States of Matter

Gases, Liquids and Solids

ANALYSIS OF IDEAL GASES Section - 1

In this section, we are going to study laws governing the behavior of gases. Gases don't have definite shape and volume. They tend to fill all the space available to them and take on the shape and volume of the container. In gases, the molecules are relatively far apart and thus influence each other to a lesser extent *(than they do so in solids and liquids).*

Three fundamental measurements that we can perform on any sample of a gas are :

Volume, Pressure and Temperature

Volume :

The volume of any sample of a gas is considered to be the space of the container that it occupies *(the space occupied by the molecules of gas is negligible as compared to the volume of container)*. The volume is expressed in liters (or ml) or m^3 (or cm^3).

$$1\text{ L} \equiv 10^3\text{ ml} \equiv 10^{-3}\text{ m}^3 \equiv 1\text{ dm}^3 \equiv 10^3\text{ cc}$$

Pressure :

The molecules of gases are in continuous random motion. They frequently collide with each other and with the walls of the container. The collisions of the molecules with the walls of the container give rise to what is called as the **Pressure**. It is measured as force per unit area and is uniform in all the directions. It is measured by instruments: **Manometer** and **Barometer** (for atmospheric pressure). It is expressed in N/m^2 or mm of Hg or atmospheres (atm) or torr.

$$1\text{ atm} = 1.013 \times 10^5\text{ N/m}^2 \equiv 1.013 \times 10^5\text{ Pa} \qquad \left(1\text{Pa} = 1\text{N/m}^2\right)$$

$$1\text{ bar} = 10^5\text{ N/m}^2$$

$$1\text{ atm} = 760\text{ mm of Hg column} = 76\text{ cm of Hg column} = 760\text{ torr} = 1.013\text{ bar}$$

Temperature :

The temperature can be discussed in terms of **hotness** or **coldness**. The measurement is based on the expansion of certain material (most often it is mercury) with increasing temperature.

One of the scale to measure the temperature is taken as **Celsius (°C) scale**. The freezing point of water is taken as 0 °C and its boiling point as 100 °C.

It was observed by Gay Lussac that the rise in volume of a given mass of gas for each degree rise in temperature is nearly equal to 1/273 times of the volume of gas at 0 °C. If V_o is the volume of gas at 0 °C and V_T is the volume of gas at T °C, then :

$$V_T = V_o\left(1 + \frac{T}{273}\right)$$

Thus, $V_T = 0$ if $T = -273$ °C i.e., the volume of a given mass of a gas is zero at constant pressure or we can say that the gas would completely disappear if $T = -273$ °C.

So T = –273 °C (or more precisely –273.15 °C) is the lowest possible temperature that can be achieved (since below – 273 °C, the volume will be negative, which is impossible). This temperature **– 273.15 °C** is called as **absolute zero**. Now a new scale called as **absolute scale** or **Kelvin scale** is defined where **–273 °C = 0 K (Kelvin).**

Note : 0 K = –273 °C or 273 K = 0 °C or 373 K = 100 °C

Also, $T(^\circ F) = 32 + \frac{9}{5} \times T(^\circ C)$ [°F ≡ Fahrenheit]

Standard Temperature and Pressure conditions (S.T.P.) :

For gases, the S.T.P. conditions are 273 K (0 °C) and 1 atm pressure. A gas at this temperature is said to be at S.T.P. (or N.T.P. ≡ Normal Temperature and Pressure) conditions.

Definition of Ideal Gas :

A gas is said to be an ideal gas if it has the following properties :

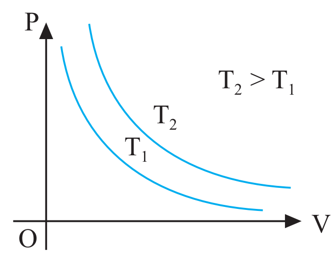
(a) There is no intermolecular forces between the gas molecules, i.e., gas molecules don't exert any kind of force on each other.

(b) Size of the gas molecules is negligible as compared to the volume occupied by the gas (i.e., container volume).

Note : The concept of Ideal gas is theoretical and no gas exists which satisfy the above requirements at all the conditions. Thus, all the gases are Real gases but they may behave as ideal under certain conditions of Pressure, Volume and Temperature.

Gas Laws (For Ideal gases only) :

Boyle's Law :



At a constant temperature (T), the pressure (P) of a given mass (or moles (n)) of any gas varies inversely with the volume (V).

Mathematically : $P \propto \frac{1}{V}$ (for given n and T)

$\Rightarrow$ **PV = constant**

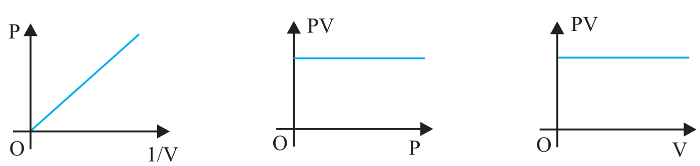
If P_1 is the pressure when volume is V_1 and P_2 is the pressure when volume is V_2 (T is same), then :

$$P_1 V_1 = P_2 V_2$$

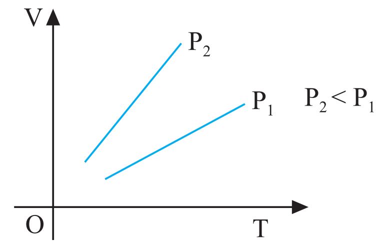
Graphically, it can be represented as shown in the figure. Each line is called as **Isotherm**.

