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 time 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.

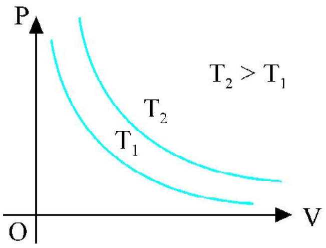
(b) Size of the gas molecules is negligible as compared to the volume occupied by the gas (i.e., container volume).

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**

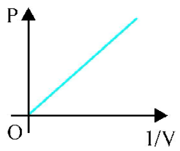
If P_1 is the pressure when volume is V_1 and P_2 is the pressure when volume is V_2 (T is same), then :

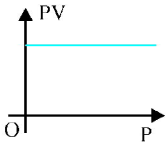
$$P_1 V_1 = P_2 V_2$$

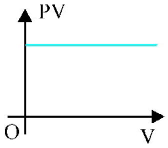
Graphically, it can be represented as shown in the figure. Each line is called as **Isotherm**.

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 :





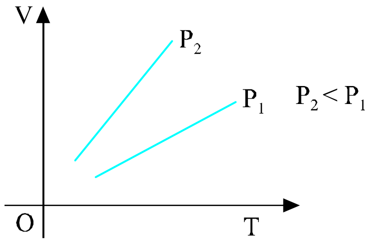


Charles Law :

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)

$$\Rightarrow \frac{V}{T} = \text{constant}$$



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 :

$$\Rightarrow \frac{V_1}{T_1} = \frac{V_2}{T_2}$$

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 :

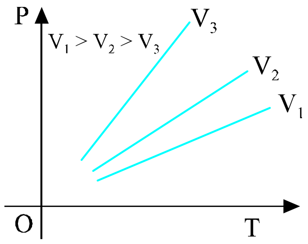
For any sample of an ideal gas, the pressure times the volume divided by the absolute temperature is a constant.

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

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)

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

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

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

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 $\frac{PV}{T} = \text{constant} = K$

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).

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

$\Rightarrow \quad \frac{PV}{T} = K = nR \quad \Rightarrow \quad PV = nRT$

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

Values of R :

Note **:** $R = \frac{PV}{nT}$

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

(ii) $R = 8.31 \frac{\text{J}}{\text{mol.K}}$ (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) $R = 2 \frac{\text{cal}}{\text{mol.K}}$ (4.184 J = 1 cal)

Different forms of Ideal Gas Equation :

(i) $PV = nRT$

(ii) $PV = \frac{g}{M_o} RT$

(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.

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

$$\Rightarrow \quad \text{Number of atoms} = \frac{256}{32} = 8$$

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.

$$\text{Now, } PV = nRT = \frac{g}{M_o} \times RT \quad \Rightarrow \quad g_X = \frac{PVM_o}{RT}$$

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

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

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.

$$P_{Total} = p_1 + p_2 + p_3 + p_4 + \ldots\ldots\ldots\ldots$$

where P_{Total} : Total pressure of the mixture and $p_1, p_2, p_3, p_4, \ldots$ 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 : $P_1 = n_1\frac{RT}{V}$ . . . (i) and $P_2 = n_2\frac{RT}{V}$ . . . (ii)

Using Dalton's Law :

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

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

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

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

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

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

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 × Total pressure exerted by the mixture in the mixture***

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

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 = $n_{SO_2}\frac{RT}{V_{vessel}}$

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

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

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

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

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.

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

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

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

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 × 2.5 = 7.5

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

Moles CO_2 formed = 2 × 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 :

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

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

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:

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

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

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

(*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:

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

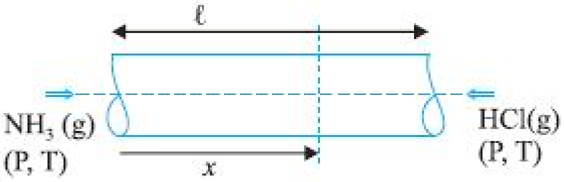
Note : Rate of effusion (r) can be defined in the following ways (depending on the analysis of a problem):

(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 ith gas in the mixture and M_i is the molar mass of the ith 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.

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

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

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

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

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

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

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

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 $PM_o = dRT$

$$\Rightarrow \quad M_o = \frac{dRT}{P} = \frac{1.5 \times 0.0821 \times 303}{720/760}$$

$(T = 30 + 273 \text{ K})$

$$\Rightarrow \quad M_o = 39.38 \text{ gm/mol}$$

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,

$$1 \times V = 0.1 \times R \times T \qquad \text{.......(i)}$$

and $$1.1 \times V = 0.1 \times R \times (T+10) \qquad \text{.......(ii)}$$

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

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

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

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

$\Rightarrow$ 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.*

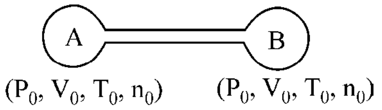
SOLUTION :

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

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

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

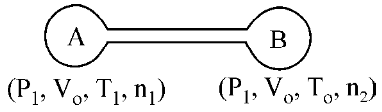
$P_1V_o = n_1RT_1$ (Finally)



$$\Rightarrow \quad \frac{P_o}{P_1} = \frac{n_o}{n_1} \times \frac{T_o}{T_1} \qquad \text{. . . . (iii)}$$

Flask B : $P_oV_o = n_oRT_o$ (Initially)

and $P_1V_o = n_2RT_o$ (Finally)



$$\Rightarrow \quad \frac{P_o}{P_1} = \frac{n_o}{n_2} \qquad \text{. . . . .(iv)}$$

Solve to get :

$n_1 = 0.3$; $n_2 = 0.4$

Using (iv),

$$P_1 = \frac{P_o\ n_2}{n_o} = 0.5 \times \frac{0.4}{0.35}\ \text{atm} = 0.56\ \text{atm}$$

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 :

$$Al + 3HCl \longrightarrow AlCl_3 + \frac{3}{2}H_2 \qquad \text{. . . . . (i)}$$

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

$$Mg + 2HCl \longrightarrow MgCl_2 + H_2 \qquad \text{. . . . . (ii)}$$

Let mass of Al be x gm

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

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

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

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

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

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

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 :

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

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.

Illustration - 8 *8.4 mL of a gaseous hydrocarbon (A) was burnt with 50 ml of O_2 in an eudiometer tube. The volume of the products after cooling to room temperature was 37.4 mL, when reacted with NaOH, the volume contracted to 3.8 ml. What is the molecular formula of A?*

SOLUTION :

Let $C_xH_{y\,(g)}$ be the hydrocarbon.

$$C_xH_{y(g)} + \left(x + \frac{y}{4}\right) O_{2(g)} \longrightarrow x\,CO_{2(g)} + \frac{y}{2}\,H_2O_{(g)}$$

[Remember this balanced combustion equation for C_xH_y]

From Gay Lussac's Law of combining volume, we get :

$$1 \text{ vol. of } C_xH_y = \left(x + \frac{y}{4}\right) \text{vol. of } O_2$$

$$\equiv x \text{ vol. of } CO_2 \equiv y/2 \text{ vol. of } H_2O$$

Contraction in volume

$= V_R - V_P = (8.4 + 50) - (37.4) = 21$ ml

From equation, we have, the contraction

$= 1 + (x + y/4) - (x + 0)$

(Note: Vol. of water is not taken as it has condensed)

$\Rightarrow$ Contraction $= 1 + y/4$

$\Rightarrow$ For 8.4 mL of C_xH_y, the contraction

$= 8.4\,(1 + y/4)$

$\Rightarrow$ $8.4\,(1 + y/4) = 21 \quad \Rightarrow \quad y = 6$

After treating with NaOH, there is a contraction of (37.4 – 3.8) = 33.6 mL, which is equal to the volume of CO_2 produced.

Volume of CO_2 produced by 8.4 ml of hydrocarbon = $8.4\,x$

$\Rightarrow \quad 8.4\,x = 33.6 \quad \Rightarrow \quad x = 4$

Another method to calculate y:

After NaOH treatment, the volume is reduced to 3.8 ml, this corresponds to the volume of O_2 unused.

Volume of O_2 unused = $50 - 8.4\,(x + y/4) = 3.8$

Solve to get : $y = 6$

Hence hydrocarbon is C_4H_6.

