GAS LAWS

1. Boyle's Law

Pressure, volume and temperature are the three parameters which determine the state of a gas. An English physicist Robert Boyle studied the relation between the pressure and the volume of a gas at constant temperature.

Boyle's law states that at any given temperature, the volume of a given mass of gas is inversely proportional to its pressure.

If V and P are the volume and pressure of certain mass of gas, then at constant temperature, according to Boyle's law,

$$V \propto 1/P \quad \therefore PV = \text{ a constant }; \quad i.e., \quad P_1V_1 = P_2V_2.$$

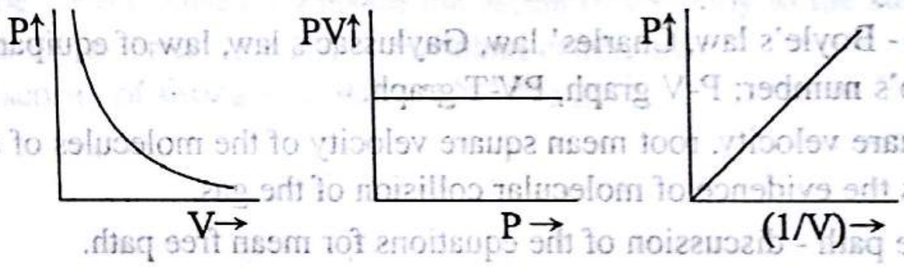

Fig. 1

For a gas, which obeys Boyle's law $P - V$ graph is a hyperbola, $PV - P$ graph is a straight line parallel to the P-axis and $P - 1/V$ graph is a straight line inclined to (1/V) axis.

Note: It can be seen that at high temperature and low pressure (large volume), the agreement between observed pressure-volume relationship and Boyle's law is good. When the volume is large (*i.e.*, low density), the molecules are far apart. Hence any effects due to forces between them are small. Thus all gases behave alike in this region. As the temperature is decreased, the gas tends to become liquid.

A gas which obeys Boyle's law at all temperatures is called an *ideal gas or a perfect gas.*

Strictly speaking there is no gas which obeys Boyle's law for a wide range of pressure and temperature.

But it is found that a gas obeys Boyle's law strictly at a certain temperature called *Boyle temperature*, which is different for different gases.

2. Charle's Laws

(a) Gay-Lussac law

For a given mass of gas, at constant pressure, the volume is directly proportional to its absolute temperature.

i.e., $V \propto T$; or $V/T =$ a constant $\therefore V_1/T_1 = V_2/T_2$

(b) For a given mass of a gas, at constant volume, the pressure is directly proportional to its absolute temperature.

i.e., $P \propto T$ $\therefore P/T =$ a constant , *i.e.,* $P_1/T_1 = P_2/T_2$

3. Avogadro's hypothesis

Equal volumes of all gases under the same pressure and temperature contain equal number of molecules.

4. Law of equipartition of energy

Total energy of a dynamical system in thermal equilibrium is equally divided among its degrees of freedom.

$$\text{Energy per degree of freedom} = (1/2)\,kT;$$

where $k = R/N$, the Boltzmann's constant and T the absolute temperature of the gas.

Note: For degrees of freedom and specific heat of gases, refer Chapter XII, page 438.

5. Graham's law of diffusion

At constant pressure, rate of diffusion (r) of a gas is inversely proportional to the square root of its density (ρ).

$$i.e.,\ r \propto 1/\sqrt{\rho}$$

6. Dalton's law of partial pressures

Total pressure of a mixture of non-reacting gases contained in the same vessel is equal to the sum of the pressures which each gas would exert if it is contained alone in the vessel.

If $P_1, P_2, P_3, \cdots$ are the partial pressures of the individual gases in a mixture of gases contained in a vessel, then, the total pressure,

$$P = P_1 + P_2 + P_3 + \cdots$$

Consider a mixture of ideal gases; μ_1 mole of gas 1, μ_2 mole of gas 2, etc. in a vessel of volume V at pressure P and temperature T. Using the perfect gas equation, $PV = \mu RT$, we get,

$$PV = (\mu_1 + \mu_2 + \ldots)RT$$

$$\therefore P = \frac{\mu_1 RT}{V} + \frac{\mu_2 RT}{V} + \ldots = P_1 + P_2 + \cdots$$

Thus we get Dalton's law of partial pressures.