Note : In the P-V curve, as we move away from origin, each isotherm represents a higher temperature.

Boyle's law can also be represented using following graphs :



Charles Law :



At a constant pressure, the volume of a given mass of any gas varies directly with the absolute temperature.

Mathematically : $V \propto T$ (for a given n and P)

$\Rightarrow \quad \dfrac{V}{T} = \text{constant}$

If V_1 and V_2 are volumes of a gas at temperature T_1 and T_2 respectively and the pressure is kept constant, then :

$\Rightarrow \quad \dfrac{V_1}{T_1} = \dfrac{V_2}{T_2}$

Graphically it is expressed as shown in the figure.

Each line is called as **Isobar**.

Note : In the V-T curve, an isobar with lesser slope will have a higher pressure.

The Combined Gas Law :

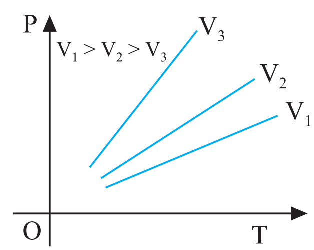
For any sample of an ideal gas, the pressure times the volume divided by the absolute temperature is a constant.

Mathematically : $\dfrac{PV}{T} = \text{constant}$

If at one condition, for a given mass of a gas P_1, V_1 and T_1 are pressure, volume and temperature respectively and at some other condition P_2, V_2 and T_2 are new pressure, volume and temperature respectively then :

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

Gay Lussac's Law :



The pressure of a given mass of any gas is directly proportional to the absolute temperature at constant volume.

Mathematically : $P \propto T$ (for constant n and V)

$\Rightarrow \quad \dfrac{P}{T} = \text{constant}$

If P_1 and P_2 are pressures of a gas at temperature T_1 and T_2 respectively and the volume is kept constant, then :

$\Rightarrow \quad \dfrac{P_1}{T_1} = \dfrac{P_2}{T_2}$

Graphically it is expressed as follows. Each line is called as **Isochor**.

Note that slope is greater for lower volume.

Note : In the P-T curve, an isochor with lesser slope will have a higher volume.

Gay Lussac's Law of Combining Volumes :

When measured at same temperature and pressure, the ratios of volumes of the gases that were reactants and of gases that were products (in a chemical reaction), were always small whole numbers.

Illustration :

(a) $2\,H_{2\,(g)} + O_{2\,(g)} \rightarrow 2\,H_2O_{\,(g)}$

2 volumes 1 volume 2 volumes **(ratio = 2 : 1 : 2)**

(b) $N_{2\,(g)} + O_{2\,(g)} \rightarrow 2\,NO_{\,(g)}$

1 volume 1 volume 2 volumes **(ratio = 1 : 1 : 2)**

(c) $CH_{4\,(g)} + 2\,O_{2\,(g)} \rightarrow CO_{2\,(g)} + 2\,H_2O_{\,(g)}$

1 volume 2 volume 1 volume 2 volume **(ratio = 1 : 2 : 1 : 2)**

Avogadro's Law :

It states that equal volume of all gases at same pressure and temperature contain equal number of molecules.

We know that 1 mole contains 6.023×10^{23} molecules (a number called as **Avogadro Number**). It is obvious that if two gases contain equal number of molecules, they must also contain the same number of moles. So, at given temperature and pressure, the volume of any gas is also proportional to the number of moles.

$\Rightarrow$ $V \propto n$ (at given T and P) *This is also a form of Avogadro's Law.*

At any given temperature and pressure, there must be some volume that will contain 6.023×10^{23} molecules or 1 mole of a gas. At S.T.P. (0°C and 1 atm), this volume is 22.4 L or 22400 mL. This is known as **Molar volume**.

Avogadro's Law can be used in determination of molecular masses of gases. As 1 mole of any gas at S.T.P. occupies 22.4 L, we can calculate the molecular weight of a gas as follows :

If M_o be the molecular weight of a gas A weighing g_A grams and occupying V_L of volume at S.T.P., then :

$$M_o = \frac{g_A \times 22.4}{V_L\,(\text{at S.T.P.})}$$

Also, $M_o = (\text{density in g/L}) \times 22.4$

The Ideal Gas Equation :

We know that $\dfrac{PV}{T} = \text{constant} = K$

The constant K depends upon the amount of gas. Now at constant P and T, V depends upon number of moles of gas (*Avogadro Law*). This implies that K is directly proportional to the number of moles (n).

$\Rightarrow$ $K \propto n$ $\Rightarrow$ $K = nR$ R : a constant independent of amount of gas.

