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313en05

THE GASEOUS AND LIQUID 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.

You are familiar with gases, liquids and solids in your daily life. You are aware that water can exist as a liquid, a solid (ice) or as a gas (vapour). These are called three *states of matter*. The properties of gaseous state can be explained in terms of large separation of molecules and very weak intermolecular forces. In this lesson, we shall also study about the intermolecular forces in liquids and see how their properties can be explained in terms of these forces.



OBJECTIVES

After reading this lesson, you will be able to:

- differentiate between the three states of matter - solid, liquid and gas;

* 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.



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- describe various intermolecular interactions;
- list the characteristic properties of gases;
- state the gas laws (Boyle's law, Charles's law, Gay Lussac's law and Avogadro's law) and express these 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;
- explain the role of Gay Lussac's law of combining volumes and Avogadro's law in developing the concept of molecule;
- state the postulates of Kinetic Molecular Theory of gases;
- explain the Maxwell's distribution of velocities; and effect of temperature and molar mass of gas on it.
- 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 Waal's equation and explain the significance of van der Waals constants and
- explain the liquifaction of gases with the help of Andrews curves.
- explain the properties of liquids in terms of their structure (molecular arrangement and intermolecular forces);
- differentiate between evaporation and boiling;
- define vapour pressure of a liquid and correlate it with its boiling point;
- define surface tension and explain the effect of various factors on it;
- explain the consequences of surface tension and
- define viscosity of a liquid and correlate it with intermolecular forces.

5.1 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 5.1.

Table 5.1 : 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. 5.1.

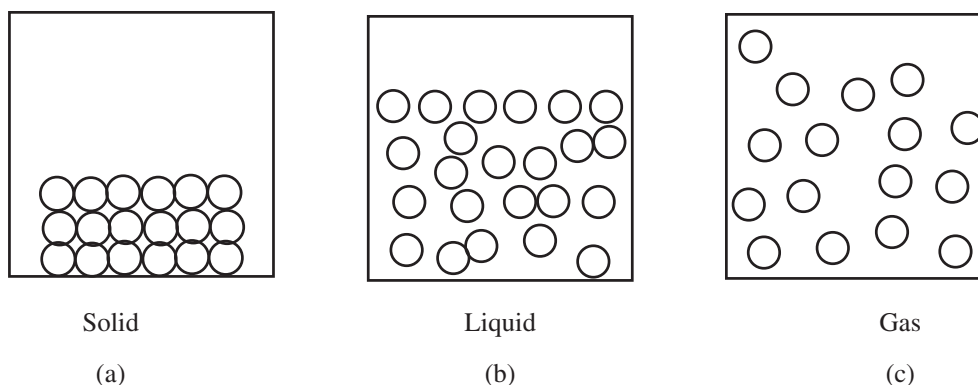


Fig. 5.1 : A simplified picture of particles in solid, liquid and gaseous state

5.2 INTERMOLECULAR INTERACTIONS

Intermolecular interactions are the interactions or forces that operate between the constituent particles of a substance, which may be atoms, molecules or ions. These forces are very weak as compared to intramolecular forces—the forces that operate within a molecule i.e. covalent and ionic bonds. These forces, though weak, are responsible for the existence of condensed phases, namely, liquids and solids.

5.2.1 Types of Intermolecular Interactions

There are four types of intermolecular interactions or forces: (i) London forces; (ii) Dipole – dipole forces; (iii) Dipole – induced dipole forces and (iv) Hydrogen



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bonding. Out of these four, the first three are collectively called **van der Waals forces**. Hydrogen bonding is a type of strong dipole – dipole forces and is *not* included in van der Waals forces. Let us now learn about these forces.

(i) London forces.

Normally we assume that electrons are evenly distributed around nucleus (Fig. 5.2(a)). However, since electrons constantly move around the nucleus, at a particular instant, the distribution of electrons may become uneven around the nucleus (Fig. 5.2 (b)) and result in generation of a dipole with a slight negative charge on one side and an equal positive charge on the opposite side. Thus, an ordinarily non-polar species like an atom of a noble gas like argon or neon becomes a polar species for an instant. This instantaneous dipole would induce dipoles in its neighbours. (Fig 5.3). These dipoles attract each other as their oppositely charged poles are near each other. The very next instant of time, this dipole disappears as the electronic distribution once again becomes symmetrical in this particular atom or molecule. With this, all the induced dipoles also disappear. However, a new instantaneous dipole appears in some other atom or molecule which induces dipoles in its neighbours.

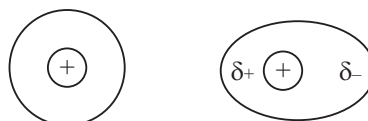


Figure 5.2: Development of instantaneous dipole

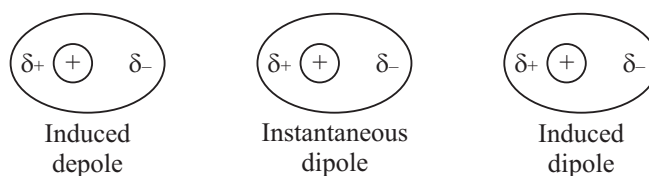


Fig. 5.3: Induced dipoles in neighbours of an atom or a molecule with instantaneous dipole.

This phenomenon continues for ever. At any given instant, a large number of such atoms or molecules distributed randomly develop instantaneous dipoles which induce dipoles in their neighbours. This results in the presence of weak interactions in the substance.

These forces are named after the Germany born physicist Fritz London. London forces are the weakest of all intermolecular forces and operate at extremely short distances. These are also called **dispersion forces**. These are the only forces that are present in atoms or non-polar molecules and are responsible for the existence of their condensed phases. These forces are present universally in all types of molecules, polar or non-polar and contribute majorly toward intermolecular forces present in them.

(ii) Dipole – Dipole Forces

If molecules of a substance are polar in nature, the positive (δ^+) end of one dipole attracts the negative (δ^-) end of the other (Fig. 5.4) Magnitude of these forces depends upon the dipole moment of the substance. These interactions are quite strong as compared to London forces and increase the melting and boiling points of polar compounds (such as ethers) as compared to those of similar non-polar compounds (such as hydrocarbons) that have nearly the same molar mass

**Fig. 5.4:** Dipole-dipole forces

	Compound	Molar Mass /(g mol ⁻¹)	Melting Point/K	Boiling point/K
n-Butane (non-polar)	C ₄ H ₁₀	58	135.2	272.6
Propanone (polar)	(CH ₃) ₂ C = O	58	179.4	329.3

In addition to the dipole-dipole forces, London or dispersion forces also operate between polar molecules.

(iii) Dipole – Induced Dipole Forces

This type of forces operate in mixtures (solutions) of two substances, out of which one is polar in nature and the other is non-polar. The polar molecules induce a dipole in the neighbouring non-polar molecules and an electrostatic force of attraction starts operating between them (Fig 5.5). Magnitude of these forces depend upon two factors

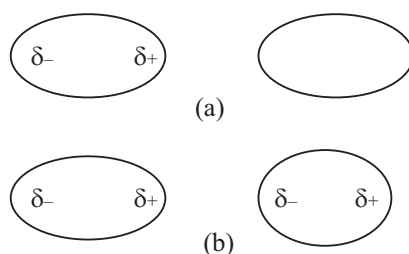


Fig. 5.5 Dipole-induced dipole forces: (a) A pair of polar and a non-polar molecules
(b) Induced dipole in the non-polar molecule

- (a) Dipole moment of the polar molecule. Greater the dipole moment, stronger is the attractive force.