Examples

X.1. The density of water is 10^3 kg m^{-3}. The density of water vapour at 100°C and 1 atm pressure is 0.6 kg m^{-3}. Estimate the fraction of molecular volume (i.e., the volume of all the molecules added) to the total volume occupied by the water vapour under the above conditions of temperature and pressure. [NCERT]

Since the molecules of a solid or liquid are closely packed, the density of a water molecule can be taken as 10^3 kg m^{-3}, the density of water. Let us estimate the volume of a water molecule.

$$\text{Mass of 1 mole of water } (H_2O) = 2 + 16 = 18\ g = 18 \times 10^{-3}\text{kg}$$

$$\text{Number of molecules of 1 mole of water} = 6 \times 10^{23}, \text{ the Avogadro's number}$$

$$\therefore \quad \text{Mass of a molecule of water} = 18 \times 10^{-3}/6 \times 10^{23} = 3 \times 10^{-26}\text{kg}$$

$$\therefore \quad \text{Volume of a water molecule} = m/d = \frac{3 \times 10^{-26}}{10^3} = 3 \times 10^{-29}\text{m}^3$$

Now, let us calculate the total actual volume of molecules in 0.6 kg of water. Consider 1 m^3 of water vapour.

$$\text{Total volume occupied by 0.6 kg of water vapour, } V = 1\text{ m}^3$$

$$\text{Mass of a molecule of water} = 3 \times 10^{-26}\text{ kg}$$

$$\text{Number of molecules in 0.6 kg of water} = 0.6/3 \times 10^{-26} = 2 \times 10^{25}$$

$$\text{Volume of a molecule} = 3 \times 10^{-29}\text{ m}^3$$

$$\therefore \quad \text{Volume of } 2 \times 10^{25} \text{ molecules, } x = 3 \times 10^{-29} \times 2 \times 10^{25} = 6 \times 10^{-4}\text{ m}^3$$

$\therefore$ Fraction of molecular volume to the total volume occupied

$$= \frac{x}{V} = \frac{6 \times 10^{-4}}{1} = 6 \times 10^{-4}.$$

X.2. Estimate the fraction of molecular volume to the actual volume occupied by oxygen gas at STP. (Radius of an oxygen molecule = 3 Å) [NCERT]

Consider 1 mole of oxygen. Let v be the volume of the molecules in 1 mole of oxygen and V the volume of 1 mole of oxygen gas.

$r = 3\text{ Å} = 3 \times 10^{-10}$ m; $\quad V = 22.4\ l = 22.4 \times 10^{-3}\text{m}^3$;

$N = 6.023 \times 10^{23}$; $\quad v/V = ?$

$$v = (4/3)\pi r^3 \times N = \frac{4 \times 3.14 \times (3 \times 10^{-10})^3 \times 6.023 \times 10^{23}}{3} = 6.81 \times 10^{-5}\text{m}^3$$

$$V = 22.4 \times 10^{-3}\text{ m}^3 \qquad \therefore v/V = \frac{6.81 \times 10^{-5}}{22.4 \times 10^{-3}} = 3.0 \times 10^{-3}$$

Perfect gas equation

According to Boyle's law, $P \propto 1/V$ (i)

According to Charles law, $P \propto T$ $\therefore P \propto T/V$ $\therefore \frac{PV}{T} = R$, a constant (ii)

This constant R is known as the gas constant. Its value depends on the mass of the gas. If one mole of a gas is considered, then the gas constant is the same for all gases and is known as the *universal gas constant.*

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

If the mass of gas is μ moles, $\mathbf{PV = \mu RT}$

Note: If one kilogram of a gas is considered, the gas constant is called ordinary gas constant r. It is different for different gases. Unit of ordinary gas constant is $\text{J kg}^{-1}\text{K}^{-1}$.

