LESSON **5**

STATES OF MATTER

1. INTRODUCTION

Matter can be classified into three categories depending upon its physical state namely solid, liquid and gaseous states. Solids have a definite volume and shape; liquids also have a definite volume but no definite shape; gases have neither a definite volume nor a definite shape.

DISTINCTION BETWEEN THREE STATES OF MATTER

Sl. No.	Solids	Liquids	Gases
1.	Particles are very Closely packed	Particles are loosely packed	Particles are very loosely packed
2.	Voids are extremely small	Voids are relatively larger	Voids are very large
3.	Inter particle forces are large	Inter particle forces are intermediate	Intermediate forces are negligible
4.	Particle motion is restricted to vibratory motion.	Particle motion is very slow	Particle motion is very rapid and also random.

MEASURABLE PROPERTIES OF GASES

Mass, volume, temperature are the important measurable properties of gases.

- **Mass:** The mass of the gas is related to the number of moles as

  $n = \dfrac{w}{M}$

  Where n = number of moles

  w = mass of gas in grams

  M = molecular mass of the gas

- **Volume:** Since gases occupy the entire space available to them, therefore the gas volume means the volume of the container in which the gas is enclosed.

  Units of Volume: Volume is generally expressed in litre or cm^3 or dm^3 $1m^3 = 10^3$ litre $= 10^3 dm^3 = 10^6 cm^3$.

- **Pressure:** The force exerted by the gas per unit area on the walls of the container is equal to its pressure.

  Units of Pressure: The pressure of a gas is expressed in atm, Pa, Nm^{-2}, bar or, lb/In^2 (psi).

  760 mm = 1 atm = 10132.5 KP_a = 101325 P_a = 101325 Nm^{-2}

760 mm of Hg = 1.01325 bar = 1013.25 milli bar = 14.7 lb/2n^2 (psi)

- **Temperature:** Temperature is defined as the degree of hotness. The SI unit of temperature is Kelvin. On the Celsius scale water freezes at 0°C and boils at 100°C where as in the Kelvin scale water freezes at 273 K and boils at 373 K.

NATURE OF GASES

If the thermal energy is much greater than the forces of attraction, then we have matter in its gaseous state. Molecules in the gaseous state move with very large speeds and the forces of attraction amongst them are not sufficient to bind the molecules at one place, with the result that the molecules move practically independent of one another. Because of this feature, gases are characterized by marked sensitivity of volume change with change of temperature and pressure. There exists no boundary surface and, therefore, gas tends to fill completely any available space, i.e. they do not possess a fixed volume.

2. EXPERIMENTALLY DERIVED GAS LAWS

2.1 BOYLE'S LAW

The English scientist Robert Boyle made the first reliable measurement of the properties of gases in the seventeenth century. According to this law "At constant temperature, the volume of a definite mass of a gas is inversely proportional to its pressure, that is,

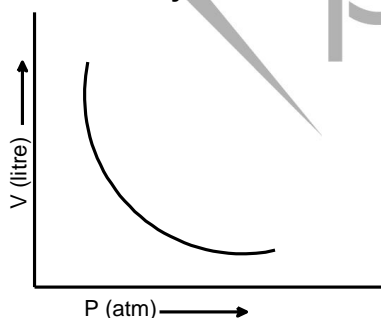$$V \propto \frac{1}{P} \qquad \ldots\ldots\ldots(2.1a)$$

$$V = \frac{K}{P} \quad \text{or} \quad PV = K$$

where K is a constant whose value depends upon (i) nature of the gas, (ii) temperature of the gas, and (iii) mass of the gas. For a given mass of a gas at constant temperature, Boyle's Law gives
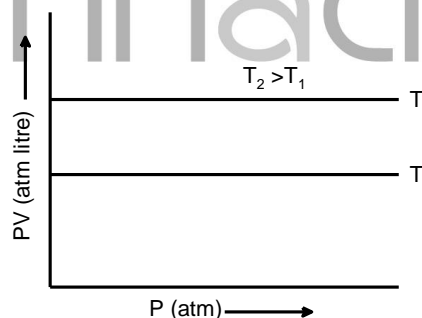
$$P_1V_1 = P_2V_2$$

where V_1 and V_2 are volumes at pressures P_1 and P_2 respectively.

Graphical Representation of Boyle's Law

(a) Plot of V against P   (b) Plot of PV against P

- Plot. (a) shows the plot of V vs P at a particular temperature. It shows that P increases V decreases. The nature of curve is a rectangular hyperbola. The general term isotherm (meaning at constant temperature) is used to describe these plots.
- Plot (b) shows the plot of PV vs P at particular temperature. It indicates that PV value remains constant inspite of regular increase in P.

2.2   CHARLES' LAW

Nearly two centuries later, a new pastime, hot air ballooning, motivated two French scientists, Jacques Charles and Joseph−Louis Gay−Lussac, to discover two additional gas laws.

Charles made measurements of a fixed mass of a gas at various temperatures under the condition of constant pressure and found that the volume of the gas is a linear function of temperature.

This can be expressed as

$$V_t = a + bt \qquad \qquad \text{..........(2.2b)}$$

where t is temperature and a and b are constants.

Equation (2.2b) has been plotted in Fig 2.2b. The intercept on the vertical axis is a and it is equal to V_0, the volume at 0°C. The slope of the plot is the derivative

$$\left(\frac{dV}{dt}\right)_P = b \; .$$

ALTERNATE FORM OF CHARLES' LAW:

Experimental data shows that for each degree rise in temperature, the volume of a gas expands $\dfrac{1}{273.15}$ of its volume at 0°C. If V_0 is the volume of a gas at 0°C, then b is given by

$$b = \frac{V_\circ / 273.15}{1^\circ C}$$

With this, equation (2.2b) becomes

$$V_t \; = V_0 + \left(\frac{V_\circ / 273.15}{1^\circ C}\right) t$$

$$= V_0 \left(1 + \frac{t / 1^\circ C}{273.15}\right)$$

$$= V_0 \left(\frac{273.15 + t / 1^\circ C}{273.15}\right) \qquad \text{..........(2.2c)}$$

It is convenient to use the absolute temperature scale on which temperatures are measured in Kelvin (K). A reading on this scale is obtained by adding 273.15 to the Celsius value. Temperature on the Kelvin scale is denoted by T. Thus,

$$T/K = 273.15 + \frac{t}{1^\circ C}$$

$$V_T = V_0 \frac{T/K}{273.15}$$

$$V_T = \left(\frac{V_\circ}{273.15\,K}\right) T$$

Since V_0, is the volume of the gas at 0°C, has a constant volume at a given pressure, the above relation can be expressed as

$$V_T = K_2T \qquad\qquad ....(2.2d)$$

where K_2 is a constant whose value depends upon the nature, mass and pressure of the gas.

Equation (2.2d) in an alternative form of Charles Law according to which the volume of a given mass of a gas at constant pressure is directly proportional to its Kelvin temperature.

A typical variation of volume of a gas with change in its Kelvin temperature is shown in Fig 2.2b.
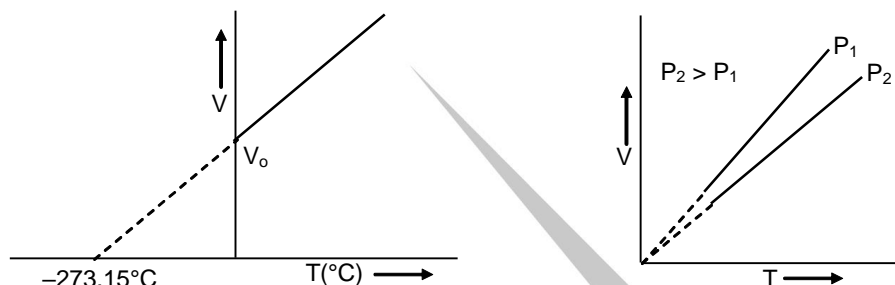

Figure 2.2b

The general term isobar, which meant at constant pressure, is assigned to these plots. Since volume is directly proportional to Kelvin temperature, the volume of a gas should theoretically be zero at Kelvin zero. However, gases liquefy and then solidify before this low temperature is reached. In fact, no substance exists as a gas at a temperature near Kelvin, zero though the straight line plots can be extrapolated to zero volume. The temperature that corresponds to zero volume is $-273.15°C$.

2.3 GAY – LUSSAC'S LAW

An expression similar to volume dependence of gas on temperature has been derived for the pressure dependence also. The pressure of a given mass of a gas at constant volume varies linearly with temperature.

$$P_t = a + bt \qquad\qquad ....(2.2e)$$

where $a = P_°$ and $b = \left(\dfrac{dP}{dt}\right)_V$. The value of the latter can be determined experimentally and is found to be ($P_°$ / 273.15°C). Thus equation (2.2e) modifies to

$$P_t = P_° + \left(\frac{P_°}{273.15}\right)\frac{t}{1°C}$$

Therefore $P_t = P_° \left(\dfrac{273.15 + t/1°C}{273.15}\right)$

$$= \frac{P_°}{273.15\,K}T$$

or $\qquad P \propto T \qquad\qquad ....(2.2f)$

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

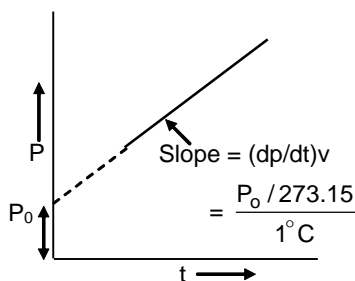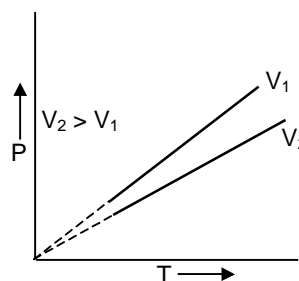Equations (2.2 e) and (2.2f) are shown graphically in Fig. 2.2c and 2.2d.

Figure 2.2c

Figure 2.2d

2.4 AVOGADRO'S LAW

According to Avogadro's law, equal number of molecules of different gases under identical conditions of temperature and pressure occupy the same volume. This shows that the volume occupied by different gases having the same number of molecules under identical conditions of temperature and pressure is independent of the nature of the gaseous molecules. Thus, whether the molecules are heavy (e.g. Br_2) or light (e.g. H_2) gases with equal number of molecules would occupy the same volume. This leads to one of the most important features of gases that the distance between molecules is much larger than the actual dimensions of molecules, since otherwise, Avogadro's law would not have been true.

$n \propto V$ (where n is the number of mole and V is the volume of gas)

2.5 EQUATION OF STATE

The results of all these laws can be combined into an expression which represents the relationship between pressure, volume and temperature and number of moles of a gas; such an expression is described as an equation of state.

Suppose the gas is in the initial state with volume V_1, pressure P_1 and temperature T_1. We then change the state of gas to a volume V_2, pressure P_2 and temperature T_2. Let us carry out this change in two steps.

(i)   First we change the pressure from P_1 to P_2 keeping the temperature T_1 constant. The resultant volume V_r as given by Boyle's law is

$$V_r = \frac{P_1 V_1}{P_2}$$

(ii)   Next, temperature is changed from T_1 to T_2, keeping the pressure P_2 constant. The final volume V_2 as given by Charle's law is

$$V_2 = \frac{V_r T_2}{T_1} = \frac{(P_1 V_1 / P_2) T_2}{T_1}$$

or $\dfrac{P_1 V_1}{T_1} = \dfrac{P_2 V_2}{T_2}$ ....(2.2g)

It also follows that no matter how we change the state of the given amount of a gas, the ratio $\dfrac{PV}{T}$ always remains constant, i.e.

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

The value of K depends on the amount of gas in the system. Since V is an extensive property (which is

mass dependent), its value at constant P and T is proportional to the amount of the gas present in the system. Then K must also be proportional to the amount of gas because P and T are intensive properties (which has no dependence on mass).

We can express this by writing K = nR, in which n is the amount of gas in a given volume of gas and R is independent of all variables and is, therefore, a universal constant. We thus have the general gas law

$$PV = nRT \qquad\qquad \text{..........(2.2h)}$$

The universal gas constant as given by equation (2.2h) is R = $\dfrac{PV}{nT}$. Thus, it has the units of (pressure × volume) divided by (amount of gas × temperature). Now the dimensions of pressure and volume are,

Pressure = (force/area) = force/(length)^2 = force × length^{-2}

volume = length^3

Thus R = $\dfrac{(\text{force} \times \text{length}^{-2})\,(\text{length}^3)}{(\text{amount of gas})\,(\text{Kelvin})}$ = $\dfrac{(\text{force} \times \text{length})}{(\text{amount of gas})\,(\text{Kelvin})}$

= $\dfrac{\text{work (or energy)}}{(\text{amount of gas})\,(\text{Kelvin})}$

Thus, the dimensions of R are energy per mole per Kelvin and hence it represents the amount of work (or energy) that can be obtained from one mole of a gas when its temperature is raised by one Kelvin.

Alternatively, Ideal Gas Equation

A gas that would obey Boyle's and Charle's law under the conditions of temperature and pressure is called an ideal gas.

Here, we combine four measurable variables P, V, T and n to give a single equation.

$V \propto n$ [P, T constant]   Avogadro's law

$V \propto T$ [n, P constant]   Charle's law

$V \propto \dfrac{1}{P}$ [n, T constant]   Boyle's law

The combined gas law can be written as $V \propto \dfrac{nT}{P}$ or $PV \propto nT$

$$PV = nRT$$

this is called ideal gas equation

where R is the constant of proportionality or universal gas constant

The value of R was found out to be

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

R = 0.0821 litre atm K^{-1} mol^{-1}

R = 2 cal K^{-1} mol^{-1}

Relation between molar mass and density (From ideal gas equation)

$$n = \dfrac{W}{M}$$

$$P = \dfrac{nRT}{V}$$

$$P = \dfrac{W}{V}\dfrac{RT}{M}$$

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$$P = d\frac{RT}{M} \Rightarrow d = \frac{PM}{RT}$$

3. CONCEPT OF IDEAL GAS

So far, we have assumed that all gases obey the gas laws under all conditions of temperature and pressure; however, for real gases this is not true. Real gases obey these laws only under limited condition of low pressures and high temperatures. They exhibit deviations from the gas laws and these deviations are greater when the temperature and pressure are close to the condition at which the gas can be condensed into a liquid. Thus Boyle's law, Charle's law and the equation of state derived based on these laws may be regarded as approximation for real gases and are expected to be applicable only at relatively low pressures and moderately high temperature. It is, nevertheless, very useful to postulate a hypothetical ideal gas, defined as a gas to which the laws of Boyle and Charles are strictly applicable under all conditions of temperatures and pressures. It is for this reason that (2.2h) is commonly referred to as the ideal gas equation. Real gases attain ideal behaviour only at very low pressures and very high temperatures.

Since equation (2.2h) is not applicable to real gases, the evaluation of the universal gas constant R cannot be done directly by utilizing the pressure, volume and temperature data of real gases. Equation (2.2h) is strictly applicable only for ideal gases and thus if the pressure and volume of one mole of an ideal gas were known at definite temperature it would be a simple matter to evaluate R from equation (2.2h). However, as no gas behaves ideally, this procedure would appear to be ruled out. But we know from experiments that gases approach ideal behaviour as the pressure is decreased. Hence, the extrapolation method (P→ 0) on the data of real gases can be utilized to determine the corresponding properties of an ideal gas. The data obtained in this manner, after extrapolation, should be independent of the characteristics of the actual gas employed for the experiment. By measuring the volume of one mole of a real gas at different pressures and constant temperature, a graph between PV and P can be drawn. On extrapolating this graph to zero pressure to correct for departures from ideal behaviour it is possible to determine the value of PV, which is expected to be applicable to one mole of an ideal gas. Since this value of PV is expected to be independent of the nature of the gas, the same value of (PV) would be obtained irrespective of the gas employed for this purpose. In other words, the graphs of PV vs P of different gases must yield the same value of $(PV)_{P\to 0}$. Infact, it is found to be so, as is evident from Fig 3.1a.
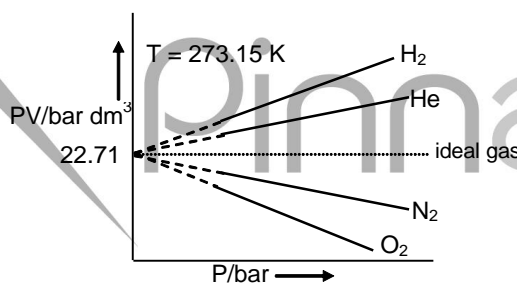
Figure 3.1a

The value of $(PV)_{P\to 0}$ at 273.15 K is found to be 22.71 dm^3 bar. Thus if P = 1 bar, then V = 22.71 dm^3, that is, the volume occupied by one mole of an ideal gas at standard temperature (273.15K) and 1 bar pressure is 22.71 dm^3.

The value of R in SI units can be worked out as follows.

$$R = \frac{PV}{nT} = \frac{(1\,bar)(22.71\,dm^3)}{(1\,mol)(273.15K)} = 0.08314\ bar\ dm^3\ K^{-1}\ mol^{-1}$$

Since 10^2 kPa = 1bar, the value of R expressed in kPa dm^3 K^{-1} mol^{-1} will be

$R = 0.08314 \ (10^2 \ kPa) \ dm^3 \ K^{-1} \ mol^{-1}$

$= 8.314 \ kPa \ dm^3 \ K^{-1} \ mol^{-1}$

$= 8.314 \ JK^{-1} \ mol^{-1}$

Illustration 1

Question: **Estimate the number of gaseous molecules left in a volume of 1mm^3 if it is pumped out to give a vacuum of 10^{-6} mm Hg at 298K.**

Solution:

$P = 10^{-6}$ mm of Hg

$= \dfrac{10^{-6} \ of \ Hg}{760 \ mm \ of \ Hg} = 1.315 \times 10^{-9}$ atm.

$V = 1mm^3 = 1 \times (10^{-3}m)^3$

$= 10^{-9}m^3 = 10^{-9} \times (10 \ dm)^3 = 10^{-6} \ dm^3 = 10^{-6} \ L$

$n = \dfrac{PV}{RT} = \dfrac{\left(1.315 \times 10^{-9} \ atm\right)\left(10^{-6} L\right)}{\left(0.0821 \ atm \ L \ mol^{-1} K^{-1}\right) \ (298K)}$

$= 5.38 \times 10^{-17}$ moles

Number of molecules $= 5.38 \times 10^{-17} \times 6.023 \times 10^{23}$

$= 3.24 \times 10^7$ **molecules**

Illustration 2

Question: **When 2 g of gaseous substance A is introduced into an initially evacuated flask kept at 25°C, the pressure is found to be 101.325 kPa. The flask is evacuated and 3 g of B is introduced. The pressure is found to be 50.602 kPa at 25°C. Calculate the ratio M_A/M_B.**

Solution:

$\dfrac{P_A V_A}{P_B V_B} = \dfrac{W_A R T_A}{M_A} \times \dfrac{M_B}{W_B R T_B} \qquad (T_A = T_B \ and \ V_A = V_B)$

$\Rightarrow \dfrac{P_A}{P_B} = \dfrac{W_A M_B}{W_B M_A}$

$\Rightarrow \dfrac{101.325 \ kPa}{50.602 \ kPa} = \dfrac{(2g) \ (M_B)}{(3g) \ (M_A)}$

$\Rightarrow \dfrac{M_A}{M_B} = \dfrac{1}{3}.$

4. LAW OF PARTIAL PRESSURES

The relation between the total pressure of a mixture of gases and the pressures of the individual gases was expressed by Dalton in the form of law of partial pressures. The partial pressure of a gas in a mixture is defined as the pressure at which the gas would exist if it is allowed to occupy the whole volume of the mixture at the same temperature.

According to Dalton's law of partial pressures, the total pressure of a mixture of gases is equal to the sum of the partial pressures of the constituent gases.

Let a mixture of non–reacting gases have n_1 moles of the first gas, n_2 moles of the second gas, and so on. Let the corresponding partial pressures be P_1, P_2…. The total pressure is given by

$$P_{total} = P_1 + P_2 + \ldots..$$

If the gases present in the mixture behave ideally, then, it is possible to write separately for each gas,

$P_1V = n_1RT$ ……..(4.1a)

$P_2V = n_2RT$ ……..(4.1b)

Hence $(P_1 + P_2 + \ldots\ldots) V = (n_1 + n_2 + \ldots\ldots) RT$

i.e., $P_{total} V = n_{total} RT$ …..(4.1c)

(where n_{total} is the total amount of gases in the mixture)

Dividing equation (4.1a) and (4.1b) by equation (4.1c), we get

$$P_1 = \frac{n_1}{n_{total}} P_{total} = X_1 P_{total} \qquad ……..(4.1d)$$

$$P_2 = \frac{n_2}{n_{Total}} P_{Total} = X_2 P_{total} \qquad ………(4.1e)$$

The fractions n_1/n_{total}, n_2/n_{total}, etc. are called the mole fractions of the respective gases. The mole fraction of a constituent of any mixture is defined as the number of moles of that constituent divided by the total number of gaseous moles of the mixture. If X's are given, it is possible to calculate the partial pressure by using equation (4.1d) and (4.1e).

The partial volume of a gas in a mixture is defined as the volume, which the gas would occupy if it were present alone in a container at temperature T and pressure P of the mixture. According to the ideal gas equation, this is given by

$$V_1 = n_1\left(\frac{RT}{P}\right) \qquad ……..(4.1\,f)$$

$$V_2 = n_2\left(\frac{RT}{P}\right) \qquad ……..(4.1\,g)$$

Adding (4.1f) and (4.1g), we get

$$V_1 + V_2 + \ldots.= (n_1 + n_2 + \ldots\ldots)\left(\frac{RT}{P}\right)$$

$$= n_{total}\frac{RT}{P} = V_{total} \qquad ….. (4.1\,h)$$

This is Amagat's law of partial volumes according to which the total volume of a mixture of gases is equal to the sum of the partial volumes of the constituent gases.

Dividing equation (4.1 f) and (4.1 g) by (4.1 f), we get

$V_1 = X_1 V_{total}$

$V_2 = X_2 V_{total}$

Illustration 3

Question: **500 ml of nitrogen at a pressure of 700 mm of mercury and 600 ml of oxygen at 800 mm of Hg are passed into 2 L evacuated flask at the same temperature. Calculate the total pressure of the mixture of gases.**

Solution:

When 500 ml of N_2 is passed into a 2 L flask, it will now occupy 2 L. Since the number of mole of N_2 is the same as before and so is the temperature,

$\therefore P_1V_1 = P_2V_2$

The new pressure of N_2 would be

$P_2 = \dfrac{P_1V_1}{V_2} = \dfrac{700 \times 500}{2000}$

$\qquad = 175$ mm of Hg.

Similarly for O_2, the new pressure would be $= \dfrac{800 \times 600}{2000} = 240$ mm of Hg

Since $P_{Total} = P_{N_2} + P_{O_2}$

$= 175 + 240 =$ **415 mm of Hg**

Alternatively:

$P_{N_2} V_{N_2} + P_{O_2} V_{O_2} = P_T V_T$

$P_T = \dfrac{500 \times 700 + 600 \times 800}{2000} =$ **415 mm Hg**.