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- (b) Polarizability of the non-polar molecule. More polarizable is the non-polar molecule, greater is the dipole moment of the induced dipole and stronger is the attractive force.

Dispersion or London forces also operate between polar and non-polar molecules and they experience the cumulative effect of both types of forces.

(iv) Hydrogen Bonding

Hydrogen bonding is responsible for abnormally high melting and boiling points of water, ethanol, ammonia, hydrogen fluoride etc. The following table gives the boiling points of hydrides of group 14, 15, 16, and 17 elements. In each group the boiling point of hydrides is increasing with molar mass from top to bottom. The trend is clearly seen in hydrides of group 14. In other groups, the trend can be seen in all the hydrides, except that of the first element in each group i.e. NH_3 (Group 15), H_2O (Group 16) and HF (Group 17) respectively. Their boiling points are exceptionally high due to the presence of hydrogen bonding in these hydrides.

Boiling Points of some Hydrides

Group 14		Group 15		Group 16		Group 17	
Hydride	B. P./K	Hydride	B.P./K	Hydride	B.P./K	Hydride	B.P./K
CH_4	109	NH_3	240	H_2O	373	HF	293
SiH_4	161	PH_3	183	H_2S	212	HCl	188
GeH_4	183	AsH_3	218	H_2Se	232	HBr	207
SnH_4	221	SbH_3	255	H_2Te	271	HI	238

Hydrogen bonding is responsible for some unusual properties of water, like its existence in liquid state over a wide range of one hundred degrees (273 K to 373 K), high heats of fusion and vaporization and its solid form (ice) being lighter than liquid water. Hydrogen bonding plays a crucial role in the structure of DNA by holding together the two helical nucleic acid chains.

5.3 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). 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.

5.3.1 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. 5.6). However when the pressure, p of the gas is plotted against $\frac{1}{V}$ a straight line is obtained (Fig. 5.7). 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. 5.8).

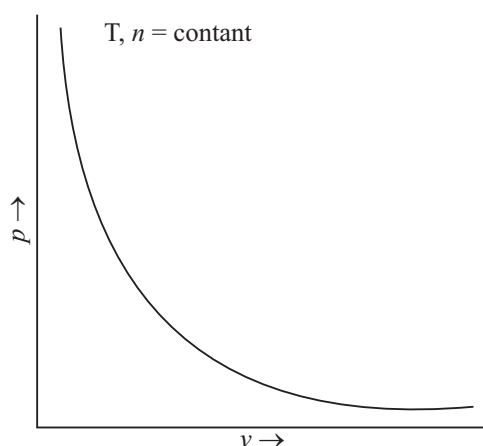


Fig. 5.6 : A graph of p versus V

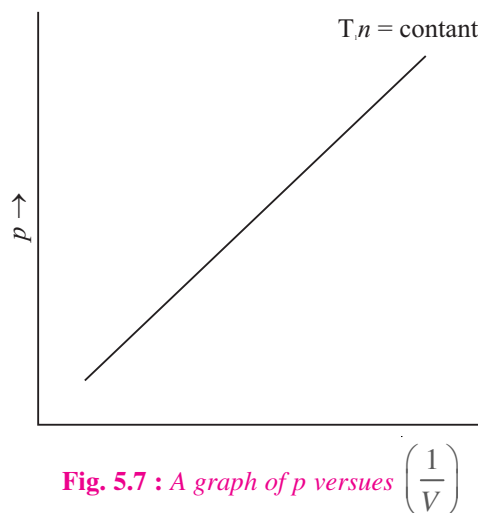


Fig. 5.7 : A graph of p versus $\left(\frac{1}{V}\right)$

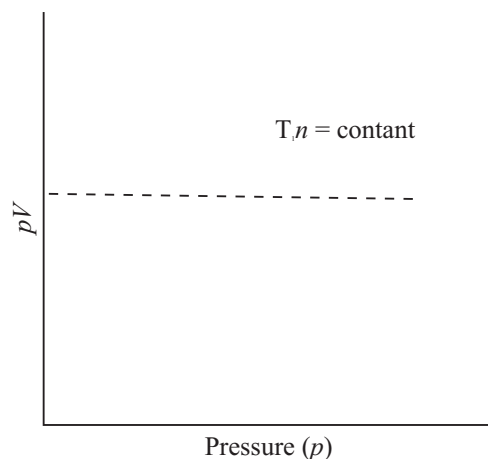


Fig. 5.8 : A graph of pV versus p



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Example 5.1 : 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 5.2 : 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

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

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.

5.3.2 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:

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

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. 5.9.

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).

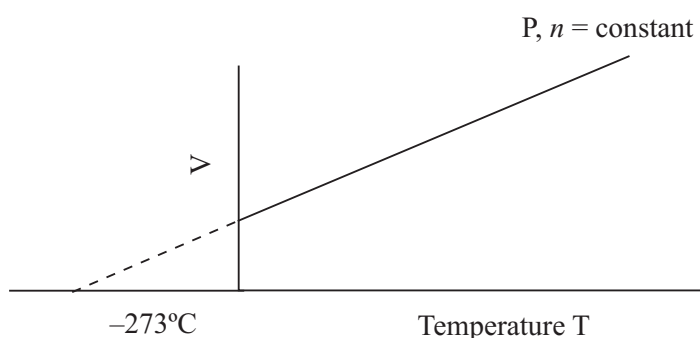


Fig. 5.9 : A graph of V versus T

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.



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5.3.3 Effect of Temperature on Pressure (Gay-Lussac's Law)

This law states that.

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

$$p \propto T$$

$$p = kT$$

Example 5.3 : 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,

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

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

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

On substituting the values we get

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

5.3.4 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

$$\therefore V \propto n$$

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

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

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**.

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 5.4 : 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 :

$$V_1 n_2 = V_2 n_1$$

$$V_2 = \frac{V_1 n_2}{n_1} = \frac{(5.0 \text{ L})(1.8 \text{ mol})}{(0.965 \text{ mol})}$$

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

Example 5.5 : 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 5.1

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?
4. What type of intermolecular interactions are present in (a) Ne gas (b) Carbon monoxide.



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5.3 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

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

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

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

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, $T = 273.15 \text{ K}$, $p = 1 \text{ bar}$ (10^5 Pa) and for 1 mol of gas ($n = 1$), $V = 22.711 \text{ L}$. Consequently,

$$\begin{aligned} R &= pV/nT = (10^5 \text{ Pa}) (22.711 \times 10^{-3} \text{ m}^3) / (1 \text{ mol}) (273.15 \text{ K}) \\ &= 8.314 \text{ J K}^{-1} \text{ mol}^{-1} \end{aligned}$$

At STP conditions used earlier (0°C and 1 atm pressure) the volume occupied by 1 mol of gas is 22.414 L

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



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

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

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

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

Example 5.6 : 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

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

5.4 DALTONS' LAW OF PARTIAL PRESSURE

The behaviour observed when two or more non-reacting gases are placed in the same 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 $n = n_A + n_B$.



