

**6****THE GASEOUS STATE**

We know that matter exist in three *different states namely solid, liquid and gas. The most familiar example to show these different states of matter is water. Water exists as a solid (ice), a liquid (water) and a gas (steam) under different conditions of temperature and pressure. The difference between these three states of matter is due to the difference in their intermolecular distances and intermolecular forces. In addition to these, temperature and pressure also play an important role in deciding the states of matter.

In this lesson we shall first discuss the differences in properties of the solid, liquid and gaseous state and the factors due to which these differences arise. We shall also study the effect of pressure and temperature on the volume of the given amount of gas. These are governed by the gas laws namely Boyles' law, Charles' law and Avogadro's law.

**Objectives**

After reading this lesson, you will be able to:

- differentiate between the three states of matter - solid, liquid and gas;
- list the characteristic properties of gases;
- state the gas laws (Boyle's law, Charles' law and Avogadro's law) and express them mathematically;
- draw the p - V , p - $1/V$, p - pV and V - T graphs;
- interpret the effect of temperature and pressure on the volume of a gas from the graph;
- derive the ideal gas equation from the gas laws;
- state the Dalton's law of partial pressure and explain its significance;
- state Graham's law of diffusion;
- state the postulates of Kinetic Molecular Theory of gases;
- explain the Maxwell's distribution of velocities;

* There is fourth state of matter called Plasma. In this state matter exists as ionised gas. This occur at very high temperature. For example matter in the sun is in the Plasma State.



- differentiate between u_{rms} , u_{mp} and u_{av} ;
- explain the deviation of real gases from ideal behaviour in term of compressibility factor;
- state the van der Waals equation and explain the significance of van der Waals constants and
- explain the liquifaction of gases with the help of Andrews curves.

6.1 The Three States of Matter

At any given conditions of temperature and pressure matter exists in one of the three states namely solid, liquid and gas. The characteristic properties of solid, liquid and gaseous state are listed in Table 6.1.

Table 6.1 : Properties of different states of matter

Property	Solid	Liquid	Gas
Shape	Definite	Indefinite; takes up the shape of the vessel.	Indefinite
Volume	Definite	Definite	Indefinite (fills the container completely)
Density	High	Less than solids but much higher than gases.	Low
Compressibility	Incompressible	largely incompressible	Highly compressible

The different characteristics of the three states of matter as listed above depend upon the relative closeness of particles that make up the substance. In solid state, the particles are held close together in a regular pattern by strong intermolecular forces. In liquid state, intermolecular forces are weak as compared to solid state hence the particles are less tightly held and allow them to move away from each other. In the gaseous state, the molecules are farthest apart as compared to solid and liquid states and the intermolecular forces are negligible so the particles move randomly. A simplified picture of particles in solid, liquid and gaseous states is represented in Fig. 6.1.

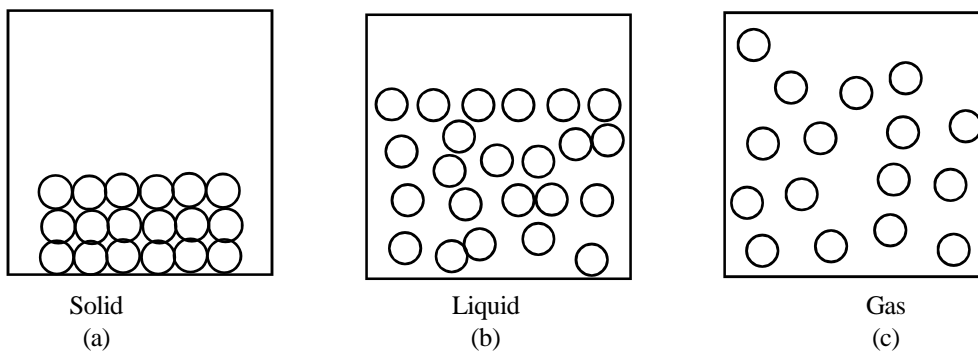


Fig. 6.1 : A simplified picture of particles in solid, liquid and gaseous state

6.2 : General Behaviour of Gases: The Gas Laws

The volume of a given mass of a gas depends upon the temperature and pressure under which the gas exists. It is, therefore, possible to describe the behaviour of gases in terms of the four variables: temperature, T ; pressure p ; volume V and amount (number of moles, n).

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For a given amount of gas the volume of gas changes with change in variables such as temperature and pressure. The relationship between any two of the variables is studied, keeping the other variable constant by various laws which are described below.

6.2.1 Effect of Pressure on the Volume of the Gas (Boyle’s law)

The effects of pressure on the volume of gas for a given amount of gas at constant temperature was studied by Robert Boyle in 1662 for different gases. He observed that if the volume of gas is doubled the pressure is halved and vice versa. Boyle’s law states that at constant temperature, the volume of a given amount of a gas is inversely proportional to its pressure.

