m_1 = Initial mass of oxygen

M = Molecular mass of oxygen = 32 g

$\therefore m_1 = n_1M = 18.276 \times 32 = 584.84$ g

After some oxygen is withdrawn from the cylinder, the pressure and temperature reduces.

Volume, V_2 = 30 litres = 30×10^{-3} m^3

Gauge pressure, P_2 = 11 atm = $11 \times 1.013 \times 10^5$ Pa

Temperature, T_2 = 17°C = 290 K

Let n_2 be the number of moles of oxygen left in the cylinder.

The gas equation is given as:

$P_2V_2 = n_2RT_2$

$$\therefore n_2 = \frac{P_2V_2}{RT_2}$$

$$= \frac{11.143 \times 10^5 \times 30 \times 10^{-3}}{8.314 \times 290} = 13.86$$

But, $n_2 = \frac{m_2}{M}$

Where,

m_2 is the mass of oxygen remaining in the cylinder

$\therefore m_2 = n_2M = 13.86 \times 32 = 453.1$ g

The mass of oxygen taken out of the cylinder is given by the relation:

Initial mass of oxygen in the cylinder – Final mass of oxygen in the cylinder

$= m_1 - m_2$

= 584.84 g – 453.1 g

= 131.74 g

= 0.131 kg

Therefore, 0.131 kg of oxygen is taken out of the cylinder.

Question 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?

<u>Answer</u>

Volume of the air bubble, $V_1 = 1.0\ cm^3 = 1.0 \times 10^{-6}\ m^3$

Bubble rises to height, $d = 40$ m

Temperature at a depth of 40 m, $T_1 = 12°C = 285$ K

Temperature at the surface of the lake, $T_2 = 35°C = 308$ K

The pressure on the surface of the lake:

$P_2 = 1\ atm = 1 \times 1.013 \times 10^5$ Pa

The pressure at the depth of 40 m:

$P_1 = 1\ atm + d\rho g$

Where,

ρ is the density of water $= 10^3\ kg/m^3$

g is the acceleration due to gravity $= 9.8\ m/s^2$

$\therefore P_1 = 1.013 \times 10^5 + 40 \times 10^3 \times 9.8 = 493300$ Pa

We have: $\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$

Where, V_2 is the volume of the air bubble when it reaches the surface

$$V_2 = \frac{P_1V_1T_2}{T_1P_2}$$

$$= \frac{(493300)(1.0 \times 10^{-6})308}{285 \times 1.013 \times 10^5}$$

$= 5.263 \times 10^{-6}\ m^3$ or $5.263\ cm^3$

Therefore, when the air bubble reaches the surface, its volume becomes $5.263\ cm^3$.

Question 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^3 at a temperature of 27 °C and 1 atm pressure.

Answer

Volume of the room, $V = 25.0\ m^3$

Temperature of the room, $T = 27°C = 300\ K$

Pressure in the room, $P = 1\ atm = 1 \times 1.013 \times 10^5\ Pa$

The ideal gas equation relating pressure (P), Volume (V), and absolute temperature (T) can be written as:

$PV = k_B NT$

Where,

K_B is Boltzmann constant = $1.38 \times 10^{-23}\ m^2\ kg\ s^{-2}\ K^{-1}$

N is the number of air molecules in the room

$$\therefore N = \frac{PV}{k_B T}$$

$$= \frac{1.013 \times 10^5 \times 25}{1.38 \times 10^{-23} \times 300} = 6.11 \times 10^{26} \text{ molecules}$$

Therefore, the total number of air molecules in the given room is 6.11×10^{26}.

Question 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).

Answer

At room temperature, $T = 27°C = 300$ K

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

Where k is Boltzmann constant = 1.38×10^{-23} m^2 kg s^{-2} K^{-1}

$\therefore \frac{3}{2}kT = \frac{3}{2} \times 1.38 \times 10^{-38} \times 300$

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

Hence, the average thermal energy of a helium atom at room temperature (27°C) is 6.21×10^{-21} J.

