

GASEOUS STATE

1. 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 his law "At constant temperature, the volume of a definite mass of a gas is inversely proportional to its pressure, that is,

$$V \propto \frac{1}{P} \quad \dots\dots\dots(2.1a)$$

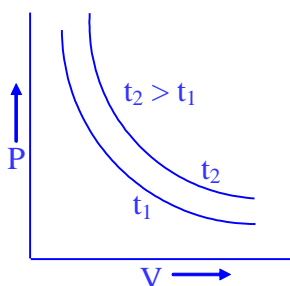
$$V = \frac{K}{P} \quad \text{or} \quad PV = K$$

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

$$P_1 V_1 = P_2 V_2$$

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

Equation (2.1a) can be represented graphically by plotting pressure vs volume



The nature of curve is a rectangular hyperbola. The general term isotherm (meaning at constant temperature) is used to describe these plots.

GASEOUS STATE

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 $V_t = a + bt$ (2.2b) where t is temperature and a and b are constants.

Equation (2.2b) has been plotted in Figure given ahead. 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 $\frac{1}{273.15}$ of its volume at 0°C . If V_0 is the volume of a gas at 0°C , then b is given by

$$b = \frac{V_0 / 273.15}{1^\circ\text{C}}$$

With this, equation (2.2b) becomes

$$\begin{aligned} V_t &= V_0 + \left(\frac{V_0 / 273.15}{1^\circ\text{C}}\right) t = V_0 \left(1 + \frac{t/1^\circ\text{C}}{273.15}\right) \\ &= V_0 \left(\frac{273.15 + t/1^\circ\text{C}}{273.15}\right) \quad \text{.....(2.2c)} \end{aligned}$$

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,

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

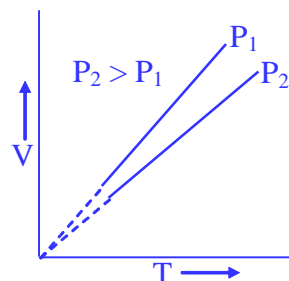
$$V_T = V_0 \frac{T/\text{K}}{273.15} = \left(\frac{V_0}{273.15 \text{ K}}\right) T$$

GASEOUS STATE

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 $V_t = K_2 T$ (2.2d) where K_2 is a constant whose value depends upon the nature, mass and pressure of the gas.

Equation (2.2d) is 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 as



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 zero Kelvin, though the straight line plots can be extrapolated to zero volume. Temperature that corresponds to zero volume is -273.15°C .

2.3 Gay – Lussac’s Law

According to Gay-Lussac’s law, pressure of a given mass of a gas at constant volume varies linearly with temperature.

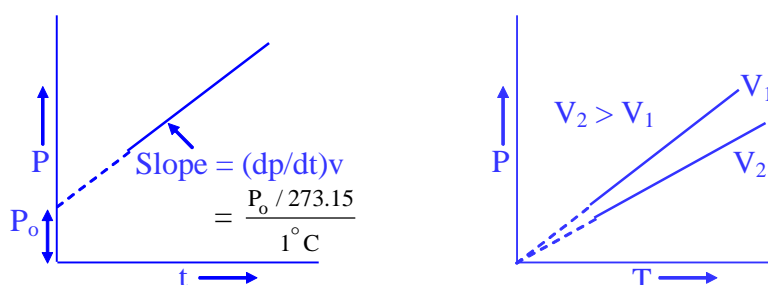
$$P_t = a + bt \quad \text{.....(2.2e)}$$

where $a = P_0$ and $b = \left(\frac{dP}{dt}\right)_v$. The value of the latter can be determined experimentally and is found to

be $(P_0 / 273.15^\circ\text{C})$. Thus equation (2.2e) modifies to $P_t = P_0 + \left(\frac{P_0}{273.15}\right) \frac{t}{1^\circ\text{C}}$

$$\text{Therefore } P_t = P_0 \left(\frac{273.15 + t / 1^\circ\text{C}}{273.15} \right) = \frac{P_0}{273.15 \text{ K}} T \quad \text{or } P \propto T \quad \text{.....(2.2f)}$$

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 as



GASEOUS STATE

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.

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

2.5 EQUATION OF STATE

The results of all those 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

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

$$\text{or } \frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2} \quad \dots\dots\dots(2.2g)$$

GASEOUS STATE

It also follows that no matter how we change the state of the given amount of a gas, the ratio $\frac{PV}{T}$ 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 amount selected from total amount).

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

$$PV = nRT \quad \dots\dots\dots(2.2h)$$

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

$$\text{Pressure} = (\text{force/area}) = \text{force}/(\text{length})^2 = \text{force} \times \text{length}^{-2}$$

$$\text{volume} = \text{length}^3$$

$$\begin{aligned} \text{Thus } R &= \frac{(\text{force} \times \text{length}^{-2}) (\text{length}^3)}{(\text{amount of gas}) (\text{Kelvin})} = \frac{(\text{force} \times \text{length})}{(\text{amount of gas}) (\text{Kelvin})} \\ &= \frac{\text{work (or energy)}}{(\text{amount of gas}) (\text{Kelvin})} \end{aligned}$$

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.

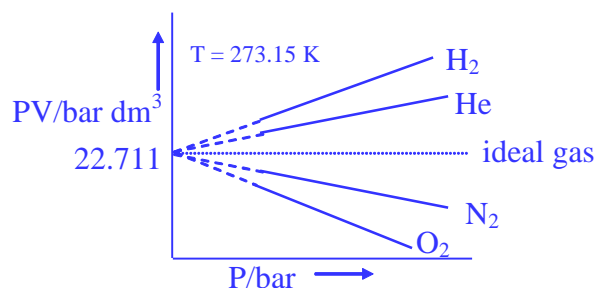
GASEOUS STATE

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, Charles'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 ($P \rightarrow 0$) 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. The graphs of PV vs P of different gases must yield the same value of $(PV)_{P \rightarrow 0}$. In fact, it is found to be so, as is evident from given figure.



GASEOUS STATE

The value of $(PV)_{P \rightarrow 0}$ at 273.15 K is found to be 22.711 dm³ bar. Thus if $P = 1$ bar, then $V = 22.711$ dm³, that is, the volume occupied by one mole of an ideal gas at standard temperature (273.15K) and 1 bar pressure is 22.711 dm³.