Illustration - 9 *15 ml of gaseous hydrocarbon required for complete combustion 357 ml of air (21 % of O_2 by volume) and the gaseous products occupied 327 ml (all volumes being measured at S.T.P.). What is the formula of hydrocarbon ?*

SOLUTION :

Let $C_xH_{y\,(g)}$ be the hydrocarbon.

$$C_xH_{y(g)} + \left(x + \frac{y}{4}\right) O_{2(g)} \longrightarrow x\,CO_{2(g)} + \frac{y}{2} H_2O_{(g)}$$

From Gay Lussac's Law of combining volume, we get :

1 vol. of $C_x H_y$

$$\equiv \left(x + \frac{y}{4}\right) \text{vol. of } O_2 \equiv x \text{ vol. of } CO_2$$

$$\equiv \frac{y}{2} \text{vol. of } H_2O$$

From equation, we have, the contraction

$= 1 + (x + y/4) - (x + 0) = 1 + y/4$

$\Rightarrow$ For 15 mL gas, contraction = $15(1 + y/4)$

Also contraction = $V_R - V_P = (15 + 357) - (327) = 45$

$\Rightarrow \quad y = 8$

The gaseous products after contraction = 327 ml

This includes volume of CO_2 plus volume of N_2 in the air (O_2 is completely used up). So let us calculate the volume of N_2 in the air.

Vol. of $O_2 = 0.21 \times 357 = 75$ ml

$\Rightarrow$ Vol. of $N_2 = 357 - 75 = 282$ ml

Now, Vol. of N_2 + Vol. of CO_2 = 327 ml

$\Rightarrow$ Vol. of $CO_2 = 327 - 282 = 45$ml

The volume of CO_2 produced = $15\,x$

$\Rightarrow \quad 15x = 45 \quad \Rightarrow \quad x = 3$

Hence the hydrocarbon is C_3H_8

Illustration - 10 *60 ml of a mixture of equal volumes of Cl_2 and an oxide of chlorine were heated and then cooled back to the original temperature. The resulting gas mixture was found to have a volume of 75 ml. On treatment with caustic soda, the volume was contracted to 15 ml. Assuming that all measurements were made at the same temperature and pressure, deduce the simplest formula of the oxide of Cl_2. (The oxide of chlorine on heating decomposes quantitative to O_2 and Cl_2).*

SOLUTION :

Let Cl_xO_y be the oxide.

$$Cl_xO_y \longrightarrow x/2\ Cl_2 + y/2\ O_2$$

1 vol. $x/2$ vol. $y/2$ vol.

$\Rightarrow$ Volume of Cl_xO_y = volume of Cl_2 = 30 ml

After cooling volume = 75 ml

This corresponds to vol. of Cl_2 initially plus vol. of Cl_2 produced and O_2 produced.

$\Rightarrow$ $V(Cl_2) + V(Cl_2\text{ produced}) + V(O_2) = 75$

$\Rightarrow$ $V(Cl_2\text{ produced}) + V(O_2) = 75 - 30 = 45$ ml

(vol. of Cl_2 initially = 30 ml)

NaOH apart from CO_2 also absorbs Cl_2. So after NaOH treatment, the residual volume corresponds to the volume of O_2 = 15 ml

$\Rightarrow$ Vol. of $Cl_2 = 45 - 15 = 30$ ml

Now from equation :

Vol. of $Cl_2 = 30\ (x/2) = 30 \Rightarrow x = 2$

Vol. of $O_2 = 30\ (y/2) = 15 \Rightarrow y = 1$

Hence formula of chloride is Cl_2O

Illustration - 11 *20 ml of a mixture of ethane (C_2H_6), ethylene (C_2H_4) and CO_2 are heated with O_2. After the explosion there was a contraction of 28 ml and after treatment with KOH there was a further contraction of 32 ml. What is the composition of the mixture ?*

SOLUTION :

Let volume of ethane = a ml

and volume of ethylene = b ml

$\Rightarrow$ Volume of CO_2 = (20 – a – b) mL

Now contraction after cooling = 28

$\Rightarrow$ $V_R - V_P = 28$

V_R = volume of ethane + volume of ethylene + volume of CO_2 + volume of O_2 used for combustion

V_P = volume of CO_2 produced (volume of H_2O is not taken as it condenses)

Considering combustion of gases :

1. $C_2H_6 + 7/2\ O_2 \longrightarrow 2\ CO_2 + 3\ H_2O$

a vol. (7/2)a vol. 2a vol.

2. $C_2H_4 + 3\ O_2 \longrightarrow 2\ CO_2 + 2\ H_2O$

b vol. 3b vol. 2b vol.

3. $CO_2 \longrightarrow CO_2$ (no reaction)

(20 – a – b) volume

$\Rightarrow$ $V_R = (a + 7/2\ a) + (b + 3b) + (20 - a - b)$

and $V_P = (2a + 2b) + (20 - a - b)$

$\Rightarrow$ $V_R - V_P = 5/2\ a + 2b = 28$

$\Rightarrow$ $\frac{5a}{2} + 2b = 28$ or $5a + 4b = 56$ ...... **(i)**

Also there is a further contraction of 32 mL on treatment with KOH.

$\Rightarrow$ Volume of CO_2 produced + Vol. of CO_2 original = 32

$\Rightarrow$ $(2a + 2b) + (20 - a - b) = 32$

$\Rightarrow$ $a + b = 12$ ...... **(ii)**

On solving **(i)** and **(ii)**, we get :

a = 8 $\Rightarrow$ Vol. of ethane = 8 ml

b = 4 $\Rightarrow$ Vol. of ethylene = 4 ml

$\Rightarrow$ Volume of CO_2 = 8 ml

Illustration - 12 *9 volumes of gaseous mixture consisting of gaseous organic compound A and just sufficient amount of O_2 required for complete combustion yielded on burning 4 volumes of CO_2, 6 volumes of water vapour and 2 volumes of N_2 all volumes measured at the same temperature and pressure. If the compound A contained only C, H and N,*

(a) How many volumes of O_2 required for complete combustion ?

(b) What is the molecular formula of the compound A ?

SOLUTION :

Let the molecular formula of A be $C_xH_yN_z$

$$C_xH_yN_z + \left(x+\frac{y}{4}\right)O_2 \longrightarrow xCO_2 + \frac{y}{2}H_2O + \frac{z}{2}N_2$$

$$1\,\text{vol}\ C_xH_yN_z \equiv \left(x+\frac{y}{4}\right)\text{vol of } O_2 \equiv x\ \text{vol}\ CO_2$$

$$\equiv \frac{y}{2}\ \text{vol of } H_2O \equiv \frac{z}{3}\ \text{vol } N_2$$

Let a volumes of $C_xH_yN_z$ were taken.

$$\text{Volume of } O_2 = a\left(x+\frac{y}{4}\right) = 9 - a$$

$\Rightarrow$ Volume of $CO_2 = ax = 4$

Volume of $H_2O = a \times \frac{y}{2} = 6$

So, $4 + 12 \times \frac{1}{4} = 9 - a$

$\Rightarrow$ $7 = 9 - a$ $\Rightarrow$ $a = 2$

Volume of $N_2 = a \times \frac{z}{2} = 2$

Thus, $x = 2$, $y = 6$, $z = 2$

$\Rightarrow$ Molecular formula of $A \equiv C_2H_6N_2$

and O_2 used $= 9 - a = 7$ volumes.

KINETIC MOLECULAR MODEL OF A GAS

Section - 3

In the previous sections, we have studied the macroscopic properties of gases and their relationships in the form of gas laws. Now, we know that for a given amount of gas, volume is directly proportional to the absolute temperature but gas laws do not provide any reason for this.

To understand the underlying principles, a theory based on a model is proposed. If the theoretical results on the basis of this particular model agree with the experimental observations, it indicates that the model is realistic. The theory that provides an explanation for the various experimental observations about a gas is based on the **Kinetic Molecular Model**.

Maxwell proposed the postulates for the behavior of gas molecules known as **Kinetic Theory of gases**.