$\Rightarrow$ $\dfrac{PV}{T} = K = nR$ $\Rightarrow$ $PV = nRT$

This is called as **ideal gas equation**. *R* is same for all gases and is known as *universal gas constant*.

Values of R :

Note : $R = \dfrac{PV}{nT}$

(i) $R = 0.0821 \dfrac{L\,atm}{mol.K}$ (use this value when P is in atm. and V is in L)

(ii) $R = 8.31 \dfrac{J}{mol.K}$ (use this value when P is in N/m^2 and V is in m^3) [This is the S.I. unit of R]

(iii) $R = 2 \dfrac{cal}{mol.K}$ (4.184 J = 1 cal)

Different forms of Ideal Gas Equation :

(i) $PV = nRT$

(ii) $PV = \dfrac{g}{M_0} RT$

(iii) $PM_0 = dRT$ (density d = g/V)

Illustrating the concept :

When 3.2 gm of sulphur is vapourised at 450 °C and 723 mm pressure, the vapour occupies a volume of 780 cm^3, what is the formula for the sulphur under these conditions ?

The molecular weight of a poly-atomic element = number of atoms × atomic mass

So let us find the molecular weight of **S** from the data given.

$$M_0 = \frac{gRT}{PV} = \frac{3.2 \times 0.0821 \times 723}{(723/760) \times (780/1000)} = 256$$

$\Rightarrow$ Number of atoms $= \dfrac{256}{32} = 8$

Hence, molecular formula of sulphur = S_8

Vapour Density :

It is defined as the ratio of the mass of the gas (X) occupying a certain volume at a certain temperature and pressure to the mass of hydrogen occupying the same volume at the same temperature and pressure.

$$\text{Now, } PV = nRT = \frac{g}{M_0} \times RT \Rightarrow g_X = \frac{PVM_0}{RT}$$

$$\text{and } g_{H_2} = \frac{PV \times 2}{RT} \quad [\because \; M_0 = 2 \text{ for } H_2 \text{ gas}]$$

$$\Rightarrow \frac{g_X}{g_{H_2}} = \frac{M_X}{2} = \text{vapour density}$$

Thus, it can be seen that vapour density of a gas does not depend on pressure or temperature or volume.

Dalton's Law of Partial Pressures :

Total pressure of a mixture of number of **non-reacting gases** is equal to the sum of pressures exerted by individual gases.

$$P_{Total} = p_1 + p_2 + p_3 + p_4 + ...$$

where P_{Total} : Total pressure of the mixture and p_1, p_2, p_3, p_4,... are the partial pressures exerted by individual gases in the mixture.

Assumption : All the gases spread uniformly to occupy the volume of the vessel.

The **partial pressure** is defined as the pressure a gas would exert if it were alone in the container at the same temperature of the mixture.

Let p_1, p_2 be the partial pressures of gases 1 and 2 present in the mixture and n_1 and n_2 be their respective moles. Let V be the volume of the container and T be the temperature at which the gases are mixed.

Then, using Gas Equation, we have : $P_1 = n_1 \dfrac{RT}{V}$ ... (i) and $P_2 = n_2 \dfrac{RT}{V}$ ... (ii)

Using Dalton's Law :

$$P_{Total} = P_1 + P_2$$

$$\Rightarrow \quad P_{Total} = n_1 \frac{RT}{V} + n_2 \frac{RT}{V}$$

$$\text{or} \quad P_{Total} = (n_1 + n_2) \frac{RT}{V} \quad \text{... (iii)}$$

From (i), (ii) and (iii), it can be seen that :

$$P_1 = \frac{n_1}{n_1 + n_2} P_{Total} \quad \text{and} \quad P_2 = \frac{n_2}{n_1 + n_2} P_{Total}$$

$$\text{or} \quad P_1 = \chi_1 P_{Total} \quad \text{and} \quad P_2 = \chi_2 P_{Total}$$

where χ_1 and χ_2 are the mole fractions of gases 1 and 2 respectively.

So in general, ***Partial pressure of a gas in a mixture = Its mole fraction in the mixture × Total pressure exerted by the mixture***

Also, % of a gas in the mixture (by moles) = $\dfrac{\text{Its partial pressure}}{\text{Total pressure}} \times 100 \equiv (\text{mole fraction of that gas}) \times 100$

Illustrating the concept :

A 2.5L flask contains 0.25 mol each of SO_2 and CO_2 gas at 27°C. Calculate the partial pressure exerted by each gas and total pressure .