On the surface of the sun, $T = 6000$ K

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

$= \frac{3}{2} \times 1.38 \times 10^{-38} \times 6000$

$= 1.241 \times 10^{-19}$ J

Hence, the average thermal energy of a helium atom on the surface of the sun is 1.241×10^{-19} J.

At temperature, $T = 10^7$ K

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

$= \frac{3}{2} \times 1.38 \times 10^{-23} \times 10^7$

$= 2.07 \times 10^{-16}$ J

Hence, the average thermal energy of a helium atom at the core of a star is 2.07×10^{-16} J.

Question 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_{rms} the largest?

Answer

Yes. All contain the same number of the respective molecules.

No. The root mean square speed of neon is the largest.

Since the three vessels have the same capacity, they have the same volume.

Hence, each gas has the same pressure, volume, and temperature.

According to Avogadro's law, the three vessels will contain an equal number of the respective molecules. This number is equal to Avogadro's number, $N = 6.023 \times 10^{23}$.

The root mean square speed (v_{rms}) of a gas of mass m, and temperature T, is given by the relation:

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

Where, k is Boltzmann constant

For the given gases, k and T are constants.

Hence v_{rms} depends only on the mass of the atoms, i.e.,

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

Therefore, the root mean square speed of the molecules in the three cases is not the same. Among neon, chlorine, and uranium hexafluoride, the mass of neon is the smallest. Hence, neon has the largest root mean square speed among the given gases.

Question 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 °C? (atomic mass of Ar = 39.9 u, of He = 4.0 u).

Answer

Temperature of the helium atom, T_{He} = –20°C= 253 K

Atomic mass of argon, M_{Ar} = 39.9 u

Atomic mass of helium, M_{He} = 4.0 u

Let, $(v_{rms})_{Ar}$ be the rms speed of argon.

Let $(v_{rms})_{He}$ be the rms speed of helium.

The rms speed of argon is given by:

$$(v_{rms})_{Ar} = \sqrt{\frac{3RT_{Ar}}{M_{Ar}}} \quad \ldots (i)$$

Where,

R is the universal gas constant

T_{Ar} is temperature of argon gas

The rms speed of helium is given by:

$$(v_{rms})_{He} = \sqrt{\frac{3RT_{He}}{M_{He}}} \quad \ldots (ii)$$

It is given that:

$(v_{rms})_{Ar} = (v_{rms})_{He}$

$$\sqrt{\frac{3RT_{Ar}}{M_{Ar}}} = \sqrt{\frac{3RT_{He}}{M_{He}}}$$

$$\frac{T_{Ar}}{M_{Ar}} = \frac{T_{He}}{M_{He}}$$

$$T_{Ar} = \frac{T_{He}}{M_{He}} \times M_{Ar}$$

$$= \frac{253}{4} \times 39.9$$

$= 2523.675 = 2.52 \times 10^3$ K

Therefore, the temperature of the argon atom is 2.52×10^3 K.

Question 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 Å. Compare the collision time with the time the molecule moves freely between two successive collisions (Molecular mass of N_2 = 28.0 u).

Answer

Mean free path = 1.11×10^{-7} m

Collision frequency = 4.58×10^9 s^{-1}

Successive collision time ≈ 500 × (Collision time)

Pressure inside the cylinder containing nitrogen, P = 2.0 atm = 2.026×10^5 Pa

Temperature inside the cylinder, T = 17°C =290 K

Radius of a nitrogen molecule, r = 1.0 Å = 1×10^{10} m

Diameter, $d = 2 \times 1 \times 10^{10} = 2 \times 10^{10}$ m

Molecular mass of nitrogen, M = 28.0 g = 28×10^{-3} kg

The root mean square speed of nitrogen is given by the relation:

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

Where,

R is the universal gas constant = 8.314 J mole^{-1} K^{-1}

$$\therefore v_{rms} = \sqrt{\frac{3 \times 8.314 \times 290}{28 \times 10^{-3}}} = 508.26 \text{ m/s}$$