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Since

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

it follows that

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

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 5.7 : 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

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

The partial pressures are therefore given by

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

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

5.5 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 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 gases 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.



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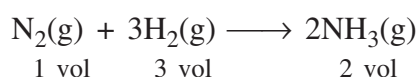
INTEXT QUESTIONS 5.2

1. What is the difference between diffusion and effusion.
2. Explain why Dalton's law is not applicable to a system of ammonia and hydrogen chloride gas.
3. 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.
4. Calculate the pressure exerted by 5.0 mol of carbon dioxide in a 1 litre flask at 47°C using ideal gas equation.

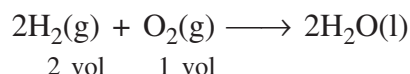
5.6 GAY LUSSAC'S LAW OF COMBINING VOLUMES

One of the laws of chemical combination is Gay Lussac's law of combining volumes.

This law states that in any chemical reaction involving gases the volumes of gaseous reactants and products (if any) bear a simple ratio to one another, when measured under similar conditions of pressure and temperature in the reaction



The ratio of volumes of nitrogen, hydrogen and ammonia is 1 : 3 : 2 when their volumes are measured at the same temperature and pressure. Similarly, in the reaction



hydrogen and oxygen always react in the ratio 2 : 1 by volume.

This law is nothing but the law of definite proportions stated in terms of volume. Gay Lussac's law when combined with gas laws led to the concept of molecules.

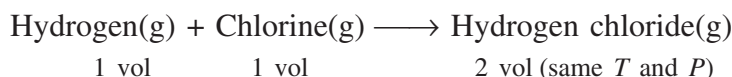
Gay Lussac's Law and the concept of molecule

Prior to the Avogadro's law, a similar hypothesis was put forward by Berzelius. "Equal volumes of all gases, under similar conditions of temperature and



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pressure contain equal number of **atoms**.” This hypothesis, when combined with the Gay-Lussac’s law led to conclusions which contradicted Dalton’s atomic theory. For example consider the gas phase reaction between hydrogen and chlorine to form hydrogen chloride

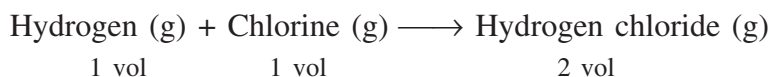


Gay Lussac’s law (experimental result)

Berzelius hypothesised	x number of hydrogen atoms	x number of chlorine atoms	$2x$ number of compound atoms of hydrogen chloride
Divided by x	1 atom of hydrogen	1 atom of chlorine	2 compound atoms of hydrogen chloride
Divided by 2	$\frac{1}{2}$ atom of hydrogen	$\frac{1}{2}$ atom of chlorine	1 compound atom of hydrogen chloride

(‘Compound atom’ was the term used by Dalton for the smallest particle of compounds before of molecule was developed)

Thus, one compound atom of hydrogen chloride contains one-half atom of each of hydrogen and chlorine. This contradicts the Dalton’s atomic theory according to which atoms are indivisible. Therefore fractional atoms ($\frac{1}{2}$ atom each of H and Cl) cannot be present in hydrogen chloride. Due to this contradiction Avogadro modified the Berzelius hypothesis by replacing the term ‘atom’ by ‘molecule’. According to Avogadro’s law, equal volumes of all gases, under similar conditions of temperature and pressure contain equal number of **molecules**”. This law when applied to the same reaction as earlier, modifies the conclusion.

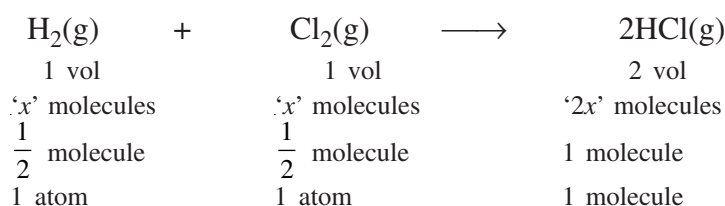


Gay Lussac’s Law

Avogadro’s law	‘ x ’ molecules of hydrogen	‘ x ’ molecules of chlorine	‘ $2x$ ’ molecules of hydrogen chloride
Divide by $2x$	$\frac{1}{2}$ molecule of hydrogen	$\frac{1}{2}$ molecule of chlorine	1 molecule of hydrogen chloride

Thus, now, one molecule of hydrogen chloride, is made from one-half molecule each of hydrogen and chlorine. ‘Molecule’ was accepted as the smallest stable

particle of matter (element or compound) which has the same properties as the bulk of the matter. Further, it was suggested that each molecule of an element may contain more than one atom of the element. Later studies showed that both, hydrogen and chlorine molecules are diatomic and contain two atoms each. Their chemical formulae are H_2 and Cl_2 respectively; one-half molecule, now, would mean one atom of H or Cl. Thus one molecule (rather than compound atom) of hydrogen chloride would be formed by one atom each of hydrogen and chlorine and its formula becomes HCl. Now we may write the reaction as



Thus Gay-Lussac's law and Avogadro's Law led to the concept of 'molecule'.

5.7 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:

- (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:

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

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



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5.7.1 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.

5.7.2 Average Velocities

This is defined as

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

and is given by the expression

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

5.8 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 5.10.

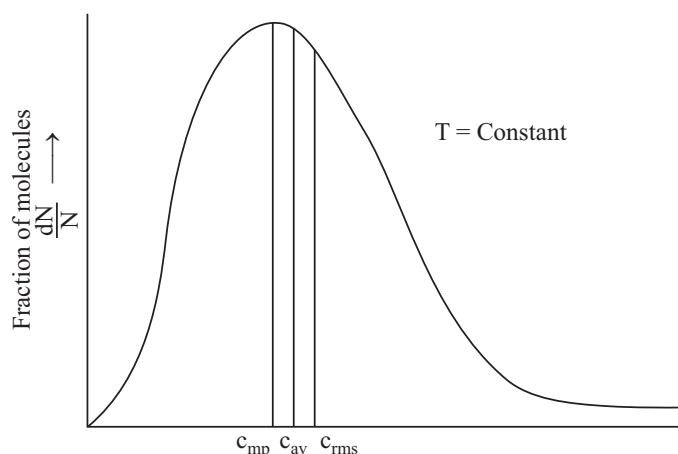


Fig. 5.10: Maxwell's distribution of speeds of molecules at a constant temperature

In the above Fig. 5.10, the maximum in the distribution curve corresponds to the speed possessed by the highest fraction of molecules. This is known as the **most probable speed** c_{mp} . Also shown in the figure are the **average speed**, c_{av} and the **root mean square (rms) speed** c_{rms} . These types of speeds are related to the temperatures, T and the molar mass, M of the gas by the following relations

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

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

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

The relative values of these speeds are

$$c_{mp} : c_{av} : c_{rms} \\ 1 : 1.13 : 1.22$$

Or $0.82 : 0.92 : 1$

From any of the above relations it can be seen that these speeds are related to the temperature and molar mass of the gas.

