

States of Matter - Gas and Liquid

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2.1 Introduction

It is not possible for any chemist to study a single molecule, but she/he can study a group of molecules existing in nature. **A group of molecules is called the matter.** The matter is made up of small particles. Matter is in three states, solid, liquid and gas, the other two states are known as plasma and Bose Einstein condensate.

Solid substances have fixed volume, definite shape and surface. Liquid substances have fixed volume and surface. They do not possess shape of their own, but take up the shape of the container in which they are poured. Gases do not have fixed volume, definite shape or surface. They acquire the shape and volume of the container. The physical state of matter can be changed by changing temperature. e.g. at 273 K temperature the H₂O is in solid state (ice), at higher than that temperature H₂O is in liquid state (water) and at 373 K temperature in gaseous state (vapour). The physical properties of a substance can be changed by changing its physical state, but the chemical properties cannot be changed. Sometimes the rate of chemical reaction changes by changing the physical state. During the chemical calculation, it is most (important) essential to have the information about the physical state of substances (reactant or product), and hence, it is essential to study the physical state of matter, factors affecting it and some important laws related to that.

The deciding factors of the physical state of matter are intermolecular forces, molecular interaction and effect of thermal energy on the motion of particles. We shall study the gaseous and liquid state of matter in this unit, so let us study these factors.

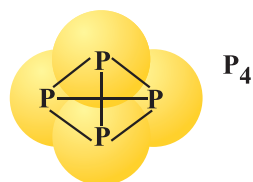
States of matter and intermolecular attractive forces : Very weak attractive force existing between molecules are called intermolecular attractive forces (van der Waals'

attractive force). It is universal and exists in all the physical states of matter. However this type of weak attractive force are hidden under strong attractive forces (chemical bonds) present in a substance. van der Waals' forces depend upon the following factors.

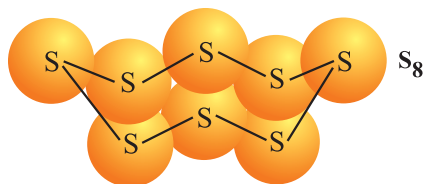
(1) shape of molecule (2) number of electrons present in (3) contact surface area of a molecule (4) average intermolecular distance.

These factors affect the physical properties of a substance viz. melting point and boiling point. e.g. (1) Melting point of yellow phosphorus (P_4) is less than that of Rhombic sulphur (S_8).

The reason for this can be understood by the following structures. Yellow phosphorus (P_4) a molecule having four P atoms and it has $4 \times 15 = 60$ electrons. Rhombic sulphur (S_8) is a molecule having 8 S atoms and it has $8 \times 16 = 128$ electrons. Thus the size (volume) and contact surface area of phosphorus is less than rhombic sulphur (S_8); hence the existing van der Waals' force in P_4 is weaker than S_8 hence the melting point of yellow phosphorus is less than rhombic sulphur.



Yellow phosphorus (P_4)



Rhombic sulphur (S_8)

The van der Waals' forces of attraction are different like (1) Dispersion forces or London forces (2) Dipole-dipole forces and (3) Dipole-induced dipole forces.

(1) Dispersion forces or the London forces : This force of attraction was first proposed by the German scientist Fritz London, so it is known as the London forces. Generally, in atoms of non-polar molecules, their electronic charge cloud is distributed symmetrically. Now, in such atoms or molecules the temporary

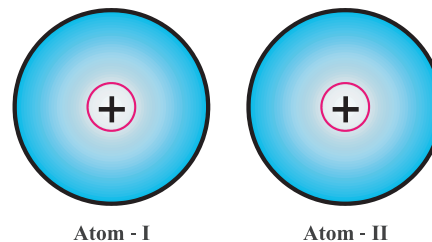


Fig 2.1 (i) The charge cloud is distributed equally in both the atoms

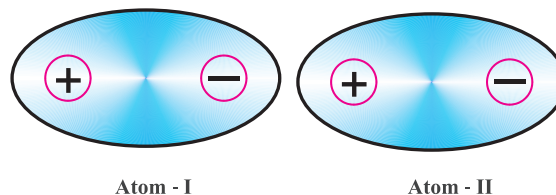


Fig 2.1 (ii) The electron density is more on right hand side in atom I. Its effect is experienced in atom II

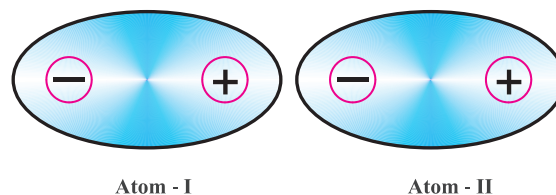
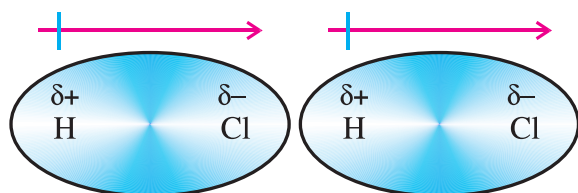


Fig 2.1 (iii) The electron density is more on left hand side. Its effect is experienced in Atom II

dipolarity is developed which can be explained as below. As shown in Figure 2.1 two atoms (atom-I and atom-II), the electron cloud is distributed symmetrically. When two such atoms come close to each other, it so happens that in one atom (atom-I) momentarily, the electronic charge density of atom-I undergoes the dispersion as shown in Figure 2.1 (ii). Hence, electron density will move towards the right hand side pole. So, the left hand side pole will be in shortage of that, therefore atom-I becomes temporarily dipolar. Now, the other atom (atom-II) which comes in its contact, it realises its effect and hence, the dispersion in the symmetrical electron density and the dipole character is induced in atom-II. The pole of right hand side of atom-I where the electron density is more and the atom II which comes in contact of that pole realises the shortage of electron density, so that, at another pole the electron density increases. Thus, the temporary dipolarity is created in atom. The opposite pole of atom-I and II comes in contact, that develops temporary force of attraction. Similarly, as shown in Figure 2.1 (iii) the temporary

can be explained. Such a force of attraction can also be explained in two molecules. This type of force of attraction in atoms or molecules, there is a temporary dispersion in electron density that affects the electron density of nearby atom or molecules. So the force of attraction develops due to such effect is called dispersion force.

(2) Dipole-Dipole forces : The molecules which are made up of the atoms having more difference in their electronegativities are always dipolar. In such molecules, which are permanently dipolar, the atom having higher electronegativity becomes partially negatively charged ($-\delta$) and atom having less electronegativity becomes partially positively charged ($+\delta$). The value of partial charges is always less than unit electronic charge 1.6×10^{-19} C. In such dipolar molecules there is a force of attraction between the poles of atoms having partially opposite charges, which is shown in Figure 2.2. In HCl molecule the chlorine atom is more electronegative than hydrogen atom, so the chlorine atom acquires partial negative charge and hydrogen atom acquires partial positive charge, hence there is a dipolar interactive attraction between two HCl molecules and such attractive forces are called dipole-dipole forces of attraction. There is also interactive London forces between such molecules so the cumulative effect of both the forces is observed. In these molecules these forces are stronger than London forces.



2.2 Dipole-Dipole mutual attractive forces in HCl molecules

(3) Dipole-Induced dipole forces : When dipolar molecules come closer to non-polar molecules, then, this type of force of attraction is observed. In dipolar molecule the density of electron cloud always distributed unevenly, also when non-polar molecule comes closer to such polar molecule, the electron density is induced unevenly in non-polar molecule, which can be explained as given below. As shown in Figure

2.3 the non-polar molecule comes in contact with B^- pole of polar molecule AB. There is an induced positive charge towards the pole of non-polar molecules which is in contact with them and the opposite pole becomes partially negative, so the dipolarity is induced in them. As a result, dipolarity can be induced between the polar molecule and non-polar molecule. They get attracted. This type of force of attraction is called dipole-induced dipole force of attraction. This type of molecules also have interactive London forces and hence, in such molecules the cumulative effect of both forces can be observed.

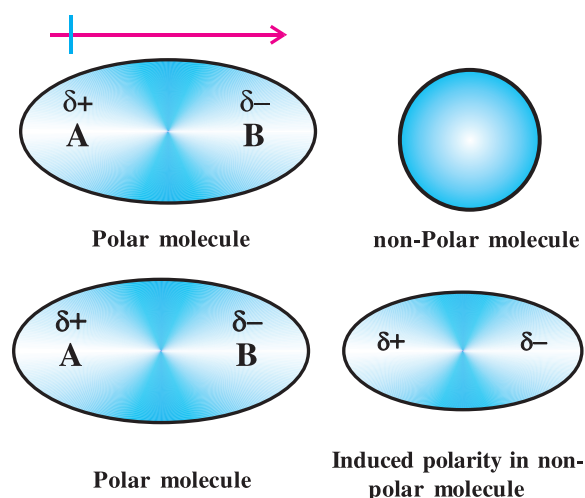


Fig. 2.3 Dipolar - Induced dipolar forces

Hydrogen bond : In intermolecular forces hydrogen bond is an important force of attraction. The first elements of group 15, 16 and 17 due to their high electronegativity, combine with hydrogen to form hydride compound in which hydrogen bond is observed. Hence, such molecules have interactive dipolar attractive forces and due to that elements of these groups show deviation in some properties. The hydrogen bond enthalpy is 10 to 100 kJ mol^{-1} . Thus, it is a weak attractive force.

Now, let us study the intermolecular repulsive forces. When two atoms or molecules come near, they repel due to same type of charges in their electron cloud. There is also repulsion between their nuclei. As the distance decreases between the two atoms or molecules, the repulsive forces rise very rapidly. Therefore, the effect of pressure is more on gas, while less in liquid and very less or negligible in solid, compared to that of gas. So if pressure is applied on solid state, the molecules do not come closer

because the molecules are close enough, so there is a repulsion in them, and if they are brought closer, then the repulsion increases more which resists the molecules to come nearer. Therefore, in solid state the effect of pressure is very less. Now, in liquid state compared to solid, the molecules are arranged little far from each other, so applying pressure on the molecules, they come closer to each other, hence effect of pressure is observed in liquid. At 293 K temperature and 1000 bar pressure applied on water, then the volume reduced only by 4%. Now, in gaseous state molecules are arranged far away and hence applying pressure, the molecules come nearer, and hence the effect of pressure is maximum on gaseous state.

The most important factor which decides the physical state of matter is the effect of thermal energy on motion of molecules. Due to this motion of molecules or atoms the energy produced is called thermal energy. It depends on the temperature of substances. On increasing the temperature the motion of molecules or atoms is increased and this motion is also called thermal motion.

Now, the intermolecular forces have tendency to keep the molecules near to each other, while the thermal energy has tendency to keep the molecules away from each other. So by balancing combination of the two opposite factors, the physical state of matter as solid, liquid or gas is decided. The gaseous molecules are arranged near to each other only by force of attraction, so they are not converted into solid or liquid spontaneously, because it is also necessary to have a change in thermal energy related to liquid and solid state. Thus, only the compression of gas will not convert gas into solid or liquid but by decreasing the temperature of gas its thermal energy can be decreased. So it can be liquefied easily. The characteristics of weak forces of attraction between the molecules of gaseous state are given below :

- (i) The volume, surface and shape of gases are not fixed but they assume the volume and shape of the container in which they are poured.
- (ii) Due to this characteristic of compression, gases show the effect of pressure and also the effect of temperature on them.
- (iii) The gaseous molecules exert equal pressure in all directions and expansion in all directions equally.
- (iv) The gaseous molecules spontaneously mix into each other easily and evenly.
- (v) The density of gas is very less compared to the density of solid or liquid.

Out of three physical states, the gaseous state is very simple because in this state the force of attraction is negligible and also indicate similarity in behaviour. Different gases have different chemical properties, still they have similarity in their behaviour. Their behaviour is described by the quantitative relation between mass, volume, temperature and pressure, and these relations can be discovered by experimental observations and such relations are called laws of gases. A number of laws of gases can be derived, while for liquid such laws derived are limited and very few for solid.

2.2 The Gas Laws

The volume of a fixed amount of gas depends upon its temperature and pressure. Both factors are different at different places and also they change with the change in atmosphere. So it is necessary to understand the relation between the volume of gas and the affecting factors and the laws of gas are derived from the study of such relations.

Boyle's law : In 1662, scientist Robert Boyle carried out experiments to study the relation between pressure and volume for fixed amount of gas and finally on the basis of experimental observations, the relation between pressure and volume of a gas was stated and it is known as Boyle's law which is given below :

“At constant temperature the pressure of a fixed amount of gas varies inversely with its volume.” Mathematically Boyle's law can be written as given below :

$$P \propto \frac{1}{V} \quad (\text{constant temperature, fixed amount})$$

$$\therefore P = K \cdot \frac{1}{V}$$

(where K is proportionality constant and it depends on the temperature and amount of the gas)

$$PV = K$$

So from Boyle's law it is said that “At constant temperature for fixed amount of gas the product of its pressure and volume is constant.”