The mean free path (l) is given by the relation:

$$l = \frac{kT}{\sqrt{2} \times d^2 \times P}$$

Where,

k is the Boltzmann constant = 1.38×10^{-23} kg m^2 s^{-2}K^{-1}

$$\therefore l = \frac{1.38 \times 10^{-23} \times 290}{\sqrt{2} \times 3.14 \times \left(2 \times 10^{-10}\right)^2 \times 2.026 \times 10^5}$$

$= 1.11 \times 10^{-7}$ m

Collision frequency $= \frac{v_{rms}}{l}$

$$= \frac{508.26}{1.11 \times 10^{-7}} = 4.58 \times 10^9 \text{ s}^{-1}$$

Collision time is given as:

$$T = \frac{d}{v_{rms}}$$

$$= \frac{2 \times 10^{-10}}{508.26} = 3.93 \times 10^{-13} \text{ s}$$

Time taken between successive collisions:

$$T' = \frac{l}{v_{rms}}$$

$$= \frac{1.11 \times 10^{-7}\,\text{m}}{508.26\ \text{m/s}} = 2.18 \times 10^{-10}\ \text{s}$$

$$\therefore \frac{T'}{T} = \frac{2.18 \times 10^{-10}}{3.93 \times 10^{-13}} \simeq 500$$

Hence, the time taken between successive collisions is 500 times the time taken for a collision.

Question 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?

Answer

Length of the narrow bore, L = 1 m = 100 cm

Length of the mercury thread, l = 76 cm

Length of the air column between mercury and the closed end, l_a = 15 cm

Since the bore is held vertically in air with the open end at the bottom, the mercury length that occupies the air space is: 100 – (76 + 15) = 9 cm

Hence, the total length of the air column = 15 + 9 = 24 cm

Let h cm of mercury flow out as a result of atmospheric pressure.

∴Length of the air column in the bore = 24 + h cm

And, length of the mercury column = 76 – h cm

Initial pressure, P_1 = 76 cm of mercury

Initial volume, V_1 = 15 cm^3

Final pressure, P_2 = 76 – (76 – h) = h cm of mercury

Final volume, $V_2 = (24 + h)\ cm^3$

Temperature remains constant throughout the process.

$\therefore P_1V_1 = P_2V_2$

$76 \times 15 = h\ (24 + h)$

$h^2 + 24h - 1140 = 0$

$$\therefore h = \frac{-24 \pm \sqrt{(24)^2 + 4 \times 1 \times 1140}}{2 \times 1}$$

= 23.8 cm or –47.8 cm

Height cannot be negative. Hence, 23.8 cm of mercury will flow out from the bore and 52.2 cm of mercury will remain in it. The length of the air column will be 24 + 23.8 = 47.8 cm.

Question 13.12:

From a certain apparatus, the diffusion rate of hydrogen has an average value of 28.7 $cm^3\ s^{-1}$. The diffusion of another gas under the same conditions is measured to have an average rate of 7.2 $cm^3\ s^{-1}$. Identify the gas.

[Hint: Use Graham's law of diffusion: $R_1/R_2 = (M_2/M_1)^{1/2}$, where R_1, R_2 are diffusion rates of gases 1 and 2, and M_1 and M_2 their respective molecular masses. The law is a simple consequence of kinetic theory.]

<u>Answer</u>

Rate of diffusion of hydrogen, $R_1 = 28.7\ cm^3\ s^{-1}$

Rate of diffusion of another gas, $R_2 = 7.2\ cm^3\ s^{-1}$

According to Graham's Law of diffusion, we have:

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

Where,

M_1 is the molecular mass of hydrogen = 2.020 g

M_2 is the molecular mass of the unknown gas

$$\therefore M_2 = M_1\left(\frac{R_1}{R_2}\right)^2$$

$$= 2.02\left(\frac{28.7}{7.2}\right)^2 = 32.09 \text{ g}$$

32 g is the molecular mass of oxygen. Hence, the unknown gas is oxygen.