Now, Partial pressure of SO_2 = $n_{SO_2} \dfrac{RT}{V_{vessel}}$

$$= 0.25 \frac{RT}{V_{vessel}} = \frac{0.25 \times 0.0821 \times 300}{2.5} = 2.46 \text{ atm}$$

and Partial pressure of $CO_2 = n_{CO_2} \dfrac{RT}{V_{vessel}}$

$$= 0.25 \frac{RT}{V_{vessel}} = \frac{0.25 \times 0.0821 \times 300}{2.5} = 2.46 \text{ atm}$$

$\Rightarrow \quad P_{Total} = 2.46 + 2.46 = 4.92 \text{ atm}$

Application of Dalton's Law of Partial Pressure

Many gases in the laboratory are collected by the downward displacement of water. The gas collected in this way also contains molecules of water that have been evaporated into the gas. The pressure exerted by these molecules depends on the temperature of water. The partial pressure of water in the gas mixture collected is called the *aqueous tension* and is equal to the vapour pressure of water at that temperature.

$\Rightarrow \quad$ Pressure of the dry gas obtained $\equiv P_{dry\ gas} = P_{observed} -$ Aqueous tension

Note : Pressure of air decreases with the increase in altitude (height from the sea level).

Illustrating the concept :

6.52 gm of a sample of oxygen is collected over water at a total pressure of 735.5 torr measured 5.45L at a temperature of 27 °C. Find the vapour pressure of water vapours.

Using gas equation, calculate the pressure of the gas and then subtract it from the pressure of the gas measured (observed).

$$P = \frac{gRT}{M_0 V} = \frac{6.52 \times 0.0821 \times 300}{32 \times 5.45} = 0.92 \text{ atm.} = 699.8 \text{ mm of Hg} \qquad [\because 1 \text{ atm} \equiv 760 \text{ mm of Hg}]$$

Now this is pressure of dry gas, hence

Vapour pressure of water $= 735.5 - 699.8 = 35.7$ mm of Hg

Illustrating the concept :

Assume that the air is essentially a mixture of nitrogen and oxygen in mole ratio of 4 : 1 by volume. Calculate the partial pressures of N_2 and O_2 on a day when the atmospheric pressure is 750 mm of Hg. Neglect the pressure of other gases.

From Dalton's Law of partial pressure, we have :

Partial pressure of nitrogen $= p_{N_2} = \chi_{N_2} \times P$ and Partial pressure of oxygen $= p_{O_2} = \chi_{O_2} \times P$

Now, $\chi_{N_2} = 4/5$, and $\chi_{O_2} = 1/5$; $P = 750$ mm of Hg

$\Rightarrow \quad p_{N_2} = \dfrac{4}{5} \times 750 = 600$ mm of Hg

and $\quad p_{O_2} = \dfrac{1}{5} \times 750 = 150$ mm of Hg

Illustrating the concept :

One of the best rocket fuels is dimethyl hydrazine (an organic compound with molecular formula : $(CH_3)_2N_2H_2$). When mixed with dinitrogen tetroxide, N_2O_4, it reacts according to the equation :

$$(CH_3)_2 N_2H_2(l) + 2N_2O_4 (l) \longrightarrow 3N_2(g) + 4H_2O(l) + 2CO_2(g)$$

If 2.5 mol of dimethyl hydrazine reacts completely with N_2O_4 and if the product gases are collected at 20°C in a 250 L vessel, what is the pressure in the vessel?

From stiochiometry of above reaction : 1 mol $(CH_3)_2N_2H_2 \equiv 3$ mol $N_2 \equiv 4$ mol $H_2O \equiv 2$ mol CO_2

Moles of N_2 formed $= 3 \times 2.5 = 7.5$

Moles H_2O formed $= 4 \times 2.5 = 10$ [H_2O will not exert any pressure at 20°C as it will become a liquid]

Moles CO_2 formed $= 2 \times 2.5 = 5$

$$\Rightarrow \quad P_{Total} = \frac{n_{Total}RT}{V} = \frac{(7.5 + 5.0) \times 0.0821 \times 293}{250} = 1.20 \text{ atm}$$

Illustrating the concept :

When 2 gm of a gaseous substance A is introduced into an initially evacuated flask at 25°C, the pressure is found to be 1 atm. 3 gm of another gaseous substance B is then added to it at the same temperature and pressure. The final pressure is found to be 1.5 atm. Assuming ideal gas behaviour, calculate the ratio of the molecular weights of A and B.

Let M_A and M_B be the molecular weights of A and B.

Using PV = nRT for A, we get :

$$1 = \frac{\frac{2}{M_A}RT}{V} \qquad \text{......(i)}$$

and using *Dalton's Law* : $P_{Total} = \frac{(n_A + n_B)RT}{V} \Rightarrow 1.5 = \frac{\left(\frac{2}{M_A} + \frac{3}{M_B}\right)RT}{V}$ ......(ii)

Solving (i) and (ii), we get : $\frac{M_A}{M_B} = \frac{1}{3}$

Graham's Law of Diffusion :

A gas expands to fill the entire container even if other gas(es) is (are) already present in the container. This process of spreading of gas is called as **diffusion**. A gas confined to a container at high pressure than the surrounding atmosphere will escape from a small hole which is opened in the container until the pressure outside and inside have been equalized. This process is called as **effusion**.

Example of effusion: Escaping of air through a punctured tyre.

Note : The process of effusion is always followed by the process of diffusion.