Dependence of molecular speeds on temperature

The temperature dependence of molecular speeds is shown in Fig. 5.11. On increasing the temperature the fraction of molecules with higher speeds increases and with some speeds decreases. The maxima shifts to higher velocity side but its height decreases.

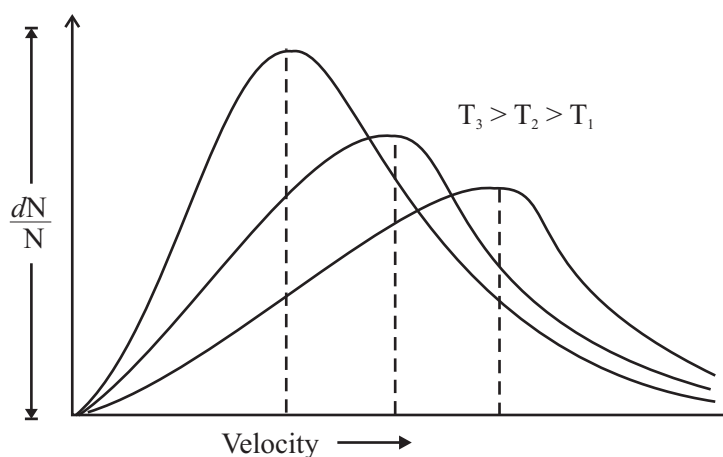


Fig. 5.11: Effect of temperature on distribution of velocities.



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Dependence of molecular speeds on molar mass of the gas

At a constant temperature any of the three types of speeds is inversely proportional to the square root of the molar mass of the gas, that is,

$$C_{\text{mp}} \propto \sqrt{\frac{1}{M}}$$

Hence, at the same temperature, the most probable speed of a lighter gas would be more than that of a heavier gas. Figure 5.12 a shows the distribution curves of H_2 and N_2 gases.

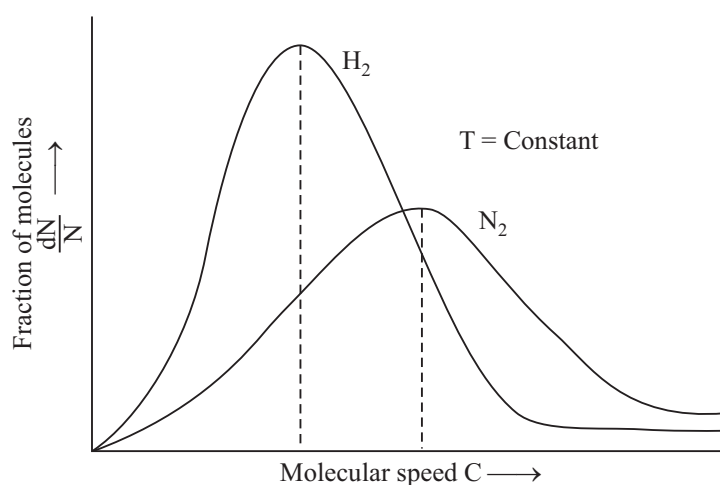


Fig. 5.12 A: Effect of molar mass of the gas on distribution of speeds.

5.9 DEVIATION FROM IDEAL GAS BEHAVIOUR

The gas laws mentioned above are strictly valid for an ideal gas under all conditions of temperature and pressure. Real 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,

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

Such a plot is shown in Fig. 5.13 for an ideal gas and a few real gases. you may note that for in ideal gas $pV = nRT$ hence $\frac{pV}{nRT} = z = 1$. Thus a straight line obtained for ideal gas in this plot, but for real gases diferent curves are obtained.

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.

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

(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

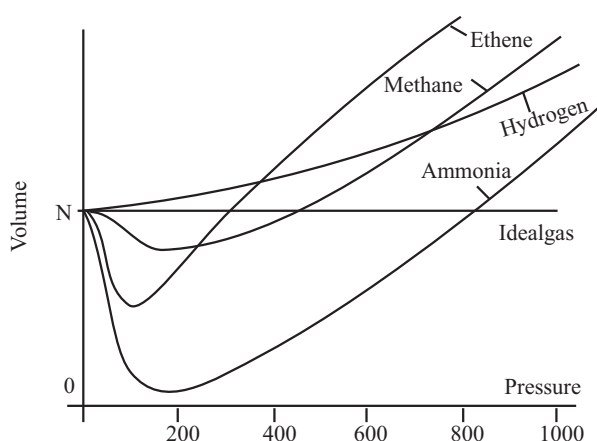


Fig. 5.13 : The plot volume versus P for real gases

5.10 LIQUEFACTION 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. 5.14). 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



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in volume. In accordance with the general rule that extremely high pressures are required to compress liquids appreciably.

Liquefaction of Gases

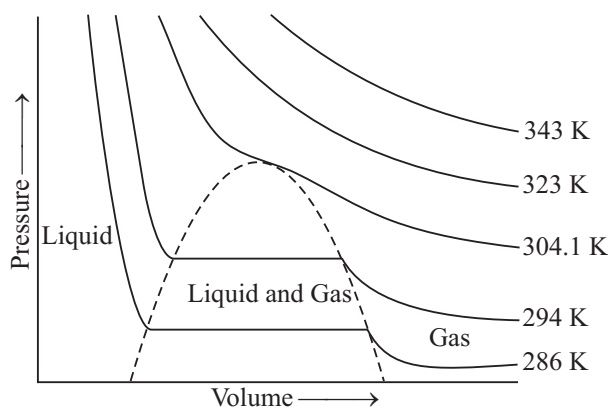


Figure 5.14: Isotherms of carbon dioxide

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

Table 5.2 : 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 5.3

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

5.11 NATURE OF LIQUIDS

Look at Figure 5.1 in which the molecular arrangement has been shown in the three states of matter. What do you notice?

In figure 5.1a, you would find that the molecules are far apart. A gaseous state can be represented by this arrangement. In liquid state (figure 5.1b), molecules are closer as compared to gaseous state. You would notice that they have very little spaces between them. However, there is no order in arrangement of molecules. Further we say that, these molecules can move about, but with lesser speeds than those in gases. They can still collide with one another as in the gaseous state. You would recall that the molecules in gases have very little attraction between them. But in liquid state the attraction between the molecules is comparatively much stronger as compared to that in the gaseous state. The attractions are strong enough to keep the molecules in aggregation. Contrary to this, in solids (Fig. 5.1a) you notice that the molecules are arranged at the closest possible distance.

Solid state is a well ordered state and has very strong intermolecular forces. You would learn more about solids in lesson 8.

We would say, in a gas there is complete chaos due to very weak intermolecular forces, whereas in solids there is a complete order due to strong forces. Liquids fall between gases and solids. Liquid molecules have some freedom of gases state and some order of solid state. Intermolecular forces in liquids are strong enough to keep the molecules close to one another but not strong enough to keep them in perfect order.