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

$$R = \frac{PV}{nT} = \frac{(1 \text{ bar})(22.711 \text{ dm}^3)}{(1 \text{ mol})(273.15 \text{ K})} = 0.08314 \text{ bar dm}^3 \text{ K}^{-1} \text{ mol}^{-1}$$

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

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

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

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

GASEOUS STATE

Illustration 1

Estimate the number of gaseous molecules left in a volume of 1mm³ if it is pumped out to give a vacuum of 10⁻⁶ mmHg at 298K.

Solution:

$$\begin{aligned}P &= 10^{-6} \text{ mm of Hg} \\&= \frac{10^{-6} \text{ of Hg}}{760 \text{ mm of Hg}} = 1.315 \times 10^{-9} \text{ atm.} \\V &= 1\text{mm}^3 = 1 \times (10^{-3}\text{m})^3 \\&= 10^{-9}\text{m}^3 = 10^{-9} \times (10 \text{ dm})^3 = 10^{-6} \text{ dm}^3 = 10^{-6} \text{ L} \\n &= \frac{PV}{RT} = \frac{(1.315 \times 10^{-9} \text{ atm})(10^{-6} \text{ L})}{(0.0821 \text{ atm L mol}^{-1} \text{ K}^{-1})(298\text{K})} \\&= 5.38 \times 10^{-17} \text{ moles} \\ \text{Number of molecules} &= 5.38 \times 10^{-17} \times 6.023 \times 10^{23} \\&= \mathbf{3.24 \times 10^7 \text{ molecules}}\end{aligned}$$

Illustration 2

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:

$$\begin{aligned}\frac{P_A V_A}{P_B V_B} &= \frac{W_A RT_A}{M_A} \times \frac{M_B}{W_B RT_B} \quad (T_A = T_B \text{ and } V_A = V_B) \\ \Rightarrow \frac{P_A}{P_B} &= \frac{W_A M_B}{W_B M_A} \\ \Rightarrow \frac{101.325 \text{ kPa}}{50.602 \text{ kPa}} &= \frac{(2\text{g}) (M_B)}{(3\text{g}) (M_A)} \\ \Rightarrow \frac{M_A}{M_B} &= \frac{1}{3}.\end{aligned}$$

GASEOUS STATE

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, \dots . The total pressure is given by

$$P_{\text{total}} = P_1 + P_2 + \dots$$

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

$$P_1 V = n_1 RT \quad \dots\dots(4.1a)$$

$$P_2 V = n_2 RT \quad \dots\dots(4.1b)$$

$$\text{Hence } (P_1 + P_2 + \dots) V = (n_1 + n_2 + \dots) RT$$

$$\text{i.e., } P_{\text{total}} V = n_{\text{total}} RT \quad \dots\dots(4.1c)$$

(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

$$P_1 = \frac{n_1}{n_{\text{total}}} P_{\text{total}} = X_1 P_{\text{total}} \quad \dots\dots(4.1d)$$

$$P_2 = \frac{n_2}{n_{\text{Total}}} P_{\text{Total}} = X_2 P_{\text{total}} \quad \dots\dots(4.1e)$$

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

$$V_1 = n_1 \left(\frac{RT}{P} \right) \quad \dots\dots(4.1 f)$$

$$V_2 = n_2 \left(\frac{RT}{P} \right) \quad \dots\dots(4.1 g)$$

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

$$V_1 + V_2 + \dots = (n_1 + n_2 + \dots) \left(\frac{RT}{P} \right) = n_{\text{total}} \frac{RT}{P} = V_{\text{total}} \quad \dots\dots (4.1 h)$$

GASEOUS STATE

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

$$V_1 = X_1 V_{\text{total}}$$

$$V_2 = X_2 V_{\text{total}}$$

Illustration 3

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 flask at same temperature. Calculate 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,

$$\therefore P_1 V_1 = P_2 V_2$$

The new pressure of N_2 would be

$$\begin{aligned} P_2 &= \frac{P_1 V_1}{V_2} = \frac{700 \times 500}{2000} \\ &= 175 \text{ mm of Hg.} \end{aligned}$$

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

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

$$= 175 + 240 = \mathbf{415 \text{ mm of Hg}}$$

Alternatively:

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

$$P_T = \frac{500 \times 700 + 600 \times 800}{2000} = \mathbf{415 \text{ mm Hg.}}$$

GASEOUS STATE

Illustration 4

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:

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

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

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

$$P_i = X_i P_{\text{total}}$$

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

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

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

Illustration 5

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:

$$P_{\text{total}} = 2 \text{ atm}$$

$$P_{CO_2} = 0.4 \text{ atm}$$

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

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

$$\text{Mole \% of } CO_2 = 0.2 \times 100 = 20\%$$

$$\text{Mole \% of } H_2 = 0.8 \times 100 = 80\%$$

Mole % is same as volume %

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

GASEOUS STATE

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,

$$\text{rate of diffusion or effusion, } r \propto \frac{1}{\sqrt{M}} \quad (\text{where } M \text{ is the molecular weight of the gas})$$

Later it was shown that

$$r = \frac{KP}{\sqrt{M}} \quad \text{where } K \text{ is a constant and } P \text{ is the pressure of the gas.}$$

Now it is believed that,

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

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 ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$)

T = Temperature of the gas (measured in K)

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

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. **It must be noted that flow of each gas is independent of presence of other gases. Net flow of each gas occurs from its higher pressure to lower 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.

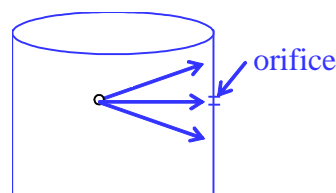
Molecular weight:

Heavier the gas, slower should be its movement.

GASEOUS STATE

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 increase the velocity,



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.