Question 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

$n_2 = n_1 \exp\,[-mg\,(h_2 - h_1)/\,k_BT]$

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:

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

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

<u>Answer</u>

According to the law of atmospheres, we have:

$n_2 = n_1 \exp\,[-mg\,(h_2 - h_1)/\,kBT]$ … (i)

Where,

n_1 is the number density at height h_1, and n_2 is the number density at height h_2

mg is the weight of the particle suspended in the gas column

Density of the medium = ρ'

Density of the suspended particle = ρ

Mass of one suspended particle = m'

Mass of the medium displaced = m

Volume of a suspended particle = V

According to Archimedes' principle for a particle suspended in a liquid column, the effective weight of the suspended particle is given as:

Weight of the medium displaced – Weight of the suspended particle

$= mg - m'g$

$$= mg - V\rho' g = mg - \left(\frac{m}{\rho}\right)\rho' g$$

$$= mg\left(1 - \frac{\rho'}{\rho}\right) \qquad \ldots (ii)$$

Gas constant, R = $k_B N$

$$k_B = \frac{R}{N} \ldots (iii)$$

Substituting equation (*ii*) in place of mg in equation (*i*) and then using equation (*iii*), we get:

$n_2 = n_1 \exp[-mg\,(h_2 - h_1)/\,k_B T]$

$$= n_1 \exp\left[-\, mg\left(1 - \frac{\rho'}{\rho}\right)(h_2 - h_1)\,\frac{N}{RT}\right]$$

$$= n_1 \exp\left[-\, mg\left(\rho - \rho'\right)(h_2 - h_1)\,\frac{N}{RT\rho}\right]$$

Question 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

[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].

Answer

Substance	**Radius (Å)**
Carbon (diamond)	1.29
Gold	1.59
Nitrogen (liquid)	1.77
Lithium	1.73
Fluorine (liquid)	1.88

Atomic mass of a substance = M

Density of the substance = ρ

Avogadro's number = $N = 6.023 \times 10^{23}$

Volume of each atom $= \frac{4}{3}\pi r^3$

Volume of N number of molecules $= \frac{4}{3}\pi r^3 N$ … (*i*)

Volume of one mole of a substance = $\frac{M}{\rho}$ … (*ii*)

$$\frac{4}{3}\pi r^3 N = \frac{M}{\rho}$$

$$\therefore r = \sqrt[3]{\frac{3M}{4\pi\rho N}}$$

<u>For carbon:</u>

$M = 12.01 \times 10^{-3}$ kg,

$\rho = 2.22 \times 10^3$ kg m^{-3}

$$\therefore r = \left(\frac{3 \times 12.01 \times 10^{-3}}{4\pi \times 2.22 \times 10^3 \times 6.023 \times 10^{23}}\right)^{\frac{1}{3}} = 1.29 \text{ Å}$$

Hence, the radius of a carbon atom is 1.29 Å.

<u>For gold:</u>

$M = 197.00 \times 10^{-3}$ kg

$\rho = 19.32 \times 10^3$ kg m^{-3}

$$\therefore r = \left(\frac{3 \times 197 \times 10^{-3}}{4\pi \times 19.32 \times 10^3 \times 6.023 \times 10^{23}}\right)^{\frac{1}{3}} = 1.59 \text{ Å}$$

Hence, the radius of a gold atom is 1.59 Å.

<u>For liquid nitrogen:</u>

$M = 14.01 \times 10^{-3}$ kg

$\rho = 1.00 \times 10^3$ kg m^{-3}

$$\therefore r = \left(\frac{3 \times 14.01 \times 10^{-3}}{4\pi \times 1.00 \times 10^3 \times 6.23 \times 10^{23}} \right)^{\frac{1}{3}} = 1.77 \text{ Å}$$

Hence, the radius of a liquid nitrogen atom is 1.77 Å.

<u>For lithium:</u>

$M = 6.94 \times 10^{-3}$ kg

$\rho = 0.53 \times 10^3$ kg m^{-3}

$$\therefore r = \left(\frac{3 \times 6.94 \times 10^{-3}}{4\pi \times 0.53 \times 10^3 \times 6.23 \times 10^{23}} \right)^{\frac{1}{3}} = 1.73 \text{ Å}$$

Hence, the radius of a lithium atom is 1.73 Å.