Now, suppose at the initial stage, at constant temperature the fixed amount of gas has its pressure and volume as P_1 and V_1 respectively and at final stage they become P_2 and V_2 then according to Boyle's law

$$P_1 V_1 = K \quad \text{(I)}$$

$$P_2 V_2 = K \quad \text{(II)}$$

From equations I and II

$$P_1 V_1 = P_2 V_2$$

(constant temperature and fixed amount)

Boyle's law can be shown by following graphs : Figure 2.4 indicates the relation between pressure and volume of gas at different constant temperature and fixed amount of gas.

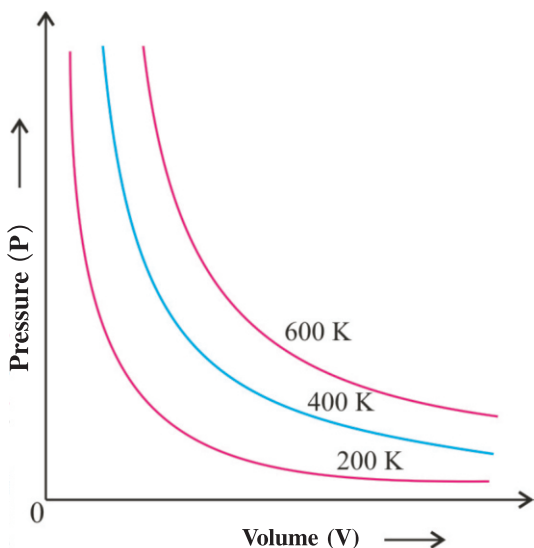


Fig. 2.4 Graph I

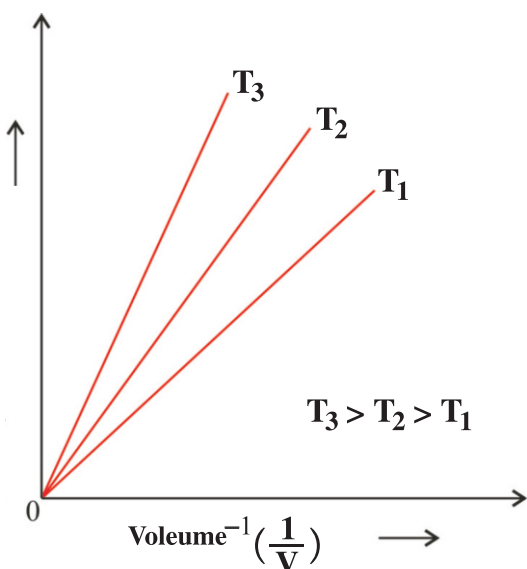


Fig. 2.5 Graph I

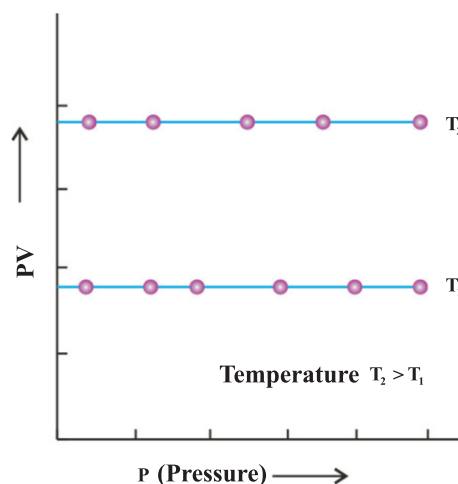


Fig. 2.6 Graph I

This graph is also called isotherm. It is clear from the isotherm graphs that at any constant temperature if the pressure increases its volume gets decreased and if the volume increases, its pressure gets decreased. This means that the product of pressure and volume becomes constant. But if the temperature changes, then, $PV = K$ in which the value of K changes which is clear from the graph in Figure 2.4.

The formula to indicate the relation between density and pressure of a gas derived from Boyle's law given below :

$$\text{According to Boyle's law } PV = K \dots (2.1)$$

Now, density

$$\therefore V = \frac{m}{d} \quad \text{(Putting this value in Boyle's law equation)}$$

$$P \cdot \frac{m}{d} = K$$

$$\therefore d = \left(\frac{m}{K}\right) \cdot P$$

Now, for fixed amount of a gas m is constant and so the value of $\frac{m}{K}$ is also constant, which is indicated by K'

$$d = K' P$$

$$\therefore d \propto P$$

$$\therefore \frac{d}{P} = K' \text{ so } \frac{d_1}{P_1} = \frac{d_2}{P_2} \text{ can be written.}$$

Hence, the relation between density and pressure of a gas which is derived from Boyle's law can be expressed as follows :

“At constant temperature for a fixed amount of gas the density of a gas varies directly as its pressure.”

The application of this relation is useful to understand the practical illustration. The pressure of air decreases on Mount Abu (nearly 0.5 bar). So, as the pressure of air decreases the density also decreases. This means that the density of O_2 in air also decreases and it becomes difficult to breath. In the same way, same type of difficulty is observed in the plane flying at height. So, in a plane attempt is made to maintain the pressure of air artificially. Eventhough by chance if any difficulty arises in breathing, then the facilities of O_2 is also available.

Example 1 : At constant temperature fixed amount of Cl_2 gas sample is filled in 2.5 litre container having pressure 4 bar. If the pressure is made 10 bar find its volume.

Solution :

According to Boyle's law

$$P_1 V_1 = P_2 V_2$$

$$P_1 = 4 \text{ bar}, V_1 = 2.5 \text{ litre}$$

$$P_2 = 10 \text{ bar}, V_2 = ?$$

$$\therefore V_2 = \frac{P_1 V_1}{P_2}$$

$$= \frac{4 \text{ bar} \times 2.5 \text{ litre}}{10 \text{ bar}} = 1 \text{ litre}$$

The volume of Cl_2 gas will be 1 litre.

Example 2 : At constant temperature fixed amount of O_2 gas having pressure 200 millibar is filled in 200 ml bottle. If the same amount of O_2 gas is filled in 2 litre bottle, find its pressure?

Solution : According to Boyle's law

$$P_1 V_1 = P_2 V_2$$

$$P_1 = 200 \text{ millibar}, V_1 = 200 \text{ ml}$$

$$P_2 = ?, V_2 = 2 \text{ litre} = 2000 \text{ ml}$$

$$P_1 V_1 = P_2 V_2$$

$$\therefore P_2 = \frac{P_1 V_1}{V_2}$$

$$= \frac{200 \times 200}{2000}$$

$$= 20 \text{ millibar}$$

The pressure of O_2 gas will be 20 millibar.

Example 3 : If the density of a gas at sea-level is 1.5 mg lit^{-1} , find the density of that gas on Mount Abu, having pressure 0.5 bar.

Solution : On sea level the pressure of gas is 1 bar. According to Boyle's law :

$$\frac{d_1}{P_1} = \frac{d_2}{P_2}$$

$$d_1 = 1.5 \text{ mg lit}^{-1}, d_2 = ?,$$

$$P_1 = 1 \text{ bar}, P_2 = 0.5 \text{ bar}$$

$$\therefore d_2 = \frac{d_1 P_2}{P_1}$$

$$= \frac{1.5 \times 0.5}{1}$$

$$= 0.75 \text{ mg litre}^{-1}$$

The density of gas will be $0.75 \text{ mg litre}^{-1}$

Absolute Zero Temperature : For fixed amount of gas at constant pressure, to understand the change in volume by changing the temperature, experiments were carried out and observations were noted. On the basis of the observations, relation between volume and temperature for gas is obtained which is known as Charles' law. From the analysis of the results the idea of absolute scale for temperature was obtained. Plotting the values of temperatures and volumes obtained from the observations as shown in Figure 2.7 graph is obtained. For the fixed

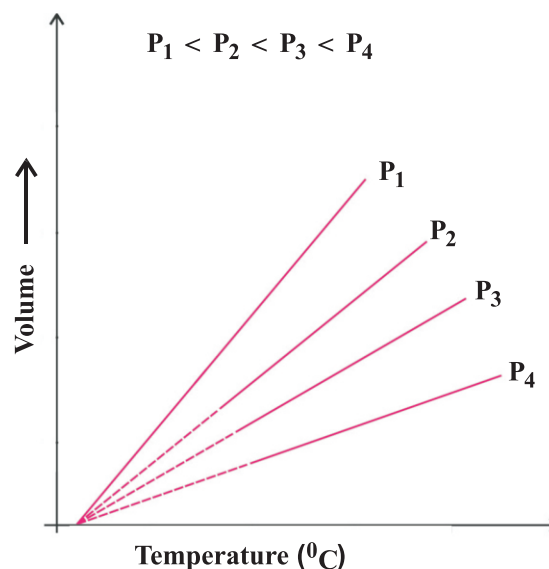


Fig. 2.7 Volume \rightarrow Temperature ($^{\circ}C$)

amount of gas, at constant pressure, if the temperature is decreased then the volume will decrease and if temperature is increased the volume will increase. Hence the volume varies directly with its temperature. The graph indicating experimentally observed values of volume and

temperature is extended towards the lower temperatures, then it touches the X-axis at -273.15°C , which indicates that theoretically at -273.15°C temperature the volume of gas should be zero and at further low temperatures the volume of gas becomes negative which is meaningless and thus at -273.15°C temperature at which the volume of gas is believed to be zero; the temperature is called absolute zero temperature. The idea of absolute zero temperature was first given by British scientist Kelvin and so this absolute zero temperature is also called Kelvin temperature. It is indicated by symbol K. When writing the Kelvin temperature, the sign for degree is not mentioned. Now, for the comparison between $^{\circ}\text{C}$ and K scale, the relation obtained is given below.

$$-273.15^{\circ}\text{C} = 0 \text{ K}$$

now, add 273.15 on both side

$$0^{\circ}\text{C} = 273.15 \text{ K}$$

similarly

$$1^{\circ}\text{C} = (1+273.15) \text{ K}$$

$t^{\circ}\text{C} = (t + 273.15) \text{ K}$ is obtained which is the relation between K and 0°C temperature. From this relation a new scale can be derived for indicating temperature, which is also known as Kelvin scale. On the basis of experimental observations a relation between absolute temperature and volume is obtained which is known as Charles' law. For convenience 273.15 value is taken nearly equal to 273 so that $t^{\circ}\text{C} = (t + 273) \text{ K}$.

The Kelvin temperature is accepted as the SI unit.

Charles' law : In 1787, scientist Charles had carried out some experiments and relation was obtained. For the fixed amount of gas at constant pressure, the relation of absolute temperature and volume of gas is known as Charles' law.

Charles' and Gay-Lussac performed several experiments and found that "At constant pressure and for fixed amount of a gas the change in volume by increasing or decreasing 1°C temperature is $\frac{1}{273}$ of the original volume of a gas."

Now, suppose at 0°C temperature the volume of gas is V_0 . So by increasing temperature by 1°C the change in volume of a gas is $(V_0 \times \frac{1}{273})$. Now if the temperature increased by $t^{\circ}\text{C}$, then the change in volume is $(V_0 \times \frac{t}{273})$. So at $t^{\circ}\text{C}$ temperature the volume

$$\text{of a gas is } \left(V_0 + \frac{V_0 \times t}{273} \right)$$

$$V_t = \left(V_0 + \frac{V_0 \times t}{273} \right)$$

$$= V_0 \left(1 + \frac{t}{273} \right) = V_0 \left(\frac{273 + t}{273} \right)$$

but $t + 273 = T_t \text{ K}$ and for 273 is T_0 , putting this value in above equation then,

$$V_t = V_0 \left(\frac{T_t}{T_0} \right)$$

$$V_t = \left(\frac{V_0 T_t}{T_0} \right)$$

$$\frac{V_t}{V_0} = \frac{T_t}{T_0} = K \quad \text{or} \quad \frac{V_t}{T_t} = \frac{V_0}{T_0} = K$$

$\therefore \frac{V}{T} = K$, $V = KT$ or $V \propto T$ (fixed amount of gas, constant pressure)

So the Charles' law can be written in this way.

"At constant pressure the volume of a fixed amount of gas varies directly to its absolute temperature."

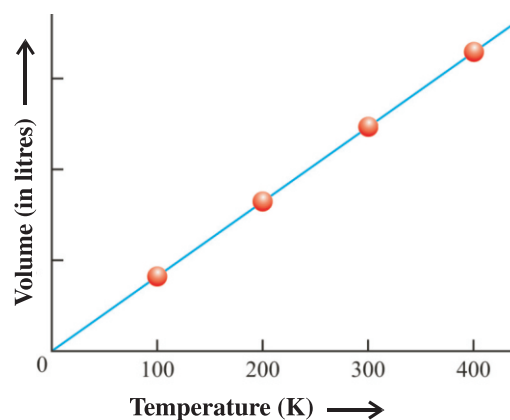


Fig. 2.8 Charles' law : volume \rightarrow Temperature (K)

Now, suppose at initial stage at constant pressure, for fixed amount of gas its volume and absolute temperature are V_1 and T_1 respectively and at final stage they are V_2 and T_2 then according to Charles' law,

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

Charles' law can be explained by graph given in Figure 2.8. It can be said that at constant pressure the volume of a fixed amount of gas varies directly with its absolute temperature which is indicated by a straight line. At different pressures $\frac{V}{T} = K$. The values of constant K are different which is also indicated in Figure 2.9 in $P_1 < P_2 < P_3 < P_4$.