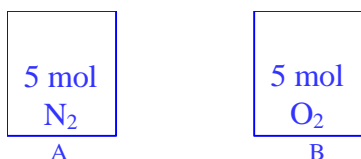
If P , A and T for two gases is same, then

$$r_1 = \frac{1}{\sqrt{M_1}} \quad r_2 = \frac{1}{\sqrt{M_2}}$$
$$\frac{r_1}{r_2} = \sqrt{\frac{M_2}{M_1}}$$

Illustration 6

Two containers A and B of equal volume at same temperature hold 5 mol N_2 and 5 mol O_2 , respectively. 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,

$$P \propto n \quad \frac{P_{N_2}}{P_{O_2}} = 1$$

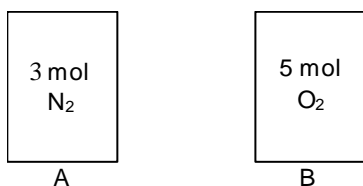
$$\frac{r_{N_2}}{r_{O_2}} = \sqrt{\frac{M_{O_2}}{M_{N_2}}} = \sqrt{\frac{32}{28}} = \sqrt{\frac{8}{7}} = 1.069$$

GASEOUS STATE

Illustration 7

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, $p \propto n$

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

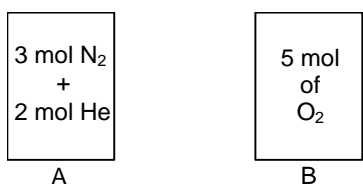
$$\frac{r_{N_2}}{r_{O_2}} = \frac{P_{N_2}}{P_{O_2}} \sqrt{\frac{M_{O_2}}{M_{N_2}}} = \frac{3}{5} \sqrt{\frac{32}{28}}$$

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

Illustration 8

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 of the same temperature. Both containers are kept separately in vacuum. Calculate the ratio of rates of gas mixture in container A to that of O_2 if the area of orifice in both containers is same.

Solution:



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.

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

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

GASEOUS STATE

$$\frac{r_{\text{mix}}}{r_{\text{O}_2}} = \frac{P_{\text{mix}}}{P_{\text{O}_2}} \sqrt{\frac{M_{\text{O}_2}}{M_{\text{mix}}}} = \sqrt{\frac{32}{18.4}} = 1.319$$

In the above solution a mistake has been made because flow of each gas is independent and should not be applied to a mixture.

$$\frac{r_{\text{mix}}}{r_{\text{O}_2}} = \frac{r_{\text{N}_2} + r_{\text{He}}}{r_{\text{O}_2}} = \frac{\frac{P_{\text{N}_2}}{\sqrt{M_{\text{N}_2}}} + \frac{P_{\text{He}}}{\sqrt{M_{\text{He}}}}}{\frac{P_{\text{O}_2}}{\sqrt{M_{\text{O}_2}}}} = \frac{\frac{3}{\sqrt{28}} + \frac{2}{\sqrt{4}}}{\frac{5}{\sqrt{32}}} = 1.773$$

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:

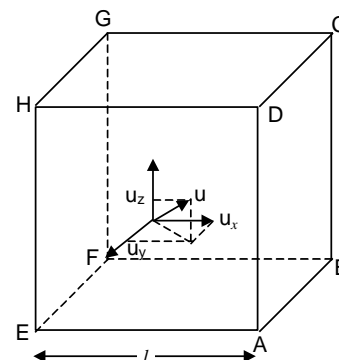
- A gas consists of a large number of very small spherical tiny particles, which may be identified with the molecules. The molecules of a given gas are completely identical in size, shape and mass.
- The volume occupied by the molecules is negligible in comparison to the volume of the gas.
- The molecules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

GASEOUS STATE

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 Figure. The component velocities are related by the expression, $u^2 = u_x^2 + u_y^2 + u_z^2$ (6.1 a)



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 $2l$ to arrive back at the wall ABCD. The number of collisions per unit time with the wall ABCD will be equal to $\frac{u_x}{2l}$

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 vessel is $\frac{mu_x^2}{l}$.

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

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

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

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

Defining the mean square speed as $\overline{u_x^2} = \frac{1}{N} \sum_{i=1}^N u_{ix}^2$ (6.1d)

GASEOUS STATE

We can write,

$$P = \frac{mN}{V} \overline{u_x^2} \quad \dots\dots(6.1e)$$

Since the direction x, y and z are equivalent, we will also have

$$\overline{u_x^2} = \overline{u_y^2} = \overline{u_z^2} \quad \dots\dots(6.1f)$$

But from equation (6.1a), we will have

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

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

$$P = \frac{mN}{V} \left(\frac{1}{3} \overline{u^2} \right)$$
$$\text{or } PV = \frac{1}{3} mN \overline{u^2} \quad \dots\dots(6.1h)$$

Illustration 9

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 $N = 10^{23}$

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

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

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

Therefore, from the kinetic gas equation

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

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

GASEOUS STATE

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

$$PV = \frac{1}{3} m N \overline{u^2} = \frac{2}{3} N \left[\frac{1}{2} m \overline{u^2} \right]$$
$$PV = \frac{2}{3} NKT \quad \dots\dots\dots(6.2a)$$

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

$$PV = \text{constant or } P \propto \frac{1}{V_1} \quad (\text{This is the expression for Boyle's law})$$

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, equation (6.2a) yields

$$V = \left(\frac{2}{3} \frac{NK}{P} \right) T \quad \text{i.e. } V = (\text{constant}) T \quad \text{or } V \propto T \quad (\text{This is the expression for Charles' law}).$$

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

$$P_1 V_1 = \frac{2}{3} N_1 K T_1 \quad \text{and} \quad P_2 V_2 = \frac{2}{3} N_2 K T_2$$

GASEOUS STATE

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

$$\frac{P_1 V_1}{P_2 V_2} = \frac{(2/3) N_1 K T_1}{(2/3) N_2 K T_2} \Rightarrow \frac{V_1}{V_2} = \frac{N_1}{N_2}$$

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.,

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

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 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.

GASEOUS STATE

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 (1.8a), 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

$$\frac{R}{N_{AV}} = \frac{8.314 \text{ JK}^{-1} \text{ mol}^{-1}}{6.023 \times 10^{23} \text{ mol}^{-1}} = 1.38 \times 10^{-23} \text{ JK}^{-1}$$

The total kinetic energy for 1 mole of the gas is $E_{\text{total}} = N_{AV} (\overline{KE}) = \frac{3}{2} RT$

Illustration 10

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:

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

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

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

$$\text{Thus } N(3/2)kT = 0.5 \times 10^4 \text{ J}$$

$$\text{Hence } T = \frac{2}{3} \frac{(0.5 \times 10^4 \text{ J})}{kN} = \frac{2}{3} \frac{(0.5 \times 10^4 \text{ J})}{(10^{23}) (1.38 \times 10^{-23} \text{ JK}^{-1})} = 2415.46 \text{ K}$$

Illustration 11

Calculate the total kinetic energy of 0.5 moles of an ideal gas at 273K.