Mathematically Boyle’s law is expressed as shown below:

$$V \propto \frac{1}{p} \quad (\text{at constant } T \text{ and } n)$$

or

$$p_1 V_1 = p_2 V_2$$

when the pressure of the gas, p is plotted against volume of the gas, V the exponential curve is obtained (Fig. 6.2). However when the pressure, p of the gas is plotted against $\frac{1}{V}$ a straight line is obtained (Fig. 6.3). If the product of pressure and volume (pV) is plotted against pressure (p) a straight line parallel to x -axis (pressure is axis) is obtained (Fig. 6.4).

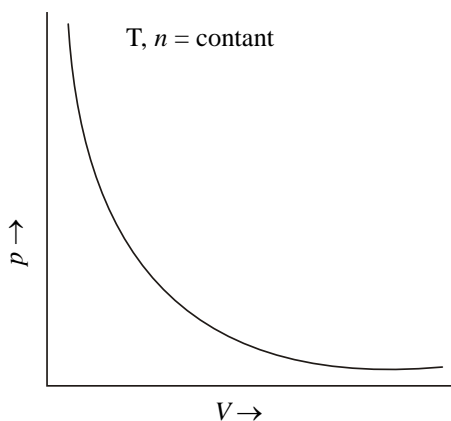


Fig.6.2 : A graph of p versus V

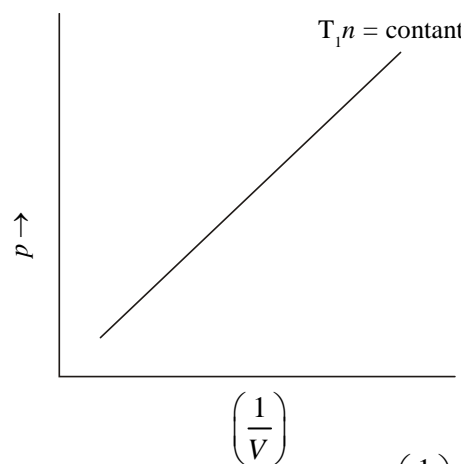


Fig.6.3 : A graph of p versus $\left(\frac{1}{V}\right)$

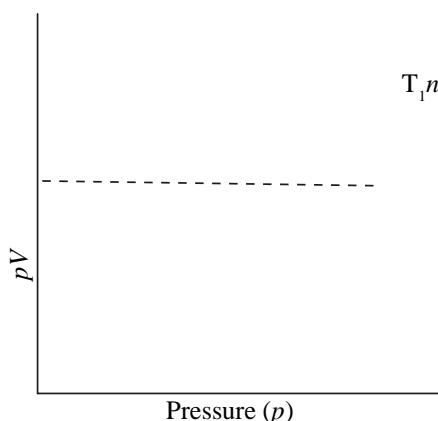


Fig.6.4 : A graph of pV versus p



Example 6.1 : The volume occupied by a given mass of a gas at 298 K is 24 mL at 1 atmospheric pressure. Calculate the volume of the gas if the pressure is increased to 1.25 atmosphere keeping temperature constant.

Solution : Given that

$$\begin{aligned} V_1 &= 25 \text{ mL} & p_1 &= 1 \text{ atm} \\ V_2 &= ? & p_2 &= 1.25 \text{ atm} \end{aligned}$$

According to Boyle's Law, $p_1 V_1 = p_2 V_2$

substituting the values of p_1 , V_1 and p_2 in the above expression we get

$$V_2 = \frac{p_1 V_1}{p_2} = \frac{(1 \text{ atm})(25 \text{ mL})}{(1.25 \text{ atm})} = 20 \text{ mL}$$

The volume occupied by the gas is 20 mL at 298 K and 1.25 atm pressure.

Example 6.2 : The volume of a certain amount of a gas is decreased to one fifth of its initial volume at a constant temperature. What is the final pressure?

Solution : Let

$$\text{Initial volume} = V_1 \qquad \text{Initial pressure} = p_1$$

$$\text{Final volume } V_2 = V_1/5 \qquad \text{Final pressure} = p_2$$

By Boyle's law, we know that at constant temperature

$$\begin{aligned} p_1 V_1 &= p_2 V_2 \\ p_2 &= \frac{p_1 V_1}{p_2} = \frac{p_1 \times V_1}{\frac{V_1}{5}} = 5p_1 \end{aligned}$$

Thus when volume is decreased to $\frac{1}{5}$ th of its initial volume, the pressure is increased by 5 times of the initial volume.

6.2.2 Effect of Temperature on the Volume of Gas (Charles' Law)

The effects of temperature on the volume of the gas was studied by Jacques Charles in 1787 and Gay Lussac in 1802 at constant pressure for different gases. Their conclusion can be given as Charles' law which states that at a constant pressure, the volume of a given amount of gas is directly proportional to the absolute temperature.