Illustration 4

Question: **Dry air has composition 78 mol % nitrogen, 21 mol % oxygen and 1 mol % other gases. Calculate the partial pressures of the components when the total pressure is 1 atm.**

Solution:

X_{N_2} (mole fraction of N_2) $= \dfrac{78}{100} = 0.78$ $\qquad [\because$ mole percent = mole fraction $\times 100]$

$X_{O_2} = \dfrac{21}{100} = 0.21$

$X_{\text{other gases}} = \dfrac{1}{100} = 0.01$

$P_i = X_i P_{total}$

$\therefore P_{N_2} = 0.78 \times (1 \text{ atm}) =$ **0.78 atm**

$P_{O_2} = 0.21 \times (1 \text{ atm}) =$ **0.21 atm**

$P_{\text{other gases}} = (0.01) \times (1 \text{ atm}) =$ **0.01 atm**

Illustration 5

Question: **In a mixture of carbon dioxide and hydrogen, the partial pressure of carbon dioxide is 0.4 atm. If the total pressure is 2 atm, What is percentage composition of the mixture by volume?**

Solution:

P_{total} = 2 atm

P_{CO_2} = 0.4 atm

$X_{CO_2} = \dfrac{P_{CO_2}}{P_{total}} = \dfrac{0.4}{2} = 0.2$

$X_{H_2} = 1 - 0.2 = 0.8$

Mole % of $CO_2 = 0.2 \times 100 = 20\%$

Mole % of $H_2 = 0.8 \times 100 = 80\%$

Mole % is same as volume %

$\therefore$ Volume % of $CO_2 = 20\%$ and volume % of $H_2 = 80\%$.

5. DIFFUSION & EFFUSION

Diffusion is the mixing of two or more gases due to partial pressure difference. A gas would move (if required against gravity also) from its region of high partial pressure to a region of low partial pressure. At the end of this process a gas would have the same partial pressure everywhere.

Effusion is leaking of gas through a small orifice into vacuum.

According to the Graham's law,

rate of diffusion or effusion, $r \propto \dfrac{1}{\sqrt{M}}$

(where M is the molecular weight of the gas)

Later it was shown that

$r = \dfrac{KP}{\sqrt{M}}$

where K is a constant and P is the pressure of the gas.

Now it is believed that,

$r = \dfrac{PA}{\sqrt{2\pi RTM}}$

r = rate of effusion or diffusion through a small orifice (measured in mol/sec)

P = Partial pressure difference of a gas (measured in Pascal)

R = Universal gas constant (8.314 J mol^{-1} K^{-1})

T = Temperature of the gas (measured in K)

M = Molecular weight of the gas(measured in Kg mol^{-1}) effusing out

A = Area of orifice (measured in m^2)

Let us now understand each parameter.

Pressure:

It is quite logical to understand that more is the partial pressure difference more will be the rate of diffusion. When a gas is kept in a container with pressure P and it is placed in an environment where the pressure of the gas is P′, then obviously the rate of gas flow should be proportional to (P−P′) and the flow will take place in the direction of high pressure to low pressure.

Area:

The rate of gas flow should be directly related to the area of the orifice. Greater the orifice area, greater should be the number of molecules coming out per unit time.

Molecular weight:

Heavier the gas, slower should be its movement.

Temperature:

It would have been expected that temperature increase should have increased the rate of gas flow from a container. This follows because increase of gas temperature, would increase the energy of the molecules and would therefore increase the velocities of gas molecules. But it should be noted that when a gas molecule moves out of a container through a small orifice, it is required to move in a very restricted path to be able to come out of the orifice. An increase in temperature no doubt would increases the velocity,
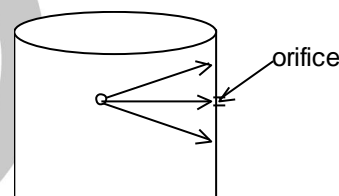
Figure 5.1a

but it would also hamper the ability of the molecule to orient itself properly with the orifice. If the orifice is large then the rate of effusion would increase with increase in temperature as the orientation would not matter much for effusion to take place.

If P, A and T for two gases is same, then

$$r_1 \propto \frac{1}{\sqrt{M_1}}$$

$$r_2 \propto \frac{1}{\sqrt{M_2}}$$

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

Illustration 6

Question: **Two containers A and B of equal volume hold 5 mol N$_2$ and 5 mol O$_2$ respectively at the same temperature. Both containers are kept separately in vacuum. Calculate the ratio of rate of diffusion of N$_2$ to that of O$_2$ if the area of orifice in both containers is same.**

Solution:
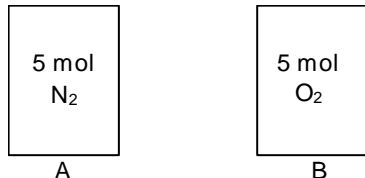
Since, the volume and temperature are same for both the containers,

$$P \propto n$$

$$\frac{P_{N_2}}{P_{O_2}} = 1$$

$$\frac{r_{N_2}}{r_{O_2}} = \sqrt{\frac{M_{O_2}}{M_{N_2}}} = \sqrt{\frac{32}{28}} = \sqrt{\frac{8}{7}} = 1.069$$

Illustration 7

Question: Two containers A and B of equal volume hold 3 mol of N_2 and 5 mol of O_2 respectively at the same temperature. Both containers are kept separately in vacuum. Calculate the ratio of rates of N_2 to that of O_2 if the area of orifice in both containers is same.

Solution:
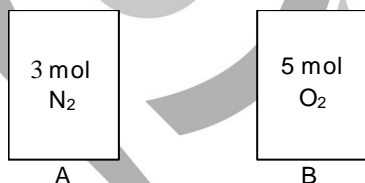
As, $p \propto n$

$$\frac{P_{N_2}}{P_{O_2}} = \frac{3}{5}$$

$$\frac{r_{N_2}}{r_{O_2}} = \frac{P_{N_2}}{P_{O_2}} \sqrt{\frac{M_{O_2}}{M_{N_2}}} = \frac{3}{5} \sqrt{\frac{32}{28}}$$

$$= \frac{3}{5} \sqrt{\frac{8}{7}} = 0.6414$$

Illustration 8

Question: Two containers A and B of equal volume hold 3 mol of N_2 + 2 mol of He and 5 mol of O_2 respectively at the same temperature. Both containers are kept separately in vacuum. Calculate the ratio of rates of effusion of gas mixture in container A to that of O_2 if the area of orifice in both containers is same.

Solution:
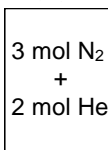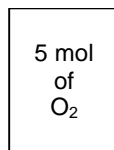
3 mol N_2 + 2 mol He	5 mol of O_2
A	B

Now, we have two gases in container A. The only difference this situation has with the previous question is that the molecular weight of the gas mixture has to be calculated.

Molecular weight of any substance is the weight in grams of 1 mole of the mixture.

3 mol of N_2 and 2 mol of He mixture weighs = $3 \times 28 + 2 \times 4 = 92$

weight of one mole of this mixture would be = $\dfrac{92}{5}$ = 18.4

$$\frac{r_{mix}}{r_{O_2}} = \frac{P_{mix}}{P_{O_2}} \sqrt{\frac{M_{O_2}}{M_{mix}}} = \sqrt{\frac{32}{18.4}} = 1.319$$

6. KINETIC THEORY OF GAS

After knowing the experimental gas laws, it is of interest to develop a theoretical model based on the structure of gases, which can correlate all the experimental facts, fortunately such a theory has been developed (known as the kinetic theory of gases) and based upon certain essential postulates (which are supposed to be applicable to an ideal gas) it is possible to derive an expression (known as the kinetic gas equation) from where all these gas laws can also be derived. Essential postulates are:

- A gas consists of a large number of very small spherical tiny particles, which may be identified with the molecules. The molecules of a given gas are completely identical in size, shape and mass.

- The volume occupied by the molecules is negligible in comparison to the volume of the gas.

- The molecules are in rapid motion, which is completely random. During their motion, they collide with one another and with the sides of the vessel. The collisions are perfectly elastic in nature.

- The laws of classical mechanics, in particular Newton's second law of motion, are applicable to the molecules in motion.

- There is no force of attraction or repulsion amongst the molecules, i.e. they are moving independent of one another.

- At any instant, a given molecule can have energy ranging from a small value to a very large value, but the average kinetic energy remains constant at a given temperature, i.e. The average kinetic energy is proportional to the absolute temperature of the gas.

6.1 DERIVATION OF THE KINETIC GAS EQUATION

Imagine a cube of edge length *l*, containing N molecules, each having a mass of m. Molecules are moving at random in all directions, with speed covering a considerable range of values.

The velocity u, of any molecule may be resolved into three component velocities designated as u_x, u_y, u_z. These are in the three directions at right angles to each other and parallel to the sides of the cube as shown in Fig 6.1 (a). The component velocities are related by the expression,

$$u^2 = u_x^2 + u_y^2 + u_z^2 \qquad \text{..... (6.1 a)}$$
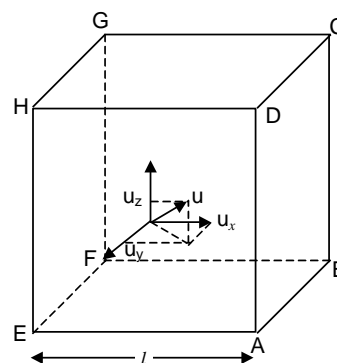
(Fig 6.1a)

Considering the *x*–component velocity of a molecule, we will have

Momentum of molecule before collision with the side ABCD $= mu_x$

Momentum of the molecule after collision with the side ABCD $= -mu_x$

Change of momentum of the molecule in a single collision with the side ABCD $= |2mu_x|$

Since *l* is the edge length of the cube, the molecule has to travel a distance 2*l* to arrive back at the wall ABCD. The number of collisions per unit time with the wall ABCD will be equal to $\dfrac{u_x}{2l}$

The total change in momentum per unit time due to such impacts is

$$2mu_x\left(\frac{u_x}{2l}\right) = \frac{mu_x^2}{l}$$

According to Newton's second law of motion

$$\begin{aligned}
\text{Force} &= \text{mass} \times \text{acceleration} \\
&= \text{mass} \times \frac{d(\text{velocity})}{dt} \\
&= \frac{d(\text{mass} \times \text{velocity})}{dt} \\
&= \frac{d(\text{momentum})}{dt} = \text{rate of change of momentum}
\end{aligned}$$

Hence, total force due to impacts of a single molecule with the wall ABCD of the vessel is $\dfrac{mu_x^2}{l}$.

The area of the wall is l^2. Hence, the pressure exerted due to the collision of *x*-component velocity of a single molecule with the side ABCD is

$$P_x = \frac{mu_x^2 / l}{l^2} = \frac{mu_x^2}{V} \qquad \text{.......(6.1b)}$$

where V is the volume of the vessel. Since each molecule will exert similar pressure, the total pressure exerted on the wall ABCD will be

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$$P = \sum_{i=1}^{N} P_{ix} = \frac{m}{V} \sum_{i=1}^{N} u_{ix}^{2} \qquad \qquad ....(6.1c)$$

Defining the mean square speed as

$$\overline{u_{x}^{2}} = \frac{1}{N} \sum_{i=1}^{N} u_{ix}^{2} \qquad \qquad ....(6.1d)$$

We can write,

$$P = \frac{mN}{V} \overline{u_{x}^{2}} \qquad \qquad ....(6.1e)$$
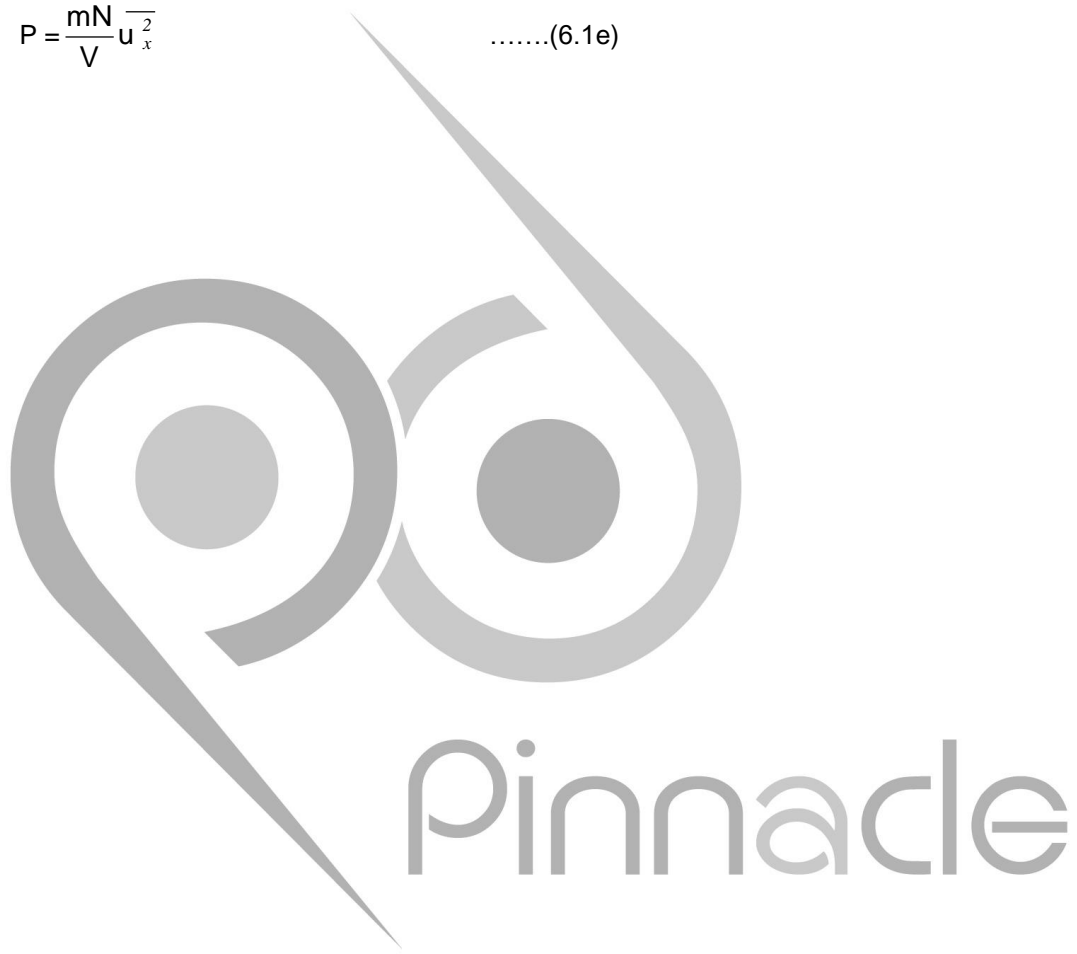
Since the direction *x*, y and z are equivalent, we will also have

$$\overline{u_x^2} = \overline{u_y^2} = \overline{u_z^2} \qquad\qquad ....(6.1f)$$

But from equation (6.1a), we will have

$$\overline{u^2} = \overline{u_x^2} + \overline{u_y^2} + \overline{u_z^2} \qquad\qquad ....(6.1g)$$

From equation (6.1f) and (6.1g), we can write

$$\overline{u_x^2} = \overline{u_y^2} = \overline{u_z^2} = \frac{1}{3}\overline{u^2}$$

Substituting this in equation (6.1e), we get

$$P = \frac{mN}{V}\left(\frac{1}{3}\overline{u^2}\right)$$

$$\text{or } PV = \frac{1}{3}mN\overline{u^2} \qquad\qquad ....(6.1h)$$

Illustration 9

Question: **Calculate the pressure exerted by 10^{23} gas particles each of mass 10^{-22} g in a container of volume 1 dm^3. The root mean square speed is 10^5 cm s^{-1}.**

Solution: From the given data, we have

$$N = 10^{23}$$

$$m = 10^{-22} \text{ g} = 10^{-25} \text{ kg}$$

$$V = 1 \text{ dm}^3 = 10^{-3} \text{ m}^3$$

$$\sqrt{\overline{u^2}} = 10^5 \text{ cm s}^{-1} = 10^3 \text{ms}^{-1}$$

Therefore, from the kinetic gas equation

$$P = \frac{1}{3}\frac{(10^{-25}\,\text{kg})(10^{23})(10^3\,\text{ms}^{-1})^2}{(10^{-3}\,\text{m}^3)} = \frac{1}{3}(10^7)\text{kgm}^{-1}\text{s}^{-2}$$

$$\mathbf{P = \frac{1}{3}\times 10^7 \ Pa}$$

6.2 SOME DERIVATIONS FROM THE KINETIC GAS EQUATION

The kinetic gas equation (6.1h) can be used to derive various gas laws and to define expressions for some useful quantities such as the root mean square speed and the average kinetic energy. Before deriving these, it is helpful to write this equation in the following form,

Average kinetic energy $\propto T$

$$\frac{1}{2}m\overline{u^2} \propto T \quad\text{or}\quad \frac{1}{2}m\overline{u^2} = KT$$

(where K is the proportionality constant)

Introducing this in equation (6.1 h) we have

$$PV = \frac{1}{3}mN\overline{u^2} = \frac{2}{3}N\left[\frac{1}{2}m\overline{u^2}\right]$$

$$= \frac{2}{3}NKT \qquad\qquad ....(6.2a)$$

Now, we proceed to derive the various gas laws from equation (6.2a)

BOYLE'S LAW

The essential conditions for Boyle's law to be applicable are:

(i) Temperature (T) should remain constant.

(ii) Mass of the gas should remain constant. In other words, the total number of molecules (N) remains unchanged.

Under these conditions, equation (6.2a) yields

$$PV = \text{constant or } P \propto \frac{1}{V_1}$$

Which is the expression for Boyle's law.

CHARLES' LAW

In this case

(i) Pressure (P) remains fixed.

(ii) Mass of the gas remains unchanged, i.e., N is constant with these conditions, equilibrium (6.2a) yields

$$V = \left(\frac{2}{3}\frac{NK}{P}\right)T \text{ i.e. } V = (\text{constant}) T \qquad \text{or } V \propto T$$

as required by Charles' law.

AVOGADRO'S LAW

It states that under similar conditions of pressure and temperature, equal volume of all gases contains equal number of molecules. Considering two gases, we have

$$P_1V_1 = \frac{2}{3}N_1KT_1 \text{ and } P_2V_2 = \frac{2}{3}N_2KT_2$$

Since $P_1 = P_2$ and $T_1 = T_2$, therefore

$$\frac{P_1V_1}{P_2V_2} = \frac{(2/3)N_1KT_1}{(2/3)N_2KT_2} \Rightarrow \frac{V_1}{V_2} = \frac{N_1}{N_2}$$

If volumes are identical, obviously $N_1 = N_2$. It also follows that mole ratio = volume ratio, when both the gases are present at the same T & P.

6.3 ROOT MEAN SQUARE SPEED

Root mean square (rms) speed is defined as the square root of the average of the squares of speeds, i.e.,

$$\sqrt{\overline{u^2}} = \sqrt{\frac{u_1^2 + u_2^2 + \ldots \ldots u_N^2}{N}}$$

From equation (6.1h), we have

$$\overline{u^2} = \frac{3PV}{mN}$$

For one mol of an ideal gas PV = RT   and   N = N_{AV}

With these, the above equation becomes

$$\overline{u^2} = \frac{3RT}{mN_{AV}} = \frac{3RT}{M}$$

where M is the molar mass of the gas.

$$\therefore \sqrt{\overline{u^2}} = \sqrt{\frac{3RT}{M}}$$

$$u_{rms} = \sqrt{\frac{3PV}{M}}$$

Based on the Maxwell distribution law (not required to be done in detail) two other forms of velocities are

$$u_{av} = \sqrt{\frac{8RT}{\pi M}}$$

$$u_{mp} = \sqrt{\frac{2RT}{M}}$$

where u_{av} is the average velocity of molecules and u_{mp} is called the most probable velocity. U_{mp} is defined as the velocity possessed by the maximum fraction of the molecules.

6.4 AVERAGE KINETIC ENERGY

The average kinetic energy $(\overline{KE})$ is defined as

$$(\overline{KE}) = \frac{1}{2}m\overline{u^2}$$

According to equation (6.2a), this is given by

$$(\overline{KE}) = \frac{3}{2}\frac{PV}{N}$$

For 1 mol of an ideal gas

$$PV = RT \text{ and } N = N_{AV}$$

With these, the above equation becomes

$$(\overline{KE}) = \frac{3}{2} \frac{RT}{N_{AV}} = \frac{3}{2}kT$$

where $k = R/N_A$ and is known as the Boltzmann constant. Its value is given by $\frac{R}{N_{AV}} = \frac{8.314 \text{ JK}^{-1}\text{mol}^{-1}}{6.023 \times 10^{23} \text{ mol}^{-1}} = 1.38 \times 10^{-23}$ JK^{-1}

The total kinetic energy for 1 mole of the gas is

$$E_{total} = N_{AV} \ (\overline{KE}) = \frac{3}{2}RT$$

Illustration 10

Question: **For a gas containing 10^{23} molecules (each having mass 10^{-22} g) in a volume of 1 dm^3, calculate the total kinetic energy of molecules if their root mean square speed is 10^5 cm s^{-1}. What will be its temperature?**

Solution: Total kinetic energy $(KE) = N\left(\frac{1}{2}m\overline{u^2}\right) = 10^{23}\left[\frac{1}{2}(10^{-25}\text{kg}) \times (10^3 \text{m s}^{-1})^2\right]$

$= 0.5 \times 10^4 \text{ kg m}^2 \text{ s}^{-2} = 0.5 \times 10^4$ J

Total kinetic energy is also equal to N(3/2)kT.

Thus N(3/2)kT = **0.5×10^4 J**

Hence T $= \frac{2}{3}\frac{(0.5 \times 10^4 \text{ J})}{kN} = \frac{2}{3}\frac{(0.5 \times 10^4 \text{ J})}{(10^{23})(1.38 \times 10^{-23}\text{ JK}^{-1})}$

= **2415.46 K**

Illustration 11

Question: **Calculate the total kinetic energy of 0.5 mol of an ideal gas at 273K.**

Solution: Total Kinetic Energy $= n\left(\frac{3}{2}RT\right) = (0.5\text{ mol})\left[\frac{3}{2} \times \left(8.314\text{JK}^{-1}\text{mol}^{-1}\right) \times (273\text{K})\right]$

= 1702.292 J

7. REAL GASES

The ideal gas laws can be derived from the kinetic theory of gases which is based on the following two important assumptions:

(i) The volume occupied by the molecules is negligible in comparison to the total volume of the gas.

(ii) The molecules exert no forces of attraction upon one another.

The molecules in gases also have weak forces of attraction (called van der Waals attraction) amongst

themselves; as otherwise, the gases could never be liquefied and solidified.

Correction for Forces of attraction:

Consider molecules of layer A & B. As can be seen in Fig. 7a, molecules of layer A, which are closest to the container wall strike the wall of the container and thereby exert a pressure P on it. This is the pressure exerted by the molecules of the real gas. The molecules of layer B attract the molecules of layer A but do not hit the container wall. This backward pull experienced by the molecules of layer A causes them to exert less pressure than what they would have exerted if there were no attractive forces.