The postulates of this model are :

- Each gas is made up of a large number of identical and small (tiny) particles known as molecules (i.e., the dimensions of these molecules are very-very small as compared to the space between them).
- The volume of a molecule is so small that it may be neglected in comparison to the total volume occupied by the gas.

- There are practically no attractive forces between the molecules. Thus, the molecules move independently.
- The molecules are never in stationary state but are believed to be in random motion in a straight line motion in all possible directions with altogether different but constant velocities. The direction of motion is changed only when it collides with the walls of container or with other molecules.
- The molecules are perfectly elastic and bear no change in energy during collisions.
- The effect of gravity on molecular motion is negligible.
- The temperature of gas is the measure of its kinetic energy. K.E. of molecules is proportional to absolute temperature of the gas.
- The pressure of the gas is due to the continuous collision of molecules on the walls of container.

Consider a container of volume V occupied by a gas.

Let m = mass of the gas in the container and N = number of molecules in the container

If m_o is the mass of one molecule $\Rightarrow$ $m = m_o N$

If N_o is the Avogadro number and M is the molecular weight of the gas,

$\Rightarrow$ $M = m_o N_o$

Root mean Square (C_{rms}) speed :

It is defined as : $c_{rms} = \sqrt{\overline{c^2}} = \sqrt{\dfrac{c_1^2 + c_2^2 + c_3^2 + \ldots\ldots\ldots + c_N^2}{N}}$

[where bar $\left(\overline{}\right)$ represents average $\Rightarrow$ $\overline{c^2}$ = Average of c^2 values]

Since the distribution is continuous, we can write : $c_{rms}^2 = \overline{c^2} = \dfrac{\int c^2\, dN_c}{N} = \dfrac{3k_B T}{m} \equiv \dfrac{3RT}{M_o}$

Where M_o = Mol. mass of the gas (in Kg)

$$\Rightarrow \quad c_{rms} = \sqrt{\frac{3RT}{M_o}}$$

Note : Derivation of the above integrals is not required.

Illustrating the concept:

The escape velocity, the velocity required by an object to escape from the gravitational field of earth, is given by $c_e = \sqrt{2gr}$ *where r = 6400 km for earth. At what temperature will the* c_{rms} *of an* H_2 *molecule attain escape velocity ? (g = 10 ms*$^{-2}$*)*

$$c_e = \sqrt{2 \times 10 \times 6400 \times 10^3} = 11313.7 \text{ ms}^{-1}$$

$$c_{rms} = \sqrt{\frac{3RT}{M_o}} = \sqrt{\frac{3 \times 8.314 \times T}{2 \times 10^{-3}}} \qquad [\text{Note : } M_{H_2} = 2 \times 10^{-3} \text{ kg}]$$

As $c_{rms} = c_e \qquad \Rightarrow \qquad T = 10263.8 \text{ K}$

Average speed (c_{avg}) :

This is defined as : $c_{avg} = \bar{c} = \dfrac{c_1 + c_2 + c_3 + \ldots.. + c_N}{N}$

For a continuous distribution, it can be written as : $c_{avg} = \dfrac{\int c\, dN_c}{N} = \sqrt{\dfrac{8RT}{\pi M_o}}$

Note : This is actually "average speed". Since, the molecule move randomly, average velocity of the gas is zero.

Illustrating the concept:

The average speed of a gas molecule is 400 m/s. Calculate its rms velocity at the same temperature.

$$c_{rms} = \sqrt{\frac{3RT}{M}} \text{ and } c_{avg} = \sqrt{\frac{8RT}{\pi M}} \qquad \Rightarrow \qquad c_{rms} = \sqrt{\frac{3\pi}{8}} \times 400 \text{ ms}^{-1} = 434.24 \text{ ms}^{-1}$$

Most Probable speed (C_{MP}) :

A very small fraction of molecules occupy either very small or very high speeds. The speed occupied by majority of molecules is known as most probable speed.

It is given by : $c_{MP} = \sqrt{\dfrac{2RT}{M_o}}$

Illustrating the concept:

For a gas consisting of only six molecular having speeds as $2\,\text{ms}^{-1}, 3\,\text{ms}^{-1}, 3\,\text{ms}^{-1}, 3\,\text{ms}^{-1}, 4\,\text{ms}^{-1}, 5\,\text{ms}^{-1}$, find c_{rms}, c_{avg} and c_{MP}.

$$c_{avg.} = \bar{c} \equiv \frac{\sum_{i=1}^{N} c_i}{N} \equiv \frac{c_1 + c_2 + \ldots + c_N}{N} = \frac{2+3+3+3+4+5}{6} = 3.33\,\text{ms}^{-1}$$

$$c_{rms} = \sqrt{\overline{c^2}} \equiv \sqrt{\frac{\sum_{i=1}^{N} c_i{}^2}{N}} \equiv \sqrt{\frac{c_1{}^2 + c_2{}^2 + \ldots + c_N{}^2}{N}} = \sqrt{\frac{2^2 + 3^2 + 3^2 + 3^2 + 4^2 + 5^2}{6}} = 3.46\ \text{ms}^{-1}$$

$c_{MP} = 3\,\text{ms}^{-1}$ (Since maximum numbers of molecules are having a speed of 3 ms^{-1})

Note :

(i) $c_{MP} < c_{avg.} < c_{rms}$

$$c_{MP} : c_{avg} : c_{rms} :: \sqrt{2} : \sqrt{\frac{8}{\pi}} : \sqrt{3}$$

$$1 : 1.128 : 1.224$$

Also, $c_{avg} = c_{rms} \times 0.9215$

(ii) c_{avg} and c_{rms} values lie in the vicinities of c_{MP} values.

(iii) The numerical values of c_{MP}, c_{avg}, c_{rms} increases with increase in temperature.

(iv) Also, it is important to note that the average translational kinetic energy of a gas molecule is given by :

$$K.E_{avg} = \frac{1}{2} m_o\, c_{rms}^2 \neq \frac{1}{2} m_o\, c_{avg}^2$$

If in a gas, there are N molecules, their total K.E. is :

$$K.E_{Total} = K.E_1 + K.E_2 + \ldots + K.E_N = \frac{1}{2} m_o c_1^2 + \frac{1}{2} m_o c_2^2 + \ldots + \frac{1}{2} m_o c_N^2$$

Thus, average kinetic energy of each molecule $= \dfrac{\frac{1}{2} m_o c_1^2 + \frac{1}{2} m_o c_2^2 + \ldots . + \frac{1}{2} m_o c_N^2}{N}$

$$= \frac{1}{2} m_o \left(\frac{c_1^2 + c_2^2 + \ldots . + c_N^2}{N} \right)$$

$$= \frac{1}{2} m_o\, c_{rms}^2$$

(v) The sharpness of maximum in curves decreases with increase in temperature which reveals that number of molecules having speeds in the vicinities of c_{MP} increase.

Kinetic Energy of Gas

The pressure exerted by the gas is :

$$P = \frac{1}{3}\frac{m_oN}{V}c^2_{rms} \quad \text{or} \quad P = \frac{1}{3}\rho c^2_{rms} \quad \text{where} \quad \rho = \text{density of gas} = \frac{m_oN}{V}$$

Using the above relation and gas laws, a relation between the average translational kinetic energy $\left(\frac{1}{2}m_oc^2_{rms}\right)$ of a molecule at the temperature, T of the gas can be derived.