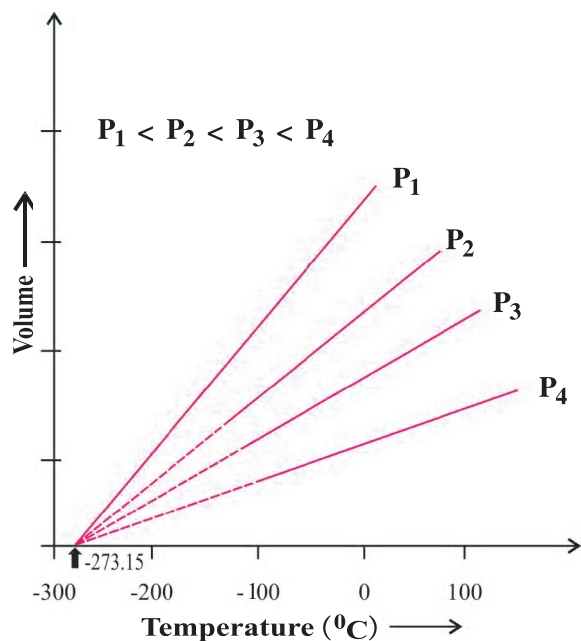


Fig. 2.9 Volume \rightarrow Temperature ($^{\circ}\text{C}$)

Example 4: At 127°C temperature the volume of O_2 gas is 3 litre. At which temperature the volume of O_2 gas will be halved ?

Solution : According to Charles' law

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

$$V_1 = 3 \text{ litre}, V_2 = \frac{3}{2} \text{ litre}$$

$$T_1 = 127 + 273 = 400 \text{ K}, T_2 = ?$$

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

$$= \frac{1.5 \times 400}{3} = 200 \text{ K}$$

$$t_2^{\circ}\text{C} = T_2 - 273 = 200 - 273 = -73^{\circ}\text{C}.$$

The temperature of O_2 gas will be -73°C .

Example 5 : At constant pressure and 125°C temperature Helium is filled in a container having volume 2 litre. If the temperature in $^{\circ}\text{C}$ is doubled then find the volume of helium gas at that temperature.

Solution : According to Charles' law

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

$$V_1 = 2 \text{ litre}, V_2 = ?$$

$$T_1 = 125 + 273 = 398 \text{ K},$$

$$T_2 = 250 + 273 = 523 \text{ K}$$

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

$$= \frac{2 \times 523}{398} = 2.628 \text{ litre}$$

\therefore The volume of helium gas will be 2.628 litre.

Gay-Lussac's law : For a fixed amount of gas and at constant volume, to find the relation between pressure and absolute temperature, Gay-Lussac carried out experiments and from the observations the relation is obtained which is given below. It is known as Gay-Lussac's law. This can be stated as follows :

“For constant volume, the pressure of a fixed amount of gas varies directly with its absolute temperature.”

Gay-Lussac's law is written mathematically as $P \propto T$ (constant volume of gas, fixed amount)

$$\therefore P = KT$$

$$\therefore \frac{P}{T} = K$$

At constant volume for a fixed amount of gas if at the initial stage the pressure and absolute temperature are P_1 and T_1 respectively and at final stage it is P_2 and T_2 , then according to

$$\text{Gay-Lussac's law } \frac{P_1}{T_1} = \frac{P_2}{T_2}$$

Gay-Lussac's law can also be explained by graph. The relation between pressure and

absolute temperature is obtained as shown in Figure 2.10. Now, at constant volume and fixed amount of gas, the values of $\frac{P}{T}$ obtained are constant at different temperatures i.e. $\frac{P}{T} = K$. The constant K is different at different constant values $V_1 < V_2 < V_3 < V_4$. This is clear from the Figure 2.10.

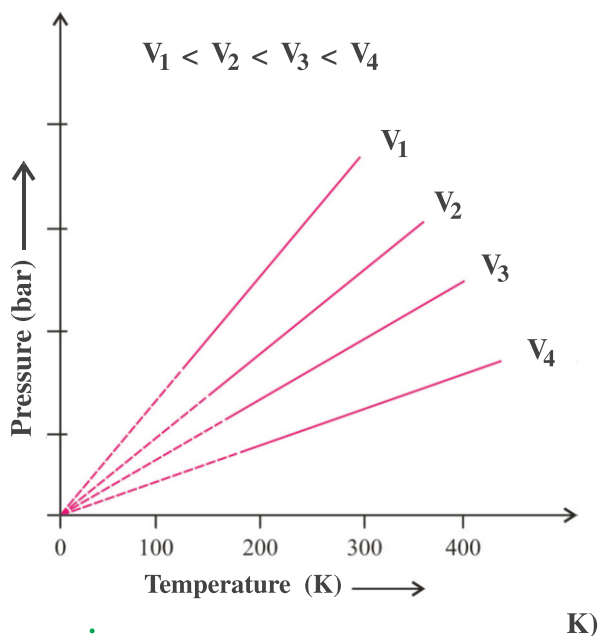


Fig. 2.10 Pressure (bar) → Temperature (K)

Example 6 : In closed vessel at 27 °C temperature N₂ is filled; having pressure 2 bar. Find the pressure of gas, if the temperature is 77 °C.

Solution :

According to Gay-Lussac's law,

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

$$P_1 = 2 \text{ bar}, P_2 = ?$$

$$T_1 = 27 + 273 = 300 \text{ K},$$

$$T_2 = 77 + 273 = 350 \text{ K}$$

$$\therefore P_2 = \frac{P_1 T_2}{T_1}$$

$$= \frac{2 \times 350}{300}$$

$$= 2.33 \text{ bar}$$

\therefore The pressure of N₂ gas 2.33 bar.

Example 7 : In a closed vessel of 400 K temperature the pressure of Cl₂ gas is 4 bar. At which °C temperature the gas is having pressure 5 bar.

Solution :

According to Gay-Lussac's law

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

$$P_1 = 4 \text{ bar}, P_2 = 5 \text{ bar},$$

$$T_1 = 400 \text{ K}, T_2 = ?$$

$$\therefore T_2 = \frac{P_2 T_1}{P_1}$$

$$= \frac{5 \times 400}{4} = 500 \text{ K}$$

$$\text{Now, } t^\circ \text{C} = T_2 - 273 = 500 - 273 = 227^\circ \text{C}.$$

\therefore The temperature of Cl₂ gas will be 227° C.

Avogadro's law : In 1811, Avogadro tried to combine the conclusions of Dalton's law and Gay-Lussac's law of combining volumes. The relation between volume of a gas and the number of molecules were given by Avogadro which is known as Avogadro's law. According to Avogadro's law, **“Equal volumes of all gases at same temperature and pressure contain equal number of molecules.”** So, at constant temperature and pressure the volume of gas (V) varies directly to the number of molecules (n).

$$\therefore V \propto n \dots$$

$\therefore V = Kn \dots$ (Mathematical form of Avogadro's law)

2.3 Standard Temperature and Pressure

The volume of a fixed amount of gas depends upon its temperature and pressure. So 0 °C or at 273 K temperature and 1 bar pressure. (10⁵ Pa) accepted as standard values by SI system, and hence, these values of temperature and pressure are known as standard temperature and pressure. **So 1 mole of any gas having same volume (for ideal gas 22.71098 litre mole⁻¹) at standard temperature (STP) and the volume at STP is known as molar volume.** The molar volumes of some gases at STP are given in table 2.1.

So, normally at STP 22.413996 litre means nearly 22.4 litre is accepted as molar volume of gas and in one mole of gas the number of molecules are 6.022×10^{23} . This constant value is known as Avogadro's number. So, at STP 22.4 litre of gas contains 6.022×10^{23} molecules.

Table 2.1

Molar volume of some gases

Gas	Volume (litremole ⁻¹)
Argon	22.37
Carbon dioxide	22.54
Dinitrogen	22.69
Dioxygen	22.69
Dihydrogen	22.72
Ideal Gas	22.71

Combined Gas Equation : Boyle's law and Charles' law state the relation of volume with pressure and with temperature respectively. So, by combining these two laws an equation is obtained which indicates the combined effect of temperature and pressure on volume for fixed amount of gas. This is known as combined gas equation or it is also called gas equation.

According to Boyle's law $V \propto \frac{1}{P}$ (Fixed amount of gas, constant temperature)

According to Charles' law $V \propto T$ (Fixed amount of gas, constant temperature)

On obtaining combined relations from both the laws, then

$$V \propto \frac{T}{P}$$

$$\therefore PV \propto T$$

$$\therefore PV = KT$$

$$\therefore \frac{PV}{T} = K \dots\dots \text{(Combined gas equation)}$$

Now, for fixed amount of gas at its initial stage the pressure, volume and absolute temperature are P_1 , V_1 and T_1 respectively and at final stage the values are P_2 , V_2 and T_2 respectively, then according to combined gas

$$\text{equation } \frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

Example 8 : At 27 °C temperature and 4 bar pressure CO is filled in 2 litre vessel. Find the pressure if it is filled in 4 litre vessel at 77 °C temperature.

Solution :

According to combined gas equation,

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

$$P_1 = 4.0 \text{ bar, } P_2 = ?$$

$$V_1 = 2 \text{ litre, } V_2 = 4.0 \text{ litre}$$

$$T_1 = 27 + 273 = 300 \text{ K,}$$

$$T_2 = 77 + 273 = 350 \text{ K}$$

$$\therefore P_2 = \frac{P_1 V_1}{T_1} \times \frac{T_2}{V_2}$$

$$= \frac{4 \times 2 \times 350}{300 \times 4} = 2.33 \text{ bar}$$

\therefore The pressure of CO gas will be 2.33 bar.

Example 9 : At 400 K temperature, 200 ml N_2 has pressure 1.5 bar. Find the volume of N_2 gas at STP.

Solution : According to combined gas equation,

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

$$P_1 = 1.5 \text{ bar, } P_2 = 1 \text{ bar}$$

$$V_1 = 200 \text{ ml, } V_2 = ?$$

$$T_1 = 400 \text{ K, } T_2 = 273 \text{ K}$$

$$V_2 = \frac{P_1 V_1}{T_1} \times \frac{T_2}{P_2}$$

$$= \frac{1.5 \times 200 \times 273}{400 \times 1} = 204.75 \text{ ml}$$

\therefore The volume of N_2 gas at STP will be 204.75 ml.

Example 10 : Find the pressure of a gas when 6.022×10^{22} molecules are placed in 2 litre vessel at 27 °C temperature.

Solution :

At STP 6.022×10^{22} molecules = 22.4 litre.

CO_2 gas 6.022×10^{22} molecules having volume at STP

$$= 22.4 \times \frac{6.022 \times 10^{22}}{6.022 \times 10^{23}} = 2.24 \text{ litre}$$

According to combined gas equation,

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

$$P_1 = 1 \text{ bar}, P_2 = ?$$

$$V_1 = 2.24 \text{ litre}, V_2 = 2 \text{ litre}$$

$$T_1 = 273 \text{ K},$$

$$T_2 = 27 + 273 = 300 \text{ K}$$

$$V_2 = \frac{P_1 V_1}{T_1} \times \frac{T_2}{P_2}$$

$$= \frac{1 \times 2.24 \times 300}{273 \times 2} = 1.231 \text{ bar}$$

∴ The pressure of CO₂ gas will be 1.231 bar.

2.4 Ideal Gas Equation

By combining Boyle's law, Charles' law and Avogadro's law, the relation obtained is called Ideal gas equation. In this equation four variables like temperature, pressure, volume and amount of gas describe gaseous state and the equation which indicates the quantitative relation between them is also called **equation of state**,

$$V \propto \frac{1}{P} \quad (\text{Boyles' law})$$

$$V \propto T \quad (\text{Charles' law})$$

$$V \propto n \quad (\text{Avogadro's law})$$

$$\therefore V \propto \frac{nT}{P}$$

$$\therefore PV \propto nT$$

$$\therefore PV = nRT$$

(where R is proportionality constant)

R is also called universal constant because the values of R is the same for all the gases. It is also the same for any temperature, pressure or volume which means it has the same constant value. The value is not changed eventhough R has different values related to difierernt unit systems.

The ideal gas equation can also be written as below, in which it indicates the relation with density and molecular mass.

$$\text{Ideal gas equation } PV = nRT$$

where n is the number of moles

but $n = \frac{m}{M}$ where m is mass of gas.