A B
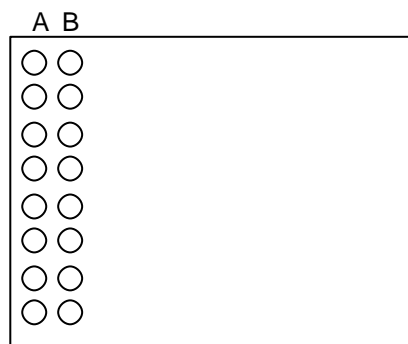
Fig. 7a

Therefore, if a real gas exerts pressure P, then an ideal gas would exert pressure P + p where p is the pressure lost by the real gas due to attractive forces.

The attractive force is mutual. That is to say that this force is between layer A and layer B molecules. Since force between two mutually attracting objects is directly proportional to the concentration of layer A and layer B molecules, since force between two mutually attracting objects is directly proportional to the magnitude of the cause of force. Thus, the pressure 'p' lost by real gas is proportional to the concentration of layer A and B molecules.

$$p \propto \frac{n}{V} \text{ (layer A)}$$

$$p \propto \frac{n}{V} \text{ (layer B)}$$

$$p \propto \frac{n^2}{V^2}$$

$$p = \frac{an^2}{V^2}$$

where a is the proportionality constant and is a measure of the forces of attraction between the molecules. Thus,

$$P_{ideal} = P_{real} + \frac{an^2}{V^2}$$

The unit of the term $\frac{an^2}{V^2}$ will be the same as that of the pressure. Thus, the SI units of 'a' will be Pa m^6 mol^{-2}. It may be conveniently expressed in k Pa dm^6 mol^{-2}.

Now, the real gas behaves same as ideal gas on removing the force of attraction. The only difference that now remains is the molecular size.

Correction for molecular size:

The container of volume V has n mole of gas molecules each of which possess a certain volume of their own. If the total volume blocked by 1 mole of molecules due to their sheer presence is taken as b, then the total volume blocked by them would be nb. We can now look at the container and see that the effective volume for the gas molecules to move is V – nb. This means that in the volume, V – nb the gas molecules have zero volume of their own.

Since $P_i V_i = nRT$

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

'b' is called the excluded volume or co-volume. The numerical value of b is four times the actual volume occupied by 1 mole of gas molecules. This can be shown as follows.

We assume that molecules are in constant motion and collide with other molecules at every instant. Moreover bi-molecular collisions are much more frequent than tri-molecular etc. Since all molecules are alike we shall assume, for the sake of simplicity (without introducing error) that molecules have fixed 'partners' for collision. That is molecule 1 & 2, 3 & 4 etc. If the total molecules are odd we can remove one molecule (removal of one molecule would hardly make a difference) to make it even. But since we have already considered that molecules collide every instant, fixing partners for collisions would introduce an error. This is because after one collision they would need to separate in order to collide again and since we have fixed partners they cannot collide with other molecules. This leads to a time interval, which is collision free. To take care of this, we now assume that molecules are stuck to each other in pairs as shown in Fig. 7b. This creates another problem that when the molecules collide they collide in all possible directions.

To simulate this we assume that the molecules that are stuck in pairs are rotating by keeping the point of contact fixed. This ensures that they occupy all possible orientations (Fig. 7c). For a third molecule the volume unavailable is the volume of the large sphere with radius 2r where r is the radius of each molecule. Therefore the volume unavailable is $\frac{4}{3}\pi(2r)^3=8\times\frac{4}{3}\pi r^3$.
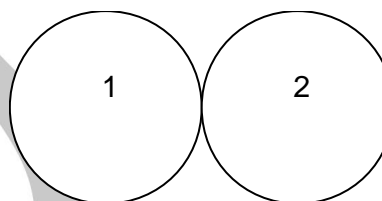
Fig. 7 b

This volume is unavailable due to two molecules. Thus, due to one molecule the volume unavailable is 4 times its volume.

$\therefore$ b = $4\times\frac{4}{3}\pi r^3\times6.023\times10^{23}$. Thus

Van der Waals equation for 1 mol of real gas is given as $\left(P+\frac{a}{V^2}\right)(V-b)=RT$.
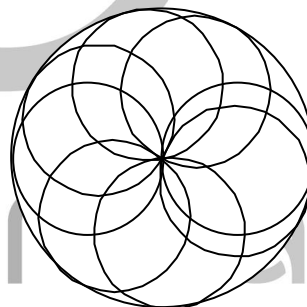
Fig. 7c

8. DEVIATION FROM IDEAL BEHAVIOR

If measurements of pressure, volume and temperature of a gas do not confirm to the ideal gas law (PV = RT), within the precision of measurements, the gas is said to deviate from ideal behaviour and exhibit non-ideal behaviour. Such gases are called real gases. At low pressures and moderately high temperatures, real gases obey ideal gas equation but as the pressure is increased or the temperature is decreased, a marked deviation from ideal behaviour is observed.

To display deviations more clearly, the ratio of the observed molar volume (V_m) to the ideal molar volume ($V_{m, ideal}$ = $\frac{RT}{P}$) is plotted as a function of pressure at constant temperature. This ratio is called the compressibility factor (Z), which is expressed as

$$Z = \frac{V_m}{V_{m,ideal}} = \frac{P \times V_m}{RT} = \frac{PV}{nRT}$$

For an ideal gas $Z = 1$ and is independent of pressure and temperature. For a real gas, $Z = f(T,P)$, a function of both temperature and pressure.

Fig. 8 a
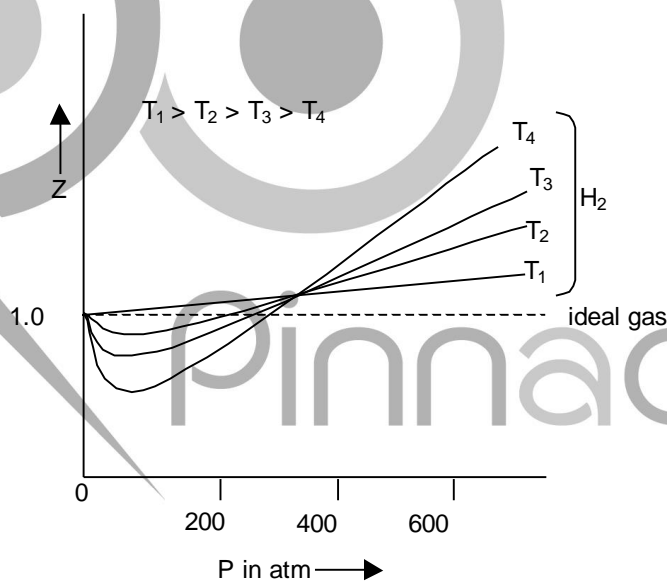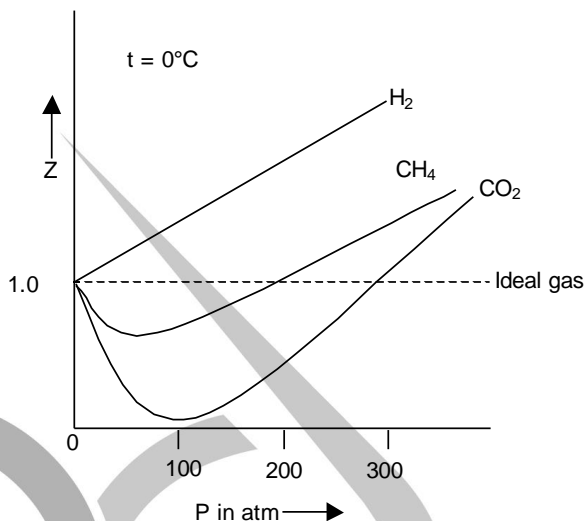
Fig. 8 b

Fig. 8 b shows a plot of Z as a function of pressure at varying temperatures. It implies that curve for a real gas has a tendency to coincide with that of an ideal gas at high temperature, i.e, at extremely high temperature; the behaviour of a real gas approaches that of an ideal gas.

Thus as the temperature is increased, the minimum in the curve vanishes and the curve remains horizontal, for which $\dfrac{PV}{nRT}$ is about unity for an appreciable range of pressure. Within this range Boyle's law is obeyed and hence the temperature is called Boyle's temperature. This temperature is characteristic for each gas. Above Boyle's temperature, slope of the curve increases continuously i.e. $Z > 1$.

Boyle's temperature = $T_B = \dfrac{a}{Rb}$

At Boyle's temperature the two effects, viz. finite size and the intermolecular attractions roughly compensate each other.

Fig. 8a shows a plot of Z as a function of pressure at 0^oC for hydrogen, ideal gas, CH_4 and CO_2. For hydrogen, Z is greater than unity (ideal value) at all pressures. For CH_4 and CO_2, Z is less than unity in the lower part of the pressure ranges but is greater than unity at very high pressures. For gases, which are easily liquefied, Z dip sharply below the ideal line, i.e., Z decreases with increase of pressure in the lower pressure range, passes through a minimum at some pressure and then increases continuously with pressure in the higher pressure region. These curves can be explained using the Van der Waals equation of real gases. The Van der Waals equation for 1 mole of a real gas is

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

The equation can be rewritten as

$$PV_m - Pb + \frac{a}{V_m} - \frac{ab}{V_m^2} = RT$$

or $PV_m = RT + Pb - \dfrac{a}{V_m} + \dfrac{ab}{V_m^2}$ ..... (8a)

Dividing Eq. (8a) by RT

$$\frac{PV_m}{RT} = \frac{RT}{RT} + \frac{Pb}{RT} - \frac{a}{V_m RT} + \frac{ab}{V_m^2 RT}$$

Z = $1 + \dfrac{Pb}{RT} - \dfrac{a}{V_m RT} + \dfrac{ab}{V_m^2 RT}$ (8b)

For H_2 gas, the value of a is extremely small (as it is very difficult to liquefy) so, all terms involving 'a' in the numerator of equation (8b) can be neglected and equation is reduced to

$$Z = 1 + \frac{Pb}{RT}$$

It clearly indicates that with the increase of pressure, Z increases and is always greater than unity.

For methane and CO_2, in the low pressure region, V_m would be very large and in comparison to V_m, 'b' can be ignored. The equation (8b) can be rewritten as

$$Z = 1 + \frac{Pb}{RT} + \left[\frac{a}{V_m RT}\left(\frac{b}{V_m} - 1\right)\right]$$

Since $b \ll V_m$, so $\dfrac{b}{V_m}$ would be extremely smaller than 1. Thus, the term $\left[\dfrac{a}{V_m RT}\left(\dfrac{b}{V_m} - 1\right)\right]$ would be

negative and greater in magnitude than positive term $\dfrac{Pb}{RT}$. Consequently, the Z is less than unity.

With the increase of pressure in the low pressure region, both the terms, $\dfrac{Pb}{RT}$ and $\left[\dfrac{a}{V_m RT}\left(\dfrac{b}{V_m} - 1\right)\right]$

increases but the increase in negative term, $\left[\dfrac{a}{V_m RT}\left(\dfrac{b}{V_m} - 1\right)\right]$ would be more than the increase in positive term,

$\left(\dfrac{Pb}{RT}\right)$, thus Z decreases continuously. But the difference between (magnitude of) increase in negative term and increase in positive term continuously decreases. When this difference becomes zero, the minima are obtained. This happens because for the same increase of pressure on a gas, the decrease in volume is not uniform. Initially the volume decreases rapidly and then the decrease in volume is less for the same increase of pressure. Then the increase in negative term is lower than the increase in positive term. Thus, Z starts increasing but is still less than unity. Then, a time comes when the magnitude of negative terms and positive terms become equal. Under such conditions, Z becomes equal to unity and when the magnitude of positive term becomes more than the negative term, the value of Z becomes greater than unity.

The nature of the curve is like this because in the low pressure region, the effect of attractive forces ('a' factor) dominates while in the high-pressure region, the size effect ('b' factor) will dominate the behaviour of the gas.

Illustration 11

Question: **The compressibility factor for nitrogen at 223 K and 800 atm is 1.95 and at 373 K and 200 atm is 1.10. A certain mass of nitrogen occupies a volume of 1.0 dm^3 at 223 K and 800 atm. Calculate the volume occupied by the same quantity of nitrogen at 373 K and 200 atm.**

Solution: The number of mole of N_2 (n) $= \dfrac{PV}{ZRT} = \dfrac{800 \times 1}{1.95 \times 0.0821 \times 223} = 22.4$ mole

Thus, the volume of N_2 at 373 K and at 200 atm would be

$$V = \frac{nZRT}{P} = \frac{22.4 \times 1.10 \times 0.0821 \times 373}{200} = \textbf{3.77 litre}$$

Illustration 12

Question: **One way of writing the equation of state for real gases is**

$$P\overline{V} = RT\left[1 + \frac{B}{\overline{V}} + ...\right]$$

where B is a constant. Derive an approximate expression for B in terms of the Van der Waal's constants 'a' and 'b'.

Solution: The Van der Waal's equation for one mole of real gas is

$$\left(P + \frac{a}{\overline{V}^2}\right)\left(\overline{V} - b\right) = RT$$

or, $\left(P + \dfrac{a}{\overline{V}^2}\right) = \dfrac{RT}{\overline{V} - b}$

$$P = \frac{RT}{\overline{V} - b} - \frac{a}{\overline{V}^2}$$

Multiplying both the sides with $\overline{V}$,

$$P\overline{V} = \frac{RT\overline{V}}{\overline{V} - b} - \frac{a}{\overline{V}}$$

$$P\overline{V} = RT\left[\frac{\overline{V}}{\overline{V} - b} - \frac{a}{\overline{V}RT}\right]$$

$$P\overline{V} = RT\left[\left(1 - \frac{b}{\overline{V}}\right)^{-1} - \frac{a}{\overline{V}RT}\right]$$

At low pressure, $\overline{V}$ is large and $\frac{b}{\overline{V}} \ll 1$. Thus, the term $\left(1 - \frac{b}{\overline{V}}\right)^{-1}$ can be expanded into a power series in $\frac{b}{\overline{V}}$.

$$\left(1 - \frac{b}{\overline{V}}\right)^{-1} = 1 + \frac{b}{\overline{V}} + \left(\frac{b}{\overline{V}}\right)^2 + ...$$

$$P\overline{V} = RT\left[1 + \frac{b}{\overline{V}} + \left(\frac{b}{\overline{V}}\right)^2 + ... - \frac{a}{\overline{V}RT}\right]$$

Ignoring b^2 and higher terms,

$$P\overline{V} = RT\left[1 + \frac{1}{\overline{V}}\left(b - \frac{a}{RT}\right) + ...\right] \qquad ....(8c)$$

Comparing Eq. (8c) with the expression given in the problem

$$B = b - \frac{a}{RT}$$

9. CRITICAL TEMPERATURE, PRESSURE AND VOLUME

A gas doesnot liquefy above a certain temperature, however high the pressure may be. This characteristic temperature is called the critical temperature (T_c).

The minimum pressure which is required for liquefaction of the gas is called the critical pressure (P_c).

The volume occupied by 1 mole of a gas at T_c and P_c is called the critical volume (V_c).

The values of various critical constants are:

$$T_c = \frac{8}{27}\frac{a}{Rb} \quad ; \quad P_c = \frac{1}{27}\frac{a}{b^2} \quad ; \quad V_c = 3b$$

10. GAS EUDIOMETRY

Gas Eudiometry involves determining the composition of gaseous mixtures, molecular formula for gases and gaseous hydrocarbons and establishing volume-volume relationship among gases.

The fundamental principle involved in gas eudiometry is the Avogadro's law. According to this law, volume of the gas is proportional to the number of moles of gas at constant temperature and pressure, i.e., volume ratio among gases is same as mole ratio at constant temperature and pressure.

In eudiometry, gaseous reactions are studied in a closed graduated tube open at one end and closed at other end. The tube is provided with platinum terminals required to produce electric spark through the mixture of gases. Such graduated tube is known as Eudiometer tube and hence the term gas eudiometry is also used for gas analysis. During eudiometry, the graduated tube is first filled with mercury. Then a known volume of the gas or gaseous mixture (which is to be studied either for molecular formula determination or composition determination) is inserted into the eudiometer tube, which displaces equivalent amount of mercury. Now a certain volume

of O_2 (in excess) is introduced and the electric spark is produced, when the combustible material gets oxidized. In general, all elements on oxidation with O_2 forms oxide with element in highest oxidation state unless & until mentioned in the problem. The volume of gases before combustion and after combustion is noted. Soon after the combustion, the reaction mixture is brought to room temperature when $H_2O(g)$ condenses to $H_2O(l)$. This leads to contraction in volume. This contraction called first contraction in volume is noted. The volumes of CO_2, other gaseous products and remaining O_2 are determined by absorbing them in suitable reagents. For example, the volume of CO_2 is determined by inserting KOH (or any other alkali) in the eudiometer tube, which absorbs all the CO_2 present. The volume of remaining O_2 is determined by introducing alkaline pyrogallol, which absorbs all the left over oxygen. There is contraction in volume noted by introducing KOH, which is referred as second contraction in volume, and contraction in volume by inserting alkaline pyrogallol is termed as third contraction in volume. From the various contractions in volume obtained, the requisite information can be derived.

- During eudiometry, the reaction mixture is brought to the room conditions after combustion in all cases. This means that if H_2O is the product, that will always exist in liquid phase.

- If reaction mixture contains nitrogen, it is not oxidized by O_2 even in presence of electric spark. This implies that in eudiometry, nitrogen is considered inert towards oxidation.

- The various reagents required for absorbing different gases are

O_2:	absorbed by alkaline pyrogallol
O_3:	absorbed by turpentine oil
NO:	absorbed by $FeSO_4$ solution
CO:	absorbed by ammoniacal Cu_2Cl_2 solution
H_2O vapour:	absorbed by conc. H_2SO_4, fused $CaCl_2$ (required when reaction mixture is not brought to room temperature)
Cl_2:	water or alkali solution
NH_3:	acid solution or $CuSO_4$ solution
CO_2 & SO_2:	alkali solution (NaOH, KOH, $Ca(OH)_2$, $Ba(OH)_2$ or ethanolamine ($HOCH_2CH_2NH_2$) etc.

Let us see the application of eudiometry in determining the composition of gaseous mixture. We are given a mixture of ethane (C_2H_6) and ethene (C_2H_4) measuring 'a' ml. The mixture is subjected to electric spark along with excess of oxygen (b ml.) On sparking, C_2H_4 and C_2H_6 both get combusted and form gaseous CO_2 and H_2O vapours. Let us assume that the volume of C_2H_4 in the mixture be 'x' ml. The combustion reactions are shown as

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

Volume reacted/produced $\quad x \qquad 3x \qquad 2x \qquad 2x$

$$C_2H_6 + \frac{7}{2}O_2 \longrightarrow 2CO_2 + 3H_2O$$

Volume reacted/produced $\quad (a-x) \quad \frac{7}{2}(a-x) \quad 2(a-x) \quad 3(a-x)$
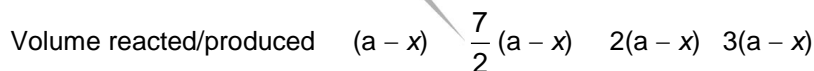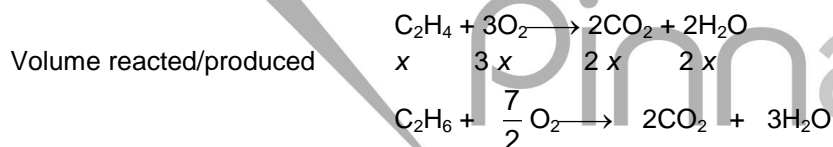
After explosion, the reaction mixture is allowed to come at room conditions, so water vapour condenses to liquid H_2O.

Volume before sparking (VBS) = a + b

Volume after sparking (VAS) = $b - 3x - \dfrac{7}{2}(a-x) + 2x + 2(a-x) = b - x - \dfrac{3}{2}(a-x)$

$\therefore$ First contraction in volume after sparking $\quad$ = VBS − VAS

$$= (a+b) - \left[b - x - \frac{3}{2}(a-x)\right]$$

$$= \left[a + x + \frac{3}{2}(a-x)\right] = \left[\frac{1}{2}(5a - x)\right]$$

Alternatively,

According to first reaction, the number of mole of reactant are same as that of the product, so as per the stoichiometry of the reaction, there is no contraction but since H_2O condenses to liquid, the contraction due to first reaction would be $2x$. According to second reaction, 9/2 mole of reactant gives 5 mole of product. This implies that there is expansion of 0.5 mole as per the stoichiometry of the reaction but as H_2O condenses to liquid, due to which there is a contraction of 3 mole. So, overall there is contraction of 2.5 mole. Thus, contraction due to second reaction would be $\frac{5}{2}(a-x)$.

Overall contraction in volume = contraction in volume due to first reaction + contraction in volume due to second reaction.

$$= \left[2x + \frac{5}{2}(a-x)\right] = \left[\frac{1}{2}(5a-x)\right]$$

Let this overall first contraction in volume noted be V ml.

$$\therefore V = \left[\frac{1}{2}(5a-x)\right]$$

Using values of V and a, x can be calculated and thus the % composition of mixture would be determined as

% of $C_2H_6 = \frac{a-x}{a} \times 100$

and % of $C_2H_4 = \frac{x}{a} \times 100$

Illustration 13

Question: **50 ml of a mixture of NH_3 and H_2 was completely decomposed by sparking into nitrogen and hydrogen. 40 ml of oxygen was added and the mixture was sparked again. After cooling to the room temperature, the mixture was shaken with alkaline pyrogallol solution and a contraction of 6 ml was observed. Calculate the % by volume of NH_3 in the original mixture.**

Solution:

Let the volume of NH_3 be x ml, than be volume of H_2 would be $(50 - x)$ ml.

On sparking,

$$NH_3(g) \longrightarrow \tfrac{1}{2}N_2(g) + \tfrac{3}{2}H_2(g)$$
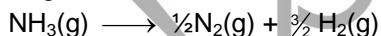
Since 40 ml of O_2 is added and sparked, it must have reacted with H_2 to form liquid water. Since 6 ml contraction in volume is there with alkaline pyrogallol, so 34 ml is the volume of O_2 used up.

$\therefore$ Total volume of H_2 would be 68 ml ($\because 2H_2 + O_2 \longrightarrow 2H_2O$)

$$\therefore (50 - x) + \frac{3}{2}x = 68$$

$$50 + \frac{x}{2} = 68; \qquad x = 36$$

$\therefore NH_3 = $ **72%**

Illustration 14

Question: **When a certain quantity of oxygen was partially ozonized in a suitable apparatus, the volume decreases by 4 ml. On addition of turpentine oil, the volume decreases further by 8 ml. Find the formula of ozone, assuming all measurements are made at the same temperature and pressure.**

Solution: The reaction occurring in the ozonizer is the conversion of oxygen to ozone and the conversion is never 100 %. Let the volume of oxygen in the beginning be 'a' ml.

$$nO_2(g) \rightleftharpoons 2O_n(g)$$

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Initial volume   a   0

Volume after attainment   a – nx 2x

of equilibrium

The initial volume reduction is due to reaction stoichiometry alone.

∴Initial volume – volume at equilibrium = 4 ml

∴ a – (a – nx + 2x) = 4

nx – 2x = 4   …….(i)

The second decrease in volume is due to the absorption of ozone by turpentine oil.