Using PV = nRT

$$\Rightarrow \quad \frac{1}{3}\frac{m_oN}{V}c^2_{rms}V = \frac{N}{N_o}RT \qquad \left[\text{Using } P = \frac{1}{3}\frac{m_oN}{V}C^2_{rms}\right]$$

Note :

$$K.E_{avg.} = \frac{1}{2}m_o\,c^2_{rms} \neq \frac{1}{2}m_o\,c^2_{avg} \qquad \left[\because \frac{c_1^2+c_2^2+\ldots+c_N^2}{N} \neq \left(\frac{c_1+c_2+\ldots+c_N}{N}\right)^2\right]$$

$$\text{or} \quad \frac{1}{3}m_o\,c^2_{rms} = \frac{1}{N_o}RT$$

$$\Rightarrow \quad \frac{1}{2}m_oc^2_{rms} = \frac{3}{2}\frac{RT}{N_o} = \frac{3}{2}k_BT$$

$\Rightarrow$ Average Translational K.E. of a molecule is directly proportional to the temperature of the gas.

$$K.E_{avg} = \frac{3}{2}k_BT \qquad \left[\text{where } k_B = \frac{R}{N_o} \text{ is known as Boltzmann constant}\right]$$

Also, K.E./mole $= \frac{3}{2}PV = \frac{3}{2}RT$

Illustration - 13 *Find the temperature at which methane and ethane will have the same rms speed as carbon dioxide at 400℃. Also calculate the mean velocity and most probable velocity of methane molecules at 400℃.*

SOLUTION :

$$c_{rms} = \sqrt{\frac{3RT}{M_o}}$$

Let 1: CO_2 and 2: Methane

For c_{rms} to be same for 1 and 2

$$\Rightarrow \quad \frac{T_1}{M_1} = \frac{T_2}{M_2}$$

(a) $T_{CH_4} = \frac{673}{44} \times 16 = 244.73\text{K}$

(b) $T_{C_2H_6} = \frac{673}{44} \times 30 = 458.86\text{K}$

$$\underset{(CH_4)}{\text{Mean speed}} = \sqrt{\frac{8RT}{\pi M_o}} = \sqrt{\frac{8 \times 8.31 \times 673}{3.14 \times 16 \times 10^{-3}}}$$

$= 943.68$ m/s

$$\underset{(CH_4)}{\text{Most probable speed}} = \sqrt{\frac{2RT}{M_o}} = \sqrt{\frac{2 \times 8.31 \times 673}{16 \times 10^{-3}}}$$

$= 836.11$ m/s

Illustration - 14 *A gas bulb of 1 L capacity contains* 2.0×10^{21} *molecules of nitrogen exerting a pressure of* 7.57×10^3 Nm^{-2}. *Calculate the root mean square (rms) speed and the temperature of the gas molecules. The ratio of the most probable speed to the root mean square speed is* 0.82, *calculate the most probable speed for these molecules at this temperature.*

SOLUTION :

$$c_{rms} = \sqrt{\frac{3RT}{M_o}} \quad T = ?$$

Using, $PV = nRT$

$$\Rightarrow \quad T = \frac{PV}{nR} = \frac{7.57\times10^3 \times 1\times10^{-3}}{\frac{2.0\times10^{21}}{6.023\times10^{23}}\times 8.314} = 274.2 \text{ K}$$

$$c_{rms} = \sqrt{\frac{3\times8.314\times274.2}{28\times10^{-3}}} = 494.22 \text{ m/s}$$

$$\text{Most probable speed } (c_{MP}) = \frac{1}{1.224}\times 494.22$$

$$= 403.77 \text{ m/s}$$

Illustration - 15 *Two gases A and B have the same magnitude of most probable speed at* 298 *K for A and* 150 *K for B. Calculate the ratio of their molor masses* $\left(\frac{M_A}{M_B}\right)$.

(A) 2 : 1 **(B)** 1 : 0.75 **(C)** 1 : 2 **(D)** 3 : 1

SOLUTION : (A)

$$\text{Most Probable} = \left(\frac{2RT}{M}\right)^{1/2}$$

$$\text{According to the problem } \frac{T_A}{M_A} = \frac{T_B}{M_B}$$

$$\therefore \quad \frac{M_A}{M_B} = \frac{T_A}{T_B} = \frac{298}{150} \approx 2$$

$$\therefore \quad M_A : M_B = 2:1$$

Illustration - 16 *What is the ratio of kinetic energy per mole of Argon at* 27°C and Helium at 127°C ?

(A) 0.75 : 1 **(B)** 1 : 1 **(C)** 1 : 0.67 **(D)** 1 : 1.25

SOLUTION : (A)

$$\text{Kinetic energy (K.E)} = \frac{3}{2}RT$$

$$KE_{Ar} = \frac{3}{2}RT_{Ar}$$

$$KE_{He} = \frac{3}{2}RT_{He}$$

$$\frac{KE_{Ar}}{KE_{He}} = \frac{T_{Ar}}{T_{He}} = \frac{300}{400} = \frac{3}{4}$$

$KE_{Ar} : KE_{He}$ is 0.75 : 1

REAL GAS ANALYSIS

Equation of state describes the variables of a gas (P, V, T) in a single equation completely. The gas equation PV = nRT is an equation of state which is followed only by ideal gases. This equation is not always applicable for a real gas (especially at high pressure and low temperature). There are many equation of states which can be used to represent a real gas but the most commonly used equation is van der Waal's Equation and is given by :

$$\left(P + \frac{an^2}{V^2}\right)(V - nb) = nRT \qquad \ldots\ldots \text{(i)}$$

where P = Real Gas Pressure ; V = Volume occupied by the Gas (≡ Container Volume)

T = Gas temperature ; R = Universal Gas Constant ; n = Moles of Gas

a, b = Characteristic constants for a gas independent of the temperature but depends on the nature of the gas.

Note : **(i)** Units of $a \equiv \frac{L^2 \text{ atm}}{\text{mol}^2}$; $b \equiv \frac{L}{\text{mol}}$

(ii) a ≡ Relates to the forces interacting between the gas molecules and modifies the pressure term. ('a' is high if the gas molecules have more attractive forces)

(iii) b ≡ Relates to the volume occupied by the gas molecules and takes into account the fact that the space actually occupied by the molecules themselves is unavailable for the molecules to move in and is given by :

b = 4 × volume of 1 mol of gas molecules.

(iv) For a given gas Van der Waal's constant 'a' is always greater than 'b'.

(v) The gas having higher values of 'a' can be liquefied easily. (to be discussed later)

Equation **(i)** is similar to the ideal gas equation with some correction factors taking into account the factors responsible for a gas to deviate from the ideal gas behaviour.

Equation **(i)** is written in a more familiar form by dividing it by "n" :

$$\Rightarrow \left(P + \frac{a}{V_m^2}\right)(V_m - b) = RT \qquad \ldots\ldots \text{(ii)}$$

where $V_m = \frac{V}{n}$ = Molar volume (volume occupied by 1 mole gas)

Pressure correction :

The term $\frac{a}{V_m^2}$ is known as Pressure correction. The pressure exerted by a real gas is always less than that by an ideal gas. So, this has to be added to the real gas pressure such that : $P_{ideal} = P_{real} + \frac{a}{V_m^2}$

Note : P_{real} is the pressure exerted by the real gas and has been denoted by 'P' in the van der Waal's equation.

Volume correction :

The term 'nb' is known as volume correction (also known as co-volume or excluded volume). The volume of the gas molecules is not zero and hence the actual compressible volume is less than V_m and thus has to be subtracted from V_m

We can also write a Universal Equation of state for any gas as :

$$PV = Z\,(nRT) \qquad \text{......(iii)}$$

where Z = compressibility factor

Note : **(i)** For ideal gas, $PV = nRT$ ⇒ $Z = 1$ at all conditions of P, V, T.

(ii) For real gas, $PV = ZnRT$

It should be clear that "Z" represents a quantitative deviation of real gas from ideal gas behaviour.

Explanation for deviation from Ideal Gas Behavior :

The deviation from ideal gas behavior is mainly due to two assumptions made while formulating the kinetic molecular theory :

(i) Molecules were considered as point masses. However all real molecules have definite volume which cannot be neglected when the volume occupied by the gas is small.

(ii) It was assumed that there are no intermolecular forces and molecules move independently. This cannot be true as otherwise gases could not condense into liquid.