$$\therefore PV = rT$$

If mass is m kg, $\mathbf{PV = mrT}$

If ρ is the density of the gas, the ordinary gas constant,

$$r = PV/T = \mathbf{P/\rho T}$$

At STP, for air , $P = 1.013 \times 10^5\ \text{Nm}^{-2}$; $\rho = 1.293\ \text{kgm}^{-3}$; $T = 273\ \text{K}$

$$r = 1.013 \times 10^5/1.293 \times 273 = \mathbf{286.97\ J\ kg^{-1}K^{-1}}$$

Relation between universal gas constant and ordinary gas constant

Universal gas constant = ordinary gas constant × molecular mass of the gas

Avogadro's number

In 1811, John Dalton, a contemporary of Avogadro, suggested that the molecules of a given chemical substance are all alike. This hypothesis, since confirmed by an overwhelming variety of evidences, makes it easy to understand why, in chemical reactions, compounds combine with each other in definite proportion by mass. It also leads directly to the concept of molecular mass and number of moles. Specifically, one mole of any pure chemical compound contains a definite number of molecules, the same number for all compounds.

The number of molecules in a mole of a gas is called Avogadro's number, N.

Thus, 0.012 kg of C^{12} contains N atoms, the mass of one C^{12} atom is $12 \times 1.6605 \times 10^{-27}$ kg.

$$\therefore N = \frac{0.012}{12 \times 1.6605 \times 10^{-27}} = 6.023 \times 10^{23}\ \text{mol}^{-1}$$

Kinetic theory of Gases

A gas is made up of a large number of tiny particles called molecules. These molecules are in a state of random motion. Molecules have a diameter of about 2×10^{-10} m and the distance between them in a gas is about ten times larger than its diameter. Hence the molecules can be thought of as moving about relatively free. German physicist R. Clausius and Scottish physicist J. C. Maxwell showed that the state of a gas and in particular the equation of state could be explained in terms of the motion of the molecules which make up the gas. The theory is based on certain basic assumptions or postulates. They are given below. Kinetic theory of gases was suggested to explain gas laws and to derive perfect gas equation.

Postulates of kinetic theory of gases

1. The molecules of a gas are hard, smooth and perfectly elastic spheres.
2. The molecules are supposed to be point masses, the size of a molecule being negligible compared to the distance between them.
3. There is no force of attraction or repulsion between molecules.
4. The molecules are in a state of random motion, moving with all possible velocities in all possible directions.
5. During their motion they collide with one another and also on the walls of the containing vessel. These collisions are elastic.
6. Between successive collisions, the molecules move in straight lines with uniform velocity. The distance travelled between two successive collisions is called free path. Average distance between successive collisions is known as *mean free path* λ.
7. Time spent in a collision is negligibly small compared to the time taken to traverse mean free path.
8. The mean kinetic energy of the molecule is a constant at a given temperature and is proportional to the absolute temperature. *i.e.*, $KE \propto T$.

Kinetic interpretation of pressure exerted by a gas

According to the kinetic theory of gases, the molecules of a gas are in random motion. During their motion, they collide each other and with the walls of the container. As they collide with the walls of the container, they exert force and hence pressure.

Thus it follows from the kinetic theory that the pressure exerted by a gas may be defined as the total momentum imparted to unit area of the walls of the container per second due to molecular impacts on the walls.

Kinetic interpretation of temperature of a gas

According to the postulates of kinetic theory of gases, the average kinetic energy of a molecule of the gas is directly proportional to the absolute temperature (T) of the gas.

$$i.e., \overline{\text{K.E}} \propto T.$$

Hence, *the temperature of a gas is a measure of the average kinetic energy of the molecules of the gas.*

Root mean square (rms) velocity of a molecule

According to the kinetic theory of gases, the molecules of a gas are in random motion. So, the average velocity of the molecules is zero. Hence we find the rms velocity of a molecule.

If $c_1, c_2, c_3, \ldots, c_n$ are the velocities of the molecules of a gas at any instant, the mean square velocity of the molecules of the gas is,

$$\overline{c^2} = \frac{c_1^2 + c_2^2 + c_3^2 + \cdots + c_n^2}{n}$$

Hence root mean square velocity of a molecule is,

$$c_{rms} = \sqrt{\frac{c_1^2 + c_2^2 + c_3^2 + \cdots + c_n^2}{n}}$$

Expression for the pressure exerted by a gas

Consider a gas inside a cubical vessel of unit side. Let m be the mass of a molecule and n be the total number of molecules in the vessel. W_1 and W_2 are two opposite walls of the vessel perpendicular to the X-axis.