∴2x = 8 and x = 4

Putting the value of x in equation (i), gives

∴nx = 4 + 8 = 12

n = $\dfrac{12}{4}$ = 3

Molecular formula of ozone is **O_3.**

Illustration 15

Question: **15 ml of an oxide of nitrogen was taken in a eudiometer tube and mixed with hydrogen till the volume was 42 ml. On sparking, the resulting mixture occupied 27 ml. To the mixture, 10 ml of oxygen was added and on explosion, again the volume fell to 19 ml. Find the formula of the oxide of nitrogen that was originally admitted in the eudiometer tube. Both the explosions led to the formation of water.**

Solution: There are 4 methods to solve this problem.

Method 1:

This is a method that is most commonly thought of by a student.

Let the oxide of nitrogen be represented as N_xO_y. On mixing with H_2, the volume was 42 ml.

∴ The volume of H_2 added was 27 ml.

On sparking, the reaction would be

$N_xO_y + yH_2 \longrightarrow yH_2O + \dfrac{x}{2} N_2$

Since on adding 10 ml of O_2, combustion still takes place, it implies that hydrogen was in excess (since N_2 will not react).

$$N_xO_y(g) + yH_2(g) \longrightarrow \dfrac{x}{2} N_2(g) + yH_2O(l)$$

Initially   15 ml   27 ml   0   0

After sparking   0   (27–15y) $\dfrac{15x}{2}$ ml –

∴ Total volume after the first explosion = $(27-15y)+\dfrac{15x}{2}=27$

∴ $\dfrac{15x}{2}-15y=0$;   ∴$x = 2y$ ……(i)

Do not immediately write the formula as N_2O, because this is a molecule and therefore N_2O is its empirical formula and not molecular formula.

In the next explosion, hydrogen reacts with 10 ml of O_2 after which the volume fell to 19 ml. Since we do not know whether O_2 or H_2 is in excess, we consider all the possibilities.

(i) *Hydrogen is in excess*

$$H_2(g) \quad + \quad \tfrac{1}{2}O_2(g) \quad \longrightarrow \quad H_2O(l)$$

Volume initially $(27-15y)$ 10   0

Volume finally $(27-15y-20)$ 0   –

∴ Final volume of gases = volume of remaining (hydrogen + nitrogen)

$$(27-15y-20)+\frac{15x}{2}=19$$

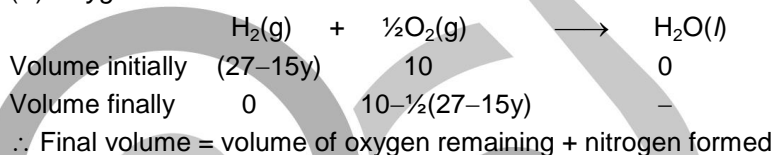$$\frac{15x}{2}-15y=12 \quad \text{this equation violates equation (i)}$$

∴ H_2 cannot be in excess.

(ii) *Hydrogen is exactly consumed by O_2*

∴ $27 - 15y = 20$; $y = \dfrac{7}{15}$.

We know that x and y have to be integers. Therefore, hydrogen can not be completely consumed by oxygen.

(iii) *Oxygen is in excess*

$$H_2(g) \quad + \quad \tfrac{1}{2}O_2(g) \quad \longrightarrow \quad H_2O(l)$$

Volume initially $(27-15y)$ 10   0

Volume finally   0 $10-\tfrac{1}{2}(27-15y)$ –

∴ Final volume = volume of oxygen remaining + nitrogen formed

$$\left[10-\frac{1}{2}(27-15y)\right]+\frac{15x}{2}=19$$
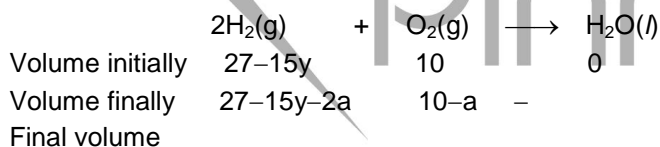
On solving $x = 2$ and $y = 1$.

∴ Formula is **N_2O**

Method 2:

Proceed till you reach equation (i)

In the second explosion, H_2 reacts with O_2 to produce H_2O.

We do not know which of these two is completely consumed. Let us therefore assume that the amount of O_2 reacted is 'a'. Then the amount of H_2 reacted will be '2a'.

$$2H_2(g) \quad + \quad O_2(g) \quad \longrightarrow \quad H_2O(l)$$

Volume initially $27-15y$ 10   0

Volume finally $27-15y-2a$ $10-a$ –

Final volume

$$27-15y - 2a + 10 - a + \frac{15x}{2} = 19$$

Since $15y-\dfrac{15x}{2}=0$, we get

$$37 - 3a = 19; \quad a = 6$$

Therefore, oxygen is left behind and its volume would be 4 ml.

∴ $4 + \dfrac{15x}{2} = 19$; $x = 2$ and y = 1.

Method 3:

At the end of first explosion, the total volume is 27 ml. Now 10 ml of O_2 is added. The total volume becomes 37 ml. After second explosion the volume becomes 19 ml. The volume decreased is 18

ml. This is due to the reaction between H_2 and O_2 only. If H_2 consumed is b ml, then O_2 consumed would be b/2 ml.
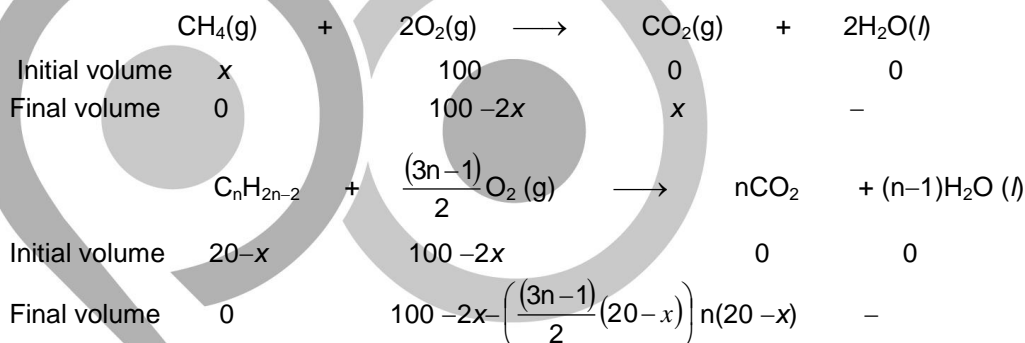
$\therefore$ b + $\dfrac{b}{2}$ = 18; b = 12 ml. This means that O_2 reacted is 6 ml and O_2 left is 4 ml.

$4 + \dfrac{15x}{2}$ = 19; x = 2 and y = 1.

Illustration 16

Question: **20 ml of a mixture of methane and a gaseous compound of acetylene series were mixed with 100 ml of oxygen and exploded to complete combustion. The volume of the products after cooling to original room temperature and pressure, was 80 ml and on treatment with potash solution a further contraction of 40 ml was observed. Calculate (a) the molecular formula of the hydrocarbon and (b) the percentage composition of the mixture.**

Solution: Let the volume of methane be x ml and the molecular formula of the unknown hydrocarbon be C_nH_{2n-2} (since it belongs to the acetylene series). Saturated hydrocarbon burnt prior to unsaturated hydrocarbon. So,

	$CH_4(g)$	+	$2O_2(g)$	$\longrightarrow$	$CO_2(g)$	+	$2H_2O(l)$
Initial volume	x		100		0		0
Final volume	0		$100-2x$		x		–

	C_nH_{2n-2}	+	$\dfrac{(3n-1)}{2}O_2\,(g)$	$\longrightarrow$	nCO_2	+	$(n-1)H_2O\,(l)$
Initial volume	$20-x$		$100-2x$		0		0
Final volume	0		$100-2x-\left[\dfrac{(3n-1)}{2}(20-x)\right]$		$n(20-x)$		–

Since the question mentions complete combustion, the amount of O_2 reacted for methane would be $2x$ and that for C_nH_{2n-2} would be $\dfrac{(3n-1)}{2}(20-x)$.

Moreover after combustion only O_2 and CO_2 are left behind [$H_2O(l)$ does not account for any volume]. On treatment with potash, there is a decrease in volume of 40 ml. This must be due to CO_2 absorption. $\therefore$ O_2 left after combustion must be 40 ml.

$$\therefore 100-2x-\frac{(3n-1)\,(20-x)}{2} = 40$$

$$2x+\frac{(3n-1)\,(20-x)}{2} = 60$$

CO_2 produced is 40 ml.

$$\therefore x + n(20-x) = 40$$

Solving these equations we get,

x = 10 ml. and n = 3

Formula of gaseous compound of acetylene series is C_3H_4,

% of CH_4 = 50 and % of C_3H_4 = 50

SOLVED OBJECTIVE EXAMPLES

Example **1**:
Helium atom is two times heavier than a hydrogen molecule. At 298 K, the average translational kinetic energy of a Helium atom is
(a) two times that of hydrogen molecule.   (b) same as that of a hydrogen molecule.
(c) four times that of a hydrogen molecule.   (d) half that of a hydrogen molecule.

Solution:

The average kinetic energy of an atom is given as $\frac{3}{2}kT$.

∴ It does not depend on mass of the atom.
∴**(b)**

Example **2**:
A balloon filled with ethylene is pricked with a sharp pointed needle and quickly dropped in a tank of H_2 gas under identical conditions. After a while the balloon will be
(a) shrunk   (b) enlarged
(c) completely collapsed   (d) remain unchanged in size

Solution:

Rate of diffusion $\propto \sqrt{\dfrac{1}{M}}$

Hence H_2 will diffuse into the balloon and its size will increase.
∴ **(b)**

Example **3**:
At which of the four conditions, the density of nitrogen will be the largest?
(a) STP   (b) 273 K and 2 atm
(c) 546 K and 1 atm   (d) 546 K and 2 atm

Solution:

Density of a gas is given by $\rho = \dfrac{PM}{RT}$. Obviously the choice that has greater $\dfrac{P}{T}$ would have greater density.

∴**(b)**

Example **4**:
The ratio of the root mean square velocity of H_2 at 50 K and that of O_2 at 800 K is
(a) 4   (b) 2   (c) 1   (d) ¼

Solution:

$u_{rms} = \sqrt{\dfrac{3RT}{M}}$; $u_{rms} \propto \sqrt{\dfrac{T}{M}}$

$\dfrac{u_{rms}(H_2 \,at\,50K)}{u_{rms}(O_2 \,at\,800K)} = \sqrt{\dfrac{50}{2} \times \dfrac{32}{800}} = 1$

∴ **(c)**

Example 5:

What percent of a sample of nitrogen must be allowed to escape if its temperature, pressure and volume are to be changed from 220° C, 3 atm and 1.65 L to 110°C, 0.7 atm and 1 L respectively?

(a) 41.4%   (b) 8.18%
(c) 4.14%   (d) 81.8%

Solution:

$$n_1 = \frac{3 \times 1.65}{R \times 493} \; ; \; n_2 = \frac{0.7 \times 1}{R \times 383}$$

Fraction remaining = $\dfrac{n_2}{n_1} = \dfrac{0.7 \times 1}{R \times 383} \times \dfrac{R \times 493}{3 \times 1.65} = 0.182$

Fraction escaped = 1 − 0.182 = 0.818
Percentage escaped = 81.8%

∴ **(d)**

Example 6:

Vander Waal equation for CH_4 at low pressure is

(a) PV = RT − Pb   (b) $PV = RT - \dfrac{a}{V}$

(c) $PV = RT + \dfrac{a}{V}$ (d) PV = RT + Pb

Solution:

$$\left(P + \frac{a}{V^2}\right)(V - b) = RT$$

At low P, volume V is high
$(V - b) \approx V$

$$\therefore \left(P + \frac{a}{V^2}\right)V = RT$$

$$PV = \left(RT - \frac{a}{V}\right)$$

∴**(b)**

Example 7:

The internal pressure loss of one mole of vander Waal gas over an ideal gas is equal to

(a) zero   (b) b^2

(c) $\dfrac{a}{V^2}$ (d) $b - \dfrac{a}{RT}$

Solution:

$\left(P + \dfrac{a}{V^2}\right)$ is the pressure of the ideal gas while P is the pressure of the real gas. ∴ $\dfrac{a}{V^2}$ is the difference.

∴**(c)**

Example 8:

The compressibility factor of a gas is less than unity at STP. Therefore,

(a) $V_m >$ 22.4 litres   (b) $V_m <$ 22.4 litres
(c) $V_m =$ 22.4 litres   (d) $V_m =$ 4.8 litres

Solution:

Since $Z = \dfrac{V_{real}}{V_{ideal}}$, if $Z < 1$ then $V_{real} < V_{ideal}$ (i.e. 22.4 litres at STP)

$\therefore$ **(b)**

Example **9:**

20 ml of a mixture of C_2H_2 and CO was exploded with 30 ml of oxygen. The gases after the reaction had a volume of 34 ml. On treatment with KOH, 8 ml of oxygen gas remain unreacted. Which of the following options show a correct composition of the mixture?
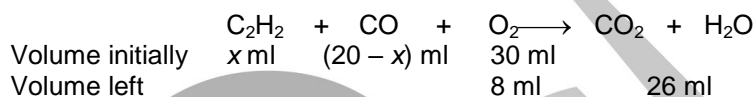
(a) $V_{C_2H_2} = 6$ **ml and** $V_{CO} = 14$ **ml** **(b)** $V_{C_2H_2} = 4$ **ml and** $V_{CO} = 16$ **ml**

(c) $V_{C_2H_2} = 2$ **ml and** $V_{CO} = 18$ **ml** **(d)** $V_{C_2H_2} = 5$ **ml and** $V_{CO} = 15$ **ml**

Solution:

$$C_2H_2 \ + \ CO \ + \ O_2 \longrightarrow \ CO_2 \ + \ H_2O$$

Volume initially x ml $(20 - x)$ ml 30 ml

Volume left 8 ml 26 ml

$2 \times$ Volume of C_2H_2 taken + volume of CO taken = Volume of CO_2.

$2x + 20 - x = 26$; $x = 6$ ml.

Volume of C_2H_2 taken = 6 ml and volume of CO taken = 14 ml.

$\therefore$ **(a)**

SOLVED SUBJECTIVE EXAMPLES

Example 1:

A spherical balloon of 21 cm diameter is to be filled up with hydrogen at STP from a cylinder containing the gas at 20 atm and 27°C. If the cylinder can hold 2.82 L of water, calculate the number of balloons that can be filled up using only the expanded value of the gas.

Solution:

We must understand first that the gas in the cylinder is at 20 atm and 27°C while its filling in the balloons requires STP conditions. If we calculate the volume of the gas at STP, it comes out to be

$$V_2 = \frac{P_1 V_1}{T_1} \times \frac{T_2}{P_2} = \frac{20 \times 2.82}{300} \times \frac{273}{1}$$

V_2 = 51.324 L

This means as we convert the gas to STP, the volume of the gas expands to 51.324 L. It is this expansion that leads to filling of the gas in balloons.

Volume of one balloon = $\frac{4}{3}\pi r^3 = \frac{4}{3} \times \frac{22}{7} \times \left(\frac{21}{2}\right)^3 = 4.851 L$

∴ Number of balloons filled up = $\frac{(51.324 - 2.82)}{4.851} \approx 10$

The numbers of balloons, which are completely filled up are **10** only.

Example 2:

An LPG (liquefied petroleum gas) cylinder weighs 14.8 kg when empty. When full, it weighs 29 kg and shows a pressure of 2.5 atm. In the course of use at 27°C, the mass of the full cylinder is reduced to 23.2 kg. Find out the volume of the gas in cubic meters used up at the normal usage conditions, and the final pressure inside the cylinder. (Assume the LPG consists of n–butane only)

Solution:

Liquefied Petroleum gas is a highly pressurised gas in the form of liquid introduced in a cylinder. Inside the cylinder, the gas exists as a liquid in equilibrium with its vapours, so that even if some gas is used up, an equivalent amount of the liquid evaporates to bring the pressure back to same.

Mass of the gas used up = (29 – 23.2) kg = 5.8 kg

Moles of the gas used up = $\frac{5.8 \times 10^3}{58} = 100 \, mole$

Using ideal gas equation, V = $\frac{nRT}{P}$

∴ V = $\frac{100 \times 0.082 \times 300}{1}$ (∵ normal usage conditions has P = 1 atm) = **2.46 m³**

Final pressure continues to be **2.5 atm** as it is LPG.

Example 3:

A container holds 3 L of $N_2(g)$ and $H_2O(l)$ at 29^oC. The pressure is found to be 1 atm. The water in the container is instantaneously split into hydrogen and oxygen by electrolysis, according to the reaction, $H_2O(l) \rightarrow H_2(g) + \frac{1}{2}O_2(g)$. After the reaction is complete, the pressure is 1.86 atm. What mass of water was present in the container. The aqueous tension of water at 29^oC is 0.04 atm.

Solution:

Total pressure in the beginning = $P_{N_2} + P_{H_2O}(l) = 1$ atm

$\therefore P_{N_2} = (1 - 0.04) = 0.96$ atm

When water is split into H_2 and $\frac{1}{2}O_2$, the total pressure is 1.86 atm.

$\therefore P_{N_2} + P_{H_2} + P_{O_2} = 1.86$

$0.96 + \left(\dfrac{3}{2}P_{H_2}\right) = 1.86 \qquad \left[\because \dfrac{P_{H_2}}{2} = P_{O_2}\right]$

$\therefore P_{H_2} = (1.86 - 0.96) \times \dfrac{2}{3} = 0.6\,\text{atm}$

Now, as $n_{H_2O} = n_{H_2}$

$\therefore n_{H_2} = \dfrac{PV}{RT} = \dfrac{0.6 \times 3}{0.082 \times 302} = 0.0726\,\text{mole}$

$\therefore$ Mass of water = $0.0726 \times 18 =$ **1.306 g**

This method looks perfectly OK. But there is one small error that has been made. The error is so small that it might be difficult to point out. Find the error on your own and only after several trails you should look at correct solution that follows now.

The error that has occurred is that the pressure of 1 atm is no doubt the pressure of N_2 and H_2O vapours but the electrolysis is done only to the H_2O (liquid) and that too instantaneously. This implies that the H_2O(vapour) that was in equilibrium with the liquid initially would be still left after the complete electrolysis of liquid water. $\therefore$ 1.86 atm is the pressure of H_2, O_2, N_2 and H_2O(vapour).

$P_{H_2} + P_{O_2} + P_{N_2} + P_{H_2O}(\text{vapour}) = 1.86$

$\dfrac{3}{2}P_{H_2} + 0.96 + 0.04 = 1.86$

$P_{H_2} = \dfrac{2}{3} \times 0.86 = 0.5734$

$n_{H_2} = \dfrac{0.5734 \times 3}{0.082 \times 302} = 0.0694\,\text{mole}$

$\therefore n_{H_2O} = 0.0694\,\text{mole}$

$\therefore$ Mass of H_2O (l) = $0.069 \times 18 =$ **1.25 g**

Alternatively,

Initially at 1 atm pressure, the mixture of $N_2(g)$ and $H_2O(l)$ is present in container. As $H_2O(l)$ is split into H_2 and O_2, pressure becomes, 1.86 atm.

According to the Dalton's law partial pressure,

Pressure due to H_2 and O_2 = 1.86 − 1 = 0.86 atm.

As H_2 and O_2 are formed in 2 : 1 molar ratio,

$\therefore$ Partial pressure of $H_2 (P_{H_2})$ = $\frac{2}{3} \times 0.86 = 0.5734$

Also, as $n_{H_2} = n_{H_2O}$

$n_{H_2} = \frac{0.5734 \times 3}{0.082 \times 302} = 0.0694 \text{mole}$

$\therefore n_{H_2O} = 0.0694 \text{mole}$

$\therefore$ Mass of H_2O (*l*) = 0.069 × 18 = **1.25 g**

Example 4:

Assume that air contains 79% N_2 and 21% O_2 by volume. Calculate the density of moist air at 25°C and 1 atm pressure when relative humidity is 60%. The vapour pressure of water at 25°C is 23.78 mm of Hg. Relative humidity is given by percentage

$$\text{relative humidity} = \frac{\text{partial pressure of water}}{\text{vapour pressure of water at that temperature}} \times 100$$

Solution:

First of all it is important to understand the distinction between vapour pressure and partial pressure of vapour.

When a liquid is in equilibrium with its vapours, the vapours exert a pressure on the surface of the liquid called vapour pressure. This is the maximum possible pressure exerted by the vapours of the liquid at that temperature. If we assume that vapours of a liquid exist in a container without the liquid, then the vapours behave just like any other gas, obeying all the gas laws. The pressure exerted by the vapours now can be anything which is less than or equal to the vapour pressure. This is called partial pressure of vapour. If the partial pressure somehow becomes more than vapour pressure, the vapours start liquefying to form liquid till vapours would be in equilibrium with liquid, exerting the vapour pressure.

In this problem, let us look at what we are supposed to calculate. We need to find the density of moist air.

From the ideal gas equation, $PV = \frac{w}{M}RT$

$\rho = \frac{w}{V} = \frac{PM}{RT}$

Therefore, we need to find the molecular weight of moist air. To find the molecular weight of a mixture of gas, we need the molar composition or mole fraction of the gas mixture.

Partial pressure of water (vapour) = $\frac{60}{100} \times \frac{23.78}{760} = = 0.0187 \text{atm}$

$\therefore$ Mole fraction of water vapour = $\frac{0.0187}{1} = 0.0187$

Pressure of ($N_2 + O_2$) = (1 − 0.0187) atm = 0.9813 atm

Let the partial pressure of N_2 be 79 x, then the partial pressure of O_2 is 21 x (they are in molar ratio of 79 : 21)

$\therefore$ 79 x + 21 x = = 0.9813

$$x = \frac{0.9813}{100}$$

x = 0.009813 atm

$\therefore P_{N_2}$ = 79x = 0.7752 atm

$\therefore P_{O_2}$ = 0.2061 atm

Mole fraction of N_2 = $\frac{0.7752}{1} = 0.7752$

and mole fraction of O_2 = $\frac{0.2061}{1} = 0.2061$

$\therefore$ Effective molecular weight of moist air = [(0.0817 × 18) + (0.7752 × 28) + (0.2061 × 32)]

= 29.77 g mol^{-1}

$\therefore \rho = \frac{1 \times 29.77}{0.082 \times 298} = \textbf{1.218 g/L}$

Example 5:

The average velocity of CO_2 at T_1 K and most probable velocity at T_2 K is 9×10^4 cm/s. Calculate the values of temperatures, T_1 and T_2 K.

Solution:

Average velocity of CO_2 at T_1 K = $\sqrt{\dfrac{8RT_1}{\pi M}}$

$9 \times 10^2 \, m/s = \sqrt{\dfrac{8RT_1}{\pi \times 44 \times 10^{-3}}} = \sqrt{\dfrac{8 \times 8.314 \times T_1}{3.14 \times 44 \times 10^{-3}}}$

T_1 = 1682.5 K

Most probable velocity of CO_2 at T_2 K = $\sqrt{\dfrac{2RT_2}{M}}$

$9 \times 10^2 = \sqrt{\dfrac{2RT_2}{M}} = \sqrt{\dfrac{2 \times 8.314 \times T_2}{44 \times 10^{-3}}}$

T_2 = 2143.37 K

Example 6:

The rate of diffusion of a sample of ozonised oxygen is 0.98 times that of pure oxygen. Find the percentage by volume of ozone in the ozonised sample.