If we assume that gas molecules are hard spheres of radius say, 2×10^{-10} m, the volume of one mole of gas molecules = (volume of each molecule) × N_o

$$= \frac{4}{3}\pi\left(2 \times 10^{-8}\right)^3 \times 6 \times 10^{23}\,\text{cm}^3 = 2.01 \times 10^{-2}\,\text{L}$$

and volume of the gas at P = 1atm and T = 0°C is nearly 22.4 L

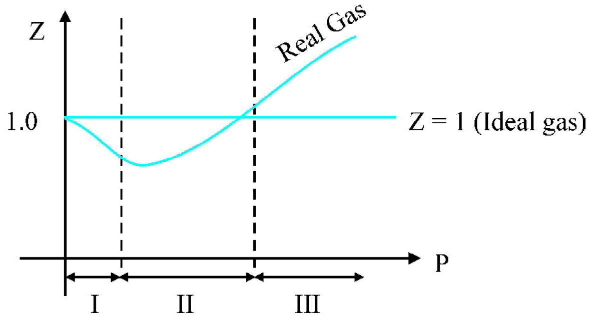
⇒ % volume occupied by gas molecules ≈ 0.09%

It can be shown that at P = 10 atm and T = 0°C, volume of the gas is nearly 2.24 L

% volume occupied by gas molecules ≈ 0.9%

Thus, as pressure increases, space available for gas molecules for free movement decreases.

With an increase in pressure, the average distance between the gas molecules decreases, then the molecular interactions start operating. Thus, the number of molecular collisions with the walls of the container gets affected resulting in smaller values of pressure than what actually would have been in the absence of intermolecular interaction.



Let us plot the variation of Z as a function of P.

We can, theoretically, describe the above behaviour by using van der Waal's equation :

This equation is a cubic in V_m. Thus, verification for the variation of Z versus P from this equation, directly, is difficult. Instead, the whole variation can be divided into three regions.

Region : I **Low Pressure :** This region is represented by that portion of the graph where $V_m - b \approx V_m$, i.e., $V_m >> b$ or when the gas has a large molar volume or very small pressure.

Thus, we have : $\left(P + \frac{a}{V_m^2}\right)(V_m) = RT$

$\Rightarrow$ $P = \frac{RT}{V_m} - \frac{a}{V_m^2}$ [Here, both P and $\frac{a}{V_m^2}$ are small numbers. So, $P + \frac{a}{V_m^2} \neq P$]

$$\Rightarrow \quad Z = \frac{PV_m}{RT} = 1 - \frac{a}{RTV_m} \qquad \ldots\ldots \text{(iv)}$$

$\Rightarrow$ In the region I, V_m is large $\Rightarrow$ $Z < 1$ but $Z \approx 1$

Thus, as P increases (V_m decreases), Z decreases [see equation (iv)]

Region : III **High Pressure :** This region is represented by that portion of the graph where

$$P + \frac{a}{V_m^2} \approx P \quad [V_m - b \neq V_m]$$

$\Rightarrow$ Van der Waal's equation reduces to : $P(V_m - b) = RT$

$\Rightarrow$ $PV_m = Pb + RT$ $\Rightarrow$ $Z = \frac{PV_m}{RT} = 1 + \frac{Pb}{RT}$ [Note : Z vs P is linear here]

Thus, as P increases, Z increases and $Z > 1$.

Region : III **Intermediate Pressure :**

In this region, neither of the two approximations are valid, i.e.,

$$V_m - b \neq V_m \quad \text{and} \quad P + \frac{a}{V_m^2} \neq P$$

So, the direct analysis is difficult.

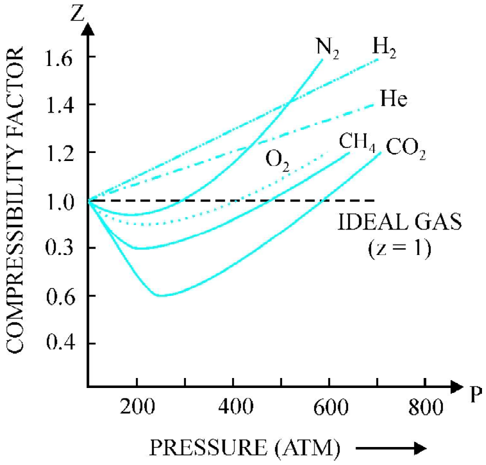
Observations from the graph :

(i) In the low pressure Region-I and in most of the Intermediate Pressure Region-II : $Z < 1$

$\Rightarrow$ Gas is more compressible. Thus, attractive forces dominate between the gas molecules

(ii) In the high Pressure Region-III, $Z > 1$

$\Rightarrow$ Gas is less compressible. Thus, repulsive forces dominate between the gas molecules.



The graph (→) shows the variation of Z vs P for different gases and following can be observed :

(i) H_2 and He gases have very low attractive forces between the gas molecules and we can assume their van der waal's gas constant 'a' ≈ 0.

$\Rightarrow$ $P(V_m - b) = RT$

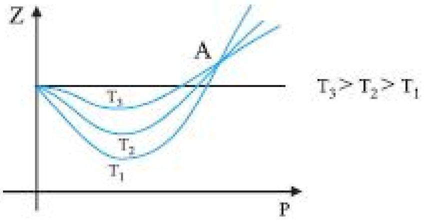
[For H_2 and He even at low Pressures we can assume

$$[P + \frac{a}{V_m^2} \approx P]$$

(ii) $Z < 1$ (as for CH_4, CO_2) can be attributed to the predominance of attractive forces among the molecules of these gases at the temperature of experimentation whereas $Z > 1$ can be attributed to the dominance of strong repulsive forces among the molecules.

(iii) All gases at sufficiently high pressure (i.e., when sizes of the molecules are comparable to the volume of the gas) will have $Z > 1$.

Variation of Z vs Temperature (T) :



In the low pressure region : $Z = 1 - \frac{a}{RTV_m}$ $(Z < 1)$

$\Rightarrow$ As T increases $\Rightarrow$ Z increases and reaches close to 1.

In the high pressure region : $Z = 1 + \frac{Pb}{RT}$ $(Z > 1)$

$\Rightarrow$ As T increases $\Rightarrow$ Z decreases and reaches close to 1.

It can be seen that Z approaches 1 as T increases and Z approaches 1 as P approaches 0.

Thus, **a real gas behaves more closely to ideal gas at low pressure and high temperature**.

Note : Large value of "a" denotes a larger dip in Z in the intermediate pressure region.

$a_{NH_3} > a_{N_2}$ as NH_3 molecules exerts attractive forces due to Hydrogen Bonding but in N_2 there are only Van der Waal's forces of attraction between the molecules which is actually small.

$b_{NH_3} < b_{N_2}$ as N_2 molecule is larger as compared to NH_3 molecule.

All isotherms in the above graph will have a common point of intersection 'A'.

Illustrating the concept :

- *Find the temperature at which 3 mole of SO_2 obeying van der Waal's equation occupies a volumes of 10 L at a pressure of 15 atm.* $\left(a = 6.71\ L^2 atm/mol^2,\ b = 0.0564\ L/mol\right)$

Using van der Waal's equation of state : $\left(P + \frac{n^2 a}{V^2}\right)(V - nb) = nRT$

we get, $\left(15 + \frac{3^2 \times 6.71}{10^2}\right)(10 - 3 \times 0.0564) = 3 \times 0.0821 \times T \quad \Rightarrow \quad T = 349.8°C$

- *The compressibility factor for 1 mole of a van der Waal's gas at 0°C and 100 atm pressure is found to be 0.5. Assuming that the volume of gas molecular is negligible, calculate the van der Waal's constant 'a'.*

Using van der Waal's equation of state : $\left(P + \frac{a}{V_m^2}\right)(V_m - b) = RT$

Now : $V_m - b \approx V_m$ (given)

$\Rightarrow$ The equation is reduced to : $\left(P + \frac{a}{V_m^2}\right)V_m = RT$ or $Z = \frac{PV_m}{RT} = 1 - \frac{a}{RTV_m}$

Also, $0.5 = \frac{100 \times V_m}{0.0821 \times 273} \quad \Rightarrow \quad V_m = 0.112\,L$

Substitute the values of V_m and T : $\Rightarrow \quad a = 1.25\ L^2\ atm\ mol^{-2}$

Illustrating the concept:

- *Calculate the pressure exerted by 5 mole of CO_2 in 1 L vessel at 47°C using van der waal's equation. Also report the pressure of gas if it behaves ideally in nature.*
  (*$a = 3.592$ atm L^2/mol^{-2}, $b = 0.0427$ L/mol*)