According to Graham's Law :

When compared at the same temperature and pressure, the rates of diffusion (or effusion) of any two gases are inversely proportional to the square roots of their densities.

$$\text{rate} \propto \frac{1}{\sqrt{\text{density}}}$$

Note : This is why lighter gases diffuse faster than the denser gases.

It t_1, t_2 are the time required for the passage of the same volume, V_m, of two gases with densities d_1 and d_2 respectively at the same temperature and pressure, through the same orifice, then:

$$\text{Rate of effusion } (r) = \frac{\text{Volume effused}}{\text{Time taken}} = \frac{V_m}{t}$$

$$\Rightarrow \qquad r_1 = \frac{V_m}{t_1} \text{ and } r_2 = \frac{V_m}{t_2}$$

$$\text{By Graham's Law : } \frac{r_1}{r_2} = \frac{V_m / t_1}{V_m / t_2} = \sqrt{\frac{d_2}{d_1}} = \sqrt{\frac{M_2}{M_1}} \qquad \Rightarrow \qquad \frac{t_2}{t_1} = \sqrt{\frac{d_2}{d_1}} = \sqrt{\frac{M_2}{M_1}}$$

(*Densities of gases at given temperature and pressure are proportional to molecular weights*)

It has been found that the rate of diffusion (r) is also proportional to the pressure of a gas (or number of molecules) at a given temperature. In that case, the rate of diffusion is given as :

$$r \propto \frac{P}{\sqrt{d}}$$

If two gases 1 and 2 at different pressures P_1 and P_2 respectively are allowed to effuse through a small hole in a container, then the ratio of rates of diffusion of two gases is given by:

$$\frac{r_1}{r_2} = \frac{P_1}{P_2}\sqrt{\frac{d_2}{d_1}} = \frac{P_1}{P_2}\sqrt{\frac{M_2}{M_1}}$$

Note : Rate of effusion (r) can be defined in the following ways (depending on the analysis of a problem):

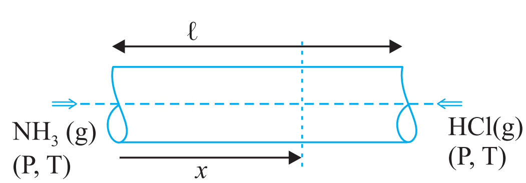
(i) $r = \frac{\text{Volume effused}}{\text{time taken}} \equiv \frac{\text{distance travelled in a tube}}{\text{time taken}}$ (if the cross sectional area is uniform).

(ii) $r = \frac{\text{moles effused}}{\text{time taken}} = \frac{\Delta n}{\Delta t}$

(iii) $r = \frac{\text{Drop in Pressure due to effusion}}{\text{time taken}} = \frac{\Delta P}{\Delta t}$

Illustrating the concept :

As shown in the figure, NH_3(g) and HCl (g) are introduced in a cylindrical container of uniform crossection. At what distance from NH_3 inlet, will NH_4Cl form ?



Using Graham's law :

$$\frac{r_{NH_3}}{r_{HCl}} = \frac{x/t}{(\ell - x)/t} = \sqrt{\frac{M_{HCl}}{M_{NH_3}}} = \sqrt{\frac{36.5}{17}} \approx 1.46$$

$$\Rightarrow \quad x = \ell\left[\frac{\sqrt{M_{HCl}/M_{NH_3}}}{1+\sqrt{M_{HCl}/M_{NH_3}}}\right] = 0.59\,\ell$$

Ammonia will diffuse faster than hydrogen chloride gas.

Application of Graham's Law of diffusion :

- Separation of isotopes and other gaseous mixture is based on this law.
- It provides a method for the determination of molar mass.

Effective molecular weight of the mixture effusing out through a hole:

Let a container A contains 3 moles of He and 2 moles of N_2 at some temperature and pressure. Suppose the container has a hole through which this gaseous mixture is effusing out.

Let us first calculate the effective molecular mass of the mixture present initially in the container.

From the very definition of molecular mass, we have :

Molecular mass is the mass of an element or compound contained in 1 mole of that element or compound.

Now, total mass of 3 moles He and 2 moles N_2 (i.e., mass of the gas mixture)

$$\equiv 3 \times 4 + 2 \times 28 = 68 \text{ gm.}$$

And the total moles of gas mixture $= 3 + 2 = 5$

Thus, molecular mass of the mixture $\equiv M_{mix} = \frac{68}{5} = 13.6$ gm/mole

We can generalize the above result as :

$$\Rightarrow \quad M_{mix} \equiv \sum_{i=1}^{n} \chi_i M_i$$

where χ_i is the mole fraction of the i^{th} gas in the mixture and M_i is the molar mass of the i^{th} gas in that mixture.