Solution:

Ozonised oxygen is a mixture of ozone and oxygen.

$$\frac{r_{mix}}{r_{O_2}} = \sqrt{\frac{32}{M_{mix}}} = 0.98$$

$$M_{mix} = \frac{32}{(0.98)^2} = 33.32 \, g/mol$$

If mole fraction of ozone is *x*, then that of oxygen would be $(1 - x)$.

$\therefore (x \times 48) + [(1 - x) \times 32] = 33.32$

$x = 0.0825$

$\therefore$ Percentage by volume of ozone = 0.0825×100 = **8.25 %**.

Example 7:

The kinetic molecular theory attributes an average kinetic theory of $\dfrac{3}{2}\dfrac{RT}{N}$ to each particle. What rms speed would a mist particle of mass 10^{-12} g have at room temperature (27^oC) according to kinetic theory of gases?

Solution:

$$u_{rms} = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3 \times 8.314 \times 300}{10^{-12} \times 6.023 \times 10^{23} \times 10^{-3}}} = \mathbf{3.52 \times 10^{-3}} \text{ m/s}$$

Example 8:

The composition of air inhaled by a human is 21% by volume O_2 and 0.03% CO_2 and that of exhaled air is 16% O_2 and 4.4% CO_2. Assuming a typical volume of 7200 L day^{-1}, what mass of O_2 is used by the body and what mass of CO_2 is generated by the body each day? Assume ideal gas behaviour for the air at 37°C and 1 atm.

Solution:

Moles of O_2 inhaled = $\dfrac{1 \times 0.21 \times 7200}{0.0821 \times 310}$ = 59.4 moles

Moles of O_2 exhaled = $\dfrac{1 \times 0.16 \times 7200}{0.0821 \times 310}$ = 45.26 moles

$\therefore$ Mass of O_2 used = $(59.4 - 45.26) \times 32$ = **452.48 g**

Moles of CO_2 inhaled = $\dfrac{1 \times 0.0003 \times 7200}{0.0821 \times 310}$ = 0.085 moles

Moles of CO_2 exhaled = $\dfrac{1 \times 0.044 \times 7200}{0.0821 \times 310}$ = 12.45 moles

$\therefore$ Mass of CO_2 generated = $(12.45 - 0.085) \times 44$ = **544.06 g**

Example 9:

The total pressure of a mixture of H_2 and O_2 is 1 atm. The mixture is allowed to react to form water, which is suddenly removed completely to leave only pure H_2 at a pressure of 0.35 atm. Assuming ideal gas behaviour and that all pressure measurements were made under the same temperature and volume conditions, calculate the composition of the original mixture?

Solution:

The total number of mole in the original mixture is
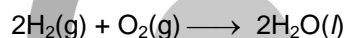
$$n_T = \frac{1.0 \times V}{RT}$$

After the reaction, the number of mole of excess H_2 is given as

$$n_{H_2}(excess) = \frac{0.35 \times V}{RT}$$

Thus, the amount of O_2 and H_2 in the original mixture that underwent reaction is

$$n_{O_2} + n_{H_2} = \left(\frac{1 \times V}{RT}\right) - \left(\frac{0.35 \times V}{RT}\right) = \frac{0.65 \times V}{RT}$$

From the chemical equation,

$$2H_2(g) + O_2(g) \longrightarrow 2H_2O(l)$$

The number of mole of H_2 used are double the mole of O_2 used. Since, H_2 is left in excess, this means that O_2 is the limiting agent. Let the mole of O_2 present in the original mixture be *x*, then the mole of H_2 consumed would be 2*x*.

$$\therefore \ x + 2x = \frac{0.65 \times V}{RT}$$

$$\therefore x = n_{O_2} = \frac{0.217 \times V}{RT}$$

and $n_{H_2}(used) = \dfrac{0.43 \times V}{RT}$

Thus, the original mixture contained

$$n_{H_2}(original\,mixture) = \left(\frac{0.43 \times V}{RT}\right) + \left(\frac{0.35 \times V}{RT}\right) = \frac{0.78 \times V}{RT}$$

and $n_{O_2}(original\ mixture) = \dfrac{0.217 \times V}{RT}$

Therefore composition of the original sample will be

$$X_{H_2} = \frac{n_{H_2}}{n_T} = \frac{0.78V/RT}{1.0V/RT} = 0.78$$

$$X_{O_2} = 1 - X_{H_2} = 1 - 0.78 = 0.22$$

$\therefore$ Percentage of H_2 in the original sample = **78%**

and percentage of O_2 in the original sample = **22%**

Example 10:

A 5 litre flask containing N_2 at 1 atm and 25°C is connected to a 4 litre flask containing N_2 at 2 atm and 0°C. After the gases are allowed to mix, keeping both flasks at their original temperatures, what will be the final pressure and the amount of N_2 in the 5 litre flask? Assume ideal gas behaviour.

Solution:

The total amount of N_2 in the combined system is given as

$$n_T = n(hot) + n(cold) = \left(\frac{P(hot)\,V(hot)}{RT(hot)}\right) + \left(\frac{P(cold)\,V(cold)}{RT(cold)}\right)$$

$$n_T = \left(\frac{1 \times 5}{0.0821 \times 298}\right) + \left(\frac{2 \times 4}{0.0821 \times 273}\right) = (0.204 + 0.357) = 0.561$$

After mixing, P(hot) = P(cold)

$$\therefore \quad \left(\frac{n'(hot)RT(hot)}{V(hot)}\right) = \left(\frac{n'(cold)RT(cold)}{V(cold)}\right)$$

Let the number of mole of N_2 left in the container at 25°C (hot container) be x, then the number of mole of N_2 in the container at 0°C (cold container) would be $0.561 - x$.
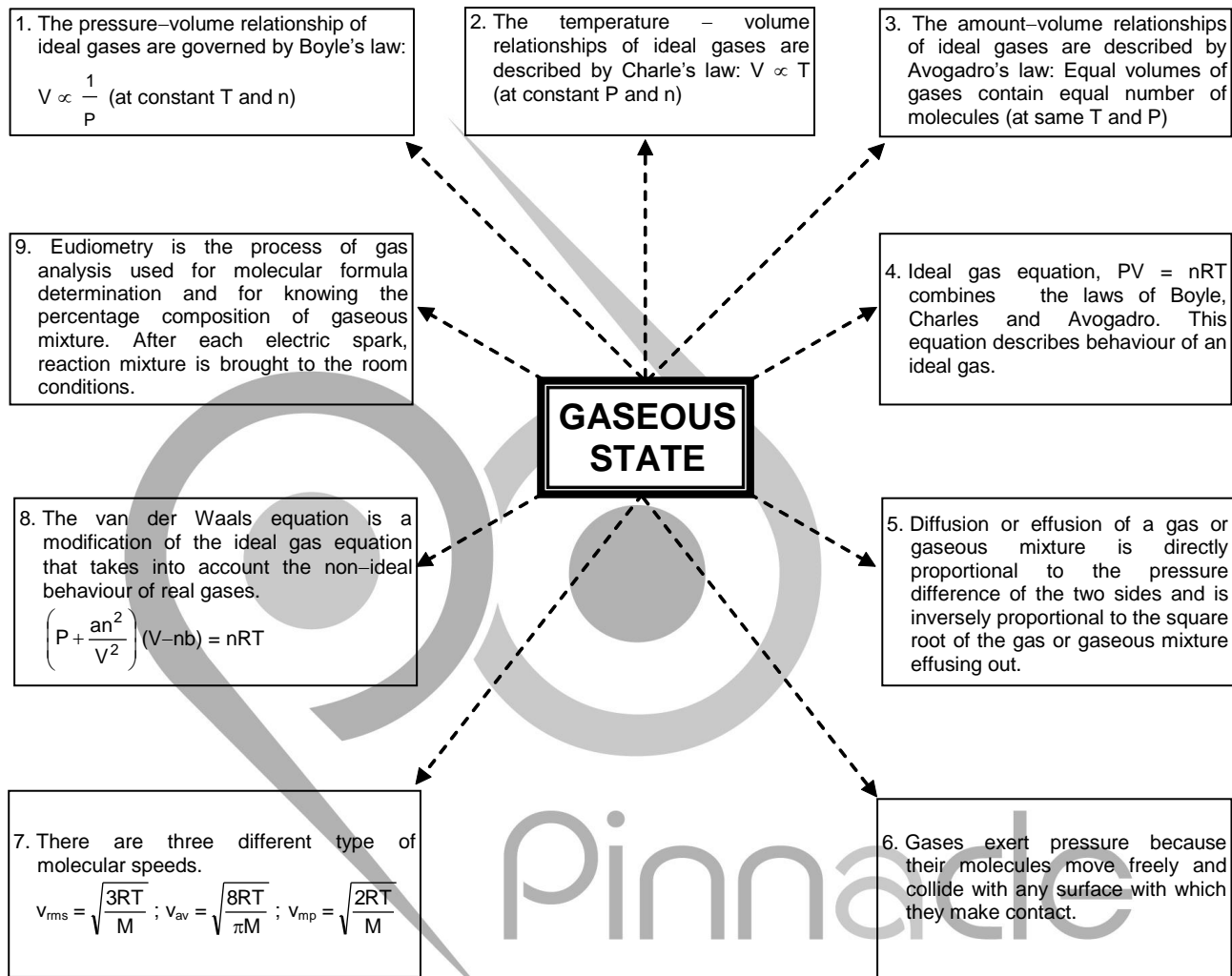
$$\frac{x \times 298}{5} = \frac{(0.561 - x)\,273}{4}$$

$\therefore \ x = 0.299$

Moles of N_2 in the 5 litre container = **0.299**

$$P(hot) = \frac{0.299 \times 0.0821 \times 298}{5} = \textbf{1.465 atm}$$

MIND MAP

1. The pressure–volume relationship of ideal gases are governed by Boyle's law:

$V \propto \dfrac{1}{P}$ (at constant T and n)

2. The temperature – volume relationships of ideal gases are described by Charle's law: $V \propto T$ (at constant P and n)

3. The amount–volume relationships of ideal gases are described by Avogadro's law: Equal volumes of gases contain equal number of molecules (at same T and P)

9. Eudiometry is the process of gas analysis used for molecular formula determination and for knowing the percentage composition of gaseous mixture. After each electric spark, reaction mixture is brought to the room conditions.

4. Ideal gas equation, PV = nRT combines the laws of Boyle, Charles and Avogadro. This equation describes behaviour of an ideal gas.

GASEOUS STATE

8. The van der Waals equation is a modification of the ideal gas equation that takes into account the non–ideal behaviour of real gases.

$\left(P + \dfrac{an^2}{V^2}\right)(V{-}nb) = nRT$

5. Diffusion or effusion of a gas or gaseous mixture is directly proportional to the pressure difference of the two sides and is inversely proportional to the square root of the gas or gaseous mixture effusing out.

7. There are three different type of molecular speeds.

$v_{rms} = \sqrt{\dfrac{3RT}{M}}$; $v_{av} = \sqrt{\dfrac{8RT}{\pi M}}$; $v_{mp} = \sqrt{\dfrac{2RT}{M}}$

6. Gases exert pressure because their molecules move freely and collide with any surface with which they make contact.
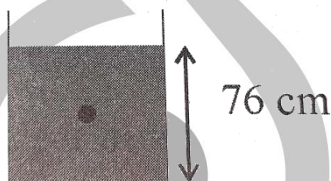
EXERCISE – I (BUILDING A FOUNDATION)

SECTION A: PRESSURE CALCULATION, BAROMETER & MANOMETER
SINGLE CORRECT ANSWER TYPE

1. An open tank is filled which Hg upto a height of 76cm. What is the pressure at the
   (i) bottom of the tank?
   (a) 3 atm
   (b) 2 atm
   (c) 4 atm
   (d) 1 atm
   (ii) Middle of the tank. (if atmospheric pressure is 1 atm)?

   76 cm

   (a) 2 atm
   (b) 1.0 atm
   (c) 2.5 atm
   (d) 1.5 atm

2. What is the the height of water upto which water must be filled to create the same pressure at the bottom.
   As in problem? $h_w d_w = h_{Hg} d_{Hg}$
   (a) 1033.6 cm
   (b) 9033.6 cm
   (c) 7033.6 cm
   (d) 8033.6 cm

3. What will be the pressure if two immiscible fluid is filled according to given diagram.
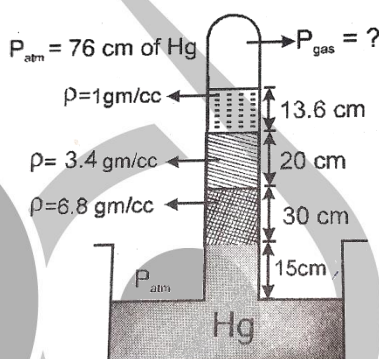   Total pressure $= h_2 d_2 g + h_1 d_1 g$

   $d_1 > d_2$

   h_2 → $h_2 d_2 g$
   h_1 → $h_1 d_1 g$
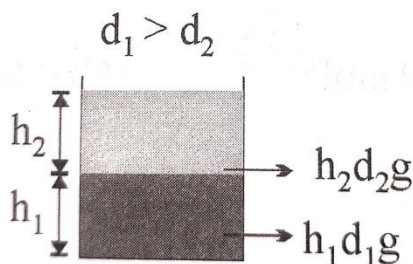
   (i) What is the pressure at the bottom of tank?
   (a) $P_{atm} + h_2 d_1 g + h_1 d_2 g$

(b) $P_{atm} + h_3d_4g + h_2d_2g$

(c) $P_{atm} + h_2d_2g + h_1d_1g$

(d) $P_{atm} + h_1d_2g + h_2d_1g$

(ii) What is the pressure at the middle point of bottom layer.

(a) $P_{atm} + h_2d_2g + \frac{h_1}{2}d_1g$

(b) $P_{atm} + h_1d_2g + \frac{h_2}{2}d_1g$

(c) $P_{atm} + h_1d_1g + \frac{h_1}{4}d_1g$

(d) $P_{atm} + h_1d_2g + \frac{h_1}{3}d_2g$

4. In the figure the pressure of the confined gas will be

(a) 30 cm of Hg

(b) 40 cm of Hg

(c) 36 cm of Hg

(d) 46 cm of Hg

5. Calculate the number of moles of gas present in the container of volume 10 L at 300 K. If the manometer containing glycerin shows 5 m difference in level as shown diagram.

(Give : $d_{glycerin} = 2.72$ g/mL; $d_{mercury} = 13.6$ g/mL.)
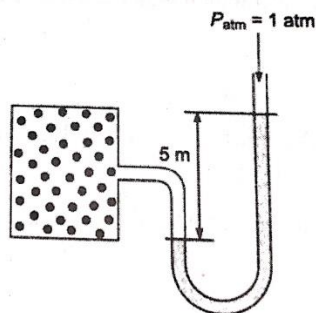
(a) 0.94 mole

(b) 0.49 mole

(c) 0.64 mole

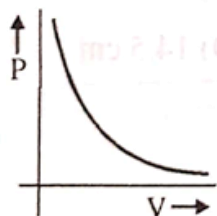(d) None of these

SECTION B: GAS LAW

SINGLE CORRECT ANSWER TYPE

1. A gas occupies one litre atmospheric pressure. What will be the volume of the same amount of gas under 750 mm of Hg at the same temperature.
   (a) 1.0133 lit.
   (b) 2.0133 lit.
   (c) 3.0133 lit.
   (d) 5.0133 lit.

2. 10 g of a gas at STP occupies 5 litres. The temp. at which the volume becomes double for the same mass of gas at the same pressure is?
   (a) 273 K
   (b) – 273° C
   (c) 273° C
   (d) 546° C

3. Figure shows graphs of pressure versus density for an ideal gas at two temperature T_1 and T_2. Which is correct:


   (a) $T_1 > T_2$
   (b) $T_1 = T_2$
   (c) $T_1 < T_2$
   (d) None of the above
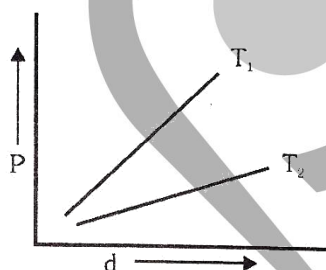
4. A gas is initially at 1 atm pressure. To compress it to 1/4 th of initial volume, what will be the pressure required? (Assume process is isothermal)
   (a) 6 atm
   (b) 4 atm
   (c) 10 atm
   (d) 8 atm

5. If the temp. of a particular amount of gas is increased from $27°C$ to 57°C, find final volume of the gas, in initial volume = 1 L and assume pressure is constant.
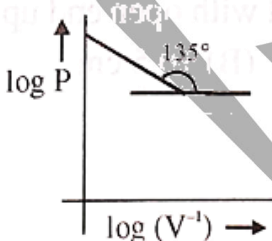   (a) 1.1 L
   (b) 2. 1 L
   (c) 3. 1 L

(d) 4. 1 L

6. Four one litre flasks are separately filled with the gases, O_2, F_2, CH_4 and CO_2 under the same conditions. The ratio of number of molecules in these gases:

   (a) $2 : 2 : 4 : 3$
   (b) $1 : 1 : 1 : 1$
   (c) $1 : 2 : 3 : 4$
   (d) $2 : 2 : 3 : 4$

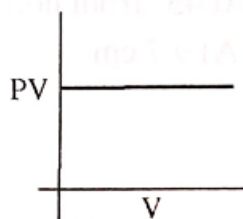7. Which of the following curve does not represent Boyle's law?
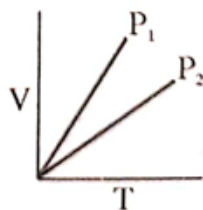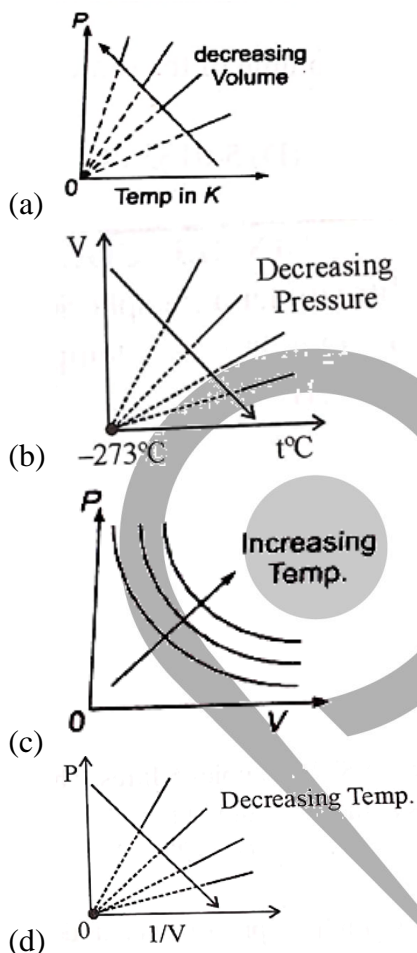

(a)
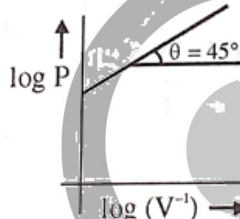
(b)

(c)

(d)

8. V versus T curves at constant pressure P_1 and P_2 for and ideal gas are shown in figure. Which is correct?

(a) $P_1 > P_2$

(b) $P_1 < P_2$

(c) $P_1 = P_2$

(d) All of these

9. Which one of these graphs for an ideal gas, the arrow indication is incorrectly marked?

(a)

(b)

(c)

(d)

10. A rubber ballon contains some solid marbles each of volume 10 ml. A gas is filled in the balloon at a pressure of 2 atm and the total volume of the balloon is 1 litre in this condition. If the external pressure is increased to 4 atm the volume of Balloon becomes 625 ml. Find the number of marbles present in the balloon.

(a) 30

(b) 20

(c) 35

(d) 25

11. A 12 cm column of air is trapped by a column of mercyry 15 cm long in a thin tube which is horizontally fixed as shown is figure.

$$P_{atm}= 750 \text{ mm}$$

$$P_{atm}$$

12 15cm
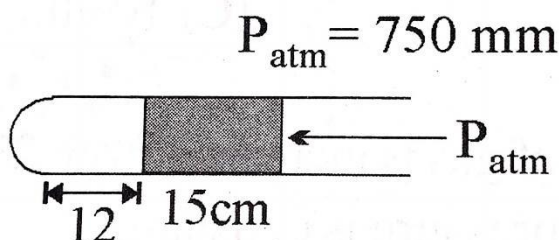
Which is the length of air colum when the tube is fixed at the same temperature.

(i) Vertically with open end up.

   (a) 10 cm

   (b) 20 cm

   (c) 30 cm

   (d) 40 cm

(ii) Vertically with open end down.

   (a) 40 cm

   (b) 15 cm

   (c) 25 cm

   (d) 35 cm

(iii) At 45° from horizontal with open end up.

   (a) 9.7 cm

   (b) 10.5 m

   (c) 15.5 cm

   (d) 14. 5 cm

SECTION C: IDEAL GAS EQUATION

SINGLE CORRECT ANSWER TYPE

1. In the gas equation $PV = nRT$ the value of universal gas constant depends upon –

   (a) The nature of the gas

   (b) The pressure of the gas

   (c) The temperature of the gas

   (d) The units of measurement

2. One litre of an unknown gas weights 1.25 g at N. T. P. which of the following gas pertains to the above data

   (a) CO_2

   (b) NO_2

   (c) N_2

   (d) O_2

3. 2.8 g of a gas at 1 atm and 273 K occupies a volume off 2.24 litres, the gas can not be:

   (a) O_2

   (b) CO

(c) N_2

(d) C_2H_4

4. Equal volumes of two gases which do not react together are enclosed in separate vessels. Their pressures are 10 mm and 400 mm respectively. If the two vessels are joined together, then what will be the pressure of the resulting mixture (temperature remaining constant)

   (a) 120 mm

   (b) 500 mm

   (c) 1000 mm

   (d) 205 mm

5. A 0.50 L container is occupied by nitrogen at a pressure of 800 torr and a temperature of 0°C. the container can only withstand a pressure of 3.0atm. What is the highest temperature (°C) to which the container may be heated?

   (a) 505

   (b) 450

   (c) 625

   (d) 560

6. Densities of two gases are in the ratio 1 : 2 and their temperatures are in the ratio 2 : 1, then the ratio of their respective molar mass at certain pressure is:

   (a) 1 : 1

   (b) 1 : 2

   (c) 2 : 1

   (d) 4 : 1

7. (i) Plot the curve between PT vs T at constant V & constant no of moles?
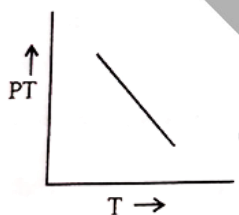
(a)
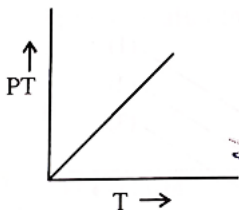
(b)
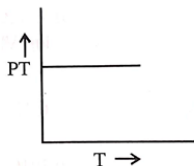
(c)
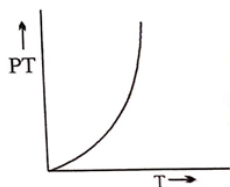
(d)

(ii) What is the number of moles of gas taken when the volume of the vessel is 82. 1m1 and $\frac{d}{dT}[PT]_{at300K} = 300$ for the given curve?