Solution:

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

$$= 1702.292 \text{ J}$$

GASEOUS STATE

7. REAL GASES

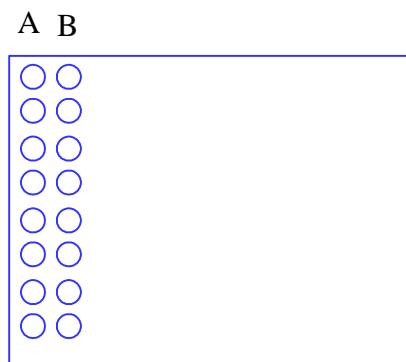
The ideal gas laws can be derived from the kinetic theory of gases which is based on the following two important assumptions:

- (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 Figure, 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.



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.

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

$$p \propto \frac{n^2}{V^2} \quad \text{or} \quad p = \frac{an^2}{V^2}$$

where a is the proportionality constant and is a measure of the forces of attraction between the molecules. Thus, $P_{\text{ideal}} = P_{\text{real}} + \frac{an^2}{V^2}$

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 $\text{Pa m}^6 \text{mol}^{-2}$. It may be conveniently expressed in $\text{k Pa dm}^6 \text{mol}^{-2}$.

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.

GASEOUS STATE

Correction for molecular size:

The container of volume V has n mole of gas molecules each of which possess 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.

$$\text{Since } P_i V_i = nRT$$

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

‘ 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 Figure. This creates another problem that when the molecules collide they collide in all possible directions.

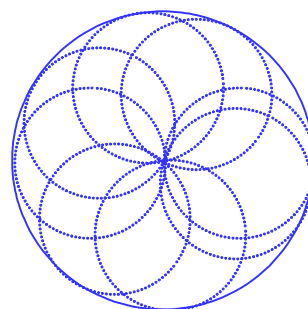
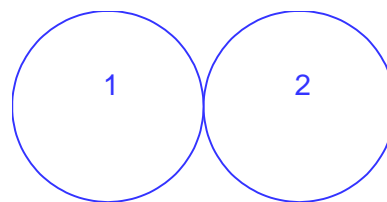
To simulate this we assume that the molecules that are stuck in pairs are rotating by keeping the point of contact fixed. This ensures that they occupy all possible orientations. For a third molecule the volume unavailable is the volume of the large sphere with radius $2r$ where r is the radius of each molecule. Therefore the volume unavailable is

$$\frac{4}{3} \pi (2r)^3 = 8 \times \frac{4}{3} \pi r^3.$$

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

$$\therefore b = 4 \times \frac{4}{3} \pi r^3 \times 6.023 \times 10^{23}. \text{ Thus Van der Waals equation for 1}$$

$$\text{mol of real gas is given as } \left(P + \frac{a}{V^2} \right) (V - b) = RT.$$



GASEOUS STATE

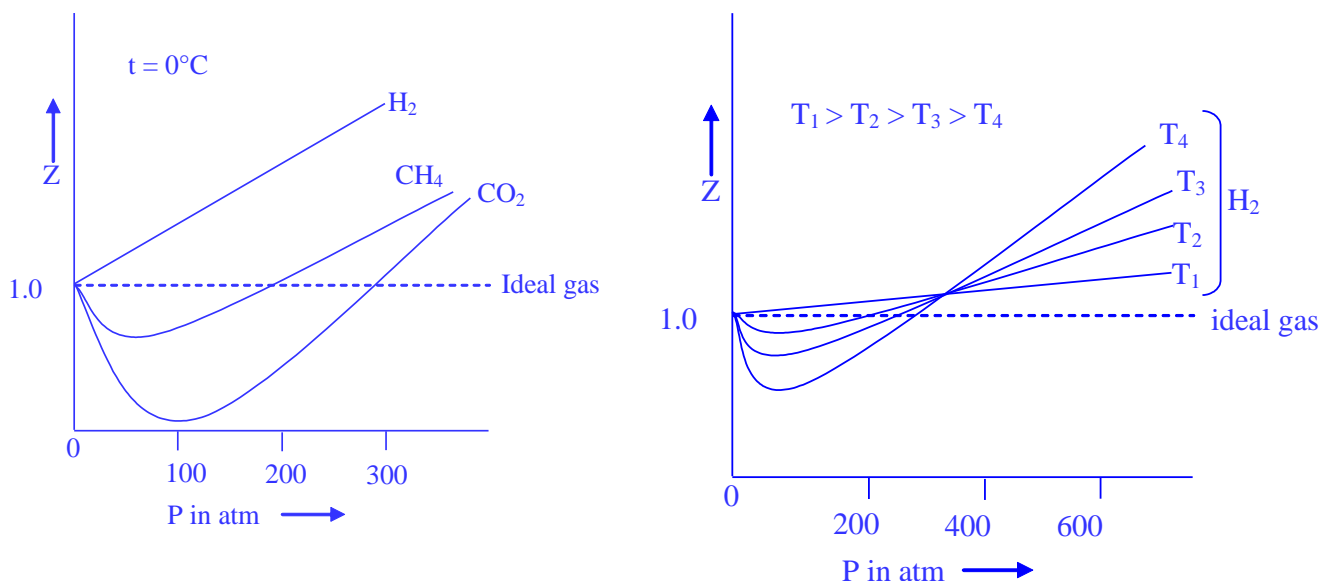
7.1 Deviation from ideal behavior

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.



Above Figures 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.

Figure shows a plot of Z as a function of pressure at 0°C 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

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

GASEOUS STATE

The equation can be rewritten as

$$PV_m - Pb + \frac{a}{V_m} - \frac{ab}{V_m^2} = RT$$
$$\text{or } PV_m = RT + Pb - \frac{a}{V_m} + \frac{ab}{V_m^2} \dots \quad (8a)$$

Dividing Eq. (8a) by RT

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

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 $\frac{b}{V_m}$ would be extremely smaller than 1. Thus, the term $\left[\frac{a}{V_m RT} \left(\frac{b}{V_m} - 1 \right) \right]$ would be negative and greater in magnitude than positive term $\frac{Pb}{RT}$. Consequently, the Z is less than unity.