M = molecular mass. Putting this value in above equation.

$$PV = \frac{mRT}{M}$$

$$\therefore P = \left(\frac{m}{V}\right) \frac{RT}{M}; \text{ but } \left(\frac{m}{V}\right) = d$$

$$P = \frac{dRT}{M} \quad (\text{where } d = \text{density})$$

m = molecular mass.

The values of gas constant R : In different unit systems the values of R gas constant (Universal constant) are different because R has unit of work energy mole⁻¹ K⁻¹. The unit of work is differernt in different systmes.

Now, let us understand the unit of R. Ideal gas equation,

$$PV = nRT$$

$$R = \frac{PV}{nT} = \frac{\text{pressure} \times \text{volume}}{\text{mole} \times \text{temperature}}$$

But pressure = force ÷ area

$$R = \frac{[\text{force} \div \text{area}] \times \text{volume}}{\text{mole} \times \text{temperature}}$$

$$= \frac{[\text{force} \div (\text{length})^2] \times (\text{length})^3}{\text{mole} \times \text{temperature}}$$

$$= \frac{\text{force} \times \text{length}}{\text{mole} \times \text{temperature}}$$

$$= \frac{\text{work energy}}{\text{mole} \times \text{temperature}}$$

(∵ force × length = work energy)

So the unit of R is work energy mole⁻¹ K⁻¹. The calculation of values of R in different units are as given below :

- (1) If the unit of pressure and volume are in atmosphere and litre respectively, then the unit of R will be in litre atmosphere mole⁻¹ K⁻¹.

volume of 1 mole gas at STP is 22.4 L.

$$\text{so, } R = \frac{PV}{nT} = \frac{1 \text{ atmosphere} \times 22.4 \text{ litre}}{1 \text{ mole} \times 273 \text{ K}}$$

$$= 0.0821 \text{ litre atmosphere mole}^{-1} \text{K}^{-1}$$

- (2) If the unit of pressure and volume are atmosphere and cm³ respectively, then the unit of R will be atm cm³ mole⁻¹ K⁻¹.

$$R = \frac{PV}{nT} = \frac{1 \text{ atmosphere} \times 22400 \text{ cm}^3}{1 \text{ mole} \times 273 \text{ K}}$$

$$= 82.1 \text{ atm cm}^3 \text{ mole}^{-1} \text{K}^{-1}$$

- (3) If the unit of pressure and volume are dyne cm⁻² and cm³ respectively, then the unit R will be erg mole⁻¹ K⁻¹.

$$R = \frac{PV}{nT} = \frac{76 \text{ cm of Hg height} \times 22400 \text{ cm}^3}{1 \text{ mole} \times 273 \text{ K}}$$

$$= \frac{76 \times 13.6 \times 981 \times 22400}{1 \times 273}$$

where 13.6 is the density of Hg and g = 981 dyne.

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

$$8.314 \text{ Joule K}^{-1} \text{ mole}^{-1}$$

$$(1 \text{ joule} = 10^7 \text{ erg})$$

- (4) Now, 4.184 J = 1 calorie

$$R = \frac{8.314}{4.184} = 1.987 \text{ calorie K}^{-1} \text{mole}^{-1}$$

$$\approx 2 \text{ calorie mole}^{-1} \text{K}^{-1}$$

$$= 2 \times 10^{-3} \text{ kilocalorie mole}^{-1} \text{K}^{-1}$$

- (5) If the unit of pressure and volume are bar and litre respectively, for ideal gas then unit of R will be bar litre mole⁻¹ K⁻¹.

$$R = \frac{PV}{nT} = \frac{1 \text{ bar} \times 22.71 \text{ litre}}{1 \text{ mole} \times 273 \text{ K}}$$

$$= 8.314 \times 10^{-2} \text{ barlitmole}^{-1} \text{K}^{-1}$$

$$= 8.314 \text{ Joulemole}^{-1} \text{K}^{-1}$$

Thus, the units of R are different according to the different units of pressure and volume which are given in Table 2.2

Table 2.2 Different values of R

Sr.	Value of R	Unit	Unit of P and V
1	0.0821	litre atm K ⁻¹ mol ⁻¹	(P in atm, V in litre)
2	82.1	ml atm K ⁻¹ mol ⁻¹	P in atm, V in cm ³
3	8.314 × 10 ⁷	erg K ⁻¹ mol ⁻¹	P in dynes cm ⁻² , V in cm ³
4	1.987	cal K ⁻¹ mol ⁻¹	P in dynes cm ⁻² , V in cm ³
5	8.3144	J K ⁻¹ mol ⁻¹	P in Pa or N m ⁻² , V in cm ³
6	8.314 × 10 ⁻²	bar lit K ⁻¹ mol ⁻¹	P in bar, V in litre

Example 11 : Find the pressure of 5 mole Cl_2 gas filled in a 2 litre vessel at 27°C temperature.

Solution :

$$PV = nRT$$

$$\therefore P = \frac{nRT}{V}$$

$$P = ?, n = 5 \text{ mole}$$

$$R = 8.314 \times 10^{-2} \text{ barlitmole}^{-1}\text{K}^{-1}$$

$$T = 27 + 273 = 300 \text{ K}, V = 2 \text{ litre}$$

$$= \frac{5 \times 8.314 \times 10^{-2} \times 300}{2}$$

$$= 62.355 \text{ bar}$$

\therefore The pressure of Cl_2 gas will be 62.355 bar.

Example 12 : Find the moles of O_2 gas having pressure 250 bar in 500 ml vessel at 350 K temperature.

Solution :

According to ideal gas equation

$$PV = nRT$$

$$\therefore n = \frac{PV}{RT}$$

$$P = 250 \text{ bar}, n = ?$$

$$R = 8.314 \times 10^{-2} \text{ barlitmole}^{-1}\text{K}^{-1}$$

$$T = 350 \text{ K}, V = 500 \text{ ml} = 0.5 \text{ litre}$$

$$= \frac{250 \times 0.5}{8.314 \times 10^{-2} \times 350} = 4.296 \text{ mol}$$

\therefore The mole of O_2 gas will be 4.296.

Example 13 : Find the temperature in $^\circ\text{C}$ for a 6.4 gm O_2 gas filled in a 200 ml vessel having pressure 50 bar.

Solution :

According to ideal gas equation,

$$PV = nRT$$

$$\therefore PV = \frac{nRT}{M} \quad (\because n = \frac{m}{M})$$

$$\therefore T = \frac{PVM}{mR}$$

$$P = 50 \text{ bar}, M = 32 \text{ grammole}^{-1}$$

$$R = 8.314 \times 10^{-2} \text{ barlitmole}^{-1}\text{K}^{-1}$$

$$m = 6.4 \text{ gram}$$

$$V = 200 \text{ ml} = 0.2 \text{ litre}, T = ?$$

$$T = \frac{50 \times 0.2 \times 32}{8.314 \times 10^{-2} \times 6.4}$$

$$= 601.4 \text{ K}$$

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

$$= 601.4 - 273 = 328.4^\circ \text{C}$$

\therefore The temperature of O_2 gas will be 328.4°C .

Example 14 : Find the pressure of neon gas having density 0.9 gm lit^{-1} at 350 K temperature.

Solution : According to ideal gas equation

$$P = \frac{dRT}{M} \quad (\because n = \frac{d}{M})$$

$$P = ?, d = 0.9 \text{ gm lit}^{-1}$$

$$R = 8.314 \times 10^{-2} \text{ bar litmole}^{-1} \text{K}^{-1}$$

$$T = 350 \text{ K}, M = 20 \text{ gm mol}^{-1}$$

$$P = \frac{0.9 \times 8.314 \times 10^{-2} \times 350}{20}$$

$$= 1.309 \text{ bar}$$

\therefore The pressure of Neon gas will be 1.309 bar.

Concept of Ideal Gas : Deviation from Ideal Gas Behaviour : In ideal gas equation, the word ideal is used, but in fact there is not a single gas which follows this equation completely. However, it is believed that real gas behaves as ideal gas at high temperature and low pressure.

The gases which obey the ideal gas equation and gas laws at all temperatures and pressure are called ideal gases. Actually not a single gas is found as an ideal gas. If the temperature is lowered and at high pressure the deviation is observed in gas laws and ideal gas equation. Hence, the gases at all temperature and pressure do not follow the ideal gas equation and these gases are called non-ideal gases or

real gases. Generally all the gases are real gases. They show ideal behavior in different proportions and out of them most of gases at low pressure and high temperature show ideal behavior. Some scientists studied gases extensively and at last concluded that all real gases at all conditions of temperature and pressure do not follow laws of ideal gas and the behaviour of real gas is deviated from an ideal gas and its study is carried out by effect of pressure and temperature.

Effect of pressure : To study the deviation in the behaviour of real gas from that of ideal gas, its idea can be obtained by plotting graph $\frac{PV}{nRT} \rightarrow Z$, $\frac{PV}{nRT}$ is called **compressibility factor**, which is indicated by Z . For ideal gas the value of Z is one, because $PV = nRT$ for ideal gas equation. Hence $\frac{PV}{nRT} = 1$, while for a real gas $Z > 1$, $Z < 1$, are possible, means that $PV \neq nRT$. As shown in figure 2.11 for H_2 and He gases always $Z > 1$ so it is called positive

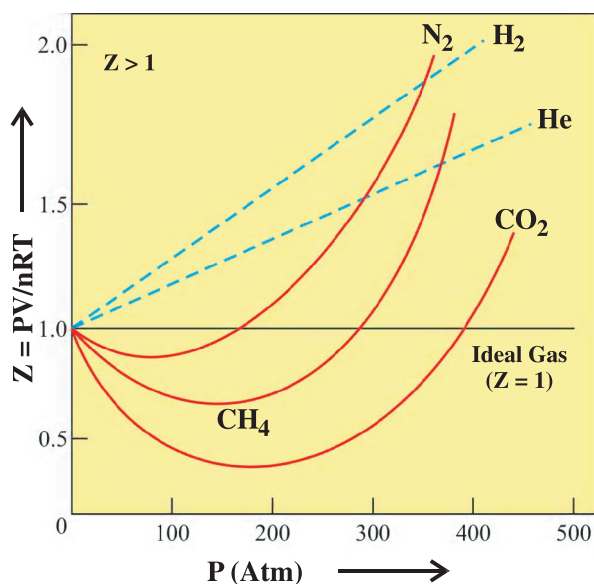


Fig. 2.11 $Z \rightarrow P$

deviation and it indicates that for all values of pressure they are less compressive than ideal gas, while for N_2 and CO gases at low pressure $Z < 1$ is called **negative deviation**. It indicates that, they are more compressive than ideal gas and at high pressure $Z > 1$ is called **positive deviation** which indicates that at high pressure, they are less compressive than ideal gases shown

in figure 2.11. For all gases the pressure is reduced and when it becomes zero, at that time $Z = 1$ means at zero pressure all gases behave as an ideal gas.

To study the deviation, the experimental data obtained for volumes of real gas at different pressures and theoretical data obtained for volumes of an ideal gas by calculation on the basis of Boyle's law at different pressures can be plotted against volume as shown in Figure 2.12. It is clear from the graph that at very high pressure, value obtained for volume of a real gas is higher than the value obtained for

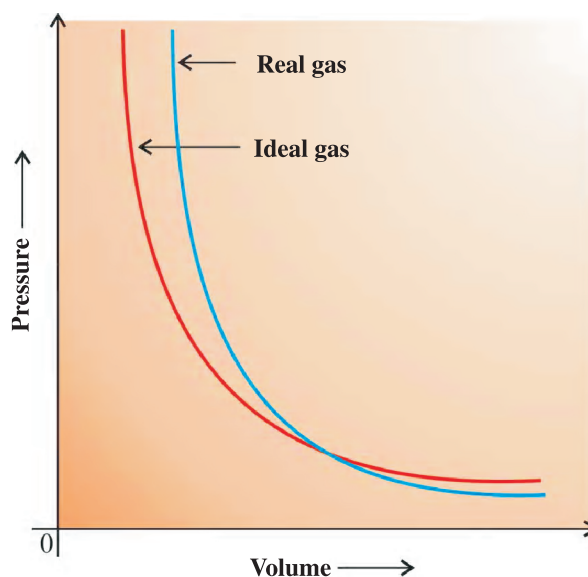


Fig. 2.12 Pressure \rightarrow Volume

volume of ideal gas and as the pressure decreases means at low pressure the volume difference for both types of gases go on decreasing and at the end, it becomes zero and so both the graphs cross each other and after that as the pressure decreases once again the difference in volume of both types of gases are observed.