So, according to Charles' Law, the volume of a gas increases as its absolute temperature is being raised, if its absolute temperature is lowered, its volume will consequently decrease. Mathematically, Charles' Law is expressed as shown below:

$$\begin{aligned} V &\propto t && \text{(at constant } p \text{ and } n) \\ V &= k \cdot t && (k \text{ is a constant}) \end{aligned}$$



Notes

Therefore,

$$V_1/t_1 = V_2/t_2$$

Graphical representation of Charles' Law is a straight line pointing away from the origin of the graph as shown in Fig. 6.5.

Here graph of the volume of a gas (V) plotted against its temperature at constant pressure and amount (in moles). Notice that the graph is a straight line with a positive gradient (slope).

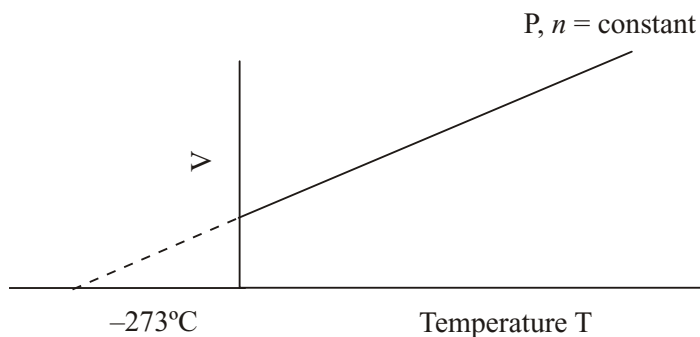


Fig. 6.5 : A graph of V versus T

Mathematically volume of a gas at temperature t is given as

$$v_t = v_0 + \frac{v_0}{273} \times t = v_0 \left(1 + \frac{t}{273} \right) = v_0 \left(\frac{273 + t}{273} \right)$$

Thus at

$$t = -273^\circ\text{C}$$

$$v_t = v_0 \left(\frac{273 - 273}{273} \right) = 0$$

This means that at -273°C , the volume of the gas is reduced to zero i.e., the gas ceases to exist. Thus this temperature (-273°C) at which the gas hypothetically ceases to exist is called **Absolute zero**. It is represented by zero K.

This is the theoretically lowest possible temperature. In actual practice, we cannot reduce the temperature of the gas to zero kelvin.

Kelvin Scale of Temperature

The scale of temperature which has -273°C as zero is called Kelvin Scale. Degree celsius is converted to Kelvin by adding 273. Thus

$$t/^\circ\text{C} + 273 = T/\text{K}$$

where

T = temperature in Kelvin

t = temperature in celsius

For example 15°C can be converted in K by adding 273 to 15.

6.2.3 Effect of Temperature on Pressure (Pressure-Temperature Law)

This law states that.



Notes

Pressure of given amount of a gas at constant volume is directly proportional to its absolute temperature.

$$p \propto T$$

$$p = kT$$

Example 6.3 : A given amount of a gas is maintained at constant pressure and occupies a volume of 2 litres at 1000°C. What would be volume if gas is cooled to 0°C keeping pressure constant.

Solution : Given that,

$$\text{Initial volume } V_1 = 2\text{L} \quad T_1 = 1000 + 273 = 1273 \text{ K}$$

$$\text{Final volume } V_2 = ? \quad T_2 = 0 + 273 = 273 \text{ K}$$

$$\text{Now using Charle's Law} \quad V_1/T_1 = V_2/T_2 \text{ or } V_2 = (V_1/T_1) \times T_2$$

On substituting the values we get

$$V_2 = (V_1/T_1) \times T_2 = (2\text{L} / 1273 \text{ K}) \times 273 \text{ K} = 0.4291 \text{ L}$$

6.2.4 Avogadro's Law

The Italian physicist Amadeo Avogadro was the first to propose, in 1811, a relationship between the volume of a gas and the number of molecules present in it. This relationship is known as Avogadro's Law. It states that :

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

Mathematically, Avogadro's law is expressed as :

$$V \propto N \text{ (at constant temperature and pressure)}$$

Where V and N are volume and number of molecules respectively.

At a given temperature and pressure, the number of molecules present in the gas is directly proportional to the number of moles.

therefore, $N \propto n$

Where n is the number of moles

$$\therefore V \propto n$$

$$\text{or} \quad \frac{V}{n} = \text{constant}$$

$$\text{Also} \quad \frac{V_1}{n_1} = \frac{V_2}{n_2}$$

He also found that the number of molecules present in 1 mole of any substance (22.4 litre of any gas at 273 K temperature and 1 atmosphere pressure) is 6.022×10^{23} molecules. This number is known as **Avogadro's number**.

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It is the number of molecules (6.022×10^{23}) of any gas present in a volume of 22.4 L (at 273 K and 1 atm) and it is the same for the lightest gas (hydrogen) as for a heavy gas such as carbon dioxide or bromine.

Example 6.4 : 0.965 mol of a gas occupies a volume of 5.0 L at 298 K/ temperature and 1 atm pressure. What would be the volume of 1.80 mol of the gas at the same temperature and pressure?