(a) $N = \frac{1}{2}$

(b) $N = \frac{1}{4}$

(c) $N = \frac{1}{6}$

(d) $N = \frac{1}{8}$

8. A high altitude balloon contains 6.81 g of helium in 1.16×10^4 L at $-23°C$. assuming ideal gas behaviour, how many grams of helium would have to be added to increase the pressure to 4.0×10^{-3} atm?

(a) 1.27

(b) 1.58

(c) 3.68

(d) 2.13

9. (i) Radius of a bubble at the bottom of the tank below was found to be 1 cm, then find the radius of the bubble at the surface of water considering the temperature at the surface & bottom being same.
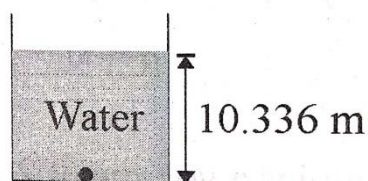
(a) $\sqrt[3]{8}$ cm

(b) $\sqrt[3]{2}$ cm

(c) $\sqrt[3]{6}$ cm

(d) $\sqrt[3]{4}$ cm

(ii) If absolute temperature at the surface is 4 times that at the bottom, then find radius of bubble at the surface.

(a) R' = 4 cm

(b) R' = 6 cm

(c) R' = 2 cm

(d) R ' = 8 cm

10. The reading of a faulty barometer is 700 mm of Hg. When actual pressure is 750 mm of Hg. The length of the air column trapped in this case is 10 cm. Find the actual value of the atmospheric

pressure when reading of this barometer is 750 mm of Hg. Assume that the length of the Barometer tube above mercury surface in the container remains constant.

(a) 860

(b) 840

(c) 830

(d) 850

SUBJECTIVE TYPE

11. The stop cock connecting the two bulbs of volume 5 litre and 10 litre containing an ideal gas at 9 atm and 6 atm respectively, is opened. What is the final pressure if the temperature remains same.

12. At constant pressure 0.0821 atm, log (V) v/s log (T) are plotted for three sample of an ideal gas as shown. Find out the no. of moles taken in sample (A), (B) and (C).
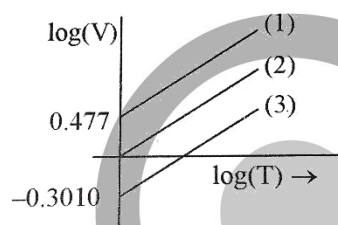
SECTION D: DALTONS LAW

SINGLE CORRECT ANSWER TYPE

1. The total pressure of a mixture of two gases is equal to:
   (a) Sum of their partial pressures
   (b) The difference in partial pressures
   (c) The product of partial pressures
   (d) The ratio of partial pressures

2. Equal masses of SO_2, CH_4 and O_2 are mixed in empty container at 298K, when total pressure is 2.1 am. The partial pressure of CH_4 in the mixture is –
   (a) 0.5 atm
   (b) 0.75 atm
   (c) 1.2 atm
   (d) 0.6 atm

3. The partial pressure of hydrogen in a flask containing 2g of H_2 & 32g of SO_2 is
   (a) $\frac{1}{16}$ of total pressure
   (b) $\frac{1}{2}$ of total pressure
   (c) $\frac{2}{3}$ of total pressure
   (d) $\frac{1}{8}$ of total pressure

4. Air contains 79% N_2 and 21% O_2 by volume. If the barometric pressure is 750 mm Hg the partial

pressure of oxygen is:

(a) 157.5 mm of Hg

(b) 175.5 mm of Hg

(c) 315.0 mm of Hg

(d) None

5. The partial pressure of hydrogen in a flask containing two grams of hydrogen and 32 gm of sulphur dioxide is:

(a) $1/16^{th}$ of the total pressure

(b) $1/9^{th}$ of the total pressure

(c) 2/3 of the total pressure

(d) $1/8^{th}$ of the total pressure

6. O_2 and SO_2 gases are filled in ratio of 1:3 by moles in a closed container of 3 L at temperature of 27° C. The partial pressure of O_2 is 0.60 atm, the concentration of SO_2 would be

(a) 0.36

(b) 0.074

(c) 3. 6

(d) 36

7. If 2 lit, of gas A at 1.5 atm and 3 lit. of gas B at 2 atm are mixed in a 5 lit. container then what is the final pressure, considering all are at same temperature.

(a) 1.6 atm

(b) 1.8 atm

(c) 1.7 atm

(d) 1.9 atm

8. 2 moles of NH_3 (g) and 1 mole of HCI(g) are taken in a container of capacity 8.21 lit. at 300 K to produce NH_3.

(a) 3 atm

(b) 4 atm

(c) 5 atm

(d) 6 atm

9. One mole of N_2 and 3 moles H_2 are taken in a container of capacity 8.21 lit. at 300K to produce NH_4 CI(s). Find the total pressure after the reaction.

Find the partials pressure of N_2 and 3 moles H_2 if partial pressure of NH_3 after sufficient time was found to be 3 atm.

$$N_2 + H_2 \rightarrow NH_3$$

(a) 2.5 atm, 5.5 atm

(b) 1.5 atm. 4.5 atm

(c) 1.1 atm, 4.8 atm

(d) 1.2 atm, 4.1 atm

SUBJECTIVE TYPE

10. A closed container containing O_2 and same liquid water was found to exert 740 mm pressure at 27° c.

(i) Then calculate the pressure exerted by O_2 if aqueous tension at 27° is 20 mm.

(ii)   What will be the final pressure if volume is reduced to half (consider volume of liquid water negligible)

(iii)   What will be the final pressure if volume is doubled.

SECTION E: DIFFUSION AND EFFUSION

1. Compare the rate of diffusion of CO with a mixture of He and CH_4 in 3 : 1 mole ratio under similar condition.

    (a) $\frac{3}{4}$

    (b) $\frac{1}{2}$

    (c) $\frac{1}{3}$

    (d) $\frac{5}{4}$

2. A mixture of H_2 and O_2 in 2 : 1 mole ratio is allowed to diffuse through a orifice. Calculate te composition of gases coming out initially.

    (a) $\frac{8}{1}$

    (b) $\frac{9}{1}$

    (c) $\frac{10}{1}$

    (d) $\frac{7}{1}$

3. A vessel contains H_2 & O_2 in the molar ratio of 8: 1 respectively. This mixture of gases is allowed to diffuse through a hole, find composition of the mixture coming out of the hole.

    (a) 32 : 1

    (b) 1 : 32

    (c) 16 : 1

    (d) 1 : 16

4. Pressure of 1 g ideal gas X at 300 K is 2 atm. When 2 g of another gas Y is introduced in the same vessel at same temperature, the pressure become 3 atm then correct relationshs between molar mass of X and Y is:

    (a) $M_Y = 2\ M_X$

    (b) $M_Y = 4\ M_X$

    (c) $M_X = 4\ M_Y$

    (d) None of these

5. 32 ml of He effuses through a fine orifice in 1 minute. Then what volume of CH_4 will diffuse in 1 minute under the similar condition.

    (a) V = 30 ml

    (b) V = 32 ml

    (c) V = 20 ml

    (d) V = 16 ml

6. A naturally occurring uranium ore contain D_2 and CH_4 in 1 : 8 mole ratio. If it is desired to enrich the D_2 to 80% of the sample (by moles) making use of relative rates of effusion of D_2 and CH_4 isotopes. How many minimum effusion steps are required.
   (a)5 steps
   (b) 21 steps
   (c)30 steps
   (d) 40 steps

7. A rigid container containing 5 mole H_2 gas at some pressure and temperature. The gas has been allowed to escape by simple process from the container due to which pressure of the gas becomes half of its initial pressure and temperature become $(2/3)^{rd}$ of its initial. The mass of gas remaining is:
   (a)7.5 g
   (b) 1.5 g
   (c)2.5 g
   (d) 3.5 g

8. The rate of diffusion of a sample of a ozonized oxygen is 0.98 times than that of oxygen. Find the % (by volume) of ozone in the ozonized sample.
   (a)8.25%
   (b) 10.25%
   (c)4.25%
   (d) 6.25%

SECTION F: CONTAINER CAPACITY, CONNECTED CONTAINER GAS PROBLEM AND PAYLOAD

SINGLE CORRECT ANSWER TYPE

1. A balloon is inflated to $\frac{7}{8}$ of its maximum volume at 27° C. Then calculate the minimum temperature above which it will burst.
   (a)320. 8 K
   (b) 340. 8 K
   (c)360. 8 K
   (d) 342. 8 K

2. A gas cylinder containing cooking gas can withstand a pressure of 18 atm. The pressure gauge of cylinder indicates 12 atm at 27° C. Due to sudden fire in building the temperature start rising at what temperature will the cylinder explode.
   (a)420 K
   (b) 410 K
   (c)450 K
   (d) 430 K

3. A tyre of maximum volume 8.21 lit. can withstand a pressure of 10 atm. Initially the tube is empty.
   (i) What is the number of the moles required to inflate completely the tube upto a pressure of 1 atm & 300 K temperature?

(a) 1/4 mol.

(b) 1/6 mol.

(c) 1/3 mol.

(d) 1/2 mol.

(ii) What is the minimum number of moles required to burst the tyre tube at 300 K?

(a) 10/3 mol

(b) 30/3 mol

(c) 20/3 mol

(d) 17/3 mol

4. An open flask contains air at 27° C. Calculate the temperature at which it should be heated so that

(i) $\frac{1}{3}$rd of air measured in the container at 27° C escape out.

  (a) 150

  (b) 250

  (c) 350

  (d) 450

(ii) $\frac{1}{3}$rd of air measured in the container at final temperature escape out.

  (a) 400

  (b) 200

  (c) 100

  (d) 300

5. A container of 8.21 lit. Capacity is filled with 1 mole of H_2 at 300 K and it is connected to another container of capacity 2×8.21 lit. Containing 4 moles of O_2 at 300 K, then what is the final pressure & partial pressure of each gas in each container?
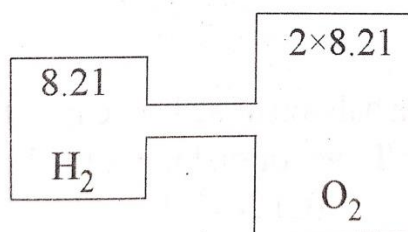
(a) $P_f = 8$ atm, $P_{H2} = 3$ atm, $P_{O2} = 4$ atm

(b) $P_f = 10$ atm, $P_{H2} = 2$ atm, $P_{O2} = 4$ atm

(c) $P_f = 6$ atm, $P_{H2} = 1$ atm, $P_{O2} = 2$ atm

(d) $P_f = 5$ atm, $P_{H2} = 1$ atm, $P_{O2} = 4$ atm

6. A 10 lit. Container consist of 1 mole of a gas at 300 K. It is connected through very small nozzle to another empty container having volume 40 lit. then calculate

(i) Ratio of moles of gas in container B & A at same T.

  (a) $\frac{4}{1}$

  (b) $\frac{5}{2}$

(c) $\dfrac{6}{1}$

(d) $\dfrac{7}{1}$

(ii)   Pressure of the gas in both container

(a) 0.9826 atm

(b) 0.7826 atm

(c) 0.3026 atm

(d) 0.4926 atm

(iii)If temperature of 40 L container is increased to 600 K keeping the other at 300 K. Find the pressure of each container.

(a) 0.830 atm

(b) 0.820 atm

(c) 0.821 atm

(d) 0.840 atm

7. A box of 1 L capacity is divided equal compartments by a thin partition which are filled with 2g H_2 and 16 g CH_4 respectively. The pressure in each compartment is recorded as P atm. The total pressure when partition is removed will be:

(a)P

(b) 2P

(c)P/2

(d) P/4

8. Consider the following apparatus. Calculate the partial pressure he helium after the opening valve. The temperature remains constant.

He
1.2 L
0.63 atm

Ne
3.4 L
2.8 atm
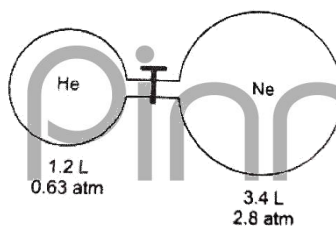
(a)0.164 atm

(b) 1.64 atm

(c)0.328 atm

(d) 1 atm

9. A balloon weighing 50 kg is filled with 685 kg of helium at 1 atm pressure and 25° C. What will be pay load if it dispalced 5108 kg of air?

(a)4373 kg

(b) 4423 kg

(c)5793 kg

(d) None of these

10. Find the payload which can be attached to a balloon of 821 lit. capacity if if is filled with Helium gas

at 3 atm and 27° C. Given diensity of air 2 g/L. wt. material of balloon = 200 g.

(a) 4042 g

(b) 3042 g

(c) 2042 g

(d) 1042 g

SECTION G: KTG

SINGLE CORRECT ANSWER TYPE

1. Which of the following is NOT a postulate of the kinetic molecular theory of gases?

   (a) The molecule possess a volume that is negligibly small compared to the container

   (b) The pressure and volume of a gas are inversely related

   (c) Gases consist of discrete particles that are in constant chaotic motion

   (d) The average kinetic energy of the molecule is directly proportional to the temperature

2. Which of the following statements about kinetic energy (K.E.) is true?

   (a) All objects moving with the same velocity have the same K.E.

   (b) The K.E. of a body will quadruple if its velocity doubles

   (c) As the velocity of a body increases, its K.E. decreases

   (d) The K.E. of a body is independent of its mass

3. The Ne atom has 10 times the mass of H_2. Which of the following statements is true?

   I.   At 25° C they both have the same average kinetic energy.

   II.   Ten moles of H_2 would have the same volumes as 1 mole of Ne at same temp. and pressure.

   III.   One mole of Ne exerts the same pressure as one mole of H_2 at STP

   IV.   A H_2 molecule travels 10 times faster than Ne atom at same temperature.

   V.   At STP, one litre of Ne has 10 times the density of 1 litre of H_2.

   (a) II, IV, V

   (b) I, III, V

   (c) I, II, III

   (d) I, II

4. Which of the following expression does not root mean square velocity –

   (a) $\left(\frac{3RT}{M_W}\right)^{\frac{1}{2}}$

   (b) $\left(\frac{3P}{DM_W}\right)^{\frac{1}{2}}$

   (c) $\left(\frac{3P}{D}\right)^{\frac{1}{2}}$

   (d) $\left(\frac{3PV_M}{M_W}\right)^{\frac{1}{2}}$

5. Average K.E. of He and Ne at 27°C is E. The average kinetic energy of NO_2 at the same temperature will be

   (a) E

(b) 22E

(c)E/22

(d) E/ $\sqrt{2}$

6. The average K.E. of He and Ne at 25°C is:

(a)$KE_{Ne} > KE_{He}$

(b) $KE_{Ne} = KE_{He}$

(c)$KE_{Ne} < KE_{He}$

(d) None of these

7. (i) Calculate the pressure exerted by 10^{23} gas molecules, each mass 10^{-22} g in a container of volume one litre. The rms velocity is 10^5 cm/sec.

(a) 3.33×10^7 dyne/cm^2

(b) 3.33×10^5 dyne/cm^2

(c) 3.33×10^3 dyne/cm^2

(d) 3.33×10^2 dyne/cm^2

(ii) What is to total kinetic energy (in cal) of these particles?

(a) 1175.0 Cal

(b) 1195.0 Cal

(c) 1155.0 Cal

(d) 1185.0 Cal

(iii)What must be the temperature?

(a) 3614.8 K

(b) 2214.8 K

(c) 1214.8 K

(d) 2414.8 K

8. Consider three one – litre flasks labeled A, B and C filled with the gases NO, NO₂, and N₂O, respectively each at 1 atm and 273 K. In which flask do the molecules have the highest average kinetic energy?

(a) Flask C

(b) All have the same

(c) Flask A

(d) None

9. If for two gases of molecular weights$M_A$andM_B at temperature $T_A$and T_B : $T_A M_B = T_B M_A$, then which property has the same magnitude for both the gases.

(a) Density

(b) Pressure

(c) KE per mol

(d) RMS speed

MULTIPLE CORRECT ANSWER TYPE

10. Indicate the correct statement for equal volumes of N₂(g) and CO₂(g) at 25°C and 1 atm.

(a) The average translational K.E., per molecule is the same for N_2 and CO_2

(b) The rms speed remains same for both N_2 and CO_2

(c) The density of N_2 is less than that of CO_2

(d) The total translational K.E., of both N_2 and CO_2 is the same

11. Select incorrect statement(s):

(a) The product of pressure and volume of fixed amount of a gas is independent of temperature

(b) The value of universal gas constant depends upon temperature, volume and number of gaseous molecules

(c) The gas constant also know as Boltzmann's constant

(d) The average kinetic energy of molecules of an ideal gas depends on temperature

SECTION H: MIXWELL'S DISTRIBUTION CURVE & MEAN FREE PATH AND FREQUENCY PARAMETER

SINGLE CORRCT ANSWER TYPE

1. At a definite temperature (T), the distribution of velocities is given by the curve. The curve that indicates that the velocities corresponding to points A, B and C are:
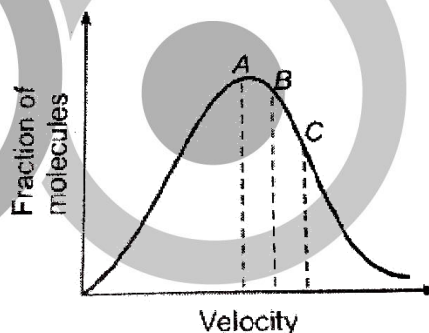
(a) Most probable, average and root mean square

(b) average, root mean square and most probable

(c) root mean square, average and most probable

(d) most probable, root mean square and average

2. At what temperature will average speed of the molecules of the second member of the series C_nH_{2n} be the same of Cl_2 at 627° C?

(a) 259.4 K

(b) 400 K

(c) 532.4 K

(d) None of these

3. If T_1, T_2 and T_3 are the temperature at which the U_{RMS}, $U_{average}$, U_{MP} of oxygen gas are all equal to 1500 m/s then the correct statement is:

(a) $T_1 > T_2 > T_3$

(b) $T_1 < T_2 < T_3$

(c) $T_1 = T_2 = T_3$

(d) None of these

4. 6×10^{22} gas molecules each of mass 10^{-24} kg are taken in a vessel of 10 litre. What is the pressure exerted by gas molecules? The root mean square speed of gas molecules is 100 m/s.
   (a) 20 Pa
   (b) 2×10^4 Pa
   (c) 2×10^5 Pa
   (d) 2×10^7 Pa

MULTIPLE CORRECT ANSWER TYPE

5. Consider the following statement regarding Maxwell's of velocities. The correct statement(s) is/are:
   (a) As temperature increases, the peak (maxima) of a curve is shifted towards right side
   (b) As temperature increases, the most probable velocity of molecules increases but fraction of molecules of most probable velocity decreases
   (c) The area under the curve at all the temperatures is the same because it represents the sum of fraction of gaseous molecules (curve between $\frac{1}{N} \times \frac{dN}{dU}$ and U)
   (d) The fractions of molecules having different velocities are different at a given temperature

6. Following represent the Maxwell distribution curve for an ideal gas at two temperature T_1 and T_2. Which of the following option(s) are true?
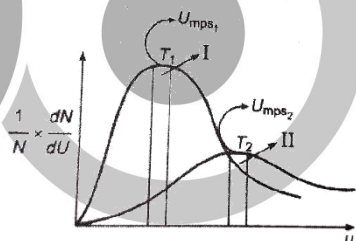
   (a) Total area under the two curves is independent of moles of gas
   (b) U_{mps} decreases as temperature decreases
   (c) $T_1 > T_2$ and hence higher the temperature, sharper the curve
   (d) The fraction of molecules having speed $= U_{mps}$ decreases as temperature increases

COMPREHENSION TYPE

Paragraph for Question no. 7 to 9

Collision cross – section is an area of an imaginary sphere of radius σ around the molecule within which the center of another molecule cannot penetrate.
The volume swept by a single molecule in unit time is
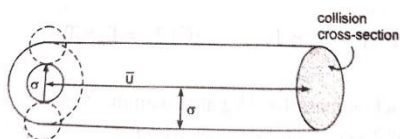
If N* is the number of molecules per unti volume, then the number of molecules within the volume V is
$$N = VN^* = (\pi\sigma^2\bar{u}) \, N^*$$
Hence, the number of collision made by a single molecules in unit time will be
$$Z = N = (\pi\sigma^2\bar{u}) \, N^*$$

In order to account for the movement of all molecules, we must consider the average velocity along the line of centres of two colliding molecules instead of the average velocity of a single molecule. If it is assumed that, on an average, molecules collide while approaching each other perpendicularly, then the average velocity along their centres is $\sqrt{2}\bar{u}$ as shown below.

Number of collision made by a single molecule with other molecules per unit time is given by

$$Z_1 = \pi\sigma^2(\overline{U_{rel}})N* = \sqrt{2}\pi\sigma^2\bar{U}N*$$
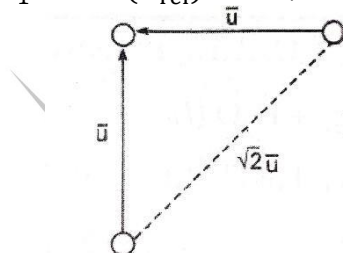
The total number of bimolecular collision Z_{11} per unit volume per unit time is given by

$$Z_{11} = \frac{1}{2}(Z_{11}N*) \text{ or } = \frac{1}{2}(\sqrt{2}\pi\sigma^2\bar{u}N*)N* = \frac{1}{\sqrt{2}}\pi\sigma^2\bar{u}N*^2$$

If the collision involve two unlike molecules ten the numebr of collision Z_{12} per unit volume per unit time is given as

$$Z_{11} = \pi\sigma_{12}^2\left(\sqrt{\frac{8KT}{\pi\mu}}\right)N_1N_2$$

Where N_1 and N_2 are the number of molecules per unit volume of the two types of molecues, σ_{12} is the average diameter of the two molecules and μ is the reduced mass.