Effect of temperature : The effect of temperature can be explained by comparing the real behaviour of N_2 gas and its ideal behaviour at different temperatures. As shown in Figure 2.13 at different temperatures for N_2 the values of PV and P are plotted. In the figure, the dotted line indicates the ideal behaviour of the gas at the same temperature. It is clear from the figure that as the temperature increases ($T_1 < T_2 < T_3 < T_4$), the depth of curved portion goes on decreasing, hence, as the temperature increases

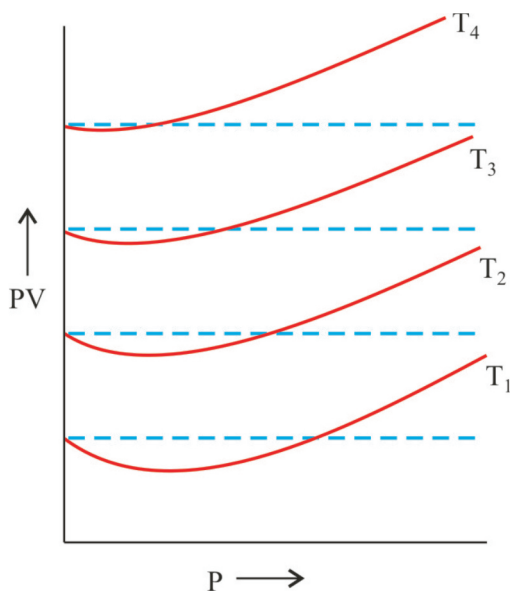


Fig. 2.13 PV \rightarrow P

the deviation of real gas compared to ideal gas behaviour goes on decreasing and at definite temperature the curve portion of graph becomes minimum and finally becomes straight line for appreciable range of pressures and at such definite temperature N_2 gas shows ideal behaviour and at this definite temperature, it follows Boyle's law. So this temperature of the gas is known as Boyle's temperature. Its values are different for different gases. For example, for N_2 gas it is 332 K and for H_2 gas it is 108 K.

Therefore, it is said that at low pressure and high temperature real gas shows ideal behaviour and at low temperature and high pressure there is a remarkable difference in its behaviour. The real gas shows deviation from ideal gas behaviour. Why? Because, out of the assumptions made in kinetic theory of gases two are not proper. These two assumptions are

(1) The force of attraction between the gaseous molecules is negligible.

(2) The volume of a molecule is negligible (which can be avoided) compared to total volume of gas.

Now, if the assumption (1) is correct then there is a negligible force of attraction so, by cooling or compressing by the effect of pressure, the molecules will never be arranged close to each other and hence, the liquefaction of gas is not possible. Similarly, liquid cannot be converted into solid by effect of temperature or pressure.

Now, if assumption (2) is correct then the theoretical and experimental graphs of volume and pressure will be same, but in fact, it is not true. The deviation is observed. So it is necessary to have correction in both the assumptions.

Now, if the force of attraction existing between gaseous molecules is as shown in Figure 2.14, then any molecules in the middle of the container have force of attraction evenly by the neighbouring molecules which are arranged in all directions. Hence, the resultant force of attraction becomes zero. Now, molecules when move towards the wall of container and ready to hit the wall means they are ready to touch the wall of container, at that time, as shown in Figure 2.14, the molecules have resultant force of attraction towards one side, i.e. it does not become zero and it tries to pull them in opposite direction from the wall. Thus with the inward

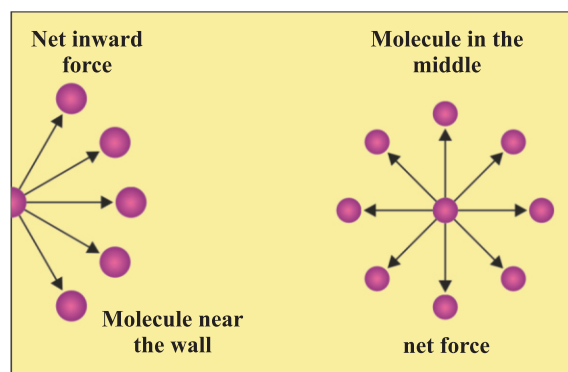


Fig. 2.14 Attraction force in molecules of gases

force of attraction, resistance is created in striking the molecules with the wall; so the measured real pressure is less than ideal pressure. So to obtain ideal pressure some correction is required in measured pressure P . (something to be added) Such suggestion is given by van der Waals and the total pressure (attraction) varies directly to square of density or inversely varies with square of its volume (V^2) so for any gas the ideal pressure value is equal to sums of real pressure and $\frac{an^2}{V^2}$

$$\therefore \text{Ideal pressure of gas} = P_{\text{real}} + \frac{an^2}{V^2}$$

where a is constant and n is number of moles of gas.

Now, if the volume of gas molecule is taken into consideration, then the total volume

occupied by the gas molecules is not available for the motion of these molecules, so to obtain the effective or ideal volume (available volume), the volume occupied by the molecules is to be subtracted from the measured volume of the gas, and thus, the volume occupied by n mole of gas is nearly nb (where b is constant) which is subtracted from total volume (V). This correction is made in ideal gas equation and so the ideal gas equation is written as given below :

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

This equation is known as **van der Waals equation** where a and b are constant and they depend on the characteristics of gas. The constant a indicates the measurement of intermolecular attractive forces which is free from effect of temperature and pressure.

At very low temperature the intermolecular attractive forces become significant when molecules are moving with low average velocity. Due to this force of attraction the molecules are pulled towards each other and hence, it creates resistance in striking with wall of container. Due to this, measured value of pressure is less than ideal pressure. So it is said that the behaviour of real gas is ideal when intermolecular forces are such that it becomes practically negligible.

Liquefaction of gas : Gas can be liquefied by lowering the temperature and increasing the pressure but for liquefaction of gas, effect of temperature is more important than effect of pressure because all gases after cooling to certain fixed temperature are liquefied under effect of pressure but in addition to that temperature, however, the pressure may be applied, even though, they are not liquefied. These temperatures are different for different gases. Hence, **the maximum temperature at which the gas gets liquefied is known as critical temperature, (T_c)**. Above the critical temperature, however, the pressure is applied even though the liquefaction of gas is not possible. So, at higher than critical temperature, the liquid state is not possible but below the critical temperature under the effect of pressure gas liquefaction is possible. **At critical temperature, the pressure is applied on gas for liquefaction, that pressure is called critical pressure (P_c) of that gas. At critical temperature and critical pressure, the**

volume occupied by 1 mole of gas is called critical volume (V_c) and this state is called critical state. Every gas has its P_c , T_c and V_c values fixed. So they are known as critical constants which are different than other gas constants. In 1869 Thomas Andrews studied the relation between pressure, volume and temperature for CO_2 gas and obtained experimental data for gaseous and liquid state of CO_2 gas. For this, he had taken a hard glass tube at constant temperature and filled with CO_2 gas. At different pressures the volume of gas was measured. After that he plotted a graph (isotherm) indicating effect of pressure on volume of gas at different constant temperature as shown in Figure 2.15. At lower temperature i.e. $13.1^\circ C$ temperature and lower pressure, at point X the

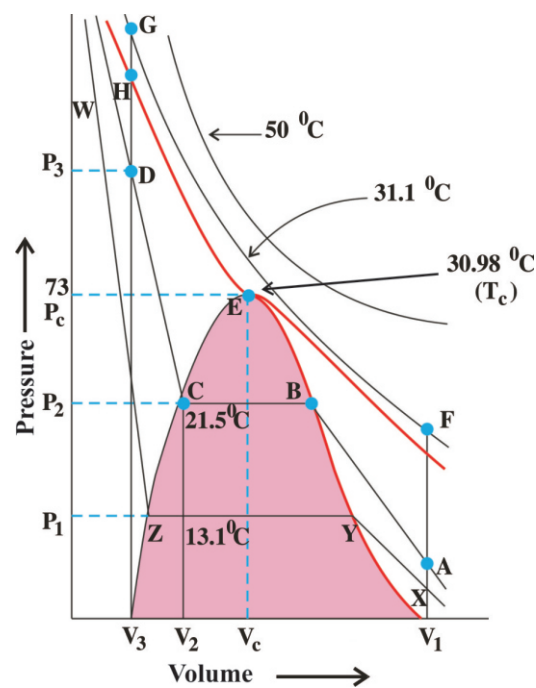


Fig. 2.15 Liquefaction of gas

CO_2 is in gaseous state. Now with increasing pressure volume of CO_2 gas decreases which is shown by XY curve. Now, at point Y, at given pressure, the liquefaction of gas starts and at point Z total gas is converted into liquid state. During this the pressure remains constant, which is clear from the figure. After that the curve ZW rises straight which indicates that after increasing the pressure on volume of liquid is very less. Thus, the isotherm obtained at $13.1^\circ C$ the XY indicates gaseous state, YZ indicates equilibrium between liquid and ZW only liquid state. YZ is horizontal which indicates that during the liquefaction of gas the pressure remains

constant. This pressure is the vapour pressure of liquid gas. Now, the isotherm obtained at 21.5°C temperature, on basis of experimental data, is the same as the isotherm obtained at 13.1°C but the horizontal portion BC which indicates the liquefaction is smaller than YZ. As the temperature increases the portion which indicates the liquefaction becomes smaller and finally at 30.98°C temperature, this portion becomes only a point E and above this temperature, i.e. 31.1°C this portion is lacking in the isotherm. So at this point of temperature the liquefaction of CO_2 is not possible. Thus at 30.98°C temperature the portion is just a point only indicating that at this point there is a liquefaction. So this temperature is known as critical temperature of CO_2 gas. Above this temperature, however, the pressure is applied, still the liquefaction of CO_2 is not possible but at 30.98°C or less than that temperature liquefaction is possible under pressure.

According to molecular kinetic theory of gases on lowering the temperature the kinetic energy of the molecules decreases and as a result slow moving molecules come closer to each other. At sufficiently low temperature some of the slow moving molecules cannot resist the force of attraction and they come closer and closer and ultimately the gas changes into the liquid state. In the same way increasing pressure, the volume decreases and so the increase in pressure and gas can also be liquefied. Thus, the combination of temperature and pressure means at critical temperature or lower than that temperature by increasing pressure the gas gets liquefied. In Table 2.3 critical temperature of some gases are given.

Table 2.3 Critical Constants

Gas-Substance	T_C (K)	P_C (Bar)	V_C $\text{dm}^3\text{mol}^{-1}$
H_2	33.2	12.97	0.0650
He	5.3	2.29	0.0577
N_2	126	33.9	0.0900
O_2	154.3	50.4	0.0744
CO_2	304.10	73.9	0.0956
H_2O	647.1	220.6	0.0450
NH_3	405.5	113.0	0.0723

In the mixture of two gases having different critical temperatures one gets liquefied faster

because on cooling the mixture, the gas starts liquefying whose critical temperature comes first so the H_2 gas starts liquefying first and at that time He gas is not liquefied.

Kinetic Energy and Molecular Speed :

Molecules are made up of particles of the substance having gaseous state. These particles are far away from each other in a large area. These particles are continuously moving in all directions. The continuous moving particles collide with each other and also with the wall of container. At that time the speeds and directions are changed, so that all particles in a container do not have same speed, but have different speeds which are continuously changing. However, at one temperature the distribution of speed of molecules is same. Maxwell and Boltzmann had studied the distribution of molecules between different possible speeds. They studied the speed of molecules and the fraction of molecules with a given speed and a graph was plotted. The graph is known as Maxwell's distribution curve as shown in Figure 2.16. The feature of molecular speed is shown below.

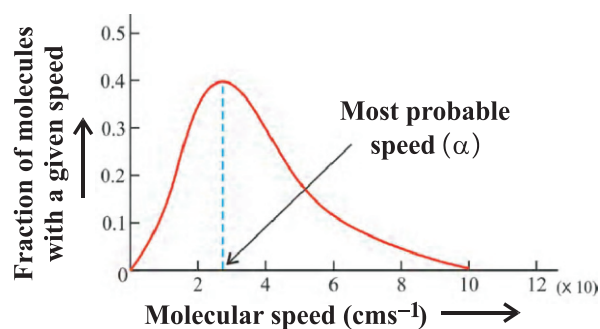


Fig 2.16

Fraction of molecules with given speed → Molecular speed

(1) The fraction of molecules with very high or low speed is very small.

(2) Increasing the speed, fraction also increases which becomes maximum and then decreases.

(3) The top portion of curve indicates maximum fraction of molecules and the speed of molecules is called most probable speed which is indicated by α . On increasing temperature the collision of molecules increases and the speed of molecules changes. On increasing temperature the most probable speed also increases which is clear from the graph in Fig 2.17. The graph is

shifted towards right side as the temperature increases and becomes more flat. If the temperature remains constant, curve of speed distribution does not change. There are three main types of speed of molecules.

- (1) most probable speed
- (2) average speed
- (3) root mean square speed.

The molecules have different kinetic energies with different types of speed.