Using van der Waal's equation of state :

$$\left(P + \frac{n^2 a}{V^2}\right)(V - nb) = nRT$$

Substituting the given values, we get :

$$\left(P + \frac{5^2 \times 3.592}{1^2}\right)(1 - 5 \times 0.0427) = 5 \times 0.0821 \times 320$$

$$\Rightarrow \qquad P = 77.218\ atm$$

If the gas behaves ideally, then using : $PV = nRT$

$$\Rightarrow \qquad P = \frac{5 \times 0.0821 \times 320}{1}\ atm = 131.36\ atm.$$

- *Van der Waal's constant b of Ar is 3.22 × 10^{-5} m^3 mol^{-1}. Calculate molecular diameter of Ar.*

  Use, b = 4 × volume occupied by the molecules in 1 mol of a gas

  $$\Rightarrow \qquad b = 4 \times N_o \times \left(\frac{4}{3}\pi r^3\right)$$

  $$3.22 \times 10^{-5} = 4 \times 6.023 \times 10^{23} \times \frac{4}{3} \times \frac{22}{7} \times r^3$$

  $$r = \left[\frac{3.22 \times 10^{-5} \times 3 \times 7}{4 \times 6.023 \times 10^{23} \times 4 \times 22}\right]^{1/3} = 0.1472 \times 10^{-9}\ m = 0.1472\ nm$$

  d = 2r = 0.2944 nm.

Critical phenomenon and Liquefaction of gases :

The phenomenon of converting a gas into liquid is known as liquefaction. The liquefaction of gas is achieved by controlling P and T as follows :

- Increasing pressure : An increase in pressure results in increase in attraction among molecules.
- Decreasing temperature : A decrease in temperature results in decrease in kinetic energy of molecules.
- The temperature of gas must be lower than its critical temperature T_C.

Note :

(i) Condition for a real gas to get liquefied is :

Low Temperature : Molecules don't have sufficient energy to overcome the attractive forces between the gas molecules.

High Pressure : Molecules are close to each other so that they can exert sufficient attraction on each other required for the liquefication of the gas.

(ii) An ideal gas can never be liquefied whatever be the temperature and pressure conditions due to the absence of the attractive forces between its gas molecules.

Critical temperature (T_C) :

It is defined as the characteristic temperature for a given gas below which a continuous increase in pressure will bring liquefaction of gas and above which no liquefaction is noticed although pressure may be increased

***For example* :** T_C for CO_2 is 31.2°C.

Critical pressure (P_C) :

It is defined as the minimum pressure applied on 1 mol of gas placed at critical temperature, to just liquefy the gas.

Critical Volume ($V_{m,C}$) :

The volume occupied by 1 mol of gas placed at critical conditions.
(i.e. $P = P_C$ and $T = T_C$).

Note : **(i)** P_C, $V_{m,C}$, T_C are characteristic values for each gas.

(ii) The numerical values of critical constants derived from Van der Waal's equation are:

$$T_C = \frac{8a}{27Rb} \;;\; P_C = \frac{a}{27b^2} \;;\; V_{m,C} = 3b$$ [a, b are the van der Waal's gas constants]

(iii) The gas having its temperature much lower than its critical temperature, less pressure is sufficient to liquefy it.

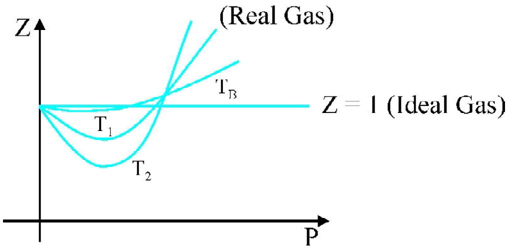
(iv) The numerical value of $\frac{RT_C}{P_C V_{m,C}} = \frac{8}{3}$ (on substituting T_C, P_C, $V_{m,C}$). Thus one can write that the value of RT/PV at critical conditions is 8/3 of normal conditions.

i.e., $$\frac{RT_C}{P_C V_{m,C}} = \frac{8}{3} = \frac{8}{3}\frac{RT}{PV}\left(\because \frac{RT}{PV} = 1\right)$$

$\Rightarrow$ At critical conditions, $$Z = \frac{P_C V_{m,C}}{RT_C} = \frac{3}{8}$$

Boyle's Temperature (T_B)

It is that temperature at which a real gas behaves ideally over a large pressure range as shown :



T_B is given by : $\frac{a}{Rb}$ where a, b are van der Waals gas constant

Note : Boyle's temperature of a gas is always higher than its critical temperature (T_C).

Collision Frequency and Mean Free Path

The collision rate (*i.e.*, the number of collisions taking place in unit time per unit volume) is called **collision frequency** (z) and is given by

$$z = \frac{\pi n^2 \sigma^2 c_{avg}}{\sqrt{2}}$$

The average of distances traveled by a molecule between successive collisions is called **mean free path** (λ).

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

where n is the number of molecules per unit molar volume.

$$n = \frac{6.02 \times 10^{23}}{0.0224} \ m^{-3}$$

c_{avg}, average velocity, σ the collision diameter *i.e.*, the minimum distance between the centres of two molecules when at the point of collision.

Also based on kinetic theory of gases, mean free path $\lambda \propto \frac{T}{P}$. Thus,

- Larger the size of the molecules, smaller the mean free path.
- Greater the number of molecules per unit volume, smaller the mean free path.
- Larger the temperature, larger the mean free path.
- Larger the pressure, smaller the mean free path.

MORE ILLUSTRATIONS

Illustration - 17 *A mixture containing 1.12L of H_2 and 1.12L of D_2 (deuterium) at S.T.P., is taken inside a bulb connected to another bulb by a stop-cock with a small opening. The second bulb is fully evacuated. The stop-cock is opened for a certain time and then closed. The first bulb is found to contain 0.05 gm of H_2. Determine the percentage composition by weight of the gases in the second bulb.*

SOLUTION :

In the first bulb :

Initial moles of $H_2 = \dfrac{1.12}{22.4} = \dfrac{1}{20}$

Initial moles of $D_2 = \dfrac{1.12}{22.4} = \dfrac{1}{20}$

Now after opening of stop-cock, mass of H_2 left in the first bulb = 0.05

⇒ Moles of $H_2 = \dfrac{0.05}{2} = \dfrac{1}{40}$

⇒ Moles of H_2 effused into second bulb

$$= \frac{1}{20} - \frac{1}{40} = \frac{1}{40}$$

Let *n* be number of moles of D_2 effused.

From Graham's Law :

$$\frac{n}{1/40} = \sqrt{\frac{2}{4}}$$

⇒ $n = \dfrac{\sqrt{2}}{80}$ = moles of D_2 in second bulb.

In the second bulb:

The mass of H_2 gas $= \dfrac{1}{40} \times 2 = 0.05\,\text{gm}$

The mass of D_2 gas $= \dfrac{\sqrt{2}}{80} \times 4 = 0.07\text{ gm}$

⇒ Total mass = 0.05 + 0.07 = 0.12 gm.

⇒ % of $H_2 = \dfrac{0.05}{0.12} \times 100 = 41.67\%$

and % of $D_2 = \dfrac{0.07}{0.12} \times 100 = 58.33\%$

Illustration - 18 *A mixture of ethane and ethene occupies 40 L at 1.0 atm and 400K. The mixture reacts completely with 130 gm of O_2 to produce CO_2 and H_2O, Assuming ideal gas behaviour, calculate the mole fractions of C_2H_4 and C_2H_6 in the mixture.*

SOLUTION :

Let x = moles of C_2H_6 and y = moles of C_2H_4

$$C_2H_6 + 7/2\ O_2 \rightarrow 2CO_2 + 3H_2O$$

$$C_2H_4 + 3O_2 \rightarrow 2CO_2 + 2H_2O$$

⇒ moles of O_2 used $= \left(\dfrac{7x}{2} + 3y\right)$

and moles of O_2 available $= \dfrac{130}{32}$

⇒ $\dfrac{7x}{2} + 3y = \dfrac{130}{32}$ ⇒ $3.5x + 3y = 4.06$

Also, $x + y = \dfrac{PV}{RT} = \dfrac{1 \times 40}{0.0821 \times 400} = 1.218$

Solving for x and y, we get :

⇒ $x = 0.812$ and $y = 0.406$

⇒ $\chi_{C_2H_6} = \dfrac{0.812}{1.218} = 0.67$ and $\chi_{C_2H_4} = 0.33$

Illustration - 19 *1 mole of CCl_4 vapours at 77°C occupies a volume of 35.0 L. If van der Waal's constants are $a = 20.39\ L^2\ atm\ mol^{-2}$ and $b = 0.1383\ L\ mol^{-1}$, calculate compressibility factor Z under,*

(a) low pressure region (b) high pressure region.