Now, to find the M_{mix} of the gas mixture effusing out, we have to determine the relative rates of effusion of the mixture components.

$$\Rightarrow \quad \frac{r_{He}}{r_{N_2}} = \frac{P_{He}}{P_{N_2}}\sqrt{\frac{M_{N_2}}{M_{He}}} \equiv \frac{n_{He}}{n_{N_2}}\sqrt{\frac{M_{N_2}}{M_{He}}}$$

$\Rightarrow \quad \dfrac{r_{He}}{r_{N_2}} = \dfrac{3}{2}\sqrt{\dfrac{28}{4}} = 3.97$

$\Rightarrow$ In the mixture effusing out : $\left(\dfrac{\text{moles He}}{\text{moles } N_2}\right)_{at\ t=0} = 3.97$

$\Rightarrow$ Mole fraction of N_2 effusing out at $t = 0 = \dfrac{\text{moles } N_2}{\text{moles } N_2 + \text{moles He}}$

$$= \frac{1}{1+3.97} = \frac{1}{4.97} = 0.2$$

$\Rightarrow \quad \chi_{N_2} = 0.2$ and $\chi_{He} = 1 - \chi_{N_2} = 0.8$

$\Rightarrow \quad M_{mix} = \chi_{He}\, M_{He} + \chi_{N_2}\, M_{N_2} = 0.8 \times 4 + 0.2 \times 28 = 8.8$ gm/mole

Illustration - 1 *At 30°C and 720 mm of Hg, the density of a gas is 1.5 g/L.Calculate molecular mass of the gas. Also find the number of molecules in 1 cc of the gas at the same temperature.*

SOLUTION :

Assuming ideal behavior and applying ideal gas equation :

$PV = nRT$

Another form of gas equation is $PM_o = dRT$

$\Rightarrow \quad M_o = \dfrac{dRT}{P} = \dfrac{1.5 \times 0.0821 \times 303}{720/760} \qquad (T = 30 + 273\text{ K})$

$\Rightarrow \quad M_o = 39.38$ gm/mol

Now number of molecules $= n \times N_A$

$$= \frac{PV}{RT} \times N_A = \frac{720/760 \times 1 \times 10^{-3}}{0.0821 \times 303} \times 6.023 \times 10^{23}$$

$$= 2.29 \times 10^{19}$$

Illustration - 2 *The pressure exerted by 12 gm of an ideal gas at temperature T in Kelvin in a vessel of volume V litre is one atm. When the temperature is increased by 10 K at the same volume, the pressure rises by 10%. Calculate the temperature T and volume V. (Molecular mass of the gas = 120 gm/mole)*

SOLUTION :

Using *Gas equation* : $PV = nRT$

We have,

$1 \times V = 0.1 \times R \times T$ .... (i)

and $\quad 1.1 \times V = 0.1 \times R \times (T + 10)$ .... (ii)

Using (i) and (ii), we have : $\dfrac{T}{T+10} = \dfrac{1}{1.1}$

$\Rightarrow \quad T = 100$ K

Putting the value of T in (i), we get :

$\Rightarrow \quad 1 \times V = 0.1 \times 0.0821 \times 100$

$V = 0.821$ L

Illustration - 3 *An open vessel at 27°C is heated until three fifth of the air has been expelled. Assuming that the volume of the vessel remains constant, find the temperature to which the vessel has been heated.*

SOLUTION :

In the given question, volume is constant. Also, as the vessel is open to atmosphere, the pressure is constant. This means that the gas equation is simply reduced to the following form:

$nT = \text{constant}$ (Use $PV = nRT$)

or $n_1 T_1 = n_2 T_2$

Now let n_1 = initial moles and n_2 = final moles

$\Rightarrow \quad n_2 = 2/5 \times n_1$ (as 3/5 th of the air has been expelled)

$$\Rightarrow \quad T_2 = \frac{n_1 T_1}{n_2} = \frac{n_1 T_1}{2/5\ n_1} = \frac{5}{2} T_1$$

$$\Rightarrow \quad T_2 = \frac{5}{2}(300) = 750\ \text{K} = 477\ °\text{C}$$

Illustration - 4 *A spherical balloon of 21 cm diameter is to be filled with H_2 at NTP from a cylinder containing the gas at 20 atm at 27°C. If the cylinder can hold 2.80L of water, calculate the number of balloons that can be filled up using pumping.*

SOLUTION :

The capacity of cylinder = 2.80 L

Let n = moles of hydrogen contained in cylinder and n_o = moles of hydrogen required to fill one balloon.

$$n = \frac{PV}{RT} = \frac{20 \times 2.80}{0.0821 \times 300} = 2.273$$

$$n_o = \frac{\text{volume of balloon}}{22400}$$

(Note: the balloons are being filled at NTP)

$$n_o = \frac{4/3\pi r^3}{22400} = \frac{4/3 \times 3.14 \times (10.5)^3}{22400} = 0.216$$

$\Rightarrow$ Number of balloons that can be filled

$$= \frac{n}{n_o} = 10.50 \approx 10$$

Illustration - 5 *A 672 mL of a mixture of oxygen-ozone at N.T.P. were found to be weigh 1 gm. Calculate the volume of ozone in the mixture.*

SOLUTION :