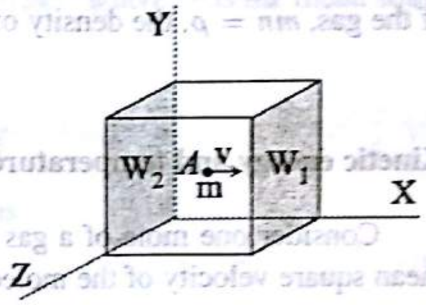

Fig. 2

Consider a molecule A moving in the X-direction with a velocity v towards the wall W_1. It hits the wall W_1 with the velocity v and rebounds with the same velocity v as the collision is perfectly elastic.

Momentum of the molecule A before collision $= mv$

Momentum of the molecule A after collision $= -mv$

Change in momentum of the molecule A due to a single collision on the wall W_1 $= -mv - mv$

$= -2mv$

$\therefore$ Change in momentum of the wall W_1 due to a single collision of the single molecule A $= 2mv$

Since the distance between the walls W_1 and W_2 is unity, the molecule A travels v times between the walls in one second.

$\therefore$ Number of collisions of the molecule A with the wall W_1 in one second $= \frac{v}{2}$

Hence, rate of change of momentum of the wall W_1; *i.e.*, the force exerted by the single molecule A on the wall W_1 $= 2mv \times \frac{v}{2} = mv^2$

Now let us consider the combined effect of the collisions of all molecules on the wall W_1. All the n molecules in the vessel are not moving along the X-axis between the walls W_1 and W_2. Since there are only three independent directions X, Y and Z, it is reasonable to assume that, at any instant, there may be $n/3$ molecules moving along the X-axis between the walls W_1 and W_2.

$\therefore$ Force exerted by the molecules on the wall $W_1 = (1/3)mnv^2$

As pressure exerted by two gases are equal, $P_1 = P_2$

$$\therefore (1/3)n_1 m_1 \overline{c_1^2} = (1/3)n_2 m_2 \overline{c_2^2} \quad (2)$$

Since the temperature is the same, the average KE of translation per molecule is the same.

$$\therefore (1/2)m_1 \overline{c_1^2} = (1/2)m_2 \overline{c_2^2} \quad (3)$$

From equations (2) and (3), $\mathbf{n_1 = n_2}$

This is *Avogadro's hypothesis.*

Expressions for the rms velocity [c_{rms} or $\overline{c}$]

(i) From the kinetic theory of gases, the pressure exerted by a gas is given by,

$$P = (1/3)\rho\overline{c^2}; \quad \mathbf{c_{rms}} = \sqrt{\mathbf{3P/\rho}}$$

(ii) $P = (1/3)\rho\overline{c^2}$; If M is the mass of the gas which occupies a volume V; $\rho = M/V$.

$$\therefore P = (1/3)(M/V)\overline{c^2} \quad \therefore PV = (1/3)\,M\overline{c^2} \quad (i)$$

But $PV = RT \therefore RT = (1/3)\,M\overline{c^2}$

$$\therefore \mathbf{c_{rms}} = \sqrt{\mathbf{3RT/M}}$$

If R is the universal gas constant, M is the mass of 1 mol of the gas (in kg)

$$\therefore c_{rms} \propto \sqrt{T} \quad \textit{i.e.}, (\mathbf{c_1/c_2})_{\mathbf{rms}} = \sqrt{\mathbf{T_1/T_2}}$$

Mean free path λ

The molecules of a gas have finite size and they are constantly in motion. During their motion they collide with one another and also on the walls of the vessel. The path covered by a molecule between any two successive collisions is a straight line and is called *free path.* The length of a free path is a matter of chance. The average of all these free paths is called *mean free path.* It is the mean distance travelled by a molecule between two successive collisions. It can be shown that the mean free path is given by the equation, $\lambda = \frac{1}{\sqrt{2}\pi d^2 n}$, where 'd' is the diameter of the molecule and 'n' the number of molecules per unit volume.