<u>For liquid fluorine:</u>

$M = 19.00 \times 10^{-3}$ kg

$\rho = 1.14 \times 10^3$ kg m^{-3}

$$\therefore r = \left(\frac{3 \times 19 \times 10^{-3}}{4\pi \times 1.14 \times 10^3 \times 6.023 \times 10^{23}} \right)^{\frac{1}{3}} = 1.88 \text{ Å}$$

Hence, the radius of a liquid fluorine atom is 1.88 Å.

UNIT IX

BEHAVIOUR OF PERFECT GAS AND KINETIC THEORY

POINTS TO REMEMBER

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

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

- **Average K.E. per molecule** of a gas $\frac{1}{2}mC^2 = \frac{3}{2}k_BT$. It is independent of the mass of the gas but depends upon the temperature of the gas.

- **Absolute zero :** It is that temperature at which the root mean square velocity of the gas molecules reduces to zero.

- **Different types of speed of gas molecules**

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

  $k_B \rightarrow$ Boltzmann's Constant

  (ii) Mean speed or average speed

  $$c_{av} = \frac{c_1 + c_2 + ...c_n}{n} = \sqrt{\frac{8k_B T}{m\pi}}$$

  (iii) Root mean square speed

  $$V_{rms} = \sqrt{\frac{V_1^2 + V_2^2 + ... + V_n^2}{n}} = \sqrt{\frac{3k_BT}{m}}$$

(iv) The number of degrees of freedom = total number of independent co-ordinates required to describe completely the position and configuration of a system.

$f = 3N - k$ For monoatomic gases, f = 3

For diatomic gases, f = 5

For linear triatomic gas molecules, f = 7

For non-linear triatomic gas molecules, f = 6

- According to the **law of equipartition of energy,** for any dynamical system in thermal equilibrium, the total energy is distributed equally amongst all the degrees of freedom. The average energy associated with each molecule per degree of freedom $= \frac{1}{2} k_B T$, where k_B is Boltzmann constant and T is temperature of the system.

- **Mean free path** of gas molecules is the average distance travelled by a molecule between two successive collisions. It is represented by λ.

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

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

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

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

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

- Behaviour of a real gas approaches the ideal gas behaviour for low pressures and high temperatures.

VERY SHORT ANSWER TYPE QUESTIONS (1 MARK)

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

2. If the number of molecule in a container is doubled. What will be the effect on the rms speed of the molecules?

3. Draw the graph between P and 1/V (reciprocal of volume) for a prefect gas at constant temperature.

4. Name the factors on which the degree of freedom of gas depends.

5. What is the volume of a gas at absolute zero of temperature?

6. How much volume does one mole of a gas occupy at NTP?

7. What is an ideal gas?

8. The absolute temperature of a gas is increased 3 times what is the effect on the root mean square velocity of the molecules?

9. What is the Kinetic Energy per unit volume of a gas whose pressure is P?

10. A container has equal number of molecules of hydrogen and carbon dioxide. If a fine hole is made in the container, then which of the two gases shall leak out rapidly?

11. What is the mean translational Kinetic energy of a perfect gas molecule at temperature T?

12. Why it is not possible to increase the temperature of a gas while keeping its volume and pressure constant.

SHORT ANSWER TYPE QUESTIONS (2 MARKS)

1. When an automobile travels for a long distance the air pressure in the tyres increases. Why?

2. A gas storage tank has a small leak. The pressure in the tank drop more quickly if the gas is hydrogen than if it is oxygen. Why?

3. Why the land has a higher temperature than the ocean during the day but a lower temperature at night.

4. Helium is a mixture of two isotopes having atomic masses 3g/mol and 4g/mol. In a sample of helium gas, which atoms move faster on average?

5. State Avogadro's law. Deduce it on the basis of Kinetic theory of gases.

6. Although the velocity of air molecules is nearly 0.5 km/s yet the smell of scent spreads at a much slower rate why.

7. The root mean square (rms) speed of oxygen molecule at certain temperature 'T' is 'V'. If temperature is doubled and oxygen gas dissociates into atomic oxygen what is the speed of atomic oxygen?