With the increase of pressure in the low pressure region, both the terms, $\frac{Pb}{RT}$ and $\left[\frac{a}{V_m RT} \left(\frac{b}{V_m} - 1 \right) \right]$ increases but the increase in negative term, $\left[\frac{a}{V_m RT} \left(\frac{b}{V_m} - 1 \right) \right]$ would be more than the increase in positive term, $\left(\frac{Pb}{RT} \right)$, 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.

GASEOUS STATE

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 12

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 dm³ at 223 K and 800 atm. Calculate the volume occupied by the same quantity of nitrogen at 373 K and 200 atm.

Solution:

$$\text{The number of mole of N}_2 (n) = \frac{PV}{ZRT} = \frac{800 \times 1}{1.95 \times 0.0821 \times 223} = 22.4 \text{ mole}$$

Thus, the volume of N₂ at 373 K and at 200 atm would be

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

Illustration 13

One way of writing the equation of state for real gases is

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

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

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

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

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

Multiplying both the sides with \bar{V} , we get $P\bar{V} = \frac{RT\bar{V}}{\bar{V} - b} - \frac{a}{\bar{V}}$

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

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

GASEOUS STATE

At low pressure, \bar{V} is large and $\frac{b}{\bar{V}} \ll 1$.

Therefore, the term $\left(1 - \frac{b}{\bar{V}}\right)^{-1}$ can be expanded into a power series in $\frac{b}{\bar{V}}$.

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

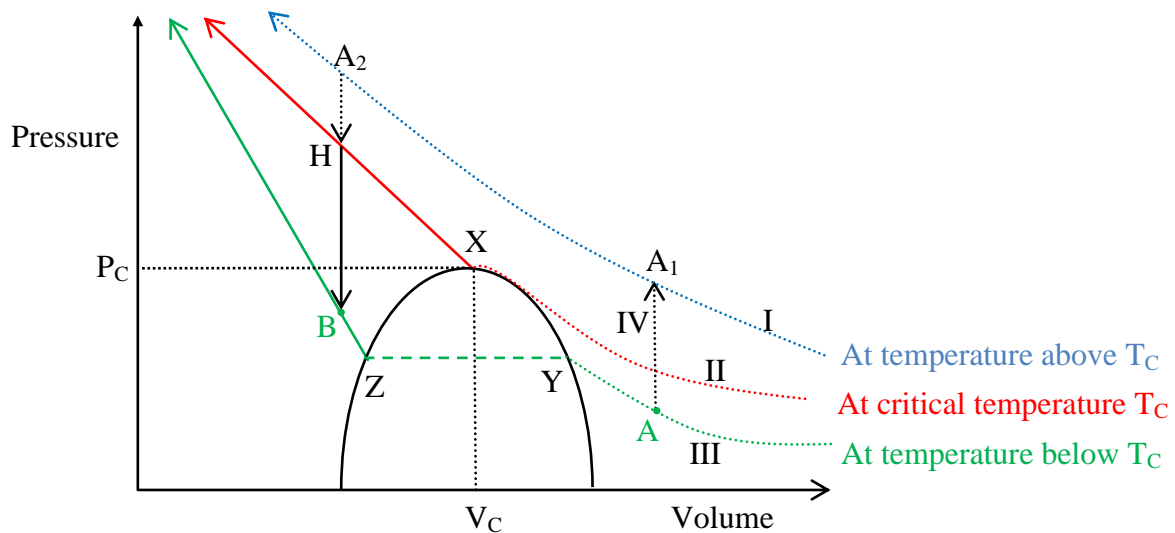
$$P\bar{V} = RT \left[1 + \frac{b}{\bar{V}} + \left(\frac{b}{\bar{V}}\right)^2 + \dots - \frac{a}{\bar{V}RT} \right]$$

Ignoring b^2 and higher terms, we get $P\bar{V} = RT \left[1 + \frac{1}{\bar{V}} \left(b - \frac{a}{RT} \right) + \dots \right] \dots (8c)$

Comparing Eq. (8c) with the expression given in the problem, we get $B = b - \frac{a}{RT}$

7.2 LIQUEFACTION OF GASES

Ideal gas cannot be liquefied under any conditions. However, real gases can be liquefied if we compress real gas below critical temperature. If we plot P versus V for any real gas at different constant temperatures, the isotherm appears like the one given below:



Isotherms of real gas at various temperatures

At high temperatures (above critical temperature) isotherms look like that of an ideal gas and the gas cannot be liquefied even at very high pressure. As the temperature is lowered, shape of the curve changes and data shows considerable deviation from ideal behaviour.

GASEOUS STATE

At Critical temperature, real gas remains gas below critical pressure i.e. P_C (Point X). At critical pressure, liquid appears for the first time. **Critical temperature is the highest temperature at which liquid is observed.** Above this temperature it is gas. **The pressure at which liquid appears at critical temperature is called critical pressure. Volume of one mole of the gas at critical temperature and critical pressure is called critical volume (V_C).** Critical temperature, pressure and volume are called critical constants. Further increase in pressure simply compresses the liquid and curve represents compressibility of the liquid. The steep line represents the isotherm of liquid. Even a slight compression results in steep rise in pressure indicating very low compressibility of liquid.

Below critical temperature, the behaviour of the gas on compression is quite different. A gas remains only upto point Y. At point Y, liquid of a particular volume appears. Further compression does not change the pressure. Liquid and gas coexist and further application of pressure results in the condensation of more gas until the point Z is reached. At point Z, all the gas has been condensed and further application of pressure merely compresses the liquid as shown by steep line. Below critical temperature each curve shows the similar trend. Only length of the horizontal line increases at lower temperatures.