Note: (Derivation of the expression for mean free path λ)

Let the molecules of the gas be assumed to be spheres of diameter d. A collision between two molecules will take place if the distance between their centres is d. Assume that only the molecule A is in motion while all other molecules are at rest. Imagine a cylindrical tube of radius d and length l. If the molecule A moves along the axis of the tube, it collides with all those molecules whose centres lie inside the cylinder.

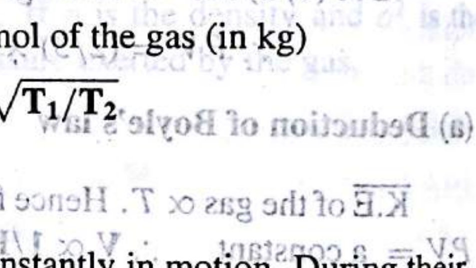

Fig. 3

Volume of the cylinder $= \pi d^2 l$

If n is the number of molecules per unit volume of the gas, then

the number of collisions of A = the number of molecules inside the cylinder

$$= \pi d^2 l \times n = \pi d^2 l n$$

Distance travelled by $A = l$

$$\therefore \quad \lambda = \frac{\text{Distance travelled}}{\text{Number of collision}} = \frac{l}{\pi d^2 l n} = \frac{1}{\pi d^2 n}$$

This equation was deduced by Clausius. In the above derivation, we have assumed that all, but one, molecules are at rest. But this assumption is not correct. Actually all molecules are in random motion. So the chances of collisions by a molecule is greater. Taking this into consideration, Maxwell derived the expression,

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

From the gas equation, $PV = RT$

$$\therefore R = \frac{PV}{T} = \frac{1.013 \times 10^5 \times 22.4 \times 10^{-3}}{273}$$
$$= 8.31 \text{ J mol}^{-1}\text{K}^{-1}$$

X.4. An air bubble of volume 1.0 cm^3 rises from the bottom of a lake 40 m deep at a temperature 12°C. To what volume does it grow when it reaches the surface which is at a temperature of 35°C. **[NCERT]**

$V_1 = 1 \text{ cm}^3 = 1 \times 10^{-6} \text{ m}^3$; $T_1 = 273 + 12 = 285 \text{ K}$

P_1 = Atmospheric pressure + pressure of 40 m of water column

$= 1.013 \times 10^5 + 40 \times 1000 \times 9.8 = 1.013 \times 10^5 + 3.92 \times 10^5$

$= 4.933 \times 10^5 \text{ Nm}^{-2}$

$P_2 = 1.013 \times 10^5$; $T_2 = 273 + 35 = 308 \text{ K}$; $V_2 = ?$

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

$$\therefore V_2 = \frac{P_1 V_1 T_2}{T_1 P_2} = \frac{4.933 \times 10^5 \times 1 \times 10^{-6} \times 308}{285 \times 1.013 \times 10^5}$$
$$= \mathbf{5.26 \times 10^{-6} \text{ m}^3}$$

X.5. Estimate the total number of air molecules (inclusive of oxygen, nitrogen, water vapour and other constituents) in a room of capacity 25 m^3 at a temperature of 27°C and 1 atm pressure. ($k = 1.38 \times 10^{-23} \text{ JK}^{-1}$) **[NCERT]**

$P = 1.013 \times 10^5 \text{ Nm}^{-2}$; $V = 25 \text{ m}^3$; $T = 273 + 27 = 300 \text{ K}$

$PV = nkT$; where n is the number of molecules of the air.

$$n = \frac{PV}{kT} = \frac{1.013 \times 10^5 \times 25}{1.38 \times 10^{-23} \times 300} = \mathbf{6.12 \times 10^{26}}$$

X.6. Estimate the average thermal energy of a helium molecule at (i) room temperature (27°C), (ii) the temperature on the surface of Sun (6000 K) and (iii) the temperature of 10 million kelvin. Given $k = 1.38 \times 10^{-23} \text{ JK}^{-1}$ **[NCERT]**

Average thermal energy of a molecule is given by $\frac{3}{2}kT$.