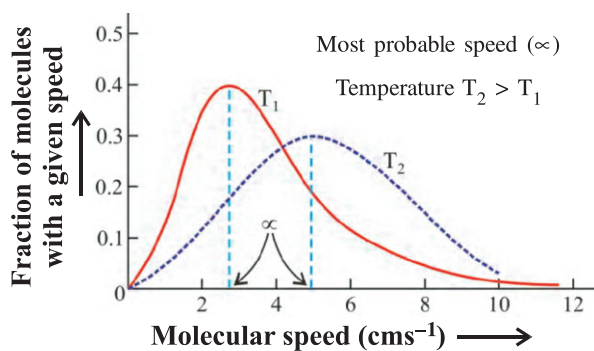


Fig. 2.17 Fraction of Molecules with a given speed → Molecular speed

“The total pressure exerted by the mixture of non-reactive gases is equal to the sum of the partial pressures of individual gas.”

Partial pressures means pressure of gases that will exert if they are filled separately in the same vessel, under the same conditions.

Suppose, in a vessel mixture of gases A, B, C, D are filled and the partial pressure are p_A , p_B , p_C , p_D respectively, then Dalton's law of partial pressure can be written in mathematical form as follows. Total pressure (P_{total}) = $p_A + p_B + p_C + p_D$

Dalton's law can be explained by the illustration given below :

As shown in Figure 2.18 take three vessels having same volume at constant temperature. Now, fill gas A in the first vessel, fill gas B in the second vessel and note down the pressure of the gases in both the vessels. Suppose the pressure of gas in the first vessel is p_A and that in the second vessel is p_B . There is no chemical reaction between gases A and B on mixing. Now, mix both gases in the third

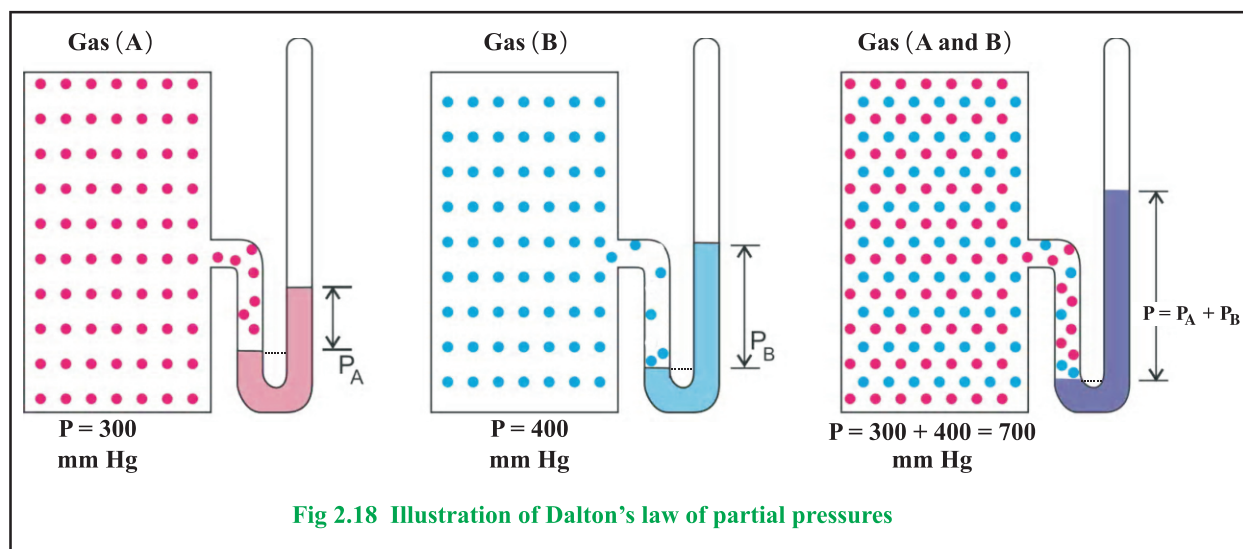


Fig 2.18 Illustration of Dalton's law of partial pressures

2.5 Dalton's Law of Partial Pressure

The component gases in a gaseous mixture behave independently in case of their properties. Moreover, if these gases are in mixture, even then all gases obey this law. Two or more gases which do not undergo chemical reactions are mixed in a closed vessel, the total pressure in a vessel can be obtained by Dalton's law of partial pressure. In 1801, Dalton stated the law of partial pressure which can be written as :

vessel and note down the pressure of a mixture of gases in third vessel which will be the total pressure. From the observation it is proved that total pressure :

$$P_{\text{total}} = p_A + p_B.$$

Sometimes the gases are collected over the water during the preparation of the gas in laboratory. The gas collected over water is saturated with water vapour at that temperature. So the measured pressure is the sum of partial

pressure of a gas collected over water and partial pressure of water vapour at that temperature. So if the measured pressure of gas is to be obtained, then subtract the water vapour pressure at that temperature which gives the partial pressure of dry gas only, e.g. 298 K temperature O_2 gas collected over water having total pressure is P_{total} , subtract the vapour pressure of water (p_{H_2O}) at same temperature, then only the pressure of dry O_2 gas (p_{O_2}) is obtained.

$$p_{O_2} = P_{\text{total}} - p_{H_2O}$$

Thus, by using Dalton's law of partial pressure the pressure of gas collected over water can be obtained.

The total pressure (P_{total}) for a mixture of gas collected in a container is obtained by using formula given below :

Suppose, in V litre container at temperature T, three different gases having number of moles n_1 , n_2 and n_3 respectively are filled. The total pressure (P_{total}) and the partial pressures of three gases are p_1 , p_2 and p_3 respectively in the container, then according to Dalton's law.

$$\text{Total pressure } (P_{\text{total}}) = p_1 + p_2 + p_3$$

$$\text{But } p_1 = \frac{n_1RT}{V}, \quad p_2 = \frac{n_2RT}{V} \quad \text{and} \quad p_3 = \frac{n_3RT}{V}$$

Putting values in above equation

$$\begin{aligned} \text{Total pressure } (P_{\text{total}}) &= \frac{n_1RT}{V} + \frac{n_2RT}{V} + \frac{n_3RT}{V} \\ &= (n_1 + n_2 + n_3) \frac{RT}{V} \end{aligned}$$

but ($n_1 + n_2 + n_3$) = total number of moles for gaseous mixture.

$$\therefore P_{\text{total}} = (\text{total number of moles}) \times \frac{RT}{V}$$

Same way from total pressure the values of partial pressure of each gas is obtained by formula given below.

Taking ratio of p_1 and P_{total}

$$\frac{p_1}{P_{\text{total}}} = \frac{n_1RT}{V} \times \frac{V}{\text{total mole} \times RT}$$

$$= \frac{n_1}{\text{total mole}}$$

$$\text{but } \frac{n_1}{\text{total mole}} = \text{mole fraction} = X_1$$

$$\therefore \frac{p_1}{P_{\text{total}}} = X_1$$

$$\therefore p_1 = X_1 \cdot P_{\text{total}}$$

In the same way

$$\therefore p_2 = X_2 \cdot P_{\text{total}}$$

$$\therefore p_3 = X_3 \cdot P_{\text{total}}$$

So the partial pressure of each gas is obtained from the total pressure and from the mole fraction of each gas. Same way, in a mixture of gases if the % by volume is given for each gas, then the partial pressure of gas is obtained by formula given below.

The partial pressure of gas (p_A) =

$$\frac{\% \text{ by volume of gas A} \times \text{total pressure}}{100}$$

Example 15 : At 27°C temperature in a 2 litre closed vessel, 10 gm H_2 and 22 gm CO_2 gases are filled. Find the partial pressure and total pressure of a mixture.

Solution :

For 10 gm H_2 gas, the mole = $\frac{m}{M}$

$$= \frac{10}{2} = 5 \text{ mole} = n_{H_2}$$

For 22 gm CO_2 gas, the mole = $\frac{m}{M}$

$$= \frac{22}{44} = 0.5 \text{ mole} = n_{CO_2}$$

Now, the partial pressure of H_2 gas (p_{H_2})
(27 + 273) = 300 K is

$$\begin{aligned} p_{H_2} &= \frac{n_{H_2}RT}{V} \\ &= \frac{5 \times 8.314 \times 10^{-2} \times 300}{2} = 62.355 \text{ bar} \end{aligned}$$

$$\begin{aligned} p_{CO_2} &= \frac{n_{CO_2}RT}{V} \\ &= \frac{0.5 \times 8.314 \times 10^{-2} \times 300}{2} = 6.236 \text{ bar} \end{aligned}$$

According to Dalton's law of partial pressure

$$\begin{aligned} P_{\text{total}} &= p_{H_2} + p_{CO_2} = (62.355 + 6.236) \text{ bar} \\ &= 68.591 \text{ bar} \end{aligned}$$

The total pressure will be 68.591 bar.

Example 16 : At 27°C temperature 4 mole Cl₂, 4 mole N₂ and 2 mole O₂ are filled in a 5 litre closed vessel. Find the total pressure of gaseous mixture.

Solution :

According to Dalton's law of partial pressure

$$= (n_{\text{Cl}_2} + n_{\text{N}_2} + n_{\text{O}_2}) \times \frac{RT}{V}$$

$$= (4 + 4 + 2) \times \frac{RT}{V}$$

(T = 27 + 273 = 300 K)

$$= \frac{10 \times 8.314 \times 10^{-2} \times 300}{5} = 49.88 \text{ bar}$$

The total pressure of gaseous mixture will be 49.88 bar.

Example 17 : In a closed vessel, at 25°C temperature 4 mole O₂, 3 mole Cl₂ and 3 mole N₂ are mixed and the total pressure found is 50 bar. Find the partial pressure of each gas.

Solution : According to Dalton's law of partial pressure

$$\text{Total number of mole} = n_{\text{O}_2} + n_{\text{Cl}_2} + n_{\text{N}_2}$$

$$= 4 + 3 + 3 = 10 \text{ mole}$$

$$p_{\text{O}_2} = \left(\frac{n_{\text{O}_2}}{\text{total mole}} \right) \cdot P_{\text{total}}$$

$$= \frac{4}{10} \times 50 = 20 \text{ bar}$$

$$p_{\text{Cl}_2} = \left(\frac{n_{\text{Cl}_2}}{\text{total mole}} \right) \cdot P_{\text{total}}$$

$$= \frac{3}{10} \times 50 = 15 \text{ bar}$$

$$p_{\text{N}_2} = \left(\frac{n_{\text{N}_2}}{\text{total mole}} \right) \cdot P_{\text{total}}$$

$$= \frac{3}{10} \times 50 = 15 \text{ bar}$$

∴ The partial pressure of O₂, Cl₂ and N₂, are 20 bar, 15 bar and 15 bar respectively.

Example 18 : At 400 K temperature in a closed vessel the % by volume of He, Ne and Ar are 40 %, 40 % and 20 % respectively. If the total pressure is 25 bar, then find the partial pressure of each gas.

Solution :

$$p_{\text{He}} = \frac{\% \text{ by volume of gas He} \times \text{total pressure}}{100}$$

$$= \frac{40}{100} \times 25 = 10 \text{ bar}$$

$$p_{\text{Ne}} = \frac{\% \text{ by volume of gas Ne} \times \text{total pressure}}{100}$$

$$= \frac{40}{100} \times 25 = 10 \text{ bar}$$

$$p_{\text{Ar}} = \frac{\% \text{ by volume of gas Ar} \times \text{total pressure}}{100}$$

$$= \frac{20}{100} \times 25 = 5 \text{ bar}$$

∴ The partial pressures of He, Ne and Ar are 10 bar, 10 bar and 5 bar respectively.

Example 19 : At 500 K temperature in 2 litre vessel 0.32 gm O₂ gas is collected over water. If the vapour pressure of water is 32 bar at 500 K, find the partial pressure of dry O₂ gas.

Solution : The pressure of O₂ gas which is collected over water is

$$P_{\text{O}_2} = \frac{mRT}{MV}$$

$$= \frac{0.32 \times 8.314 \times 10^{-2} \times 500}{32 \times 2} = 0.2079 \text{ bar}$$

But, the O₂ gas is collected over water, so this is combined pressure of dry O₂ and water vapour.

$$\text{The water vapour pressure} = 32 \text{ millitre}$$

$$= 0.032 \text{ litre}$$

$$P_{\text{O}_2} = P_{\text{O}_2(\text{dry})} + P_{\text{H}_2\text{O}}$$

$$P_{\text{O}_2(\text{dry})} = P_{\text{O}_2} - P_{\text{H}_2\text{O}}$$

$$= (0.2079 - 0.032) = 0.1759 \text{ bar}$$

The partial pressure of dry O₂ gas is 0.1759 bar.