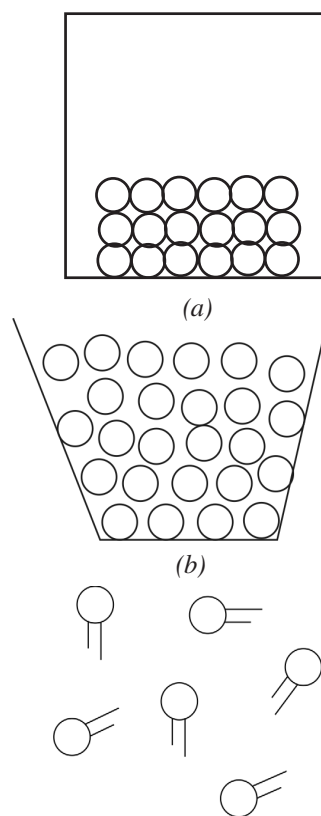


Fig. 5.15 : Arrangement of molecules in (a) solids; (b) liquids and (c) gases



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5.12 PROPERTIES OF LIQUIDS

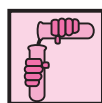
In this section you would learn how the properties of liquids can be explained in terms of molecular arrangement and intermolecular forces. Let us consider a few properties of liquids as examples.

5.12.1 Volume and Shape

You would recall that the liquids (for example water) take the shape of the container in which they are kept. However, they have a definite volume. How can you explain the properties of definite volume and variable shape? In liquids, the attractive forces are strong enough to keep the molecules moving within a definite boundary. Thus, they maintain a definite volume. These intermolecular forces are not strong enough to keep them in definite positions. The molecules can, therefore, move around and take the shape of the container in which they are kept.

5.12.2 Compressibility

Compressibility of a substance is its ability to be squeezed when a force is applied on it. Let us study the compressibility of liquids with the help of the following activity.

**ACTIVITY 5.1**

Aim: To study the compressibility of water.

What is required?

A 5 mL syringe and water.

What to do?

- (i) Take the syringe and fill it with water by pulling out the plunger.
- (ii) Note the volume of water.
- (iii) Press the plunger while blocking the nozzle of the syringe with a finger.

What to observe?

Observe the volume of water in the syringe while pressing the plunger. Does the volume of water change by pressing the plunger? You would observe that it does not change.

The above activity clearly shows that liquids are largely incompressible. It is because there is very little empty space between the molecules. In contrast, the gases are highly compressible because of large empty spaces between their molecules.

The large difference in the free space in gaseous and liquid states becomes evident from the fact that the volume occupied by a given amount of a substance in liquid state is *100-1000 times less* than that in the gaseous state.

5.12.3 Diffusion

Diffusion is the process of spreading of a substance from a region of higher concentration to a region of lower concentration. Let us study the phenomenon of diffusion in liquids with the help of the following activity.



ACTIVITY 5.2

Aim : To study the phenomenon of diffusion through water.

What is required?

A glass, water, blue ink and a dropper.

What to do?

- (i) Take some water in the glass.
- (ii) Add a few drops of blue ink into water with the help of a dropper.

What to observe?

Observe the water and ink in the beaker.

Initially the ink does not mix with water. After some time it starts spreading slowly. After a few hours the whole of water in the glass becomes coloured due to diffusion of ink through water.

The above activity demonstrates that diffusion occurs in liquids. Why does it happen? Because the molecules of both the liquids are moving and help in the diffusion process.

5.12.4 Evaporation

You know that water left in an open pan evaporates slowly until the pan becomes dry. Evaporation is the process by which a liquid changes into vapour. It occurs at all temperatures from freezing point to boiling point of the liquid.

In a liquid, at any temperature, a small fraction of the molecules is moving with relatively high velocity. Such molecules have high kinetic energy. These can overcome the intermolecular attractive forces and escape through the surface of the liquid.

Rate of evaporation of a liquid depends on a number of factors. For example, more is the surface area, faster will be the evaporation. For faster drying, we



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increase the surface area by spreading the wet clothes. If we supply heat to the liquid, evaporation is faster. The wet clothes dry faster in the sun. The increase in temperature increases the kinetic energy of the molecules of the liquid and the liquid evaporates at a faster rate. We feel cool after the bath. Why do we feel so? It is because during evaporation water takes the heat from our body and we feel cold.

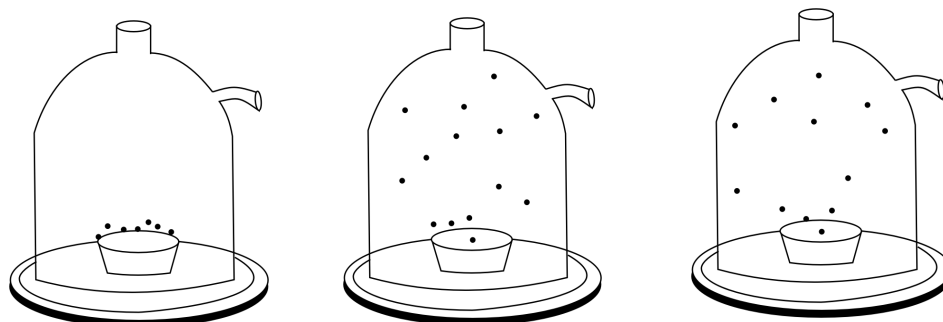
Now let us compare the rate of evaporation of two liquids, for example, water and alcohol. Which of these two liquids evaporates faster? You must have experienced that alcohol evaporates faster. Why does this happen? The number of molecules escaping from a liquid depends upon the attractive forces. When these forces are stronger, fewer molecules escape. In alcohol, these attractive forces are weaker than those in the water. Hence, alcohol evaporates faster than water.

5.13 VAPOUR PRESSURE AND BOILING POINT

In the previous section you have learnt that liquids evaporate when kept in an open vessel. Different liquids evaporate to different extent under similar conditions. The extent of evaporation of a liquid is measured with the help of **vapour pressure** of a liquid. In this section, you will study about it and also about the boiling point of a liquid.

5.13.1 Vapour Pressure of a Liquid

You know that a liquid placed in an open vessel evaporates completely. If, however, the liquid is allowed to evaporate in a closed vessel, say in stoppered bottle or a bell jar, evaporation occurs, but after some time the level of the liquid does not change any further and becomes constant. Let us understand how does it happen. In the closed vessel, the molecules evaporating from the liquid surface are confined to a limited space. These molecules may collide among themselves or with the molecules of air and some of them may start moving towards the surface of the liquid and enter into it. This is known as condensation. In the



Initially molecules evaporate

After some time condensation begins

At equilibrium the rates of evaporation and condensation become equal

Fig. 5.16 : Establishing (vapour liquid) equilibrium under a evacuated jar

beginning, rate of evaporation is greater than the rate of condensation. But as more and more molecules accumulate in the space above the liquid, rate of condensation gradually increases. After some time, rate of evaporation becomes equal to the rate of condensation and an equilibrium state is reached (Fig. 5.16). The number of molecules in the vapour above the liquid becomes constant. These molecules exert certain pressure over the surface of the liquid. This pressure is known as **equilibrium vapour pressure, saturated vapour pressure** or simply as **vapour pressure**. The vapour pressure of a liquid has a characteristic value at a given temperature. For example, vapour pressure of water is 17.5 Torr and that of benzene is 75.00 Torr at 20° C. The vapour pressure of a liquid increases with increase in temperature. It is so because at a higher temperature more molecules have sufficiently high energy to overcome the forces of attraction and escape to form vapour. A plot of vapour pressure as a function of temperature is called **vapour pressure curve**. Figure 5.17 depicts the vapour pressure curves of some liquids.