(*i*) Energy at 27°C $= \frac{3}{2} \times 1.38 \times 10^{-23} \times 300 = \mathbf{6.21 \times 10^{-21} \text{ J}}$

(*ii*) Energy at 6000 K $= \frac{3}{2} \times 1.38 \times 10^{-23} \times 6000 = \mathbf{1.24 \times 10^{-19} \text{ J}}$

(*iii*) Energy at 10^7 K $= \frac{3}{2} \times 1.38 \times 10^{-23} \times 10 \times 10^6 = \mathbf{2.07 \times 10^{-16} \text{ J}}$

X.7. A flask contains argon and chlorine in the ratio 2 : 1 by mass. The temperature of the mixture is 27°C. Obtain the ratio of (i) average kinetic energy per molecule and (ii) ratio of root mean square speed (v_{rms}) of the molecules of the two gases. Atomic mass of argon = 39.9; Molecular mass of chlorine = 70.9 **[NCERT]**

(i) The average kinetic energy per molecule of a gas depends only on the temperature. It does not depend on the nature of the gas. Since the argon and chlorine in the flask are at the same temperature, the ratio of the average kinetic energy per molecule of the gases will be 1 : 1

(ii) The average K.E. of a molecule $= \frac{1}{2} m\overline{c^2} = \frac{3}{2} kT$

since T is a constant, $\overline{KE}$ for Ar = KE for Cl_2 $\therefore \frac{1}{2} m_{Ar}\overline{c^2}_{Ar} = \frac{1}{2} m_{Cl_2}\overline{c^2}_{Cl_2}$

$$\frac{\overline{c^2}_{Ar}}{\overline{c^2}_{Cl_2}} = \frac{m_{Cl_2}}{m_{Ar}} = \frac{70.9}{39.9} = 1.78$$

$$\therefore \left(\frac{c_{Ar}}{c_{Cl_2}}\right)_{rms} = \sqrt{1.78} = \mathbf{1.33}$$

X.8. Calculate the rms velocity of hydrogen at STP given its density at STP $= 8.99 \times 10^{-2}\ \text{kgm}^{-3}$

Standard atmospheric pressure $= P = 1.013 \times 10^5\ \text{Nm}^{-2}$

Density $= \rho = 8.99 \times 10^{-2}\ \text{Kgm}^{-3}$

$$c_{rms} = \sqrt{\frac{3P}{\rho}} = \sqrt{\frac{3 \times 1.013 \times 10^5}{8.99 \times 10^{-2}}} = \mathbf{1839\ ms^{-1}}$$

X.9. Calculate the r.m.s. velocity of a gas at 300 K given its molecular mass = 32 and $R = 8.3\ \text{J mol}^{-1}\text{K}^{-1}$.

$M = 0.032\ \text{kg};\ R = 8.3\ \text{J mol}^{-1}\text{K}^{-1};\ T = 300\ \text{K}$

$$\bar{c} = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3 \times 8.3 \times 300}{0.032}} = \mathbf{483.15\ ms^{-1}}$$

X.10. At what temperature will the rms velocity of hydrogen be double its value at STP when pressure remains constant.

Let x be the rms velocity of hydrogen at STP ($T_1 = 273$ K). Let T_2 be the temperature at which rms velocity becomes double (*i.e.*, $2x$)

$$c_{rms} \propto \sqrt{T} \quad \therefore x \propto \sqrt{T_1} \text{ and } 2x \propto \sqrt{T_2} \quad \therefore \frac{2x}{x} = \sqrt{\frac{T_2}{T_1}}$$

$$\therefore T_2 = 4 \times T_1 = 4 \times 273 = \mathbf{1092\ K}$$

X.11. At what temperature will oxygen molecules have the same rms velocity as hydrogen molecules at 60°C. Molecular mass of hydrogen and oxygen are 2 and 32 respectively.

$$c_{rms} = \sqrt{\frac{3RT}{M}};\quad T_1 = 60°\text{C} = 333\ \text{K};\quad M_H = 0.002\ \text{kg};$$

$$M_O = 0.032\ \text{kg};\quad T_2 = ?$$

$$(c_{rms})_H = \sqrt{\frac{3RT_1}{M_H}};\quad (c_{rms})_O = \sqrt{\frac{3RT_2}{M_O}}$$

Let the rms velocity of hydrogen at T_1 K is equal to that of oxygen at T_2 K.