Solution :

$$V_1 n_2 = V_2 n_1$$

$$\frac{V_2 n_2}{n_1} = \frac{(5.0\text{L}) (1.8 \text{ mol})}{(0.965 \text{ mol})}$$

$$V_2 = 9.33 \text{ L}$$

Example 6.5 : Compare the volumes of 16 g of oxygen and 14 g nitrogen at the same temperature and pressure.

Solution : Number of moles of $\text{O}_2 = 16 \text{ g}/32 \text{ g mol}^{-1} = 0.5 \text{ mol}$

Number of moles of $\text{N}_2 = 14 \text{ g}/28 \text{ g mol}^{-1} = 0.5 \text{ mol}$

Since the two gases are at the same temperature and pressure, and contain equal number of mole, hence according to the Avogadro's Law they should also occupy the same volume.



Intext Question 6.1

1. The density of a gas is usually less than that of the liquid. Explain.
.....
2. Calculate the pressure (atm) required to compress 500 mL of gas at 0.20 atm into a volume of 10 mL.
.....
3. Equal volumes of oxygen gas and an unknown gas weigh 2.00 and 1.75 g respectively under the same experimental conditions. What is the molar mass of the unknown gas?
.....

6.3 The Ideal Gas Equation

Boyle's Law, Charles' Law and Avogadro's Law can be combined to give a single equation which represents the relation between the pressure, volume and kelvin temperature of a given amount of a gas under different conditions. Thus

$$V \propto 1/p \quad \text{at constant temperature (Boyles' Law)}$$

$$V \propto T \quad \text{at constant pressure (Charles' Law)}$$

$$V \propto n \quad \text{at constant temperature and pressure (Avogadros' Law)}$$

All the three expressions can be combined into a single expression

$$V \propto nT/P \text{ or } pV \propto nT$$

$$\text{or } pV = \text{constant} \times nT$$

The constant in this equation is called ‘**universal gas constant**’ or ‘**molar gas constant**’, represented by R . Thus we can write for 1 mole of a gas

$$pV = RT$$

Correspondingly, for n moles of a gas we have

$$pV = nRT$$

This is known as the ideal gas equation because it holds only when gases are behaving as ‘ideal’ gases.

Since for a given mass of gas we can write

$$pV/T = \text{a constant, we have}$$

$$p_1 V_1/T_1 = p_2 V_2/T_2$$

Where p_1 , V_1 and T_1 refer to one set of conditions and p_2 , V_2 and T_2 refer to a different set of conditions.

The numerical value of R can be found by substituting experimental quantities in the equation. At STP, $T = 273.15$ K, $p = 1$ atm and for 1 mol of gas ($n = 1$), $V = 22.414$ L. Consequently,

$$\begin{aligned} R = pV/nT &= (1 \text{ atm}) (22.414\text{L}) / (1 \text{ mol}) (273.15\text{K}) \\ &= 0.082057 \text{ L atm mol}^{-1} \text{ K}^{-1} \end{aligned}$$

The value of R depends on the units adopted for the quantities in the equation $pV = nRT$. The various values are:

$$R = 0.082057 \text{ L atm K}^{-1} \text{ mol}^{-1} \text{ (for calculation purpose the value is taken as } 0.0821 \text{ L atm K}^{-1} \text{ mol}^{-1}\text{)}$$

$$R = 8.314 \times 10^7 \text{ erg K}^{-1} \text{ mol}^{-1}$$

$$R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$R = 1.987 \text{ cal K}^{-1} \text{ mol}^{-1}$$

Example 6.6 : At 273 K, 10 mol of a gas is confined in container of volume 224 L. Calculate the pressure of the gas. $R = 0.0821 \text{ L atm mol}^{-1} \text{ K}^{-1}$.

Solution : The ideal gas equation $pV = nRT$ will be used here

$$n = 10 \text{ mol, } R = 0.0821 \text{ atm L K}^{-1} \text{ mol}^{-1}$$

$$V = 224 \text{ L} \quad T = 273\text{K} \quad p = ?$$

On substituting these values in the above equation we get

$$p = nRT/V = (10 \text{ mol} \times 0.0821 \text{ atm L mol}^{-1} \text{ K}^{-1} \times 273\text{K}) / 224\text{L} = 0.99998 \text{ atm} = 1 \text{ atm}$$

6.4 Daltons’ Law of Partial Pressure

The behaviour observed when two or more non-reacting gases are placed in the same



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container is given by Dalton's Law of partial pressures. Dalton's Law states that.

The total pressure exerted by a mixture of non-reacting gases is equal to the sum of the partial pressures of the various gases present in the mixture.

The partial pressure is defined as the pressure the gas would exert if it was alone in the container. Suppose a sample of hydrogen is pumped into a one litre box and its pressure is found to be 0.065 atm. Suppose, further a sample of argon is pumped into a second one litre box and its pressure is found to be 0.027 atm. If both samples are now transferred to a third one litre box, the pressure is observed to be 0.092 atm. For the general case, Dalton's Law can be written as

$$P_{\text{total}} = p_A + p_B + p_C + \dots$$

Where p_A, p_B, p_C, \dots are the partial pressure of gases A, B, C, respectively. This gas laws provide a simple way of calculating the partial pressure of each component, given the composition of the mixture and the total pressure. First we introduce the mole fractions X_A and X_B . These are defined as

$$X_A = \frac{n_A}{n} \quad \text{and} \quad X_B = \frac{n_B}{n}$$

Where n_A and n_B are the number of moles of gas A and B respectively and $n = n_A + n_B$.