The mean free path is the avarage distance travelled by a molecule between two sucessive collisions. We can express it is follows:

$$\lambda = \frac{\text{Average distance travelled per unit time}}{\text{No.of collsions made by a single molecule per unit time}} = \frac{\bar{u}}{Z_1}$$

or $\lambda = \frac{\bar{u}}{\sqrt{2}\pi\sigma^2\bar{u}N*} \Rightarrow \frac{1}{\sqrt{2}\pi\sigma^2N*}$

7. For a given gas the mean free path at a particular pressure is
   (a) Independent of temperatrue
   (b) Decreases with rise in temperature
   (c) Increase with rise in temperature
   (d) Directly proportional to T^2

   Direction for question no.8 and 9.
   Three ideal gas samples in separate equal volume containers are taken and following data is given:

	Pressure	Temperature	Mean freee paths	Mol.wt
Gas A	1 atm	1600 k	0.16 nm	20
Gas B	2 atm	200 K	o.16 nm	40
Gas C	4 atm	400 K	0.04 NM	80

8. Calculate ratio of collsion frequencies (Z_{11}) (A: B: C) of following for the three gases.
   (a) $1:2:4$
   (b) $4:2:1$
   (c) $1:4:16$

(d) $16 : 4 : 1$

9. Calculate the ratio of number of collisions by one molecule per sec (Z_1).

   (a) $4 : 1 : 4$

   (b) $1 : 4 : 4$

   (c) $4 : 3 : 2$

   (d) $1 : 2 : 4$

SECTION I: EUDIOMETRY

SINGLE CORRECT ANSWER TYPE

1. $C_6H_5OH(g) + O_2(g) \rightarrow CO_2(g) + H_2O(l)$

   Magnitude of volume change if 30 ml of C_6H_5OH (g) is burnt with excess amount of oxygen, is

   (a) 30 ml

   (b) 60 ml

   (c) 20 ml

   (d) 10 ml

2. 0.90 g of a solid organic compound (molecular weight = 90) containing C, H and O was heated with oxygen corresponding to a volume of 224 mL at STP. After the combustion the total volume of the gases was 560 mL at STP. On treatment with KOH the volume decreased to 112 mL. Determine the molecular formula of the compound.

   (a) $C_2H_2O_2$

   (b) $C_2H_4O_2$

   (c) $C_4H_2O_2$

   (d) $C_2H_2O_2$

3. 5 mL of a gas containing C and H was mixed with an excess of oxygen (30 mL) and the mixture exploded by means of an electric spark. After the explosion the volume of the mixed gases remaining was 25 mL. On adding a concentrated solution of KOH, the volume further diminished to 15 mL, the residual gas being pure oxygen. All volumes have been reduced to NTP. Calculate the molecular formula of the hydrocarbon gas.

   (a) C_2H_2

   (b) C_2H_4

   (c) C_2H_6

   (d) C_2H_8

4. The % by volume of C_4H_{10} in a gaseous mixture of C_4H_{10} and CO is 40. When 200 ml of the mixture is burnt in excess of O_2, find volume (in ml) of CO_2 produced.

   (a) 220

   (b) 340

   (c) 440

   (d) 560

5. When 20 ml of mixture of O_2 and O_3 is heated, the volume becomes 29 ml and disappears in alkaline pyrogallol solution. What is the volume percent of O_2 in the original mixture?

(a) 90%

(b) 10%

(c) 18%

(d) 2%

6. A mixture of C_2H_2 and C_3H_8 occupied a certain volume at 80 mm Hg. The mixture was completely burnt to CO_2 and H_2O (I). The pressure of CO_2 was found to be 230 mm Hg at the same temperature and volume, the fraction of C_2H_2 in mixture is

(a) 0.125

(b) 0.5

(c) 0.85

(d) 0.25

7. A mixture of CH_4 and C_2H_2 occupied a certain volume at a total pressure of 63 mm. The sample ws burnt to CO_2 and H_2O and CO_2 alone was collected and its pressure was found to be 69 mm in the same volume and at the same temperature as the original mixture. What fraction of the mixture was methane?

(a) 0.90

(b) 0.80

(c) 0.70

(d) 0.60

Paragraph For Question no. 8 to 11

A 10 ml mixture of N_2, a alkane & O_2 undergo combustion in Eudiometry tube. There was contraction of 2 ml, when residual gases are passed through KOH. To the remaining mixture comprising of only one gas excess H_2 was added & after combustion the gas produced is absorbed by water, causing a reduction in volume of 8 ml.

8. Gas produced after introduction of H_2 in the mixture?

(a) H_2O

(b) CH_4

(c) CO_2

(d) NH_3

9. Volume of N_2 present in the mixture?

(a) 2 ml

(b) 4 ml

(c) 6 ml

(d) 8 ml

10. Volume of O_2 remained after the first combustion?

(a) 4 ml

(b) 2 ml

(c) 0

(d) 8 ml

11. Identify the hydrocarbon.

(a) CH_4

(b) C_2H_6

(c) C_3H_8

(d) C_4H_{10}

SECTION J: REAL GAS

SINGLE CORRET ANSWER TYPE

1. A real gas obeying Vander waal equation will resemble ideal gas if the
   (a) Constants a and b are negligibly small
   (b) A is large and b is small
   (c) A is small and b is large
   (d) Constant a and b are large

2. The compressibility factor of real gas is usually greater than one $(Z > 1)$ at high temperature and high pressure. This is because
   (a) The constant a is negligible while b is not
   (b) The constant b is negligible while a is not
   (c) Both a and b negligible
   (d) Both a and b are no negligible

3. The value of Vander waal's constant 'a' for the gases O_2, N_2, NH_3 and CH_4 are 1.36, 1.39, 4.17 and 2.253 p atm, m^{-2}, respectively. The gas which can most easily be liquefied is
   (a) O_2
   (b) N_2
   (c) NH_3
   (d) CH_4

4. What is not true about the Vander waal constant 'b' among the statements given below?
   I. It is called excluded volume
   II. It is accounts for the Interparticle forces
   III. Its units are mol dm^{-3}
   IV. Its value depends on molecular size
   (a) I, II
   (b) II, IV
   (c) II, III
   (d) I, IV

5. Vander waal's constant for three different gases are given

Gas	a	b
X	3.0	0.0025
Y	10.0	0.030
Z	6.0	0.035

   Which is correct?
   (a) Maximum critical temperature – Y
   (b) Most ideal behaviour – X

(c) Maximum molecular volume – Z

(d) All are correct

6. Consider an ideal gas contained in a vessel. If the intermolecular interaction suddenly begins to act, which of the following will happen:

(a) The observed pressure decreases

(b) The observed pressure increases

(c) The observed pressure remains same

(d) None of these

7. A real gas obeying Vander Waals equation will resemble ideal gas, if the:

(a) Constants a & b are small

(b) A is large & b is small

(c) A is small & b is large

(d) Constant a & b are large

8. Calculate the compressibility factor for CO_2, if one mole of it occupies 0.4 litre at 300 K and 40 atm. Comment on the result:

(a) 0.40, CO_2 is more compressible than ideal gas

(b) 0.65, CO_2 is more compressible than ideal gas

(c) 0.55, CO_2 is more compressible than ideal gas

(d) 0.62, CO_2 is more compressible than ideal gas

9. Calculate the radius of He atoms if its vander Waal's constant 'b' is 24 $mlmol^{-1}$;

(a) 1.355 A°

(b) 1.314A°

(c) 1.255 A°

(d) 0.355 A°

10. The critical constant for water are 374°C, 218 atm and 0.0566 litre mol^{-1}. Calculate a & b.

(a) $A = 1.095$ $litre^2$ atm mol^{-1}, $b = 0.0185$ litre mol^{-1}

(b) $A = 1.92litre^2$ atm mol^{-2}, $b = 0.185$ litre mol^{-1}

(c) $A = 2.095$ $litre^2$ atm mol^{-2}, $b = 0.0189$ litre mol^{-1}

(d) $A = 2.95$ $litre^2$ atm mol^{-2}, $b = 0.1185$ litre mol^{-1}

11. The compressibility of a gas is less than unity at STP. Therefore:

(a) $V_m > 22.4$ L

(b) $V_m < 22.4$ L

(c) $V_m = 22.4$ L

(d) $V_m \geq 22.4$ L

12. If two moles of an ideal gas at 546 K occupies a volume of 44.8 litres, the pressure must be:

(a) 2 atm

(b) 3 atm

(c) 4 atm

(d) 1 atm

13. At ATP the order of root mean square velocity of molecules of H_2, O_2 and HBr is:

(a) $H_2 > N_2 > O_2 > HBr$

(b) $HBr > O_2 > N_2 > H_2$

(c) $HBr : H_2 > O_2 \ N_2$

(d) $N_2 > O_2 > H_2 > HBr$

14. Consider the following statements:

The coefficient B in the virile equation on state

$$PV_m = RT \left(1 + \frac{B}{V_m} + \frac{C}{V_m^2} + \cdots \ldots \ldots \ldots \ldots \right)$$

a. Is independent of temperature

b. Is equal to zero boyle temperature

c. Has the dimension of molar volume

Which of the above statements are correct.

(a) a and b

(b) a and c

(c) b and c

(d) a, b and c

15. consider the following statements: If the vander Waal's parameters of two gases given as

a (atm $lit^2 mol^{-2}$)   b (lit mol^{-1})

Gas X : 6. 5   0.056

Gas Y : 8.0   0.011

Then a :V_C (X) <V_C (Y)

B :p_C (X) <p_C (Y)

C :T_C (X) <T_C (Y)

Select correct alternate:

(a) a alone

(b) a and b

(c) a, b and c

(d) b and c

16. the temperature at which a real gas obeys the ideal gas laws over a wide range of pressure is:

(a) critical temperature

(b) Boyle temperature

(c) Boiling temperature

(d) Reduced temperature

MULTIPLE CORRECT ANSWER TYPE

17. Which of the following statement(s) is/are true?

(a) A real gas can be liquefied if its temperature is greater than its critical temperature.

(b) Kinetic energy of gaseous molecules is zero at 0° C.

(c) The term $V_m - b$ in vander waals equation represents the available volume where molecules of the gas can move.

(d) For a vander waals gas $V_c = 3b$, $p_c = a/27 b^2$, $T_c = 8a/27b$ R. numerically the compressibility factor of a vander waals gas at the critical points is Z = 0.375.

18. Among the four statements given below for real gases, which are incorrect:
    (a) The molecules causes attractive interactions.
    (b) They show deviation from ideal gas laws.
    (c) The molecules are almost volume less points.
    (d) The molecules have negligible mass.

19. When a gas is expanded at constant temperature:
    (a) The pressure decreases
    (b) The kinetic energy of the molecules remains the same
    (c) The kinetic energy of the molecules decreases
    (d) The number of molecules of the gas decreases

20. Which of the following are correct statements:
    (a) Vander waals constant 'a' is a measure of attractive force
    (b) Vander waals constant 'b' is also called co – volume or excluded volume
    (c) 'b' is expressed in L mol^{-1}
    (d) 'a' is expressed in atm L^{2}mol^{-2}

21. Three gases of densities A(0.82), B(0.25), C(0.51) are enclosed in a vessel of 4L capacity. Pick up the correct statement:
    (a) Gas A will tend to lie at the bottom
    (b) The number of atoms of various gases A, B, C are same
    (c) The gases will diffuse to form homogeneous mixture.
    (d) The average kinetic energy of each gas is same.

22. Which of the following statement(s) is true
    (a) A gas with a = 0 can be very easily liquefied.
    (b) Mean free path increases with the increase in temperature at constant pressure.
    (c) The behaviour of a real gas approach ideal gas at high temperature & low pressure.
    (d) Real gases deviate form ideal behaviour their molecules cause attractive interaction on one another.

EXERCISE – II (READY FOR CHALLENGES)

LEVEL-I

1. 1 litre CO and 1.75 litre CH_4 at the same temperature and pressure were mixed together. What is the relation between the masses of two gases in the mixture?

(a) $m_{CO} > m_{CH_4}$

(b) $m_{CH_4} = m_{CO}$

(c) $m_{CO} < m_{CH_4}$

(d) $m_{CO} = 2m_{CH_4}$

2. For a given mass of a gas, if pressure is reduced to half and temperature is doubled, then the volume 'V' will become

(a) 4V

(b) $2V^2$

(c) V/4

(d) 8V

3. 4 g of H_2 and 32 g of SO_2 are present in a gaseous mixture at N.T.P. The partial pressure of H_2 is

(a) equal to that of SO_2

(b) equal to that of SO_2

(c) three times that of SO_2

(d) four times that of SO_2

4. At what temperature will the total kinetic energy of 0.3 mole of He be the same as the total kinetic energy of 0.40 mole of Ar at 400 K?

(a) 400 K

(b) 373 K

(c) 533.33 K

(d) 300 K

5. The rms speed of hydrogen is $\sqrt{7}$ times the rms speed of nitrogen. If 'T' is the temperature of the gas

(a) $T(H_2) = T(N_2)$

(b) $T(H_2) > T(N_2)$

(c) $T(H_2) < T(N_2)$

(d) $T(H_2) = \sqrt{7}\ T(N_2)$

6. Which of the following gas has higher value of the vander waals constant 'b'?

(a) N_2 (b) O_2

(c) O_3 (d) F_2

7. A mixture of gases contains 55% nitrogen, 25% oxygen and 20% carbon dioxide by mole. The partial pressure of oxygen is 200 Torr. The partial pressure of carbon dioxide would be

(a) 760 Torr (b) 800 Torr

(c) 200 Torr (d) 160 Torr

8. A certain saturated hydrocarbon effuses 0.525 times as fast as methane under identical conditions. The molecular formula of the hydrocarbon (a compound made up of only carbon and hydrogen) is

(a) C_4H_8 (b) C_4H_{10}

(c) C_3H_6 (d) C_3H_8

9. If the rate of effusion of NH_3 is 3.32 times faster than that of an unknown gas when both gases are at same temperature and pressure, what is molecular weight of the unknown gas?

(a) 45.5 (b) 100

(c) 112   (d) 187.4

10. If for two gases of molecular weights are 'M_A' and 'M_B' at temperature 'T_A' and 'T_B' respectively. If $T_A M_B = T_B M_A$, then which property has the same magnitude for both the gases:
(a) Density
(b) Pressure
(c) KE per mol
(d) RMS speed

11. If pressure of a gas contained in a closed vessel is increased by 0.4% when heated by 1°C its initial temperature must be
(a) 250 K
(b) 250° C
(c) 2500 K
(d) 25° C

12. Consider the gaseous reaction, $N_2 + 3H_2 \longrightarrow 2NH_3$.
1 mol N_2 and 4 mole H_2 are taken in 15 L flask at 27°C. After the completion of the reaction, 5L of H_2O is added to the reaction vessel, pressure setup in the flask would be (assume conversion to be 100%)

(a) $\dfrac{3 \times 0.0821 \times 300}{15}$ atm
(b) $\dfrac{2 \times 0.0821 \times 300}{10}$ atm

(c) $\dfrac{1 \times 0.0821 \times 300}{15}$ atm
(d) $\dfrac{1 \times 0.0821 \times 300}{10}$ atm

13. If 'b' is the excluded volume then available volume for 'N' molecules in 'V' litre container is

(a) $(V - b)$
(b) $\left(V - \dfrac{N_o}{N} b \right)$

(c) $\left(V - \dfrac{N}{N_o} b \right)$
(d) none of these

(N_o = Avogadro's number)

14. 20 ml of O_2 contracts to 17 ml when subjected to silent electric discharge in an ozoniser. What further contraction would be observed if the partially ozonised oxygen is treated with oil of cinnamon (which absorbs ozone). All volumes are reported at the same temperature and pressure.
(a) 2 ml
(b) 8 ml
(c) 6 ml
(d) 4 ml

15. 0.5 mole of each of H_2, SO_2 and CH_4 are kept in a container. A hole was made in the container. After 3 hours, the order of partial pressures in the container will be
(a) $P_{SO_2} > P_{CH_4} > P_{H_2}$
(b) $P_{H_2} > P_{SO_2} > P_{CH_4}$
(c) $P_{CH_4} > P_{SO_2} > P_{H_2}$
(d) $P_{CH_4} > P_{H_2} > P_{SO_2}$

16. At what temperature would the volume of a given mass of a gas at constant pressure be twice its volume at 0°C?
(a) 546°C
(b) 100°C
(c) 273°C
(d) 373°C

17. At low pressure vander Waal's equation for 3 moles of a real gas will have its simplified form

(a) $\dfrac{PV}{RT + Pb} = 3$
(b) $\dfrac{PV}{RT - \dfrac{3a}{V}} = 3$

(c) $\dfrac{PV}{RT + 3Pb} = 1$
(d) $\dfrac{PV}{RT - \dfrac{a}{V}} = 3$

18. 10 g each of the following gases at 87°C and 755 mm Hg pressure are taken. Which of them will have the least volume
    (a) HF
    (b) HCl
    (c) HBr
    (d) HI

19. Under identical experimental condition which of following pair of gas will be most easy to separate by diffusion process?
    (a) $U^{235}F_6$ and $U^{238}F_6$
    (b) O_2 and N_2
    (c) H_2 and D_2
    (d) CO_2 and C_3H_8

20. NH_3 is liquefied more easily than N_2, hence
    (a) $a_{NH_3} > a_{N_2}$ and $b_{NH_3} > b_{N_2}$
    (b) $a_{NH_3} > a_{N_2}$ but $b_{NH_3} < b_{N_2}$
    (c) $a_{NH_3} < a_{N_2}$ but $b_{NH_3} > b_{N_2}$
    (d) None

21. An unknown gas effuses through a small hole one half as fast as methane CH_4, under the same conditions. What is the molar mass of the unknown gas?
    (a) 4 g/mol
    (b) 8 g/mol
    (c) 32 g/mol
    (d) 64 g/mol

22. If the pressure of a given mass of gas is reduced to half and temperature is doubled simultaneously, the volume will be
    (a) same as original volume
    (b) ¼th of original volume
    (c) twice of original volume
    (d) none of these

23. The temperature of an ideal gas is reduced from 927°C to 27°C. The r.m.s. velocity of the molecules becomes
    (a) double the initial value
    (b) half of the initial value
    (c) four times the initial value
    (d) ten times the initial value

24. A vessel containing 1.0 g of oxygen at a pressure of 10 atm and a temperature of 47°C. The pressure drops to 5/8th of its original value and temperature falls to 27°C due to leakage of the gas, then mass of oxygen leaked out will be
    (a) 0.22 g
    (b) 0.82 g
    (c) 0.432 g
    (d) 0.33 g

25. Which gas contains larger number of molecules?
    (a) 4 g H_2O
    (b) 2 g CH_4
    (c) 4 g PCl_5
    (d) 2 g PH_3

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LEVEL-II

1. The temperature of a given mass of a gas is increased from 19°C to 20°C at constant pressure. The volume V of the gas is increased
   (a) to V(20/19).
   (b) by 1/273.15 of its volume at 0°C.
   (c) by 1/273.15 of its volume at 0 K.
   (d) by a factor of 1/273.15 of its volume at 19°C.

2. Two balloons are filled with equal moles of hydrogen and helium. Which balloon will contract faster, if the same size holes are made in both of them?
   (a) Balloon filled with hydrogen gas.
   (b) Balloon filled with helium gas.
   (c) Both will contract at the same time
   (d) Hydrogen filled balloon will contract but helium filled balloon will not contract.

3. Oxygen and cyclopropane at partial pressure of 570 torr and 170 torr respectively are mixed in a gas cylinder. The ratio of the number of moles of cyclopropane to the number of moles of oxygen is
   (a) 0.23
   (b) 0.30
   (c) 0.39
   (d) 3.35

4. A bottle of dry NH_3 and another bottle of dry HCl at same temperature and pressure, connected through a long tube are opened simultaneously at both the ends. The white ring (NH_4Cl) first formed will be
   (a) at the center of the tube
   (b) near the HCl bottle
   (c) near the ammonia bottle(d) throughout the length of the tube

5. An open vessel containing air is heated from 300 K to 400 K. The fraction of air, which goes out with respect to originally present is
   (a) 3/4
   (b) 1/4
   (c) 2/3
   (d) 1/8

6. Which curve does not represent Boyle's law

   (a)

   (b)

   (c)

   (d)
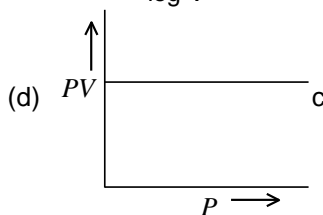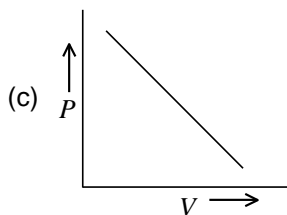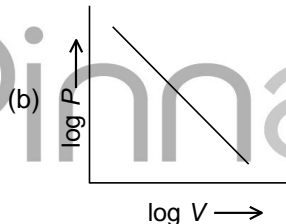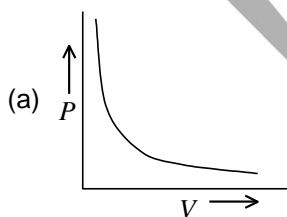
7. Under what conditions will a pure sample of an ideal gas not only exhibit a pressure of 1 atm but also a concentration of 1 mole litre^{-1} ($R = 0.082$ litre atm mol^{-1} deg^{-1})
(a) at STP
(b) when V = 22.4 litre
(c) when T = 12.18 K
(d) impossible under any condition

8. The temperature of an ideal gas is increased from 140 K to 560 K. If at 140 K the root mean square velocity of the gas molecules is u, at 560 K it becomes
(a) 5u
(b) 2u
(c) u/2
(d) u/4

9. 4.0 g of argon has pressure 'P' at temperature 'T' K in a vessel. On keeping the sample at 50° higher temperature, 0.8 g gas was given out to maintain the pressure 'P'. The original temperature was
(a) 73 K
(b) 100 K
(c) 200 K
(d) 510 K

10. The circulation of blood in human body supplies O_2 and releases CO_2. The concentration of O_2 and CO_2 is variable but on the average, 100 mL blood contains 0.02 g of O_2 and 0.08 g of CO_2. The volume of O_2 and CO_2 at 1 atm and at a body temperature of 37°C, assuming 10 litre blood in human body, would be
(a) 2 litre, 4 litre
(b) 1.5 litre, 4.5 litre
(c) 1.59 litre, 4.63 litre
(d) 3.82 litre, 4.63 litre

11. The pressure of the atmosphere 100 miles above the surface of earth is about 7.6×10^{-6} mm of Hg and its temperature is –23°C. How many molecules are there in 1 ml of a gas at this altitude?
(a) 2.93×10^{11}
(b) 7.58×10^{10}
(c) 0.05×10^{11}
(d) 2.07×10^{10}

12. By what ratio will the average velocity of the molecules in a gas change when the temperature is raised from 50°C to 373°C?
(a) $\dfrac{1.21}{1}$
(b) $\dfrac{1.46}{1}$
(c) $\dfrac{1.414}{1}$
(d) $\dfrac{4}{1}$

13. The composition of the equilibrium mixture $Cl_2 \rightleftharpoons 2Cl$, attained at 1200°C, is determined by measuring the rate of effusion through a narrow aperture. At 1.80 mm of Hg pressure, the mixture effuses 1.16 times as fast as krypton (atomic mass = 84) under the same conditions, what will be the fraction of chlorine molecules dissociated into atoms.
(a) 1.37%
(b) 13.7%
(c) 26%
(d) 26.4%

14. The density of phosphorus vapour at 310°C and 775 torr is 2.64 g/*l*. What is the molecular formula of phosphorus?
(a) P
(b) P_2
(c) P_4
(d) P_8

15. Dalton's law of partial pressure is not applicable to, (at normal conditions)
(a) He and O_2 mixture
(b) H_2 and Cl_2 mixture
(c) H_2 and He mixture
(d) H_2 and CO_2 mixture

16. A gas cylinder containing cooking gas can withstand a pressure of 14.9 atm. The pressure gauge of cylinder indicates 12 atm at 27°C. Due to sudden fire in building the temperature starts rising. The temperature above which the cylinder explodes is
(a) 42.5°C
(b) 67.8°C
(c) 99.5°C
(d) 25.7°C

17. A cylinder with a movable piston is filled at 25°C with a gas that occupies a volume of 30.5 cm^3. If the maximum capacity of the cylinder is 45.8 cm^3, what is the highest temperature to which the cylinder can be heated at constant pressure without having the piston come out?
(a) 50°C
(b) 147.5°C
(c) 174.5°C
(d) 120°C

18. A gaseous hydrocarbon required two and half times of its volume of O_2 for complete combustion and produced double its volume of CO_2. The molecular formula of the gas is
(a) CH_4
(b) C_2H_6
(c) C_2H_2
(d) C_2H_4

19. 1 L of N_2 and $\dfrac{7}{8}$ L of O_2 at the same temperature and pressure were mixed together. What is the relationship between masses of the two gases in the mixture?
(a) $Mass_{N_2} = 3\ Mass_{O_2}$
(b) $Mass_{N_2} = 8\ Mass_{O_2}$
(c) $Mass_{N_2} = Mass_{O_2}$
(d) $Mass_{N_2} = 16\ Mass_{O_2}$

20. At constant pressure what would be the percentage decrease in the density of an ideal gas for a 10% increase in the temperature.
(a) 10%
(b) 9.1%
(c) 11%
(d) 12.09%

ONE OR MORE THAN ONE CHOICE CORRECT

1. Point A in the given curve shifts to higher value of velocity if
(a) T is increased.
(b) P is decreased at constant pressure.
(c) V is decreased at constant pressure.
(d) molecular weight M is decreased.