At critical point horizontal portion of the isotherm merges into one point. Thus we see that a point like A represents gaseous state. A point like B represents liquid state and a point under the dome shaped area represents existence of liquid and gas in equilibrium. All the gases upon compression at constant temperature (isothermal compression) show the same behaviour. Also above discussion shows that gases should be cooled below their critical temperature for liquefaction. Critical temperature of a gas is highest temperature at which liquefaction of the gas first occurs. Liquefaction of so called permanent gases (i.e., gases which show continuous positive deviation in Z value) requires cooling as well as considerable compression. Compression brings the molecules in close vicinity and cooling slows down the movement of molecules therefore, intermolecular interactions may hold the closely and slowly moving molecules together and the gas liquefies. It is possible to change a gas into liquid (or a liquid into gas) by a process in which always a single phase is present. For example we can move from point A to A_1 vertically by increasing the temperature at constant volume then we can reach the point A_2 by compressing the gas at the constant temperature along this isotherm (The pressure will increase). Now we can move vertically down towards B by lowering the temperature at constant volume. As soon as we cross the point H on the critical isotherm we get liquid. We end up with liquid but in this series of changes we do not pass through two-phase region.

GASEOUS STATE

If process is carried out at the critical temperature, substance always remains in one phase. Thus there is continuity between the gaseous and liquid state. The term fluid is used for either a liquid or a gas to recognize this continuity. Thus a liquid can be viewed as a very dense gas. Liquid and gas can be distinguished only when the fluid is below its critical temperature and its pressure and volume lie under the dome, since in that situation liquid and gas are in equilibrium and a surface separating the two phases is visible. In the absence of this surface there is no fundamental way of distinguishing between two states. At critical temperature, liquid passes into gaseous state imperceptibly and continuously; the surface separating two phases disappears. A gas below the critical temperature can be liquefied by applying pressure, and is called vapour of the substance. Critical constants for some common substances are given in table given on next page.

Critical Constants for some substances

Substance	T_C / K	P_C / bar	$V_C / \text{dm}^3\text{mol}^{-1}$
H ₂	33.2	12.97	0.0650
He	5.3	2.29	0.0577
N ₂	126.0	33.9	0.0900
O ₂	154.3	50.4	0.0744
CO ₂	304.1	73.9	0.0956
H ₂ O	647.1	220.6	0.0450
NH ₃	405.5	113.0	0.0723

$$\text{Critical Temperature } (T_C) = \frac{8a}{27Rb},$$

$$\text{Critical Pressure } (P_C) = \frac{a}{27b^2}$$

$$\text{Critical Volume } (V_C) = 3b,$$

$$\text{For 1 mole of gas under critical conditions, } P_C V_C = ZRT_C$$

$$\frac{a}{27b^2} \times 3b = Z \times R \times \frac{a}{27Rb} \quad Z = \frac{3}{8}$$

$$\text{Under Critical conditions, } Z = (3/8)$$

GASEOUS STATE

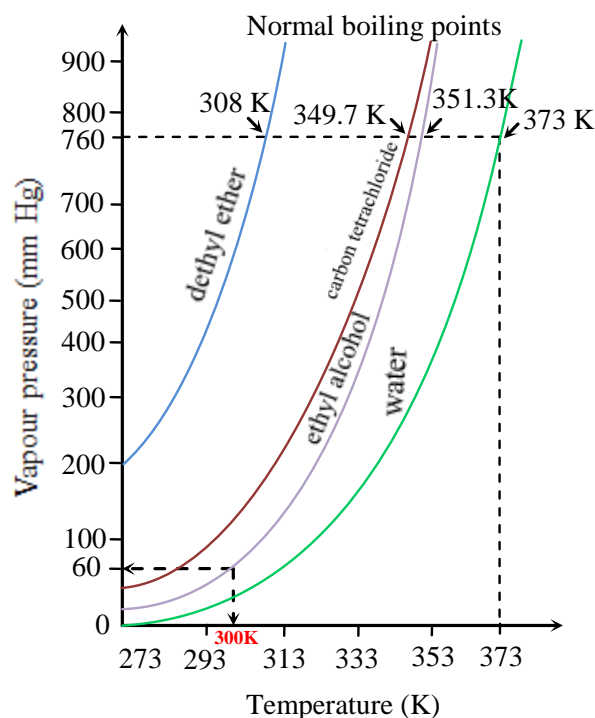
8 LIQUID STATE

Intermolecular forces are stronger in liquid state than in gaseous state. Molecules in liquids are so close that there is very little empty space between them and under normal conditions liquids are denser than gases. Molecules of liquids are held together by attractive intermolecular forces. Liquids have definite volume because molecules do not separate from each other. However, molecules of liquids can move past one another freely, therefore, liquids can flow, can be poured and can assume the shape of the container in which these are stored. In the following sections we will look into some of the physical properties of the liquids such as vapour pressure, surface tension and viscosity.

8.1 Vapour Pressure

If an evacuated container is partially filled with a liquid, a portion of liquid evaporates to fill the remaining volume of the container with vapour. Initially the liquid evaporates and pressure exerted by vapours on the walls of the container (vapour pressure) increases. After some time it becomes constant and equilibrium is established between liquid phase and vapour phase. Vapour pressure at this stage is known as equilibrium vapour pressure or saturated vapour pressure.

Since process of vapourisation is temperature dependent; the temperature must be mentioned while reporting the vapour pressure of a liquid. When a liquid is heated in an open vessel, the liquid vapourises from the surface. At the temperature at which vapour pressure of the liquid becomes equal to the external pressure, vapourisation can occur throughout the bulk of the liquid and vapours expand freely into the surroundings. The condition of free vapourisation throughout the liquid is called boiling. The temperature at which vapour pressure of liquid is equal to the external pressure is called boiling temperature at that pressure. Vapour pressure of some common liquids at various temperatures is shown in given figure. At 1 atm pressure, boiling temperature is called normal boiling point.



Vapour Pressure versus Temperature Curve

GASEOUS STATE

If pressure is 1 bar then the boiling point is called standard boiling point of the liquid. Standard boiling point of the liquid is slightly lower than the normal boiling point because 1 bar pressure is slightly less than 1 atm pressure. The normal boiling point of water is 100 °C (373 K), its standard boiling point is 99.6 °C (372.6 K).

At high altitudes atmospheric pressure is low. Therefore liquids at high altitudes boil at lower temperatures in comparison to that at sea level. Since water boils at low temperature on hills, the pressure cooker is used for cooking food. In hospitals surgical instruments are sterilized in autoclaves in which boiling point of water is increased by increasing the pressure above the atmospheric pressure by using a weight covering the vent.