Let V mL of ozone are there in the mixture

$\Rightarrow$ volume of oxygen = (672 – V) mL

$$\text{Mass of ozone at N.T.P.} = \frac{V}{22400} \times 48$$

$$\text{Mass of oxygen at N.T.P.} = \frac{672 - V}{22400} \times 32$$

$$\Rightarrow \quad \frac{V}{22400} \times 48 + \frac{672 - V}{22400} \times 32 = 1$$

$\Rightarrow$ On solving we get : V = 56 ml

Illustration - 6 *Two flasks of equal volume connected by a narrow tube (of negligible volume) are at 27°C and contain 0.70 mole of H_2 at 0.5 atm pressure. One of the flask is then immersed into a bath kept at 127°C, while the other remains at 27°C. Calculate the final pressure and the number of moles of H_2 in each flask.*

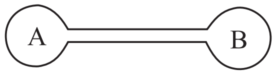
SOLUTION :

Moles of H_2 initially $= 0.7 = 2n_o$ ..... **(i)**

$\Rightarrow \quad n_1 + n_2 = 2n_o$ ..... **(ii)**

Flask A : $\quad P_oV_o = n_o RT_o \quad$ (Initially)

$P_1V_o = n_1RT_1 \quad$ (Finally)

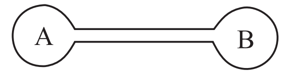


$(P_o, V_o, T_o, n_o) \quad (P_o, V_o, T_o, n_o)$

$\Rightarrow \quad \dfrac{P_o}{P_1} = \dfrac{n_o}{n_1} \times \dfrac{T_o}{T_1}$ .....**(iii)**

Flask B : $\quad P_oV_o = n_oRT_o \quad$ (Initially)

and $\quad P_1V_o = n_2RT_o \quad$ (Finally)



$(P_1, V_o, T_1, n_1) \quad (P_1, V_o, T_o, n_2)$

$\Rightarrow \quad \dfrac{P_o}{P_1} = \dfrac{n_o}{n_2}$ .....**(iv)**

Solve to get :

$n_1 = 0.3 \; ; \; n_2 = 0.4$

Using **(iv)**, $P_1 = \dfrac{P_o\, n_2}{n_o} = 0.5 \times \dfrac{0.4}{0.35}$ atm $= 0.56$ atm

Illustration - 7 *1 gm of an alloy of Al and Mg reacts with excess HCl to form $AlCl_3$, $MgCl_2$ and H_2. The evolved H_2 collected over mercury at 27°C occupied 1200 mL at 684 mm Hg. What is the composition of alloy?*

SOLUTION :

$Al + 3HCl \longrightarrow AlCl_3 + \dfrac{3}{2}H_2$ ..... **(i)**

Also, $\quad$ Moles of $H_2 \equiv \dfrac{PV}{RT} = \dfrac{\dfrac{684}{760} \times 1.2}{0.0821 \times 300} = 0.044$

$Mg + 2HCl \longrightarrow MgCl_2 + H_2$ ..... **(ii)**

Let mass of Al be x gm

$\therefore$ Mass of Mg will be $(1 - x)$ gm

From stoichiometry of reactions **(i)** & **(ii)** ;

$\Rightarrow \quad$ Moles $H_2 = \dfrac{3}{2} \times \dfrac{x}{27} + \dfrac{(1-x)}{24} \times 1 = 0.044$

$\Rightarrow \quad 0.0555\,x + 0.0416 + (1 - x) = 0.044$

$\Rightarrow \quad 0.0139x = 2.4 \times 10^{-3} \quad \Rightarrow \quad x = 0.172$ gm

Thus, % Al = 17.2 % and % Mg = 82.8 %

IN-CHAPTER EXERCISE - A

1. *Fill in the blanks :*

(a) *A cooking gas cylinder can withstand a pressure of 15 atm. At 27°C the pressure of the gas in cylinder is 12 atm. The minimum temperature above which it will burst out is____________°C*

(b) *At constant temperature 250 mL of Argon at 760 mm Hg pressure and 60 mL of nitrogen at 500 mm pressure are put together in one litre flask. The final pressure is _______ mm Hg.*

(c) *Oxygen is present in 1 litre flask at a pressure of 7.6×10^{-10} mm of Hg. The number of oxygen molecules in the flask at 0°C are ______________.*

2. *The moles and weight of hydrogen gas contained in a 10 L flask at a pressure of 75 cm of Hg and at temperature 25°C is ___________ and ____________.*

3. *The density of the mixture of nitrogen and oxygen is 1.15 g/L at 750 mm of Hg at 27°C. The percentage composition of these gases in the mixture is ___________ and _________. Assume the gases behave ideally.*

4. *Choose the correct option for each of the following. Only one option is correct. The questions marked with * may have more than one correct options.*

(i) *The ratio of speeds of diffusion of two gases A and B is 1 : 4. If the ratio of their mass present in the mixture is 2 : 3, then which of the following is the ratio of their mole-fractions ?*