8. Two vessels of the same volume are filled with the same gas at the same temperature. If the pressure of the gas in these vessels be in the ratio 1 : 2 then state

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

   (ii) The ratio of the number of molecules.

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

10. A gas is filled in a cylinder fitted with a piston at a definite temperature and pressure. Why the pressure of the gas decreases when the piston is pulled out.

SHORT ANSWER TYPE QUESTIONS (3 MARKS)

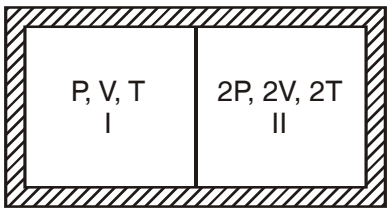
1. On what parameters does the λ (mean free path) depends.

2. Equal masses of oxygen and helium gases are supplied equal amount of heat. Which gas will undergo a greater temperature rise and why?

3. Why evaporation causes cooling?

4. Two thermally insulated vessels 1 and 2 are filled, with air at temperatures (T_1, T_2), volume (V_1, V_2) at pressure (P_1, P_2) respectively. If the value joining the two vessels is opened what is temperature of the vessel at equilibrium.

5. A partition divides a container having insulated walls into two compartments I and II. The same gas fills the two compartment. What is the ratio of the number of molecules in compartments I and II?



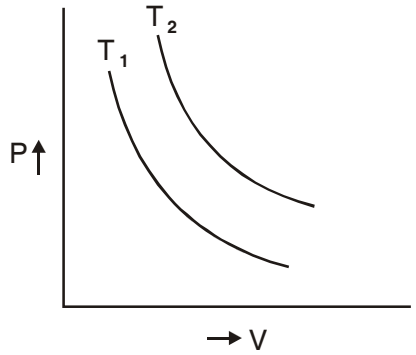
6. Prove that for a perfect gas having n degree of freedom

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

where C_p and C_v have their usual meaning.

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

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



9. Three vessels of equal capacity have gases at the same temperature and pressure. The first vessel contains neon (monatomic) the second contains chlorine (diatomic) and the third contains uranium hexafluoride (polyatomic). Do the vessels contain equal number of respective molecules? Is the root mean square speed of molecules the same in the three cases? If not in which case is V_{rms} the largest?

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

LONG ANSWER TYPE QUESTIONS (5 MARKS)

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.

2. What is meant by mean free path of a gas molecule? Derive an expression for it.

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

4. What do you understand by mean speed, root mean square speed and most probable speed of a gas. The velocities of ten particles in m/s are 0, 2, 3, 4, 4, 4, 5, 5, 6, 9 calculate.

   (i) Average speed (ii) r.m.s. speed

5. What is law of equipartition of energy? Find the value of $\gamma = C_p/C_v$ for diatomic and monatomic gas. Where symbol have usual meaning.

NUMERICALS

1. An air bubble of volume 1.0 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?

2. 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.

3. 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 l mol^{-1} K^{-1}.

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 drop to 17°C. Estimate the mass of oxygen taken out of the cylinder

   (R = 8.31 J mol^{-1} $^{k-1}$)

   (molecular mass of O_2 = 32)

5. At what temperature the rms speed of oxygen atom equal to r.m.s. speed of heliums gas atom at –10°C

   Atomic mass of helium = 4

   Atomic mass of oxygen = 32

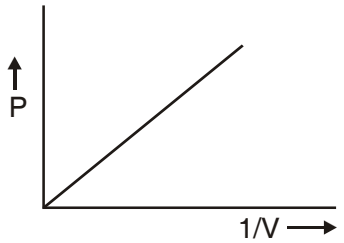
6. Estimate the total number of molecules inclusive of oxygen, nitrogen, water vapour and other constituents in a room of capacity 25.0 m^3 at a temperature of 27°C and 1 atom-pheric pressure.