2. Which of the following processes would lead to an increase in the average speed of the molecules of an ideal gas system?
(a) Decreasing the temperature of the system.
(b) Compressing the gas with a piston adiabatically.
(c) Expanding the gas into a vacuum.
(d) Heating the system keeping V and P constant.
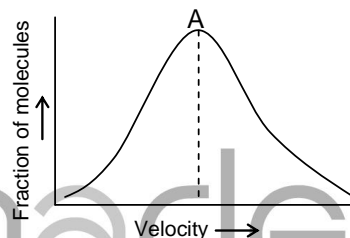
3. According to the kinetic theory of gases
   (a) pressure of a gas is due to collisions of molecules with each other.
   (b) kinetic energy is proportional to square root of the temperature.
   (c) pressure of a gas is due to collisions of molecules against the sides of the container.
   (d) there is no force of attraction between gas molecules.

4. For two gases, A and B with molecular weights M_A and M_B, it is observed that at a certain temperature T, the mean velocity of A is equal to the V_{rms} of B. Thus the mean velocity of A can be made equal to the mean velocity of B, if
   (a) Temperature of A is raised to T' while B is maintained at T.
   (b) Temperature of A is lowered to T_2 while B is at T.
   (c) Both A and B are raised to a higher temperature.
   (d) Heat energy is supplied to B.

5. Which of the following statements is true?
   (a) the ratio of the mean speed to the rms speed is independent of the temperature.
   (b) the square of the mean speed of the molecules of a gas is equal to the square of rms speed at a certain temperature for the same gas.
   (c) mean kinetic energy of the gas molecules at any given temperature is independent of the mean speed.
   (d) the difference between rms speed and mean speed at any temperature for different gases diminishes as larger and yet larger molar masses are considered.

6. If for two gases of molecular weights M_A and M_B at temperature T_A and T_B, it is observed that $T_A M_B = T_B M_A$, then which property has the same magnitude for both the gases.
   (a) PV if mass of gases taken are same   (b) Pressure
   (c) KE per mol   (d) V_{rms}

7. Molecular attraction and size of the molecules in a gas are not negligible at
   (a) Critical point   (b) High pressure.
   (c) High temperature and low pressure   (d) low temperature and high pressure

8. If 10 g of a gas at atmospheric pressure is cooled from 273°C to 0°C, keeping the volume constant, its pressure would become
   (a) $\dfrac{1}{273}$ atm   (b) 2 atm   (c) $\dfrac{1}{2}$ atm   (d) 5.06×10^4 N/m^2

9. Select correct statements :
   (a) Vapour may be condensed to liquid by the application of pressure.
   (b) To liquefy a gas one must lower the temperature below T_c and apply pressure.
   (c) At T_c there is no distinction between liquid and vapour state.
   (d) At T_c, density of liquid is very high as compared to its gaseous state.

10. Which of the following statement is/are correct?
    (a) All real gases are less compressible than ideal gas at high pressure.
    (b) Hydrogen and helium are more compressible than ideal gas for all values of pressure.
    (c) Except H_2 and He, the compressibility factor $Z = \left(\dfrac{PV}{nRT}\right) < 1$ for all gases at low pressure.
    (d) The compressibility factor of real gases is independent of temperature.

MATCH THE FOLLOWING

Note: Each statement in column I has one or more than one match in column II.

1.

Column I	Column II
I. Critical temperature	**(A)** Gas cannot be liquefied above this temperature.
II. Boyle's temperature	**(B)** Deviate from ideal gas equation.
III. Compressibility factor (Z) < 1	**(C)** Gas follows the ideal gas equation.
IV. High temperature and low pressure	**(D)** Assumption of no intermolecular force of attraction is valid.
	(E) $V_{real} < V_{ideal}$

REASONING TYPE

Directions: Read the following questions and choose

    (A) **If both the statements are true and statement-2** is the correct explanation of **statement-1**.

    (B) **If both the statements are true but statement-2** is not the correct explanation of **statement-1**.

    (C) **If statement-1** is True and **statement-2** is False.

    (D) **If statement-1** is False **and statement-2** is True.

1. **Statement-1:** All molecules of an ideal gas move with the same speed.

    Statement-2: There is no attraction between the molecules in an ideal gas.

    (a) (A)   (b) (B)   (c) (C)   (d) (D)

2. **Statement-1:** In van der Waals equation

$$\left(P + \frac{a}{V^2} \right)(V - b) = RT$$

    pressure correction, $\left(\dfrac{a}{V^2} \right)$, is due to force of attraction between molecules.

    Statement-2: Volume of gas molecules cannot be neglected due to force of attraction.

    (a) (A)   (b) (B)   (c) (C)   (d) (D)

3. **Statement-1:** Under identical conditions a lighter gas diffuses more rapidly than a heavier gas.

    Statement-2: Under identical conditions, the rate of diffusion of gases is inversely proportional to the square root of their density.

    (a) (A)   (b) (B)   (c) (C)   (d) (D)

4. **Statement-1:** A gas can be liquefied at any temperature below its critical temperature.

    Statement-2: Liquification of a gas takes place when the average kinetic energy of the molecules is low.

(a) (A)　　　　　　　(b) (B)　　　　　　　(c) (C)　　　　　　　(d) (D)

5.　**Statement-1:** At absolute zero temperature, pressure, kinetic energy and heat content of gas is reduced to zero.

　Statement-2: At absolute zero temperature velocity reduces to zero.

(a) (A)　　　　　　　(b) (B)　　　　　　　(c) (C)　　　　　　　(d) (D)

LINKED COMPREHENSION TYPE

　　　The figure given below shows three glass chambers that are connected by valves of negligible volume. At the outset of an experiment, the valves are closed and the chambers contain the gases as detailed in the diagram. All the chambers are at the temperature of 300K and external pressure of 1.0 atm.

P_{ext} = 1.0 atm　　　　　　　Throughout T = 300K

Valve-1　　　　Valve-2

He
4.1 atm

N_2
0.82 atm

Vacuum

6.0 L

10.0 L

4.0 L

A　　　　　　B　　　　　　C
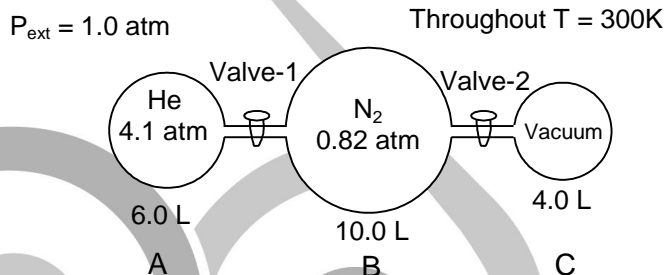
1.　Which of the following represents the total kinetic energy of all the gas molecules after both valves are opened? ($R = 0.082$ atm L $K^{-1}mol^{-1}$ = 8.314 L $K^{-1}mol^{-1}$)
(a) 2836.2 J
(b) 3280.0 J
(c) 4520.6 J
(d) 4982.4 J

2.　Suppose that after both valves are opened, the entire apparatus is cooled to lower the final internal pressure to 1.0 atm. What is the contribution of N_2 gas to this final pressure?
(a) 0.40 atm
(b) 0.35 atm
(c) 0.30 atm
(d) 0.25 atm

3.　What is the total pressure in chamber B if only valve–1 is opened?
(a) 0.31 atm
(b) 2.05 atm
(c) 2.46 atm
(d) 3.10 atm

EXERCISE – III (CROSSING THE HURDLES)

SUBJECTIVE PROBLEMS

1. 4:1 molar mixture of He and CH_4 is contained in a vessel at 20 bar pressure. Due to a hole in the vessel the gas mixture leaks out. What is the composition of the mixture effusing out initially?

2. A sample of oxygen is collected by displacing water from an inverted tube. The temperature is 25°C, the pressure is 750 mm and the volume occupied is 280 ml. What is the true volume of O_2 at STP? (Aqueous tension at 25°C = 23.8 mm)

3. At room temperature, NH_3 gas at 1 atm and HCl gas at P atm are allowed to effuse through identical pinholes from opposite ends of a glass tube of 1 metre length and of uniform cross section. NH_4Cl is first formed at a distance of 60 cm from the end through which HCl gas is sent in. What is the value of P?

4. 40 ml of a mixture of H_2 & O_2 was placed in a gas burette at 18°C and 1 atm. A spark was produced so that the formation of water was complete. The remaining pure gas had a volume of 10 ml at 18°C & 1 atm. If the remaining gas was H_2, what was the initial mole % of H_2 in mixture?

5. When 2 g of a gas 'A' is introduced into an evacuated flask kept at 25°C, the pressure is found to be 1 atm. If 3 g of another gas 'B' is then added to the same flask, the total pressure becomes 1.5 atm. Assuming ideal gas behaviour, calculate the ratio of molar masses $M_A : M_B$.

6. A mixture of $NH_3(g)$ and $N_2H_4(g)$ is placed in a sealed container at 300 K. The total pressure is 0.5 atm. The container is heated to 1200 K, when both substances decompose completely according to the equations,

    $2NH_3(g) \longrightarrow N_2(g) + 3H_2(g)$
    $N_2H_4(g) \longrightarrow N_2(g) + 2H_2(g)$.

    After decomposition is complete, the total pressure at 1200 K is found to be 4.5 atm. Find the mole per cent of $N_2H_4(g)$ in the original mixture.

7. A mixture of 0.5 mole of CO & 0.5 mole of CO_2 is taken in a vessel and allowed to effuse out through a pin hole into another vessel which has vacuum. If a total of 'A' mole has effused out in time 't', show that $M_1A + M_2(1-A) = 36$, where M_1 and M_2 are the mean molar masses of the mixture that has effused out & the mixture still remaining in the vessel, respectively.

8. A flask of capacity one litre contain NH_3 at 1 atm & 25°C. A spark is passed through until all the NH_3 is decomposed into N_2 & H_2. Calculate (a) the pressure of gases left at 25°C. (b) the moles of N_2 & H_2 formed.

9. 120 mL of NH_3 at 25°C and 750 Torr was mixed with 165 mL of O_2 at 50°C and 635 Torr and transferred to a 300 mL reaction vessel where they were allowed to react according to the equation,

    $4NH_3(g) + 5O_2(g) \longrightarrow 4NO(g) + 6H_2O(g)$

    What was the total pressure (in Torr) in the reaction vessel at 150°C after the reaction is over? Assume that the reaction goes to completion.

10. The radius of a Xe atom is 1.3×10^{-8} cm. A 100 cm^3 container is filled with Xe at a pressure of 1.0 atm and a temperature of 273 K. Calculate the fraction of the volume of container occupied by Xe atoms.

11. A cylinder contains 100 g of an ideal gas (molecular weight 40 g mol^{-1}) at 27°C and 2 atm pressure. In transportation, the cylinder fell and a dent was created but the valve attached to cylinder cannot keep the pressure greater than 2 atm, so 10 g of the gas leaked out. Calculate

    (a) Volume of the cylinder before and after dent.

    (b) What would have been the pressure after dent assuming temperature remained constant during this

process assuming that the gas did not leak out?

12. A gaseous compound X contained 44.4% C, 51.9% N and 3.7% H. Under like conditions 30 cm^3 of X diffused through a pinhole in 25 sec and the same volume of H_2 diffused in 4.81 sec. Deduce molecular formula of X.

13. 5 ml of a gaseous hydrocarbon was exposed to 30 ml of O_2. The resultant gas, on cooling is found to measure 25 ml, of which 10 ml was absorbed by NaOH and the remainder by pyrogallol. Determine molecular formula of the hydrocarbon. All measurements are made at constant pressure and temperature.

14. A 0.750 g sample of solid benzoic acid, $C_7H_6O_2$, was placed in a 0.500 L pressurized reaction vessel filled with O_2 at 10.0 atm pressure and 25°C. To the extent of the availability of oxygen, the benzoic acid was burned completely to water and CO_2. What was the final mole fraction of CO_2 and H_2O vapour in the resulting gas mixture brought to the initial temperature? The vapour pressure of water at 25°C is 23.8 torr. Neglect both the volume occupied by nongaseous substances and the solubility of CO_2 in H_2O. (The water pressure in the gas phase cannot exceed the vapor pressure of water, so most of the water is condensed to the liquid.)

15. A 50 mL sample of a hydrogen–oxygen mixture was placed in a gas burette at 18°C and confined at barometric pressure. A spark was passed through the sample so that the formation of water could go to completion. The resulting pure gas has a volume of 10 mL at barometric pressure. What was the initial mole fraction of hydrogen in the mixture (a) if the residual gas after sparking was hydrogen (b) if the residual gas was oxygen?

ANSWERS

EXERCISE – I

PRESSURE CALCULATION, BAROMETER & MANOMETER

Ques.	1.	2.	3.	4.	5.
Ans.	(i) b, (ii) d	a	(i) c, (ii) a	b	a

GAS LAW

Ques.	1.	2.	3.	4.	5.	6.	7.	8.	9.	10.
Ans.	a	c	a	b	a	b	c	b	b	d

Ques.	11.
Ans.	(i) – A, (ii) – B, (iii) – B

IDEAL GAS EQUATION

Ques.	1.	2.	3.	4.	5.	6.	7.	8.	9.
Ans.	d	c	a	d	a	a	(i)– d, (ii) – a	d	(i)– b, (ii) – c

Ques.	10.	11.	12.
Ans.	d	7 atm	Sample (A) n = 3 mol, Sample (B) n = 1 mol, Sample (C) n = $\frac{1}{2}$ mol]

DALTONS LAW

Ques.	1.	2.	3.	4.	5.	6.	7.	8.	9.
Ans.	a	c	c	a	c	b	b	a	b

Ques.	10.
Ans.	P_{O_2} P_{H_2O} (i) 720 mm 20 mm (ii) 1440 mm 20 mm (iii) 360 mm 20 mm

DIFFUSION AND EFFUSION

Ques.	1.	2.	3.	4.	5.	6.	7.	8.
Ans.	b	a	a	b	d	a	a	a

CONTAINER CAPACITY, CONNECTED CONTAINER GAS PROBLEM AND PAYLOAD

Ques.	1.	2.	3.	4.	5.
Ans.	d	c	(i) – c, (ii) – a	(i) – d, (ii) – a,	d
Ques.	6.		7.	8.	9.	10.
Ans.	(i) – a, (ii) –d, (iii) c		a	a	a	d

KTG

Ques.	1.	2.	3.	4.	5.	6.
Ans.	b	b	b	b	a	b
Ques.	7.		8.	9.	10.	11.
Ans.	(i) –a, (ii) –b, (iii) – d		b	d	a, c, d	a, b, c

MAXWELL'S DISTRIBUTION CURVE & MEAN FREE PATH AND FREQUENCY PARAMETER

Ques.	1.	2.	3.	4.	5.	6.	7.	8.	9.
Ans.	a	c	b	b	a, b, c, d	a, b, d	c	c	a

EUDIOMETRY

Ques.	1.	2.	3.	4.	5.	6.	7.	8.	9.	10.
Ans.	b	a	b	c	b	a	a	d	b	c
Ques.	11.									
Ans.	a									

REAL GAS

Ques.	1.	2.	3.	4.	5.	6.	7.	8.	9.	10.
Ans.	a	a	c	c	d	a	a	b	a	c
Ques.	11.	12.	13.	14.	15.	16.	17.	18.	19.	20.
Ans.	b	a	a	c	d	b	c, d	c, d	a, b	a, b, c, d
Ques.	21.	22.								
Ans.	c, d	b, c, d								

EXERCISE – II

LEVEL-I

Ques.	1.	2.	3.	4.	5.	6.	7.	8.	9.	10.
Ans.	b	a	d	c	c	c	d	b	d	d
Ques.	11.	12.	13.	14.	15.	16.	17.	18.	19.	20.
Ans.	a	d	c	c	a	c	b	d	c	b
Ques.	21.	22.	23.	24.	25.					
Ans.	d	d	b	d	a					

LEVEL-II

Ques.	1.	2.	3.	4.	5.	6.	7.	8.	9.	10.
Ans.	b	a	b	b	b	c	c	b	c	c
Ques.	11.	12.	13.	14.	15.	16.	17.	18.	19.	20.
Ans.	a	c	b	c	b	c	c	c	c	b

ONE OR MORE THAN ONE CHOICE CORRECT

Ques.	23.	24.	25.	26.	27.
Ans.	a, d	b, d	c, d	b, d	a, c, d
Ques.	28.	29.	30.	31.	32.
Ans.	a, d	a, b, d	c, d	a, b, c	a, c

MATCH THE FOLLOWING

1.
I – (A), (B) ; II – (C), (D) ; III – (A), (B), (E) ; IV – (C), (D)

REASONING TYPE

Ques.	1.	2.	3.	4.	5.
Ans.	d	c	a	a	a

LINKED COMPREHENSION TYPE

Ques.	1.	2.	3.
Ans.	d	d	b

EXERCISE – III

SUBJECTIVE PROBLEMS

1.   He = 88.88%, CH_4 = 11.12%

2.   245.1 ml

3.   2.2 atm

4.   75%

5.   1 : 3

6.   25%

8.   (a) P_{Total} = 2 atm (b) n_{N_2} = 2.044×10^{-2}, n_{H_2} = 6.13×10^{-2}

9. P_{Total} = 981.36 Torr

10. 9.88×10^{-4}

11.   (a) 30.78 dm^3, 27.71 dm^3 (b) 2.22 atm.

12. $C_2H_2N_2$

13. C_2H_4

14.   0.214, 0.0032

15.   (a) 0.733 (b) 0.533

PROFICIENCY TEST– I

The following 10 questions deal with the basic concepts of this section. Answer the following briefly. Go to the next section only if your score is greater than or equal to 8. Do not consult the study material while attempting the questions.

1. According to Charles' law, the increase in volume for each degree rise in temperature is_____ time of its original volume at 0°C.

2. True/False: The dimensions of gas constant R is energy per mole.

3. Real gases behave ideally when pressure is_____.

4. True/False: Partial pressure $P_i = X_i P_T$ where X_i is mole fraction of the gas and P_T is the total pressure.

5. True/False: Volume fraction = $\dfrac{1}{\text{mole fraction}}$.

6. True/False: If temperature is increased, the rate of gas coming out of a container through a small orifice increases.

7. The value of PV when P → 0 for 1 mole a gas at 273.15 K is _____.

8. R = _____ J/mol. K

9. For two gases $\dfrac{r_1}{r_2} = \sqrt{\dfrac{M_2}{M_1}}$ is true when the temperature, pressure difference and _____ are same for both the gases.

10. True/False: According to Gay–Lusaac law, $V \propto T$ at constant P and n.

ANSWERS TO PROFICIENCY TEST– I

1. $\dfrac{1}{273.15}$

2. False, it is energy per mole per Kelvin.

3. low

4. True

5. False, volume fraction = mole fraction

6. False.

7. $22.71 \ dm^3$ bar

8. 8.314

9. Area of orifice

10. False, it is $P \propto T$ when V and n are constants.

PROFICIENCY TEST– **II**

The following 10 questions deal with the basic concepts of this section. Answer the following briefly. Go to the next section only if your score is greater than or equal to 8. Do not consult the study material while attempting the questions.

1. True/False One of the assumptions of Kinetic theory of gas is that the molecular size is comparable with the volume of the gas.

2. According to kinetic gas equation PV = _____

3. U_{av} = _____

4. U_{rms} = _____

5. U_{mp} = _____

6. Average translational kinetic energy per mole of gas = _____

7. Boltzmann constant = _____ J K^{-1}.

8. True/False: The average translational kinetic energy of the gases is directly proportional to mass of gas.

9. True/False: The pressure exerted by the gas is due to collisions of the gas molecules on the walls of the container.

10. True/False: u_{av} of gas molecule in sample is more than u_{mp} but less than u_{rms}.

ANSWERS TO PROFICIENCY TEST– **II**

1. False

2. $PV = \dfrac{1}{3}mN\overline{u^2}$

3. $\sqrt{\dfrac{8RT}{\pi M}}$

4. $\sqrt{\dfrac{3RT}{M}}$

5. $\sqrt{\dfrac{2RT}{M}}$

6. $\dfrac{3}{2}RT$

7. $\dfrac{R}{N_A} = 1.38 \times 10^{-23} \text{ J K}^{-1}$

8. False

9. True

10. True

PROFICIENCY TEST– III

The following 10 questions deal with the basic concepts of this section. Answer the following briefly. Go to the next section only if your score is greater than or equal to 8. Do not consult the study material while attempting the questions.

1. The gas molecule can be liquefied and solidified due to presence of _____ forces of attraction.

2. The numerical value of 'b' is _____ times the actual volume occupied by one mole of gas molecule.

3. The ratio of molar volume to ideal molar volume is called _____

4. For hydrogen gas Z is _____ unity at all pressure.

5. True/False: For real gases, at high temperature $Z \to 0$.

6. Unit of 'a' would be _____

7. True/False: Small value of 'a' means, gas can be easily liquified.

8. True/False: Oxygen can be absorbed by turpentine oil.

9. True/False: In eudiometry, the contraction in volume is due to condensation of water vapour and change in number of gas moles during the reaction.

10. x ml of C_2H_2 is completely burnt in presence of 2.5 ml of O_2. Due to the condensation of water, contraction in volume will be _____ .

ANSWERS TO PROFICIENCY TEST– III

1. Vander Waal's (weak)

2. Four

3. Compressibility factor (Z)

4. Greater than

5. False

6. atm lit^2 mol^{-2}

7. False

8. False

9. True

10. x