Since

$$p_A = n_A RT/V, \quad p_B = n_B RT/V \quad \text{and} \quad p = n RT/V,$$

it follows that

$$p_A = X_A p \quad \text{and} \quad p_B = X_B p$$

This is an exceptionally useful (and simple) way of calculating at partial pressures when the composition and total (measured) pressure of a mixture of gas is known.

Example 6.7 : Atmosphere is often considered mainly as a mixture of nitrogen and oxygen: 76.8% by mass of nitrogen and 23.2% by mass of oxygen. Calculate the partial pressure of each gas when the total pressure is 1 atm.

Solution : The number of moles of each component is

$$p_{N_2} = 76.8 \text{ g} / 28 \text{ g mol}^{-1} = 2.74 \text{ mol}$$

$$p_{O_2} = 23.2 \text{ g} / 32 \text{ g mol}^{-1} = 0.725 \text{ mol}$$

The mole fractions of the components are therefore

$$X_{N_2} = \frac{2.74}{2.74 + 0.725} = 0.791 ; \quad X_{O_2} = \frac{0.725}{2.74 + 0.725} = 0.209$$

The partial pressures are therefore given by

$$p_{N_2} = 0.791 \times 1 \text{ atm} = 0.791 \text{ atm}$$

$$p_{O_2} = 0.209 \times 1 \text{ atm} = 0.209 \text{ atm}$$

6.5 Graham's Law of Diffusion

If we open a bottle of perfume in one corner of a room or burn an incense stick we can feel the smell of the perfume or the incense stick all over the room also. The smell of



perfume or incense stick spreads from one point of the room to the other by mixing with air. This free intermingling of gases when placed in contact with each other is known as **diffusion**.

Diffusion occurs in liquids as well as in gases. **Effusion** is the escape of a gas through a small hole, as in case of a puncture in a tyre.

The experimental observation of the rate of effusion of gases through a small hole in the side of the led Graham (1829) to formulate the following law:

At constant temperature and pressure, the rate of diffusion of a gas is inversely proportional to the square root of its density. Graham's law is applicable to both diffusion and effusion.

If the time for a given volume of gas A to escape is t_A , while the time for the same volume of gas B to escape is t_B , it follows, that,

$t_A/t_B = (\text{rate})_B / (\text{rate})_A = \sqrt{\rho_A / \rho_B}$ where ρ_A and ρ_B are the densities of gases A and B respectively.

The ratio of the densities of the molecules is the same as the ratio of the molecular masses of the gases at the same temperature and pressure.

hence, $t_A/t_B = (\text{rate})_B / (\text{rate})_A = \rho_A / \rho_B = \sqrt{M_A / M_B}$ where M_A and M_B are the molecular masses of gases A and B respectively.



Intext Questions 6.2

- What is the difference between diffusion and effusion.
.....
- Explain why Daltons' law is not applicable to a system of ammonia and hydrogen chloride gas.
.....
- The rates of diffusion of CO_2 and O_3 were found to be 0.29 and 0.271. What is the molecular mass of O_3 if the molecular mass of CO_2 is 44.
.....
- Calculate the pressure exerted by 5.0 mol of carbon dioxide in a 1 litre flask at 47°C using ideal gas equation.
.....

6.6 Kinetic Molecular Theory of Gases (Accounting For the Gas Laws)

To explain the behaviour of the gases theoretically, Clausius, Maxwell and Boltzmann made the following assumptions:

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- (1) Gases consist of large number of tiny particles called molecules.
- (2) The gas molecules are so small and so far apart that the total volume of the molecules is a negligible fraction of the total volume occupied by the gas.
- (3) The molecules are in a state of constant, rapid and random motion colliding with one another and with the walls of the container.
- (4) There are no attractive or repulsive forces between the molecules of the gas.
- (5) The collisions of the molecules among themselves and with the walls of the containing vessel are perfectly elastic, so that there is no loss of energy during collisions.
- (6) The pressure exerted by a gas is due to the bombardment of the molecules on the walls of the containing vessel.
- (7) The kinetic energy of a gas is directly proportional to the absolute temperature of the gas.

On the basis of this model, it is possible to derive the following expression for a gas:

$$pV = \frac{1}{3} m N \overline{C^2}$$

Where p is pressure, V denotes volume, m is the mass of a gas molecule, N is the total number of molecules, and \overline{C} is the root mean square velocity of the gas molecules.

6.6.1 Root Mean Square Velocity

Root mean square velocity is the square root of the average of the squares of all the molecular velocities. Mathematically,

$$\text{RMS Velocity} = \sqrt{(C_1^2 + C_2^2 + \dots + C_N^2)/N}$$

where C_1, C_2, \dots, C_N the molecular velocities.