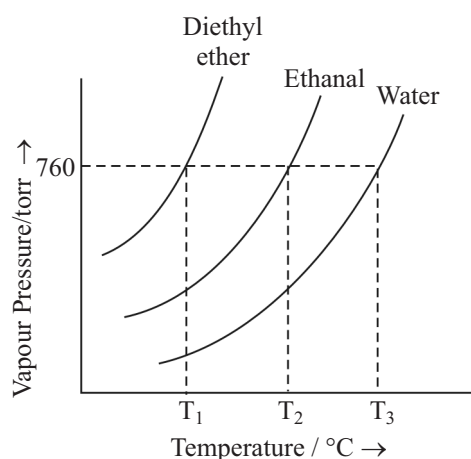


Fig. 5.17 : Vapour pressure curves of some liquids.

What would happen if we remove some of the vapour from the closed vessel. Would the vapour pressure of the liquid increase, decrease or remain constant? Vapour pressure of the liquid would remain constant at that temperature. In the beginning, the vapour pressure would decrease after the removal of the vapour, but soon more liquid would evaporate to maintain the equilibrium and the original vapour pressure would be restored. So the vapour pressure of a liquid has a definite value at a particular temperature.

5.13.2 Boiling

You must have seen the formation of bubbles at the base of a vessel, in which a liquid is heated. The rate of formation of bubbles increases with increase in heat supplied. What are the bubbles made up of? The first bubbles that you see are of the air, which is driven out of the liquid by increase in temperature. After some



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time, bubbles of the liquid are formed throughout vapour. These bubbles rise to the surface and break. When this happens, we say that the liquid is boiling. The bubbles in the liquid rise and break form only if its vapour pressure is equal to the atmospheric pressure.

The temperature at which boiling occurs is called the **boiling point** of the liquid. At this temperature the vapour pressure of the liquid is equal to the atmospheric pressure. The boiling point, therefore, depends upon the atmospheric pressure. For example, water boils at 100°C at 760 Torr and at 97.7°C at 700 Torr.

The normal boiling point of a liquid is defined as the temperature at which the vapour pressure of a liquid is equal to one atmosphere or 760 Torr.

The boiling point of a liquid depends upon its nature. A more volatile liquid would boil at a lower temperature than a less volatile liquid. You can again refer to figure 5.3 and note that diethyl ether boils at a much lower temperature than water, because it is highly volatile liquid. The boiling point of ethanol lies in between those of diethyl ether and water. Vapour pressures or boiling points of liquids give us an idea of the strength of attractive forces between molecules in liquids. Liquids having lower boiling points have weaker attractive forces in comparison to those having higher boiling points.

You can make a liquid boil at temperature other than its normal boiling point. How? Simply alter the pressure above the liquid. If you increase this pressure, you can increase the boiling point and if you can decrease this pressure you decrease the boiling point. On the mountains, the atmospheric pressure decreases and therefore boiling point of water also decreases. People living on hills face problem in cooking their meals. They, therefore, use pressure cooker. How food is cooked faster in it? The lid of pressure cooker does not allow water vapours to escape. On heating the water vapours accumulate and the inside pressure increases. This makes the water boil at a higher temperature and the food is cooked faster.

5.13.3 Evaporation and Boiling

Evaporation and boiling, both involve conversion of a liquid into vapour and appear to be similar. However, they differ from each other in some aspects. Evaporation occurs at all temperatures from freezing point of a liquid to its boiling point, while boiling occurs at a definite temperature only i.e, at its boiling point. Evaporation occurs slowly while boiling is a fast process. Evaporation of a liquid occurs at its surface alone while boiling occurs throughout the liquid. These differences between evaporation and boiling have been summarized in Table 5.3.

Table 5.3 : Differences between evaporation and boiling

S.No.	Evaporation	Boiling
1.	It takes place at all temperatures.	It takes place at a definite temperature.
2.	It is a slow process.	It is a fast process
3.	It occurs only at the surface of the liquid.	It occurs throughout the liquid.



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INTEXT QUESTIONS 5.1

1. Match the following.

Column I

- (i) Liquids have a definite volume.
- (ii) Liquids acquire the shape of their container.
- (iii) Liquids are largely incompressible.

Column II

- (A) The molecules in a liquid can move about.
- (B) The molecules in liquids are close and have very little free space.
- (C) The inter molecular forces liquids strong enough to keep the molecules moving with in a definite space.

2. When a liquid is heated till it starts boiling.

- (i) What are the small bubbles that appears initially at the bottom and sides of the vessel made up of?
- (ii) What are the large bubbles that form in the boiling liquid made up of?

3. Liquids A, B and C boil at 65°C, 120°C and 90°C respectively. Arrange them in the decreasing order of the strength of intermolecular forces.

5.14 SURFACE TENSION

Liquids show the effects of inter molecular forces most dramatically in another property, namely, **surface tension**. Any molecule in the interior of liquid is equally attracted by neighbour molecules from all sides and it does not experience any 'net' force. On the other hand, any molecule at the surface of a liquid is attracted by other molecules at the surface of the liquid or below it. Due to the



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imbalance of forces, any molecule at the surface experiences a net inward pull (Figure 5.18). As a result, the surface is under tension as if the liquid were covered with a tight skin (or stretched membrane). The phenomenon is called *surface tension*. Quantitatively, the **surface tension** is defined as the force acting on an imaginary line of unit length drawn on the surface of the liquid and acting perpendicular to it towards the liquid side as shown in Figure 5.5. It is represented by the Greek letter *gamma*, γ . Its SI unit is newton per metre (N m^{-1}) and CGS unit is dyne per centimetre (dyne cm^{-1}). The two units are related as : $1 \text{ N m}^{-1} = 10^3 \text{ dyne cm}^{-1}$

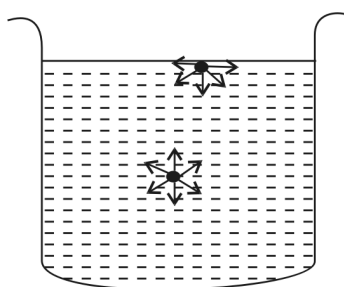


Fig. 5.18 : Forces acting on molecules, at the surface and in bulk of liquids

Surface molecules of a liquid experience a constant inward force. Therefore they have a higher energy than the molecules in the bulk of the liquid. Due to this reason liquids tend to have minimum number of molecules at their surface. This is achieved by *minimising the surface area*. In order to increase the *surface area* more molecules must come to the surface. This can happen only if some energy is supplied or work is done. *The energy supplied (or work done) for increasing the surface area of a liquid by a unit amount is known as its surface energy*. Its units are joule per square metre J m^{-2} or N m^{-1} (since $1\text{J} = 1\text{N m}$). Thus dimensionally, the surface tension and surface energy are similar quantities and they have the same numerical value.