Boiling does not occur when liquid is heated in a closed vessel. On heating continuously vapour pressure increases. At first a clear boundary is visible between liquid and vapour phase because liquid is more dense than vapour. As the temperature increases more and more molecules go to vapour phase and density of vapours rises.

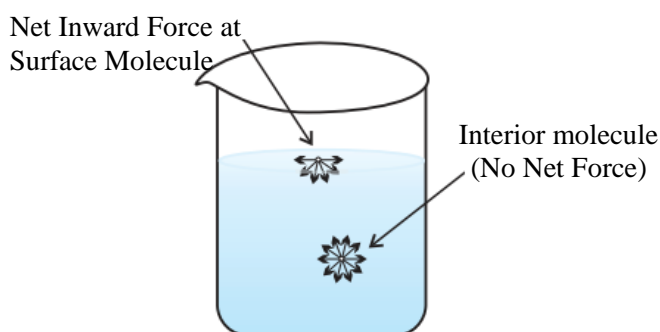
At the same time liquid becomes less dense. It expands because molecules move apart. When density of liquid and vapours becomes the same; the clear boundary between liquid and vapours disappears. This temperature is called critical temperature about which we have already discussed.

8.2 Surface Tension

It is well known fact that liquids assume the shape of the container. Why is it then small drops of mercury form spherical bead instead of spreading on the surface? Why do particles of soil at the bottom of river remain separated but they stick together when taken out? Why does a liquid rise (or fall) in a thin capillary as soon as the capillary touches the surface of the liquid? All these phenomena are caused due to the characteristic property of liquids, called surface tension. A molecule in the bulk of liquid experiences equal intermolecular forces from all sides. The molecule, therefore, does not experience any net force. But for the molecule on the surface of liquid, net attractive force is towards the interior of the liquid (as shown in figure), due to the molecules below it (Since there are no molecules above it). Due to these inward forces at the surface molecules, liquids tend to minimize their surface area. The molecules on the surface experience a net downward force and have more energy than the molecules in the bulk, which do not experience any net force. Therefore, liquids tend to have minimum number of molecules at their surface. If surface of the liquid is increased by pulling a molecule from the bulk, attractive forces will have to be overcome. This will require expenditure of

GASEOUS STATE

energy. The energy required to increase the surface area of the liquid by one unit is defined as surface energy. Its dimensions are Jm^{-2} .



Forces acting on a molecule on liquid surface and on a molecule inside the liquid

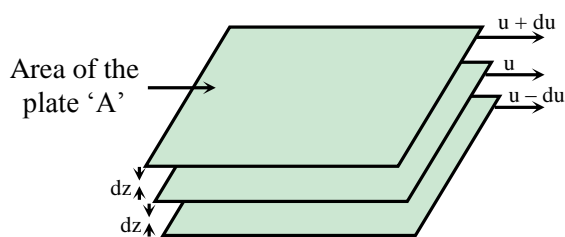
Surface tension is defined as the force acting per unit length perpendicular to the line drawn on the surface of liquid. It is denoted by Greek letter γ (Gamma). It has dimensions of kg s^{-2} and in SI unit it is expressed as N m^{-1} . The lowest energy state of the liquid will be when surface area is minimum. Spherical shape satisfies this condition; that is why mercury drops are spherical in shape. This is the reason that sharp glass edges are heated for making them smooth. On heating, the glass melts and the surface of the liquid tends to take the rounded shape at the edges, which makes the edges smooth. This is called fire polishing of glass. Liquid tends to rise (or fall) in the capillary because of surface tension. Liquids wet the things because they spread across their surfaces as thin film. Moist soil grains are pulled together because surface area of thin film of water is reduced. It is surface tension which gives stretching property to the surface of a liquid. On flat surface, droplets are slightly flattened by the effect of gravity; but in the gravity free environments drops are perfectly spherical. The magnitude of surface tension of a liquid depends on the attractive forces between the molecules. When the attractive forces are large, the surface tension is large. Increase in temperature increases the kinetic energy of the molecules and effectiveness of intermolecular attraction decreases, so surface tension decreases as the temperature is raised.

8.3 Viscosity

It is one of the characteristic properties of liquids. Viscosity is a measure of resistance to flow which arises due to the internal friction between layers of fluid as they slip past one another while liquid flows. Strong intermolecular forces between molecules hold them together and resist movement of layers past one another. When a liquid flows over a fixed surface, the layer of molecules in the immediate contact of surface is stationary. The velocity of upper layers increases as the distance of

GASEOUS STATE

layers from the fixed layer increases. This type of flow in which there is a regular gradation of velocity in passing from one layer to the next is called laminar flow. If we choose any layer in the flowing liquid (see figure), the layer above it accelerates its flow and the layer below this retards its flow.



Gradation of velocity in the laminar flow

If the velocity of the layer at a distance dz is changed by a value du then velocity gradient is given by the amount du/dz . A force is required to maintain the flow of layers. This force is proportional to the area of contact of layers and velocity gradient i.e.

$$F \propto A \text{ (A is the area of contact)}$$

$$F \propto (du/dz) \text{ (where, } du/dz \text{ is velocity gradient; the change in velocity with distance)}$$

$$F \propto A \cdot \frac{du}{dz} \quad \text{or} \quad F = \eta A \cdot \frac{du}{dz}$$

Where ' η ' is proportionality constant and is called coefficient of viscosity. Viscosity coefficient is the force when velocity gradient is unity and the area of contact is unit area. Thus ' η ' is measure of viscosity. SI unit of viscosity coefficient is newton second per square metre (N s m^{-2}) = pascal second ($\text{Pa s} = 1\text{kg m}^{-1}\text{s}^{-1}$). In cgs system the unit of coefficient of viscosity is poise (named after great scientist Jean Louise Poiseuille).

$$1 \text{ poise} = 1 \text{ g cm}^{-1}\text{s}^{-1} = 10^{-1}\text{kg m}^{-1}\text{s}^{-1}$$

Greater the viscosity, the more slowly the liquid flows. Hydrogen bonding and van der Waals forces are strong enough to cause high viscosity. Glass is an extremely viscous liquid. It is so viscous that many of its properties resemble solids. However, property of flow of glass can be experienced by measuring the thickness of windowpanes of old buildings. These become thicker at the bottom than at the top. Viscosity of liquids decreases as the temperature rises because at high temperature molecules have high kinetic energy and can overcome the intermolecular forces to slip past one another between the layers.