7. 0.014 kg of nitrogen is enclosed in a vessel at a temperature of 27°C. How much heat has to be transferred to the gas to double the rms speed of its molecules.

ANSWERS (1 MARK)

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

2. No effect

3. 

4. Atomicity and temperature

5. 0

6. 22.4 litre

7. Gas in which intermolecular forces are absent

8. increases $\sqrt{3}$ times

9. 3P/2

10. Hydrogen (rms speed is greater)

11. $\frac{3}{2}RT$

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

    P and V are constant then T is also constant.

ANSWERS (2 MARKS)

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

2. Rate of diffusion of a gas is inversely proportional to the square root of the density. So hydrogen leaked out more rapidly.

3. Specific Heat of water is more than land (earth). Therefore for given heat change in temp. of land is more than ocean (water).

6. The air molecules travel along a zigzag path due to frequent collision as a result their displacement per unit time is very small.

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

   $C^1 = 2V$

8. $P = \frac{1}{3}\frac{mnc^2}{V}$ $\qquad P \alpha nc^2$; $ca\sqrt{T}$

   as the temperature is same rms speeds are same.

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

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

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

ANSWERS (3 MARKS)

1. (i) diameter of molecule (iii) $\gamma \propto \frac{1}{P}$

2. (ii) $\lambda \propto T$ (iv) $\lambda \propto \frac{1}{\int}$ (v) $\lambda \propto \frac{1}{n}$ (iv) $\lambda \propto m$

3. During evaporation fast moving molecules escape a liquid surface so the average kinetic energy of the molecules left behind is decreased thus the temperature of the liquid is lowered.

4. number of mole = Constant

$\mu_1 + \mu_2 = \mu$

$$\frac{P_1V_1}{R\,T_1} + \frac{P_2V_2}{RT_2} = \frac{P(V_1 + V_2)}{RT}$$

from Boyles law $P(V_1 + V_2) = P_1V_1 + P_2V_2$

5. $n = \frac{pV}{kT}$ $\qquad h' = \frac{2p\ 2v}{kT}$

$n / n' = \frac{1}{4}$

8. $T = \frac{PV}{\mu R}$ $T \alpha P V$ (man is constant)(μ is constant)

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

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

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

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

ANSWERS NUMERICALS

1. $v_1 = 10^{-6}m^3$

Pressure on bubble P_1 = water pressure + Atmospheric pressure

$= \rho gh + Patm$

$= 4.93 \times 10^5$ Pa

$T_1 = 285$ k. $T_2 = 308$ k

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$$

$$V_2 = \frac{4.93 \times 10_5 \times 1 \times 10^{-6} \times 308}{285 \times 1.01 \times 10^5} = 5.3 \times 10^{-6} m^3$$

2. According to kinetic theory of gases,

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

At constant temperature, v^2_{rms} is constant. A V is also constant, so $P \propto M$

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

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

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

4. V_1 = 30 litre = 30 × 10^3 cm^3 = 3 × 10^{-2} m^3

P_1 = 15 × 1.013 × 10^5 N/m^2

T_1 = 300 K

$$\mu_1 = \frac{P_1V_1}{RT_1} = 18.3$$

$$\mu_2 = \frac{P_2V_2}{RT_2}$$

P_2 = 11 × 1.013 × 10^5 N/m^2

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

$T_2 = 290\ k$

$\mu_2 = 13.9$

$= 18.3 - 13.9 = 4.4$

Mans of gas taken out of cylinder = 4.4 × 32 g

= 140.8 g

= 0.140 kg.

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

Let r.m.s speed of oxygen is $(Vrms)_1$ and of helium is $(Vrms)_2$ is equal at temperature T_1 and T_2 respectively.

$$\frac{(Vrms)_1}{(Vrms)_2} = \sqrt{\frac{M_2T_1}{M_1T_2}}$$

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

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

6. As Boltzmann's constant,

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

Now $PV = nRT = nk_B\ NT$

∴ The number of molecules in the room

$$= nN = \frac{PV}{Tk_B}$$

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

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

7. Number of mole in 0.014 kg of Nitrogen.

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

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

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

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

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

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