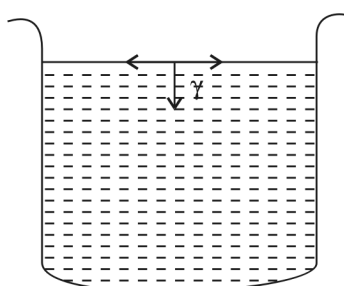


Fig. 5.19 : Surface tension force acting on the surface of a liquid.

Effect of Temperature

On raising the temperature surface tension of a liquid decreases. It completely vanishes at the critical temperature. This happens due to the following two factors:

- On heating, the liquids expand. This increases the intermolecular distances.
- On heating, the average kinetic energy of molecules and hence their chaotic motion increases.

Due to both of these factors, the intermolecular forces become weak and the surface tension decreases.

Effect of Adding Surface Active Solutes

The solutes which get more concentrated on the surface of the liquid than in the bulk are called **surface active solutes** or **surfactants**. Alcohols are examples of such substances. Their addition to a liquid lowers its surface tension. The cleaning action of soaps and detergents is based on this fact.

Some Effects of Surface Tension

Surface tension results in many interesting and important properties of liquids. Let us now study some of them.

(i) Spherical Shape of liquid drops

You have already learnt that liquids tend to have a minimum surface area. For a given volume, the geometrical shape having minimum surface area is a sphere. Hence, liquids have a natural tendency to form spherical drops, when no external force acts on them. Rain drops are distorted spheres and the distortion is due to the friction of air.

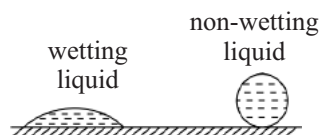


Fig. 5.20 : Wetting and non-wetting liquids on the surface of a solid.

(ii) Wetting and Non-wetting properties

When a drop of liquid is placed on a solid surface, the force of gravity should cause it to spread out and form a thin layer (Fig. 5.20). Such a liquid is called a **wetting liquid**. This happens in case of most of the liquids. For example, drops of water or alcohol spread out on the surface of glass. Some liquids behave differently. When a drop of mercury is placed on the surface of glass, it does not spread out (Fig. 5.20). Such liquids are called **non-wetting liquids**.



Notes



Notes

Wetting or non-wetting nature of a liquid depends upon two types of forces. The intermolecular attractive forces between molecules of a liquid are called **cohesive force** while those between the molecules of the liquid and the solid (whose surface is in contact with the liquid) are called **adhesive forces**. If adhesive forces are stronger than cohesive forces, the liquid would be wetting in nature and when cohesive forces are stronger than adhesive forces it would be non-wetting in nature on the surface of a particular solid.

(iii) Capillary Action

Let us carry out the following activity.

**ACTIVITY 5.3**

Aim : To study the capillary action.

What is required?

Glass capillary tubes, water, mercury and two petri dishes.

What to do?

- (i) Take some water in a petri dish
- (ii) Dip one end of a 3-4 cm long capillary in it.
- (iii) Take some mercury in another petri dish.
- (iv) Dip one end of another 3-4 cm long capillary in it.

What to observe?

Observe the levels of water and mercury in the capillaries. Is it below or above the levels of the liquids in petri dishes?

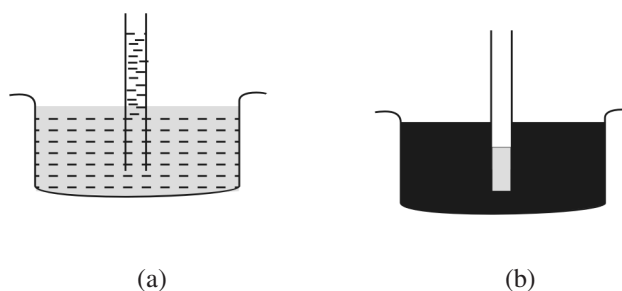


Fig. 5.21 : Capillary Action

You would observe that when one end of a capillary tube is dipped in water, it rises in the capillary as shown in Fig. 5.21(a). On the other hand when one end of

a capillary tube is dipped in mercury, its level falls in the capillary as in Fig. 5.21(b).

The phenomenon of rise or fall of a liquid in a capillary is known as **capillary action**. The rise of water in the glass capillary is due to its wetting nature as the adhesive forces are stronger than cohesive forces. Water tends to increase the area of contact with glass wall of the capillary by rising in it. Mercury being non-wetting with respect of glass (its cohesive forces are stronger than adhesive forces) tends to minimise the area of contact by depressing inside the capillary

(iv) Curved meniscus

When a wetting liquid such as water is taken in a glass tube, the liquid tends to rise slightly along the walls of the tube for increasing its area of contact with glass. The surface of the liquid (meniscus) becomes curved. It is concave in shape [Fig. 5.22(a)]. When a non-wetting liquid like mercury is taken a glass tube, it tends to decrease its area of contact and depresses along the walls of the glass tube. The meniscus is convex in shape in this case [Fig. 5.22(b)].

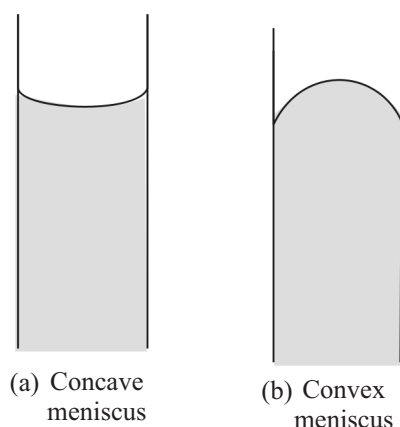


Fig. 5.22 : Curved meniscus of liquids

5.15 VISCOSITY

Every liquid has the ability to flow. It is due to the fact that molecules in a liquid move freely, although within a limited space. Water flows down a hill *under gravitational force* or through pipes when forced by a pump. Some external force is always required for a liquid to flow. Some liquids like glycerol or honey flow slowly while others like water and alcohol flow rapidly. This difference is due to the *internal resistance to flow* which is called **viscosity**. The liquids with higher viscosity flow slowly and are more viscous in nature like glycerol or honey. Water and alcohol have lower viscosity and are less viscous in nature.



Notes



Notes

They flow more rapidly.

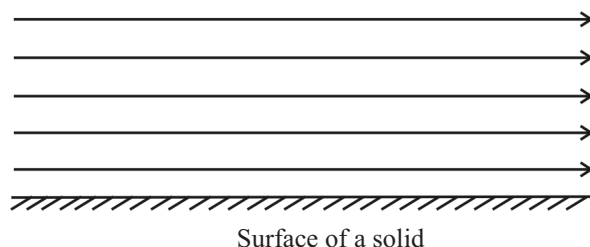


Fig. 5.23 : Flow of different layers of a liquid

The viscosity is related to the intermolecular forces. Stronger the intermolecular forces more viscous are the liquids. Let us understand this with the help of Figure 5.9. When a liquid flows steadily, it flows in different layers with one layer sliding over the other. Such a flow is known as **laminar flow**. Consider a liquid flowing steadily on a plane surface. The layer closest to it is almost stationary due to adhesive forces. As the distance of the layer from the surface increases, its velocity increases. Thus different layers move with different velocities. Due to intermolecular forces (cohesive forces) each layer experiences a force of friction from its adjacent layers. This force of friction, f between two layers depends upon:

- (i) area of contact between them A .
- (ii) distance between the layers, dx .
- (iii) difference in velocity between the layers, du .