6.6.2 Average Velocities

This is defined as

$$u_{av} = \frac{u_1 + u_2 + \dots + u_N}{N}$$

and is given by the expression

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

6.7 Distribution of Molecular Speeds

According to Maxwell in a gas all the molecules are in a state of constant rapid random motion and they collide with one another and with the walls of the vessel. During collision the redistribution of the energy takes place. As a result their speed and the kinetic energy



changes. Therefore at any instant different molecules have different speed and hence different kinetic energy. At the given temperature even though the speed of the individual molecule continuously changes, the fraction of the molecules having the same speed remains constant and this is known as **Maxwell-Boltzmann Distribution Law**.

At the given temperature this fraction is denoted by $\frac{dN}{N}$ where dN is number of molecules having the same velocity and N is the total number of the molecules present in the gas. At the given temperature this fraction of the molecule is plotted against the molecular speed as shown as figure 6.6.

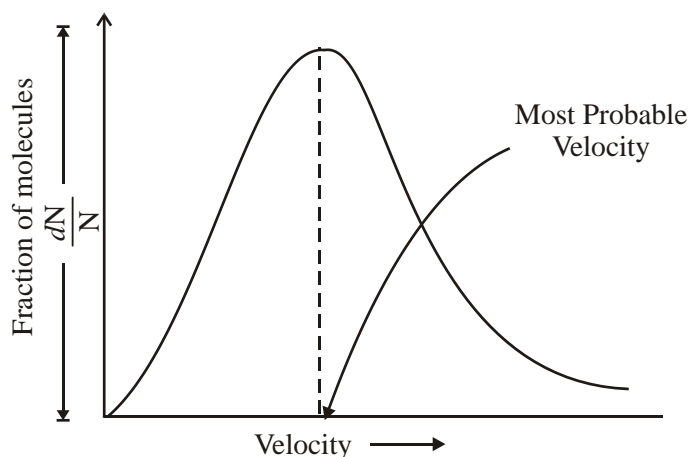


Fig. 6.6 : Maxwells' distribution of velocities at constant temperature

In above Fig. 6.6 the maximum in the distribution curve corresponds to the speed possessed by the highest fraction of the molecule, this is known as **most probable speed**. It may be noted that if the temperature is increased the fraction of the molecule with higher speeds increases thus the most probable speed increases with increase of temperature. The temperature dependence of the distribution of the speed is as shown in Fig. 6.7.

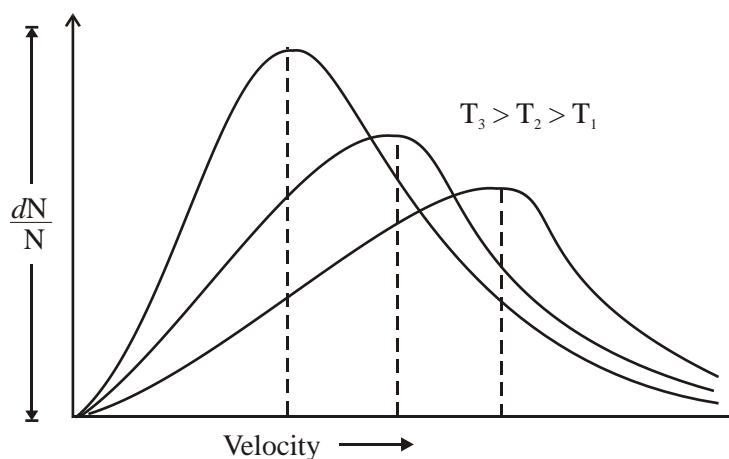


Fig. 6.7 : Effect of temperature on distribution of velocities.



At the given temperature the most probable speed is given by the following expression.

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

the three speeds, root mean square speed, average speed and most probable speed are related by the following expressions

$$u_{rms} : u_{av} : u_{mp} :: \sqrt{3} : \sqrt{8/\pi} : \sqrt{2}$$

and also 1.224 : 1.128 : 1, so

$$u_{rms} > u_{av} > u_{mp}$$

The most probable velocity u_{mp} increases with the use in temperature of a gas.

6.8 Deviation From Ideal Gas Behaviour

The gas laws mentioned above are strictly valid for an ideal gas under all conditions of temperature and pressure. Reas gases show deviations from these laws at low temperature

and high pressure. These deviations can be shown clearly by plotting $\frac{pV}{nRT}$ as a function of pressure at constant temperature,

$$\frac{pV}{nRT} = \frac{V_{observed}}{V_{ideal}} = Z \text{ (compressibility factor)}$$

Gases deviate from ideal behaviour due to the following faulty assumptions of kinetic theory :

1. Volume of the molecules of a gas is negligibly small in comparison to the space occupied by the gas.
2. There is no force of attraction between the molecules of a gas.