2.6 Graham's Law of Gaseous Diffusion

In laboratory, at one corner, if a bottle of H₂S water is kept open, then within short time the smell of it will spread in the entire laboratory. If a flask filled with brown colour NO₂ gas is attached with flask containing H₂ gas, although the pressure of both flasks are equal, after sometime both the flasks will have same colour intensity (light brown). This happens because the mixture of gaseous molecules have

characteristic to mix uniformly and that results into homogenous system. Such a characteristic of diffusion of gas is called gaseous diffusion. **So the diffusion of gas means, it is a process in which two or more gases mix spontaneously to form homogeneous system.** They mix spontaneously without taking into consideration the density of mixing gases. This happens because in a gaseous state of substances there is a lot of empty space between the molecules. So the molecules of different gases come in contact with each other and the molecules move and diffuse in the empty space. This process continues till the homogeneous system is formed. Thus, the motion of gaseous molecules is called diffusion and its rate is called rate of the diffusion.

It is proved by the experiment that all gases possess relation between their diffusion rate and their density; higher the density of gas, lower is the rate of the diffusion. By studying this diffusion of gas, Graham in 1928, presented a relation between diffusion rate of gas and its density which is known Graham's law of diffusion of gases. This can be stated as :

“The rate of diffusion of various gases varies inversely proportional to the square root of their densities.”

If the density of gas is (d) and rate of diffusion is (r), then the mathematical form of Graham's law is

$$r \propto \frac{1}{\sqrt{d}}$$

On the basis of measurement of diffusion rate of gas, the molecular mass of the gas can be determined. For this, the diffusion rates of two gases are compared after carrying out the experiment at same temperature and pressure.

Suppose, r_1 and r_2 are the diffusion rates of gas-1 and gas-2 respectively and the densities of these two gases at the same temperature and pressure are d_1 and d_2 respectively, then the following equation can be written from the definition of Graham's law of diffusion of gases.

$$\frac{r_1}{r_2} = \sqrt{\frac{d_2}{d_1}}$$

Now, at the same temperature and pressure the density of a gas varies directly to its molecular mass.

$$\therefore d \propto M$$

Now, $r \propto \frac{1}{\sqrt{d}}$ and $d \propto M$, so by combining these two,

$$r \propto \frac{1}{\sqrt{M}}$$

Now, for two different gases, comparing the rates of diffusion,

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

$$\therefore \frac{d_2}{d_1} = \frac{M_2}{M_1}$$

Hence, it can be proved that at same temperature and pressure, the ratio of the densities of any two gases is equal to the ratio of their molecular masses.

It can be proved from this equation that if the diffusion rates of two gases are measured and if the molecular mass of one gas is known, then the molecular mass of the other gas can be obtained.

The volume of the diffused gas in a unit time is called rate of diffusion.

$$\therefore \text{Rate of diffusion (r)} = \frac{\text{volume of gas diffused (V)}}{\text{time required for diffusion (t)}}$$

$$r = \frac{V}{t}$$

For two gases at the same temperature

and pressure the rates of diffusion are

$$\text{and } r_2 = \frac{V_2}{t_2}$$

$$\frac{r_1}{r_2} = \frac{V_1/t_1}{V_2/t_2} = \sqrt{\frac{M_2}{M_1}} = \sqrt{\frac{d_2}{d_1}}$$

$$\frac{r_1}{r_2} = \frac{V_1 \cdot t_2}{V_2 \cdot t_1} = \sqrt{\frac{M_2}{M_1}} = \sqrt{\frac{d_2}{d_1}}$$

For convenience during the experiment the time taken by two gases for diffusion of equal volumes are measured or the volume of two diffusion gases are measured in equal time. So, during calculation of such experimental observation, the above equation can also be written as below :

$$\frac{V_1 \cdot t_2}{V_2 \cdot t_1} = \sqrt{\frac{M_2}{M_1}} = \sqrt{\frac{d_2}{d_1}}$$

$$\text{If } t_1 = t_2 \text{ then } \frac{V_1}{V_2} = \sqrt{\frac{M_2}{M_1}} = \sqrt{\frac{d_2}{d_1}}$$

$$\text{If } V_1 = V_2 \text{ then } \frac{t_2}{t_1} = \sqrt{\frac{M_2}{M_1}} = \sqrt{\frac{d_2}{d_1}}$$

To determine the ratio of rate of diffusion for two gases, experiment can be carried out in laboratory. For that, at the same temperature and pressure the volume of two gases diffusing at the same time are measured; the experiment performed is as follows :

Experiment : In laboratory to determine the rate of diffusion of NH_3 and HCl gases, the experiment performed is shown in Figure 2.19. A glass tube 100 cm in length and uniform diameter is taken. At the P end of the tube a cotton plug dipped in aqueous ammonia and at the Q end cotton plug dipped in hydrochloric acid are fixed at the same time. As the two gases will diffuse a thin layer of white fumes of ammonium chloride will be formed at the place R as shown in Figure 2.19. Note down this point R and measure the distance PR and QR.

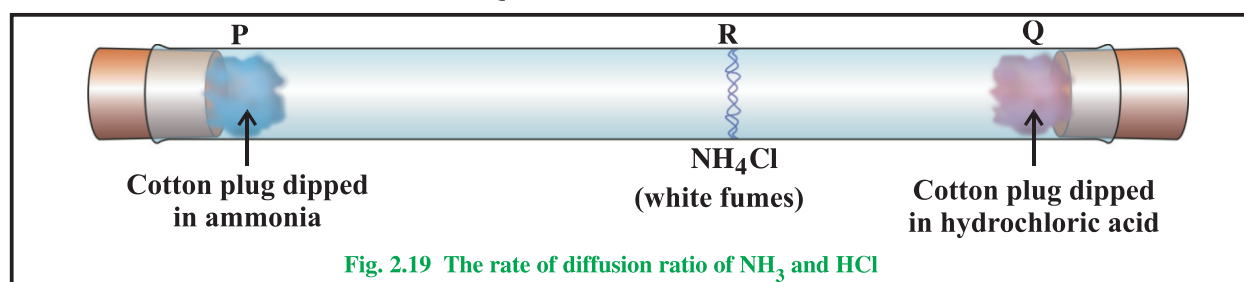


Fig. 2.19 The rate of diffusion ratio of NH_3 and HCl

Reaction :



The white fumes of ammonium chloride is seen, there is a diffusion of ammonia gas which occupies distance PR and the diffusion of hydrochloric acid gas occupies distance QR. As the diameter of the tube is uniform,

$$\frac{V_{\text{NH}_3}}{V_{\text{HCl}}} = \frac{\text{Distance PR}}{\text{Distance QR}}$$

After doing the experiment three times the

average ratio of distances $\frac{\text{PR}}{\text{QR}}$ comes out to be

about 1.46 ± 0.01 . According to Graham's law of diffusion of gases, it indicates the ratio of diffusion rates for $\text{NH}_{3(g)}$ and $\text{HCl}_{(g)}$.

Importance of Graham's law of gaseous diffusion : The importance of Graham's law of gaseous diffusion is given below :

(i) To separate the mixture of two isotopes, e.g. Uranium metal has two isotopes ^{235}U and ^{238}U . ^{235}U is more important in production of nuclear energy. The proportion of ^{235}U in uranium metal is only 0.7 %.

The uranium hexafluoride (UF_6) is a volatile compound. Uranium hexafluoride is prepared from uranium metal. The difference between the molecular masses of $^{235}\text{UF}_6$ and $^{238}\text{UF}_6$ is very less. Hence, the ratio of rate of diffusion of these gases is 1.0047.

Now, if the mixture of $^{235}\text{UF}_6$ and $^{238}\text{UF}_6$ gas filled in a porous vessel and allowed to have the diffusion the amount of $^{235}\text{UF}_6$ of less molecular mass will be somewhat faster in diffusion rate than $^{238}\text{UF}_6$. A series of experiments were carried out. This type of work is carried out in a laboratory extended to a kilometer distance at Oak Ridge in Tennessee

State of U.S.A. The experiment of diffusion of this gas through porous membrane is distributed (extended) to about a kilometer. After a long time pure $^{235}\text{UF}_6$ is obtained which is decomposed to get pure ^{235}U . Thus, the isotopes of uranium are separated by gaseous diffusion.

(ii) Graham's law of gaseous diffusion is used in finding out the molecular masses of gases and the density of gases.

(iii) Graham's law of gaseous diffusion is used in determining the rate of diffusion ratio for any two gases.

Example 20 : Under the uniform experimental conditions, find the rate of diffusion ratio for O_3 and SO_2 gases.

Solution : The molecular masses of O_3 and SO_2 are 48 and 64 g mol^{-1} respectively. So according to Graham's law of gaseous diffusion.

$$\frac{r_{O_3}}{r_{SO_2}} = \sqrt{\frac{M_{SO_2}}{M_{O_3}}}$$

$$= \sqrt{\frac{64}{48}} = 1.1547$$

\therefore The rate of diffusion ratio of O_3 and SO_2 is 1.1547.

Example 21 : The time taken by O_2 gas to travel from sun to earth is 80 seconds. Find the time taken by helium gas from the same source.

Solution : Here, the distance for diffusion of both the gases is equal. So, according to Graham's law of diffusion,

$$\frac{t_{O_2}}{t_{He}} = \sqrt{\frac{M_{O_2}}{M_{He}}}$$

$$\frac{80}{t_{He}} = \sqrt{\frac{32}{4}} = \sqrt{8}$$

(As the molecular mass of O_2 and He are 32 and 4 g mol^{-1} respectively)

$$\therefore t_{He} = \frac{80}{\sqrt{8}}$$

$$= 28.288 \text{ second} \cong 28.29 \text{ second}$$

\therefore The time taken by helium gas is 28.29 second.

Example 22 : The volumes occupied by N_2 and unknown gas in same time are 50 ml and 70 ml respectively. Find the molecular mass of unknown gas.

Solution : According to Graham's law of gaseous diffusion :

$$\frac{r_{N_2}}{r_{\text{unknown gas}}} = \frac{V_{N_2}}{V_{\text{unknown gas}}} = \sqrt{\frac{M_{\text{unknown gas}}}{M_{N_2}}}$$

$$\therefore \frac{50}{70} = \sqrt{\frac{M_{\text{unknown gas}}}{28}}$$

$$\therefore M_{\text{unknown gas}} = \frac{2500 \times 28}{4900}$$

$$= 14.29 \text{ g mol}^{-1}$$

\therefore The molecular mass of unknown gas is 14.29 g mol^{-1} .

2.7 Avogadro's Hypothesis

Avogadro proposed a hypothesis, in 1811. It can be expressed as "The number of molecules of any gas in same volume at standard temperature and pressure is same."

Simple gas equation is one of the methods to present the Avogadro's hypothesis. All the relations derived from Avogadro's hypothesis are included in this equation. This gas equation is applicable to all the gases in favourable conditions. The presentation of this equation in the form of symbol can be made as follows.

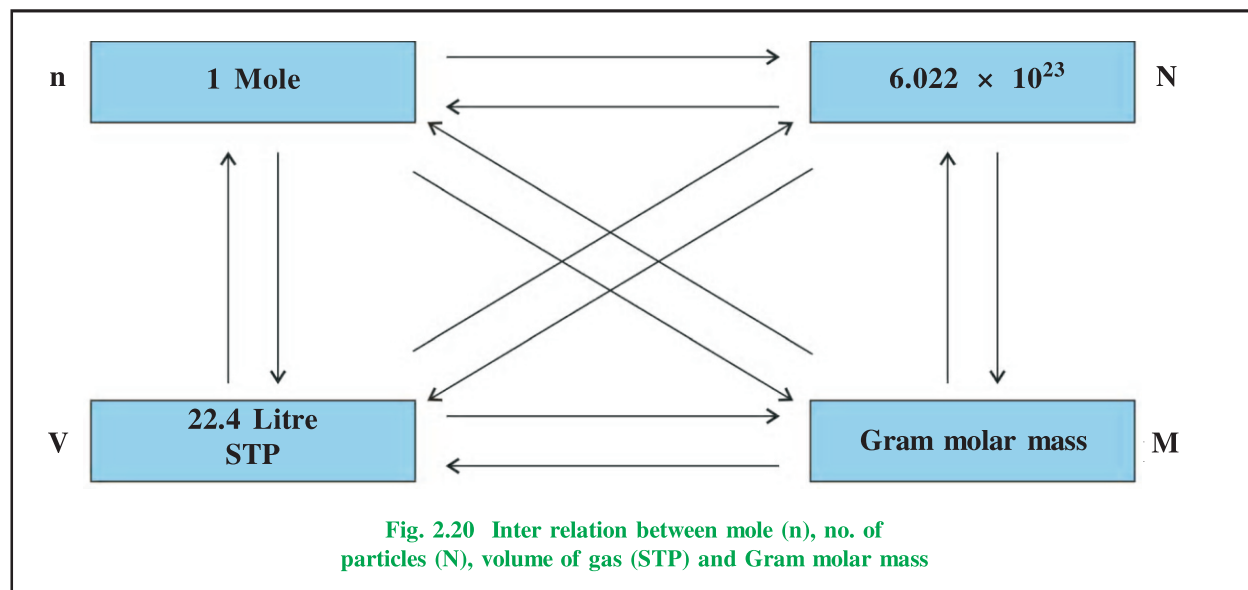
In a V litre volume of any gas at P bar pressure and T Kelvin temperature, n moles of molecules = $n \times N$ (where $N = 6.02 \times 10^{23}$ is known as Avogadro's number or Avogadro's constant).