GASEOUS STATE

9. 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 gases 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 form oxide with element in highest oxidation state unless & until mentioned in the problem. 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 volume of gases before combustion and after combustion and cooling is noted.

The volume of any gaseous substance in eudiometer is determined by absorbing that gas 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.

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 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)

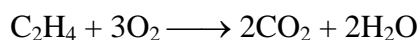
GASEOUS STATE

Cl₂: absorbed by water or alkali solution

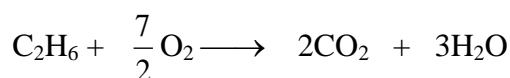
NH₃: absorbed by acid solution or CuSO₄ solution

CO₂ & SO₂: absorbed by alkali solution (NaOH, KOH, Ca(OH)₂ or ethanolamine (HOCH₂CH₂NH₂).

Let us see the application of eudiometry in determining the composition of gaseous mixture. We are given a mixture of ethane (C₂H₆) and ethene (C₂H₄) measuring 'a' ml. The mixture is subjected to electric spark along with excess of oxygen (b ml.) On sparking, C₂H₄ and C₂H₆ both get combusted and form gaseous CO₂ and H₂O vapours. Let us assume that the volume of C₂H₄ in the mixture be 'x' ml. The combustion reactions are shown as



Volume reacted/produced x 3x 2x 2x



Volume reacted/produced (a - x) $\frac{7}{2}(a - x)$ 2(a - x) 3(a - x)

After explosion, the reaction mixture is allowed to come at room conditions, so water vapour condenses to liquid H₂O.

Volume before sparking (VBS) = a + b

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

∴ First contraction in volume after sparking = VBS - VAS

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

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 H₂O 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 H₂O 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.

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

GASEOUS STATE

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

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

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

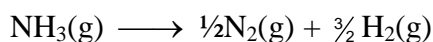
Illustration 14

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, then the volume of H_2 would be $(50 - x)$ ml.

On sparking,



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 ($\because 2H_2 + O_2 \longrightarrow 2H_2O$)

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

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

$$\therefore NH_3 = 72\%$$

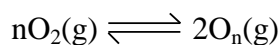
GASEOUS STATE

Illustration 15

When a certain quantity of oxygen was ozonized in a suitable apparatus, the volume decreased by 4 ml. On addition of turpentine oil, the volume decreased further by 8 ml. Find the formula of ozone, assuming all measurements were 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.



Initial volume	a	0
Volume after attainment of equilibrium	$a - nx$	$2x$

The initial volume reduction is due to reaction stoichiometry alone.

\therefore Initial volume – volume at equilibrium = 4 ml

$$\therefore a - (a - nx + 2x) = 4$$

$$nx - 2x = 4 \quad \dots\dots(i)$$

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

$$\therefore 2x = 8 \text{ and } x = 4$$

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

$$\therefore nx = 4 + 8 = 12$$

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

Molecular formula of ozone is O_3 .

GASEOUS STATE

Illustration 16

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 3 methods to solve this problem.

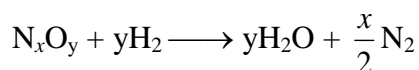
Method 1:

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.

\therefore The volume of H_2 added was 27 ml.

On sparking, the reaction would be



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	$\frac{x}{2}N_2(g)$	+	$yH_2O(l)$
Initially	15 ml		27 ml		0		0
After sparking	0		$(27-15y)$		$\frac{15x}{2}$ ml		–

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

$$\therefore \frac{15x}{2} - 15y = 0; \quad \therefore x = 2y \quad \dots\dots(i)$$

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*

	$H_2(g)$	+	$\frac{1}{2}O_2(g)$	\longrightarrow	$H_2O(l)$
Volume initially	$(27-15y)$		10		0
Volume finally	$(27-15y-20)$		0		–

\therefore Final volume of gases = volume of remaining (hydrogen + nitrogen)

GASEOUS STATE

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

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

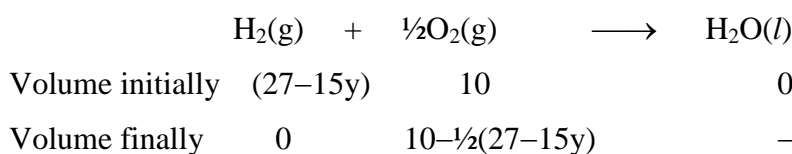
\therefore H_2 cannot be in excess.

(ii) *Hydrogen is exactly consumed by O_2*

$$\therefore 27 - 15y = 20; \quad y = \frac{7}{15}.$$

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

(iii) *Oxygen is in excess*



\therefore 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 $y = 1$.

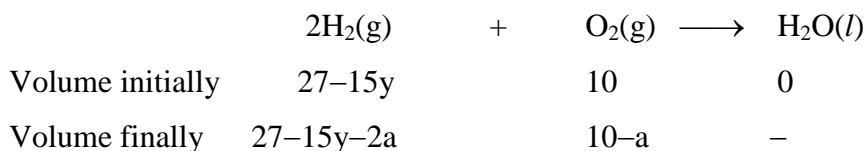
\therefore Formula is N_2O

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'.



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

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

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

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

$$\therefore 4 + \frac{15x}{2} = 19; \quad x = 2 \text{ and } y = 1.$$

GASEOUS STATE

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.

$$\therefore b + \frac{b}{2} = 18; \quad b = 12 \text{ ml. This means that } O_2 \text{ reacted is 6 ml and } O_2 \text{ left is 4 ml.}$$

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

Illustration 17

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}	+	$\frac{(3n-1)}{2} O_2 (g)$	\longrightarrow	nCO_2	+	$(n-1)H_2O (l)$
Initial volume	$20-x$		$100 - 2x$		0		0
Final volume	0		$100 - 2x - \left(\frac{(3n-1)}{2} (20-x) \right)$		$n(20-x)$		—

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 $\frac{(3n-1)}{2} (20-x)$.

GASEOUS STATE

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.

$$\therefore 100 - 2x - \frac{(3n-1)(20-x)}{2} = 40 \quad \text{i.e.} \quad 2x - \frac{(3n-1)(20-x)}{2} = 60$$

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 $C_3H_4 = 50$