Contrary to assumption(1), the volume occupied by the molecules of a gas becomes significant at high pressures. If nb is the volume occupied by the molecules, the actual volume of the gas is $(V - nb)$. Assumption (2) too doesn't hold good as at high pressures molecular interactions start operating. Molecules are dragged back by other molecules which affects the pressure exerted by them on the walls of the container.

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

(P_{real} is observed pressure and $\frac{an^2}{V^2}$ is correction term)

In view of the corrections for pressure and volume, ideal gas equation can be rewritten as

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

This is known as van der Waals equation

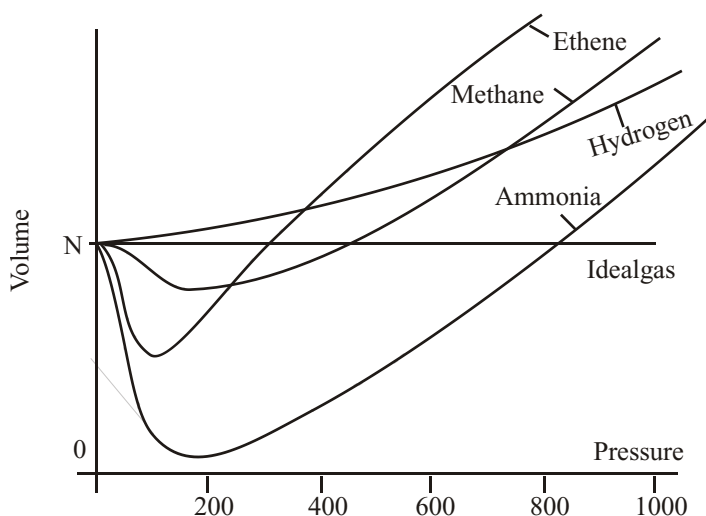


Fig. 6.8 : The plot volume versus P for real gases

6.9 Liquifaction of Gas

Any gas can be liquified at atmospheric pressure if it is cooled sufficiently. Many gases (but not all) can be liquified at ordinary temperature by compressing them.

The conditions of temperature and pressure under which gases liquify were first investigated by Andrews in 1869.

Andrews subjected CO_2 to various pressures at different temperatures and plotted the effect of pressure on volume (Fig. 6.9). The curve obtained at a given temperature is called an *isotherm*. As can be seen in the figure, at 321 K the volume of the gas decreased with the increased pressure approximately in accordance with the Boyle's Law. At 294 K, however, the volume first decreases in accordance with Boyle's Law until the pressure was increased to about 60 atm. At this pressure there was a sudden break in the curve and liquid carbon dioxide appeared. The pressure remained constant until all the gas had been converted into liquid. Subsequent increase of pressure caused practically no change in volume. In accordance with the general rule that extremely high pressures are required to compress liquids appreciably.

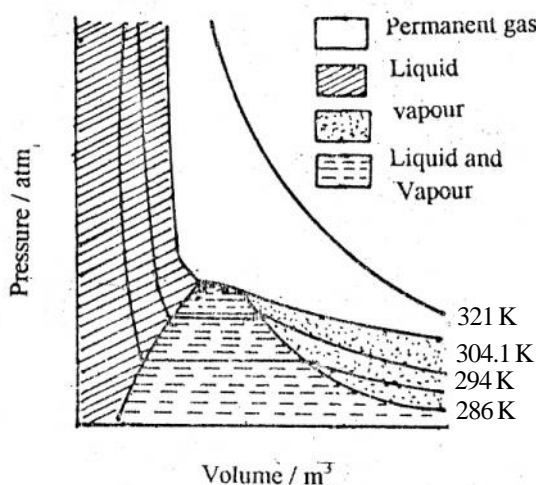


Fig. 6.9 : Isotherms of carbon dioxide

Similar changes took place when the isotherms were constructed for temperatures below 294 K, except that the pressure required to liquify the gas became smaller as the temperature decreased. Andrews found that liquifaction could be brought about at all temperatures below 304.1 K. But above this temperature no liquifaction occurred no matter how much

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pressure was increased. This temperature was therefore called the **critical temperature** for CO_2 . The pressure required to liquify the gas at the critical temperature was called **critical pressure**, and the volume of 1 mole of the substance at the critical temperature and pressure, the **critical volume**.

The temperature above which a gas cannot be liquified, however large the pressure may be is known as critical temperature.

Table 6.2 list values of the critical temperature and pressure critical volume for some common substances.

Table 6.2 : Critical temperatures and critical pressures

Substance	Critical Temperature (K)	Critical Pressure (atm)
Water, H_2O	647	217.7
Sulphur dioxide, SO_2	430	77.7
Ammonia, NH_3	406	112.5
Hydrogen Chloride, HCl	324	81.6
Carbon dioxide, CO_2	304	73.0
Oxygen, O_2	154	49.7
Nitrogen, N_2	126	33.5
Hydrogen, H_2	33	12.8



Intext Questions 6.3

- What are the conditions under which real gases behave as ideal gas.
.....
- Which term in van der waals equation accounts for the molecular volume.
.....
- Calculate the root mean square velocity of ozone kept in a closed vessel at 20°C and 1 atm pressure.
.....
- What is compressibility factor.
.....