SOLUTION :

(a) Under low pressure region, V_m is high

$(V_m - b) \approx V_m$

$$\Rightarrow \quad \left(P + \frac{a}{V_m^2}\right)V_m = RT$$

$$\Rightarrow \quad PV_m + \frac{a}{V_m} = RT$$

$$Z = 1 - \frac{20.39}{0.0821 \times 350 \times 35} = 0.98$$

$$\left[\because \ Z = 1 - \frac{a}{RTV_m}\right]$$

(b) Under high pressure region P is high,

$$\left(P + \frac{a}{V_m^2}\right) \approx P$$

$\therefore \quad P(V_m - b) = RT \quad$ or $\quad PV_m - Pb = RT$

$$\Rightarrow \quad P = \frac{RT}{V_m - b}$$

$$\Rightarrow \quad Z = \frac{PV_m}{RT} = \frac{V_m}{V_m - b} = \frac{1}{1 - \dfrac{b}{V_m}}$$

$$\Rightarrow \quad Z = \frac{1}{1 - \dfrac{0.138}{35}} = 1.004$$

Illustration - 20 *At 20°C, two balloons of equal volume and porosity are filled to a pressure of 2 atm, one with 14 kg N_2 and other with 1 kg of H_2. The N_2 balloon leaks to a pressure of 1/2 atm in 1 hr. How long will it take for H_2 balloon to reach a pressure of 1/2 atm ?*

SOLUTION :

Note : $\dfrac{r_1}{r_2} = \sqrt{\dfrac{M_2}{M_1}}$

$$\Rightarrow \quad \frac{n_1/t_1}{n_2/t_2} = \sqrt{\frac{M_2}{M_1}}$$

$$\Rightarrow \quad \frac{(w_1/M_1)/t_1}{(w_2/M_2)/t_2} = \sqrt{\frac{M_2}{M_1}}$$

$$\Rightarrow \quad \frac{w_1/t_1}{w_2/t_2} = \sqrt{\frac{M_1}{M_2}}$$

where w_1, w_2 are the weights of gas 1 and 2 effused in time t_1 and t_2 respectively.

At constant V and T for a gas $P \propto w$

Thus, for N_2 : $P_1 = 2$ atm. $\quad P_2 = \dfrac{1}{2}$ atm. at $\quad t = 1$ hr

$w_1 = 14$ kg $\quad w_2 = ?$

$$\because \quad \frac{P_1}{P_2} = \frac{w_1}{w_2}$$

$$\Rightarrow \quad \frac{2}{1/2} = \frac{14}{w_2} \quad \Rightarrow \quad w_2 = \frac{14}{4}\ kg\ N_2$$

$$\text{Wt. of } N_2 \text{ diffused} = 14 - \frac{14}{4} = \frac{42}{4} = \frac{21}{2}\ kg$$

Similarly, for H_2 : $P_1 = 2$ atm, $\quad P_2 = \dfrac{1}{2}$ atm, at $t = t$ hr

$w_1 = 1$ kg $\quad w_2 = ?$

$$\Rightarrow \quad \frac{P_1}{P_2} = \frac{w_1}{w_2} \quad \Rightarrow \quad \frac{2}{1/2} = \frac{1}{w_2} \quad \Rightarrow \quad w_2 = \frac{1}{4}\ kg$$

Wt. of H_2 diffused $\Rightarrow 1-\frac{1}{4}=\frac{3}{4}$ kg

Now $\frac{r_{N_2}}{r_{H_2}}=\sqrt{\left(\frac{M_{H_2}}{M_{N_2}}\right)}$ for diffusion of N_2 and H_2

or $\frac{w_{N_2}}{w_{H_2}}\times\frac{t_{H_2}}{t_{N_2}}=\sqrt{\frac{M_{N_2}}{M_{H_2}}}$

$\Rightarrow \frac{21/2}{3/4}\times\frac{t_{H_2}}{60}=\sqrt{\frac{28}{2}}$

$\Rightarrow t_{H_2}=\frac{60}{\sqrt{14}}$ min

Alternative approach :

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

$$\frac{\Delta P_1/t_1}{\Delta P_2/t_2}=\frac{P_1}{P_2}\sqrt{\frac{M_2}{M_1}}$$

Here : $\Delta P_1=\Delta P_2=2-\frac{1}{2}$ atm and

$P_1=P_2=2$ atm

$\Rightarrow \frac{t_2}{t_1}=\sqrt{\frac{M_2}{M_1}}$

$\Rightarrow t_{H_2}=t_{N_2}\sqrt{\frac{M_{H_2}}{M_{N_2}}}=\frac{60}{\sqrt{14}}$ min

Illustration - 21 *A gaseous mixture of helium and oxygen is found to have a density of 0.518 g dm^{-3} at 25°C and 720 torr. What is the per cent by mass of helium in this mixture ?*

SOLUTION :

We know, $PM_o = dRT$

$\Rightarrow \frac{720}{760}\times M_o = 0.518\times 0.0821\times 298$

$\Rightarrow M_o = 13.37$ g/mol

Let mole fraction of He in mixture be α.

$\Rightarrow \chi_{He}=\alpha,\quad \chi_{O_2}=(1-\alpha)$

Average molecular mass $=\alpha\times M_{He}+(1-\alpha)\,M_{O_2}$

$\Rightarrow 13.37=\alpha\times 4+(1-\alpha)\,32$

$\Rightarrow \alpha = 0.666$

% by mass of He $=\frac{0.666\times 4}{0.666\times 4+0.334\times 32}\times 100$

$= 19.95\%$

THE LIQUID STATE

Section - 5

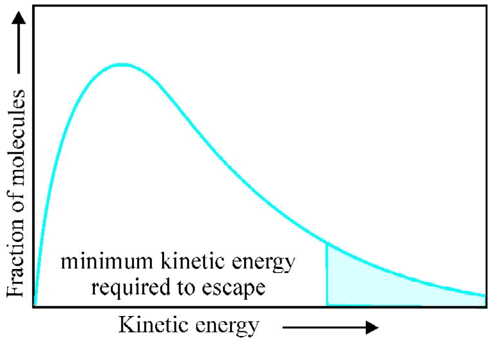
The liquid state is intermediate between gaseous and solid states. In the gaseous state the molecular interactions are very weak practically negligible and molecules are in random motion. Molecules continue to move unless they are reflected back by the walls of the vessel. Otherwise molecules would continue to move and the gas would expand to any volume. This is why gases do not have a definite volume.

In case of liquid, the molecular interactions are quite strong and a given quantity of liquid occupies a definite volume. Molecules of the liquid have so much freedom that they can flow readily and take up the shape of the container due to continuous breaking and making of weak van der Waal's bonds between the neighbouring molecules.

Molecules in solids completely lack in translation motion. The thermal motion of the molecules is so greatly reduced that they can only oscillate with respect to their fixed positions in the crystals. Each molecule in a solid has generally 6 to 12 nearest neighbours called coordination number. In the liquid state the coordination number of a molecule is not fixed but is only slightly less than in solid. The distance between the nearest neighbours in liquid is only slightly higher than that in solids. This is why there is very little expansion of solids on melting.

Vapour Pressure

The kinetic theory is the idea that there is distribution of kinetic energies and hence the molecular speeds, depending on the absolute temperature. Therefore, in any gas, liquid or solid at room temperature, a small fraction of molecules have relatively high kinetic energy. Some of these high energy molecules at the liquid surface become free resulting into its evaporation. With the departure of high energy molecules the average kinetic energy decreases leading to a fall in temperature of the liquid. This explains why evaporation causes cooling.