$$\text{Then } \sqrt{\frac{3RT_1}{M_H}} = \sqrt{\frac{3RT_2}{M_0}}; \quad \frac{T_1}{M_H} = \frac{T_2}{M_0}$$

$$\therefore T_2 = T_1 \frac{M_0}{M_H} = \frac{333 \times 0.032}{0.002} = \mathbf{5328\,K}$$

X.12. ***A vessel contains two non-reacting gases neon (mono-atomic) and oxygen (diatomic). The ratio of their partial pressures is 3 : 2. Estimate (a) the ratio of the number of molecules and (b) the ratio of the mass density of neon and oxygen in the vessel. Atomic mass of Neon = 20.2. Molecular mass of $O_2 = 32$. [NCERT]**

Partial pressure of a gas in a mixture is the pressure it would have exerted for the same volume and temperature if it alone occupied the vessel.

$$P_1 V = \mu_1 RT; \quad P_2 V = \mu_2 RT$$

$$\frac{P_1}{P_2} = \frac{\mu_1}{\mu_2} = \frac{3}{2}$$

$$\text{But, } \mu_1 = \frac{N_1}{N}; \quad \mu_2 = \frac{N_2}{N};$$

where N_1 and N_2 are the number of molecules and N, the Avogadro number

$$(a) \therefore \frac{N_1}{N_2} = \frac{\mu_1}{\mu_2} = \mathbf{\frac{3}{2}}$$

(*b*) If m_1 and m_2 are the masses of neon and oxygen, $\mu_1 = \frac{m_1}{M_1}$ and $\mu_2 = \frac{m_2}{M_2}$, where M_1 and M_2 are the molecular masses of neon and oxygen.

If ρ_1 and ρ_2 are their mass densities,

$$\frac{\rho_1}{\rho_2} = \frac{m_1/V}{m_2/V} = \frac{m_1}{m_2} = \frac{\mu_1 M_1}{\mu_2 M_2} = \frac{3}{2} \times \frac{20.2}{32} = \mathbf{0.947}$$

X.13. **Molar volume of an ideal gas is the volume occupied by 1 mole of the gas at STP. Show that it is 22.4 litre. [NCERT]**

By the gas equation , $PV = \mu RT$

When $\mu = 1$, $V =$ Volume of 1 mole of the gas

$$V = \frac{RT}{P} = \frac{8.3 \times 273}{1.013 \times 10^5}$$

$$= 2.239 \times 10^{-2}\,m^3 = \mathbf{22.39\ litre}$$

X.14. **An oxygen cylinder of volume 30 litre has an initial pressure of 15 atm and temperature 27°C. After some oxygen is withdrawn from the cylinder the pressure drops to 11 atm and temperature to 17°C. Estimate the mass of oxygen taken out of the cylinder. R=8.3 J mol^{-1} K^{-1}. Molecular mass = 32. [NCERT]**

$$P_1 = 15 \times 1.013 \times 10^5\,Nm^{-2}; \; V_1 = 30 \times 10^{-3}\,m^3, \quad T_1 = 300\,K$$

$$PV = \mu RT \quad \mu = \frac{PV}{RT}$$

Let μ_1 be the number of moles of oxygen initially present.

$$\mu_1 = \frac{PV}{RT} = \frac{15 \times 1.013 \times 10^5 \times 30 \times 10^{-3}}{8.3 \times 300} = 18.3$$

Initial mass of oxygen $= 18.3 \times 0.032 = 0.586\,\text{kg}$

Let μ_2 be the number of moles of oxygen left.

$$\mu_2 = \frac{11 \times 1.013 \times 10^5 \times 30 \times 10^{-3}}{8.3 \times 290} = 13.85$$

Final mass of oxygen $= 13.85 \times 0.032 = 0.443\,\text{kg}$

Mass of gas taken out $= 0.586 - 0.443 = \mathbf{0.143\,kg}$

IMPORTANT POINTS

1. *Boyle's law:* $P_1V_1 = P_2V_2$ *(at constant temperature).*
2. *Charles laws: (a) Gay – Lussac law* $V_1/T_1 = V_2/T_2$ *(at constant pressure) (b)* $P_1/T_1 = P_2/T_2$ *(at constant volume)*
3. *Energy per degree of freedom* $= (1/2)kT$;