These quantities are related as

$$f = \eta A \frac{du}{dx}$$

Here η (Greek letter 'eta') is called the coefficient of viscosity and $\frac{du}{dx}$ is the *velocity gradient* between the layers.

If $A = 1 \text{ cm}^2$, $du = 1 \text{ cm s}^{-1}$ and $dx = 1 \text{ cm}$, then

$$f = \eta$$

Thus, coefficient of viscosity is the force of friction between two parallel layers of the liquid which have 1 cm^2 area of contact, are separated by 1 cm and have a velocity difference of 1 cm s^{-1} . It may be noted that f is also equal to the **external force** which is required to overcome the force of friction and maintain the steady flow between two parallel layers having A area of contact, and which are dx distance apart and moving with a velocity difference of du .

Units

CGS unit of viscosity is $\text{dyne cm}^{-2}\text{s}$. This unit is also known as **poise (P)**. The SI unit of viscosity is $\text{N m}^{-2}\text{s}$ or Pa s . The two units are related as :

$$1 \text{ Pa s} = 10 \text{ P}$$

The unit poise is found to be too large and its submultiples **centipoise** ($1 \text{ cP} = 10^{-2} \text{ P}$) and **milli poise** ($1 \text{ mP} = 10^{-3} \text{ P}$) are used for liquids and micropoise ($\mu\text{P} = 10^{-6} \text{ P}$) is used for gases.

Effect of Temperature

Viscosity of a liquid decreases on raising the temperature. It is due to decrease in intermolecular forces on heating as discussed in previous section (Section 5.4).

**INTEXT QUESTIONS 5.5**

- Fill in the blanks.
 - A molecule at the surface of a liquid has energy than the one within the liquid.
 - Surface tension of liquid on cooling.
 - Meniscus of a non-wetting liquid is in shape while that of a wetting liquid is in shape.
 - When one end of a glass capillary tube was dipped in a liquid, the level of liquid inside the capillary was observed to fall. The adhesive forces in this liquid are than the cohesive forces between the liquid and glass.
 - Liquid X is more viscous than liquid Y. The intermolecular forces in Y are than in X.
- What are the SI units of
 - Surface tension.
 - Coefficient of viscosity
- Why do liquids have a tendency to acquire minimum surface area?

**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.



Notes

MODULE - 3

States of Matter

The Gaseous and Liquid State



Notes

- Intermolecular interactions present depend upon the nature of the substance. Various types of interactions are London or dispersion forces, dipole-dipole dipole induced dipole forces and hydrogen bonding.
- 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.
- Gay Lussac's law of combining volume and Avogadre's law led to the concept of molecule.
- 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.
- In liquids the intermolecular force are quite strong as compared to gases but weak enough to allow the molecules to move within a limited space and the intermolecular distance is short.
- Liquids have definite volume but no definite shape, are almost incompressible and can diffuse.
- Liquids evaporate and exert a definite vapour pressure at specified temperature.
- Boiling point is the temperature at which the vapour pressure of the liquid becomes equal to the external pressure.
- Surface tension is the force acting on an imaginary line of unit length drawn on the surface of the liquid and acting perpendicular to it towards the liquid side.
- Due to surface tension, liquids tend to have minimum surface area and show the phenomena of capillary rise or fall and curved meniscus.
- Viscosity is the internal force of friction to the flow of liquid.



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 (0°C , 1 bar pressure)?
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 Waal's 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?
11. Explain the following properties of liquids on the basis of their structure:
(i) Volume (ii) Shape (iii) Compressibility (iv) Ability to flow
12. Why diffusion can occur in liquids. Explain.
13. Define (i) vapour pressure and (ii) boiling point.
14. Differentiate between evaporation and boiling.
15. Explain the effect of temperature on vapour pressure of a liquid.
16. Define surface tension and give its CGS and SI units.
17. What is surface energy?
18. Why is energy required to increase the surface area of a liquid?
19. What is the effect of addition of a surface active substance on the surface tension of a liquid.
20. Why are liquid drops spherical in shape?
21. What are wetting and non-wetting liquids?
22. The cohesive forces acting in liquids A and B are C_1 and C_2 respectively and $C_1 > C_2$ Which of them would have higher surface tension.
23. Liquid A rises in glass capillary tube. If one drop of it is put on a plane glass surface, would it spread out or not. Explain.
24. A liquid forms a convex meniscus in glass tube. Comment on its nature.
25. Define viscosity.
26. What is coefficient of viscosity?



Notes



Notes

27. Give CGS and SI units of coefficient of viscosity.
28. What is the effect of temperature on (i) vapour pressure (ii) surface tension and (iii) viscosity of a liquid?



ANSWERS TO INTEXT QUESTIONS

5.1

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

moles of O_2 = moles of unknown gas

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

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

Molar mass of unknown gas is 28.

4. (a) Dispersion or London Forces (b) dipole-dipole interactions and dispersion forces.

5.2

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.

$$3. \quad \frac{r_{O_3}}{r_{CO_2}} = \left(\frac{M_{CO_2}}{M_{O_3}} \right)^{1/2}$$

$$\frac{0.271}{0.290} = \left(\frac{44}{M_{O_3}} \right)^{1/2}$$

Squaring both sides

$$\frac{(0.271)^2}{(0.290)^2} = \frac{44}{M_{O_3}}$$

$$M_{O_3} = \frac{44 \times 0.29 \times 0.29}{0.271 \times 0.271} = 50.4$$

Molecular mass of $O_3 = 50.4$

4. By ideal gas equation

$$pV = nRT$$

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

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

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

5.3

1. Low pressure and high temperature.
2. b

$$\begin{aligned} 3. \quad u_{rms} &= \sqrt{\frac{3RT}{M}} \\ &= \sqrt{\frac{3 (8.314 \text{ Jk}^{-1} \text{ mol}^{-1}) (293 \text{ K})}{(0.048 \text{ kg mol}^{-1})}} \\ &= \sqrt{\frac{(8.314 \text{ Kg m}^2 \text{ s}^{-2} \text{ K}^{-1} \text{ mol}^{-1}) (293 \text{ K})}{0.048 \text{ Kg mol}^{-1}}} \\ &= 390.3 \text{ ms}^{-1} \end{aligned}$$

4. $Z = \frac{pV_m}{RT}$ = where V_m = molar volume
Z is compressibility factor.

5.4

1. (i) C; (ii) A; (iii) B
2. (i) Air (ii) Liquid.
3. $B > C > A$



Notes



Notes

5.5

- more
 - increases
 - convex; concave
 - stronger
 - weaker
- N m^{-1} ; $\text{N m}^{-2}\text{s}$
- Molecules in the surface of a liquid have higher energy due to an inward force on them. Therefore liquids tend to have minimum number of molecules in the surface or have minimum surface area.