In a closed vessel, some free space above the liquid, the evaporated molecules cannot escape to the atmosphere. Initially the vapour pressure increases and then comes to a constant value. The volume of the liquid decreases initially and then becomes constant over a period of time. Increase in pressure means more number of collisions with the walls of the container.

Inside a closed vessel, the liquid and its vapours are in *dynamic equilibrium*. The pressure exerted by the vapours is then known as *equilibrium vapour pressure*. Since the vapour pressure is a kinetic phenomena, it is independent of the amount of a liquid .It only depends on the temperature. The temperature must, therefore, be specified with the vapour pressure of a liquid.

A liquid is said to be at its boiling temperature if its vapour pressure is equal to external pressure. Therefore, the boiling point of water in particular and of liquids in general decreases as altitude of a place increases where the external pressure is less than one atmospheric pressure

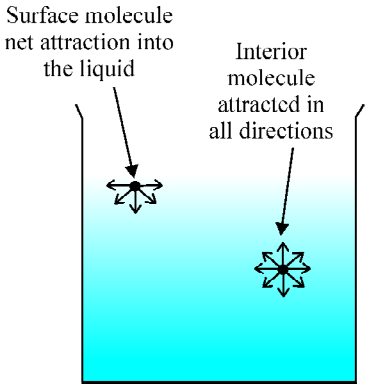
Vapour pressure of solids

When a solid is directly converted to its vapour state, then the process is called *sublimation*. Substances like ammonium chloride, iodine, camphor, solid carbon dioxide sublime at ordinary temperature and pressure. The white cloud like trail that we see coming out of the high flying jet is water vapours issuing from the exhausts of high flying jets, getting converted directly into microcrystalline ice which is slowly reconverted into water vapour without passing through the liquid state. This property of sublimation is used in the process called **freeze drying.**

Surface Tension

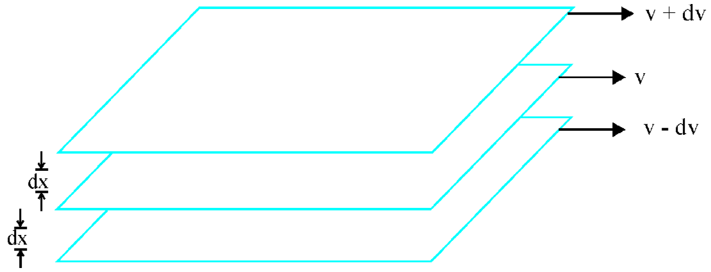
Surface tension is one of the characteristic properties of liquids. Each molecule in the liquid state is influenced by the nearest neighbour molecules. A molecule in the bulk of liquid experiences equal attractive forces from all sides. There is no resultant force on the molecule which tries to move it in any direction, whereas for a molecule at the surface of the liquid, the net attraction towards the liquid is greater than that towards the vapour state.

The energy required to increase the surface area of the liquid by one unit, is defined as its surface tension. It is represented by the *Greek letter* γ (gamma). The liquid surface, in the absence of any other force tends to attain a minimum area. Mathematically it can be shown that for a given volume, the sphere has a minimum area. Hence the water drop acquires a spherical shape. Liquid in a capillary tube rises due to its surface tension. Surface tension is also defined as the force acting per unit length perpendicular to the line drawn on the surface. The units of surface tension is Nm^{-1} .



Viscosity of liquids

The ease with which a fluid can flow is determined by its property called *viscosity*. Viscosity arises due to the internal friction between layers of fluids as they pass over each other. When a liquid is steadily flowing over a fixed horizontal surface the layer immediately in contact with the surface is stationary. The velocity of the layers increases with the distance from the fixed surface. if we select a layer, the layer immediately below tries to retard its flow(velocity),while the one above tries to accelerate the flow. Force required to maintain the flow in the three layers described above is directly proportional to the area of contact and velocity gradient.



Velocity gradient = dv/dx

Frictional force, $F \alpha A\left(\frac{dv}{dx}\right)$

Force is proportional to area in contact and velocity gradient, i.e.,

$F \propto A$ (Area) ......(i)

and $F \propto \frac{dv}{dx}$ (velocity gradient) ......(ii)

On combining (i) & (ii) , we get : $F \propto \frac{dv}{dx}$

$$\Rightarrow \quad F = \eta A \frac{dv}{dx}$$

where η is a constant, called as the coefficient of viscosity and it has the unit of poise, $g\ cm^{-1}s^{-1}$.

THE SOLID STATE

Section - 6

The substance is said to be in solid state if the molecular interaction energy predominates over the disruptive thermal energy.

Covalent Solids

A covalent solid is a giant molecule having a three dimensional network of covalent bonds. Examples are diamond, silicon carbide, silica. These are generally very hard.

Ionic Solids

Ionic solids are three dimensional arrangements of cations and anions bound by coulombic forces .The crystal on the whole are electrically neutral. Such solids are characterized by high melting and boiling points. The ionic solids do not conduct electricity as ions present therein are not free to move. Examples are sodium chloride, barium oxide and calcium fluoride.

Metallic Solids

Metals are orderly collection of positive ions surrounded by and held together by free electrons, each metal atom donating one or more electrons. The bonding is not directional. The metals are good conductors of heat and electricity. They are highly malleable and ductile. These sets of properties can be attributed to this structure of metals. Metals like sodium crystallize- in simple cubic lattice. The presence of a sea of mobile electrons in a metal accounts for its high electrical and thermal conductivity.

Molecular Solids

Many combinations of elements result into covalent molecules. These are discrete units capable of independent existence. Thus we have molecules like di-hydrogen, di-nitrogen, methane etc. which are called covalent compounds. They have weak molecular interaction. Even mono-atomic molecules like the noble gases, form molecular solids. These solids are characterized by low melting points.

THINGS TO REMEMBER

2. Boyle's Law : $PV = \text{constant}$ (Keeping T and n constant)

3. Charle's Law : $\frac{V}{T} = \text{constant}$ (Keeping P and n constant)

4. Combined Gas Law : $\frac{PV}{T} = \text{constant}$ (Keeping n constant)

5. Gay Lussac's Law : $\frac{P}{T} = \text{constant}$ (Keeping V and n constant)

6. 1 mol Ideal Gas = 22.4 L at STP.

7. Ideal gas Equation : $PV = nRT$ or $PV_m = RT$ $(V_m = V/n)$

8. Dalton's law of Partial Pressure :

$$P_{Total} = \frac{(n_1 + n_2 + \ldots)}{V}RT \quad \text{Partial pressure of a gas} = \chi_{Gas} \times P_{Total}$$

9. Graham's Law of Diffusion : Rate of diffusion/effusion $= \frac{\Delta n}{\Delta t}$ or $\frac{\Delta P}{\Delta t}$ or $\frac{\Delta V}{\Delta t}$

$$= \frac{P}{\sqrt{M}}$$

10. Maxwell's speed distribution : $C_{rms} = \sqrt{\frac{3RT}{M_o}}$; $C_{avg} = \sqrt{\frac{8RT}{\pi M_o}}$; $C_{MP} = \sqrt{\frac{2RT}{M_o}}$

[T is in Kelvin : M_o is in kg/mol : R = 8.314 kJ/mol]

11. Kinetic Energy of Gas : $KE_{avg} = \frac{3}{2}k_BT$

12. Real Gas Equation : $\left(P + \frac{an^2}{V^2}\right)(V - nb) = nRT$ and $Z = \frac{PV_m}{RT}$

b = 4 × volume of 1 mol of gas molecules.

13. Critical constants for a real gas $T_C = \frac{8a}{27Rb}$; $P_C = \frac{a}{27b^2}$, $V_{m,\,C} = 3b$

14.

$$\text{Real Gas} \xrightarrow{\text{High T and Low P}} \text{Ideal Gas}$$

$$\text{Real Gas} \xrightarrow{\text{Low T and High P}} \text{Liquify}$$

In low Pressure Region : $\left(P + \frac{a}{V_m^2}\right)V_m = RT$ & $Z = 1 - \frac{a}{RTV_m}$

In High Pressure Region : $P(V_m - b) = RT$ & $Z = 1 + \frac{Pb}{RT}$