(A) 24 : 1 **(B)** 1 : 24 **(C)** 32 : 1 **(D)** 3 : 17

(ii) *The density of the gaseous mixture (He and N_2) is $\frac{10}{22.4}\,g/L$ at NTP. What is the percentage composition of He and N_2 by volume in this mixture respectively ?*

(A) 75%, 25% **(B)** 25%, 75% **(C)** 30%, 70% **(D)** 40%, 60%

(iii) *According to Charles law V = KT where K is a constant. The unit of K is :*

(A) $m^3\ K^{-1}$ **(B)** $m^{-3}\ K$ **(C)** $m^3\ K^2$ **(D)** $m^{-3}\ K^{-2}$

(iv) *A 10 g of a gas at atmospheric pressure is cooled from 273°C to 0°C keeping volume constant, its pressure would become :*

(A) 1/2 atm **(B)** 1/273 atm **(C)** 2 atm **(D)** 273 atm

(v) *400 cm^3 of oxygen at 27°C were cooled to – 3°C without change in pressure. The contraction in volume will be :*

(A) 40 cm^3 **(B)** 30 cm^3 **(C)** 44.4 cm^3 **(D)** 60 cm^3

(vi) *The vapour density of gas is 11.2. The volume occupied by 11.2 g of this gas at S.T.P. is:*

(A) 22.4 L **(B)** 11.2 L **(C)** 1 L **(D)** 2.24 L

(vii) *Given the reaction* $C(s) + H_2O(l) \longrightarrow CO(g) + H_2(g)$

Calculate the volume of gases produced at STP from 48.0 g of carbon

(A) 179.2 L **(B)** 89.6 L **(C)** 44.8 L **(D)** 22.4 L

***(viii)** *Which of the following statements are correct ?*

(A) He diffuses at a rate of 8.65 times as much as CO does
(B) He escapes at a rate of 2.65 times as fact as CO does
(C) He escapes at a rate of 4 times as CO_2 does
(D) He escapes at a rate 4 times as fast as SO_2 does

(ix) *There are 201 equidistant rows of spectators sitting in a hall. A magician releases laughing gas N_2O from the front and the tear gas (M_o = 176) from the rear of the hall simultaneously which row spectators will have a tendency to smile and weep simultaneously ?*

(A) 130 **(B)** 134 **(C)** 120 **(D)** 100

(x) *Which of the following properties can be seen exclusively in gases only ?*

(A) They intermix spontaneously
(B) They fill the whole vessel in which they are placed
(C) They exert pressure on the walls of the container
(D) Their molecules are constantly in a state of motion

(xi) *If equal volumes of oxygen and nitrogen are mixed together, the vapour density of the mixture, at constant temperature and pressure is :*

(A) 8.2 **(B)** 7.5 **(C)** 15 **(D)** 23

(xii) *Equal weights of O_2 and SO_2 are enclosed in a container when O_2 exerts a partial pressure of 0.67 atm. This will remain the same even on :*

(A) *Adding equal weights of O_2 and SO_2* **(B)** *Removing equal weights each of O_2 and SO_2*

(C) *Removing equal moles of O_2 and SO_2* **(D)** *Doubling both volume and temperature*

(xiii) *Two cylinders A and B contain the same gas at the same temperature. The pressure and volume of A are both twice those of B. Then the ratio of the number of molecules of A and B is :*

(A) 1 : 4 **(B)** 4 : 1 **(C)** 2 : 1 **(D)** 1 : 2

(xiv) *The rms speed of CH_4 at $T_1 K$ and SO_2 at $T_2 K$ are the same. The ratio T_1/T_2 is :*

(A) 0.25 **(B)** 0.30 **(C)** 0.20 **(D)** 0.35

(xv) *At what temperature would the most probable speed of CO_2 molecules be twice that at 323 K ?*

(A) 911°C **(B)** 1091°C **(C)** 1272K **(D)** 1019°C

EUDIOMETRY — Section - 2

Application of Gay Lussac's Law of combining Volumes

It is a method used to analyze the gaseous mixtures of hydrocarbons and to determine their molecular formulae.

Here, the combustible gases (i.e., hydrocarbons) are exploded in a tube with the excess of O_2 so that C and H in the gas are converted to $CO_2(g)$ and $H_2O(g)$ respectively. After cooling and contraction, the volume of contents of the tube are measured (this does not include H_2O as it condenses). At this stage, the contents include CO_2 (g), unused O_2 (if any left) and N_2 (if any in the air).

Now NaOH is used to separate out CO_2 ($2\,NaOH + CO_2 \longrightarrow Na_2CO_3 + H_2O$). As a result a further contraction in volume takes place. After this, the unused O_2 is left which is generally absorbed by the pyrogallol solution. In general after cooling, the contraction in volume is given as :

$\Delta V = V_R - V_P$ (V_R : volume of reactants, V_P : volume of products after cooling)

Note : NaOH also absorbs Cl_2, apart from CO_2

From the measurements made, and applying Gay Lussac's Law of combining volumes, we can calculate molecular formulae and compositions of gaseous mixtures. Please read the given Illustrations on the next page carefully to understand the application of law.