   $k = R/N = 1.38 \times 10^{-23}\ \text{J K}^{-1}$, *the Boltzmann's constant.*
4. *Ideal gas equation:*

$$PV = RT \text{ (for 1 mole of a gas)}$$

$$PV = \mu RT \quad \text{(for } \mu \text{ mole of the gas)}$$

$PV = nkT$ *(n = number of molecules of the gas)*

$$\therefore P_1V_1/T_1 = P_2V_2/T_2; \quad R = 8.31\ \text{J/mol/K}$$

5. $P = (1/3)mn\overline{c^2} = (1/3)\rho\overline{c^2}$
6. $\bar{c} = \sqrt{3P/\rho} = \sqrt{3RT/M}$; *P should be in* Nm^{-2} *(Pa)*

$$1\ \text{atm} = 1.013 \times 10^5\ \text{Pa}$$

$$\overline{v} = \sqrt{\frac{8RT}{\pi M}}; \quad v_p = \sqrt{\frac{2RT}{M}}$$

7. $\overline{\text{K.E}}$ *of a molecule* $= (3/2)kT$

   $\overline{\text{K.E}}$ *of 1 mole of a gas* $= (3/2)RT$
8. $\lambda = 1/\sqrt{2}\pi d^2 n$
9. *Maxwellian distribution law:* $n(v) = 4\pi N(m/2\pi kT)^{3/2}v^2e^{-mv^2/2kT}$

D. Essays

1. State the important postulates of kinetic theory of gases. Derive an expression for the pressure exerted by a gas.
2. Derive expressions for (a) *rms* velocity and (b) kinetic energy of a molecule of a gas.
3. Discuss briefly the Maxwellian speed distribution. From this obtain expression for mean velocity, *rms* velocity and most probable velocity of the molecules of a gas.

E. Problems

1. Calculate the rms velocity of methane molecules present in the atmosphere of Jupiter whose atmospheric temperature is $-130°C$. Molecular mass of methane = 16; $R = 8.3\ J\ mol^{-1}K^{-1}$.

   [Ans: $471.8\ ms^{-1}$]

2. If the rms velocity of hydrogen molecule at STP is $1.84 \times 10^3\ ms^{-1}$, calculate the rms velocity of oxygen at STP [Molecular mass of hydrogen and oxygen are 2 and 32 respectively].

   [Ans: $460\ ms^{-1}$]

3. Calculate the kinetic energy of 0.002 kg of helium at 200 K. $R = 8.3\ J\ mol^{-1}\ K^{-1}$.

   [Ans: 1.245×10^3 J]

4. At what temperature, the pressure remaining constant, will the r.m.s. velocity of a gas be half its value at 273 K?

   [Ans: 68.25 K]

5. The mean kinetic energy of a molecule of hydrogen at 0°C is 5.64×10^{-21} J and $R = 8.3\ J\ mol^{-1}K^{-1}$. Calculate Avogadro number.

   [Ans: $6.023 \times 10^{23}\ mol^{-1}$]

6. At what temperature will the average speed of oxygen molecules be sufficient to escape from the earth? Given escape velocity of earth = $11.1\ kms^{-1}$, mass of oxygen molecule = 5.34×10^{-26} kg, $k = 1.38 \times 10^{-23}\ JK^{-1}$.

   [Hint: $(3/2)\,kT = \frac{1}{2}mv_e^2$]

   [Ans: 1.6×10^5 K]

7. Calculate the temperature at which the rms velocity of gas molecules is double the value at 27°C, pressure remaining constant.

   [Ans: 927°C]

8. Given Boltzmann's constant = $1.38 \times 10^{-23}\ JK^{-1}$, calculate the kinetic energy of translation of an oxygen molecule at 300 K

   [Ans: 6.21×10^{-21} J]

9. At what temperature is the *rms* speed of an atom of argon gas equal to the *rms* speed of a helium gas atom at $-20°C$? (Atomic mass of Ar = 39.9 u, of He = 4.04) [NCERT]

   Hint: $\sqrt{T_1/M_1} = \sqrt{T_2/M_2}$

   [Ans: 2.52×10^3 K]