What You Have Learnt

- Matter exists in three states, namely, solid, liquid and gas.
- The three states of matter differ in the relative closeness of the molecules constituting them.
- There exists a definite relationship between the pressure, volume, temperature and number of moles of a gas and they are given by Boyle's law, Charle's law and Avogadro's law.



- The gases obeying gas laws are known as ideal gases.
- Dalton's law give the relationship between partial pressures exerted by the non-reacting gases to the total pressure.
- Most of the gases deviate from the ideal behaviour. The deviations of gases from ideal behaviour is due to the wrong assumptions of kinetic molecular theory.
- Real gases can be liquified under appropriate conditions.



Terminal Exercise

1. Draw the graphs of the following :
 - a) p vs V at constant T and n
 - b) $1/V$ vs p at constant T and n
 - c) T vs V at constant p
2. What is the volume occupied by one mole of a gas at STP?
3. The volume of a sample of a gas is 500 mL at a pressure of 1.5 atm. If the temperature is kept constant, what will be the volume of that gas at
 - (i) 1 atm.
 - (ii) 5.0 atm.
4. List the wrong assumptions of kinetic theory of gases which led to van der Waals equation.
5. What is the standard temperature and pressure?
6. What is the lowest possible temperature?
7. CO_2 can not be liquefied at 35°C , however large the pressure may be, Why?
8. A sample of nitrogen gas weighing 9.3 g at a pressure 0.99 atm occupies a volume of 12.4 litres when its temperature is 55K. What will be its volume when the temperature is 220 K? Assume pressure is kept constant.
9. Calculate the volume of one mole of oxygen at 27°C and 2 atm pressure, given that the volume of oxygen at STP is 22.4 litres.
10. What is the Maxwell-Boltzmann Law?



Answers to Intext Questions

6.1

1. Due to more intermolecular distances in gaseous molecule compared to liquid.
2. Boyle Law equation is

$$p_1 V_1 = p_2 V_2$$

$$(.20 \text{ atm}) (500 \text{ mL}) = p_2 (10 \text{ mL})$$

$$p_2 = \frac{(0.20 \text{ atm}) (500 \text{ ml})}{10 \text{ ml}}$$

$$p_2 = 10 \text{ atm.}$$

3. By Avogadro's Law

$$\text{moles of O}_2 = \text{moles of unknown gas}$$

States of matter



Notes

$$\frac{2.00 \text{ g}}{32 \text{ g mole}^{-1}} = \frac{1.75 \text{ g}}{\text{Molecular weight of unknown gas}}$$

$$\text{Molar mass of unknown gas} = \frac{1.75 \times 32}{2.00} = 28 \text{ g mol}^{-1}$$

Molar mass of unknown gas is 28.

6.2

1. Movement of gas molecules through another gas is called diffusion. When gas escapes from a container through a very small opening it is called effusion.
2. Ammonia and hydrogen chloride gases are reacting gases and Dalton's Law is applicable to mixture of non-reacting gases.

$$3. \frac{r_{\text{O}_3}}{r_{\text{CO}_2}} = \left(\frac{M_{\text{CO}_2}}{M_{\text{O}_3}} \right)^{1/2}$$

$$\frac{0.271}{0.290} = \left(\frac{44}{M_{\text{O}_3}} \right)^{1/2}$$

Squaring both sides

$$\frac{(0.271)^2}{(0.290)^2} = \frac{44}{M_{\text{O}_3}}$$

$$M_{\text{O}_3} = \frac{44 \times 0.29 \times 0.29}{0.271 \times 0.271} = 50.4$$

Molecular mass of O₃ = 50.4

4. By ideal gas equation

$$pV = nRT$$

$$p \times 1.0 = (5.0 \text{ mol}) (0.0821 \text{ L atm K}^{-1} \text{ mol}^{-1}) 320 \text{ K}$$

$$p = \frac{(5.0 \text{ mol}) (0.0821 \text{ L atm K}^{-1} \text{ mol}^{-1}) 320 \text{ K}}{1.0 \text{ L}}$$

$$p = 131.3 \text{ atm.}$$

6.3

1. Low pressure and high temperature.
2. b

$$3. u_{rms} = \sqrt{\frac{3RT}{M}}$$

$$= \sqrt{\frac{3 (8.314 \text{ Jk}^{-1} \text{ mol}^{-1}) (293 \text{ K})}{(0.048 \text{ kg mol}^{-1})}} = \sqrt{\frac{(8.314 \text{ Kg m}^2 \text{ s}^{-2} \text{ K}^{-1} \text{ mol}^{-1}) (293 \text{ K})}{0.048 \text{ Kg mol}^{-1}}}$$

$$= 390.3 \text{ ms}^{-1}$$

$$4. Z = \frac{pV_m}{RT} = \text{where } V_m = \text{molar volume}$$

Z is compressibility factor.