One important dimension resulting from Avogadro's hypothesis is molar volume. Molar volume can be explained by using simple gas equation. **Molar volume means the volume occupied by the molar mass expressed in gram of a gas.** The volume of 1 mole at 273 K temperature and 1 bar pressure can be found by general gas equation and is called molar volume. The 22.4 litre value is accepted as a standard value. **The molar volume is also known as gram molar volume.** The presentation of Avogadro's hypothesis on the basis of molar volume can be made as follows.

"In 22.4 litre of any gas at 273 K temperature and 1 bar pressure (STP) contain 1 mole molecules." This statement can be given alternatively as the mass of 22.4 litre of any gas at 273 K temperature and one bar pressure is its molecular mass. According to Avogadro's hypothesis, **"The number of molecules in one molar volume of any gas is 6.022×10^{23} ."**

"The mass in gram of one mole of any substance is its molar mass."

The relations among mole number(n), number of particle (N), Volume (V) of STP and molecular mass (M) are given in Figure 2.20.



Example 23 : Find the number of molecules, atoms and total number of atoms in 20 gram CaCO_3 .

Solution : The molecular mass of CaCO_3 is 100 g mol^{-1}

$$\begin{aligned} \therefore \text{Mole of } \text{CaCO}_3 &= \frac{m}{M} = \frac{20}{100} \\ &= 0.2 \text{ mole} \end{aligned}$$

$$\begin{aligned} \text{Now, the number of } \text{CaCO}_3 \text{ molecules} \\ &= \text{mole} \times \text{Avogadro's number} \\ &= 0.2 \times 6.022 \times 10^{23} \\ &= 1.2044 \times 10^{23} \text{ molecules} \end{aligned}$$

One molecule of CaCO_3 is having one atom Ca, one atom C and three atoms of oxygen and total number of atoms is 5.

$$\begin{aligned} \text{So the number of Ca atoms} &= \\ &= \text{molecules } 1.2044 \times 10^{23} \times 1 \\ &= 1.2044 \times 10^{23} \end{aligned}$$

$$\begin{aligned} \text{The number of C atoms} &= \\ &= \text{molecules } 1.2044 \times 10^{23} \times 1 \\ &= 1.2044 \times 10^{23} \end{aligned}$$

$$\begin{aligned} \text{The number of O atoms} &= \\ &= \text{molecules } 1.2044 \times 10^{23} \times 3 \\ &= 3.6132 \times 10^{23} \end{aligned}$$

$$\begin{aligned} \text{Total number of atoms in } \text{CaCO}_3 \\ &= \text{no. of molecules} \times 5 \\ &= 1.2044 \times 10^{23} \times 5 \\ &= 6.022 \times 10^{23} \end{aligned}$$

Example 24 : Find the number of molecules, number of atoms and total number of atoms in 5.6 litre of CH_4 at STP.

Solution :

$$\text{Mole of } \text{CH}_4 = n = \frac{V}{22.4} = \frac{5.6}{22.4} = 0.25$$

$$\begin{aligned} \text{The number of molecules in } \text{CH}_4 \\ &= \text{mole} \times \text{Avogadro's number} \\ &= 0.25 \times 6.022 \times 10^{23} \\ &= 1.5055 \times 10^{23} \text{ molecules} \end{aligned}$$

Now, one molecule of CH_4 has one carbon atom and four hydrogen atoms and total number of atoms are five.

$$\begin{aligned} \text{The number of C atoms} &= 1.5055 \times 10^{23} \times 1 \\ &= 1.5055 \times 10^{23} \end{aligned}$$

$$\begin{aligned} \text{The number of H atoms} &= 1.5055 \times 10^{23} \times 4 \\ &= 1.5055 \times 10^{23} \times 4 \\ &= 6.022 \times 10^{23} \end{aligned}$$

$$\begin{aligned} \text{Total number of atoms} &= 1.5055 \times 10^{23} \times 5 \\ &= 7.5275 \times 10^{23} \end{aligned}$$

Example 25 : Find the volume at STP and mass of 6.022×10^{22} molecules of O_2 .

Solution :

$$\begin{aligned} \text{mole of } O_2 &= \frac{\text{No. of molecules of } O_2}{\text{Avogadro's number}} \\ &= \frac{6.022 \times 10^{22}}{6.022 \times 10^{23}} = 0.1 \text{ mole} \end{aligned}$$

$$\begin{aligned} \text{Volume of } O_2 \text{ at STP} &= \text{mole} \times 22.4 \text{ ltr.} \\ &= 0.1 \times 22.4 \\ &= 2.24 \text{ litre} \end{aligned}$$

$$\begin{aligned} \text{Mass of } O_2 &= \text{mole} \times \text{molecular mass} \\ &= 0.1 \times 32 = 3.2 \text{ grams.} \end{aligned}$$

2.8 Liquid State and its Physical Properties

The liquid has a fixed volume but not a definite shape. It takes the shape of container in which it is poured. As compared to the gaseous state the molecules are arranged near each other in the liquid state. In the liquid state the intermolecular distance between two molecules is less compared to the gaseous state. So the force of attraction is more compared to the gaseous state, but less compared to the solid state and as a result the liquid has fixed volume but not a definite shape. In the liquid state the arrangement of molecules is more in order compared to the gaseous state, but less in order compared to the solid state. Thus, the liquid state is the linking middle state between the solid and the gaseous states. Each liquid state has measurable characteristics of physical properties as mentioned below :

(i) Fixed volume : Liquid has fixed volume. It never expands like gas when it is filled in a vessel. In liquid one surface is free while the remaining surfaces depend on the vessel. As the liquid has fixed volume, the volume will not change by changing the vessels. e.g. 500 ml water poured in beaker, conical flask, bowl bucket, its volume remains only 500 ml. There is no change in volume but it assumes the shape of vessels in which it is poured.

(ii) Fluidity : Liquid can flow and can be poured from one container to another. It assumes the shape of the container because liquid possesses the properties of fluidity.

(iii) Non-compressibility : Compared to gas, the compressive character is very less in liquid. For example at 298 K temperature, if double pressure is exerted on gaseous state the volume becomes half, while in liquid if the pressure is doubled, the volume decreases by 0.0045 % only. If 1000 bar pressure is applied on water at 293 K temperature, then its volume decreases by only 4 %. Thus, compared to gas the liquid has property of non-compressibility.

(iv) Diffusion : If a cylindrical vessel is half filled with water and ethyl alcohol is added carefully from the inner side of the cylinder, the ethyl alcohol keeps floating on the surface of water and a separate surface between the two can be clearly observed. If this system is kept for sometime, gradually the separate surface will become invisible and ultimately it will disappear. Hence, it can be said that ethyl alcohol diffuses in water. If this system is kept for longer time, then both the liquids form homogeneous mixture. The diffusion is shown in liquid compared to gas, because in liquid the molecules are arranged close to each other, so when they diffuse, they undergo collision with the neighbouring molecules which are obstructive in diffusion. Moreover, the intermolecular attractive forces are more in liquid compared to gas which also restricts the molecules in fast diffusion, so the diffusion becomes slow. Moreover, in liquid the rate of diffusion increases with increasing temperature because the kinetic energy of molecules increases due to increase in temperature, so the molecules move faster. The diffusion character is observed in molecules of liquid having same polarity like polar liquid cohesion contact with another polar liquid. Then diffusion takes place, but when comes in contact with non-polar liquid then diffusion will not take place and vice versa is also true.

(v) Evaporation : If the liquid is poured on an open surface it will evaporate as the time passes. The reason is that certain liquid gets converted on its own into gaseous state at normal temperature. This phenomenon is called evaporation. More or less evaporation is there at all temperatures. Like gaseous molecules, the speed of all liquid molecules are not the same as some molecules have maximum speed; some

have medium speed and some have minimum. Now, those molecules with maximum speed have also the maximum kinetic energy and such molecules undergo evaporation and they escape from the liquid surface (into vapour) and as a result the speed of remaining molecules become less so the kinetic energy also becomes less and hence, the temperature decreases. Due to evaporation of liquid the temperature decreases and hence it creates cooling. The evaporation depends upon temperature, strength of intermolecular attractive forces and exposed surface area of liquid.

(vi) Vapour pressure : As the gas in closed container shows pressure, similarly the liquid also shows pressure in a closed container. Due to evaporation the molecules escape from liquid surface but do not leave the container and they are collected in the vapour state above the surface of the liquid. The vapour state molecules move randomly in all directions and collide with one another, with wall of the container and also with the liquid surface. During this, some slow moving molecules when collide with surface of liquid may be recaptured by the intermolecular attraction get and converted into liquid known as condensation. Initially the rate of evaporation and condensation are not equal, but after sometime the rates become equal and this stage is known as dynamic equilibrium and now, the

concentration of the molecules in vapour state becomes constant and the pressure exerted by the vapour molecules is in equilibrium with its liquid called vapour pressure. The vapour pressure depends on the nature of liquid. This means that it depends upon the intermolecular attraction forces of the liquid molecules. Weaker the intermolecular attractive forces, higher is the vapour pressure. Higher the temperature of liquid more is the vapour pressure.

(vii) Surface tension : The molecules of a liquid on one side of hypothetical unit length line on free surface of liquid exerts the force parallel to the surface and perpendicular to the molecules, on the other side of the line is called surface tension of liquid. Due to surface tension the drop is always spherical and the water (liquid) rises in a capillary tube upto certain level (height).

(viii) Viscosity : There is a viscosity between any two successive layers in a movement (conduction) as a result there exists a touching friction resistance force on the contact surface. Such internal resistance force is called viscosity force. **The property of having such a force existing in the liquid is called viscosity.** The viscosity depends on intermolecular forces. As the intermolecular forces increase the viscosity also increases. Viscosity decreases with increase in the temperature.

SUMMARY

The group of molecules is called matter. Matter is made up of small particles. Matter is in three states, Solid, liquid and gas. The other two states are known as Plasma and Bose, Einstein condensate. The physical state of the matter changes by changing temperature. The physical properties of a substance are changed by changing its physical state but the chemical properties do not change, sometimes the rate of chemical reaction changes by changing the physical state. During the chemical calculation, it is most essential to have the information about the physical state of substances (reactant or product) and hence it is essential to study the physical state of matter, factors affecting and related some important laws. The deciding factors of the physical state of matter are intermolecular forces, molecular interaction and the effect of thermal energy on the motion of particles.

The Dutch scientist van der Waals suggested that the weak forces of attraction exist between the molecules, which cannot be explained by any other chemical attraction is known as van der Waals attractive forces. This force is universal. This force of attraction is exerted upto 4.5×10^{-10} distance in substance. van der Waals forces depend upon the shape of molecules, number of electrons present in molecules, contact surface of molecules and

average intermolecular distance. The van der Waals forces of attraction are different like (i) Dispersion forces or London forces. (2) Dipole-dipole forces and (3) Dipole-induced dipole forces.

Dispersion forces of attraction was first of all proposed by the German scientist Fritz London so it is known as London forces. This type of force of attraction is observed in atoms or molecules, there is a temporary dispersion in electron density that affect the electron density of nearby atom or molecule so the force of attraction is developed and so such effect is called dispersion force. The dipole-dipole forces are observed in permanently dipolar molecules. Such dipolar molecules also have interactive London forces so the cumulative effect of both forces are observed. The dipole-dipole force is stronger than London forces. The dipole-induced dipole forces are observed when dipolar molecules come near to non-polar molecules. This type of molecules also have London forces and hence the cumulative effect of both forces are observed. The hydrogen bonding is an important intermolecular force. The first elements of groups 5, 6 and 7 due to their high electronegativity combine with hydrogen to form hydride compounds, in which hydrogen bond is observed. There also exists an intermolecular repulsive forces; and based on that the effect of pressure on solid, liquid and gaseous state explained very easily. The most important factor which decides the physical, state of matter is the effect of thermal energy, on motion of molecules due to this motion of molecules or atoms the energy produced is called thermal energy to keep the molecules near to each other while the thermal energy has tendency to keep the molecules away from each other. By balancing combination of the two opposite factors, the physical state of matter as solid, liquid or gas is decided. Due to weak forces of attraction between molecules of gaseous state have some characteristics. The behaviour of gas is described by the quantitative relation between mass, volume, temperature and pressure and these relations are discovered by experimental observations and such relations are called laws of gases. The relation between pressure and volume of a gas was studied and it is known as Boyle's law. At constant temperature for a fixed amount gas, pressure (P) varies inversely with its volume (V). Mathematically the Boyle's law is written as $PV = K$ or $P_1V_1 = P_2V_2$. The equation $d/P = K$ devised from Boyle's law where d is the density. The Kelvin temperature is accepted as an SI unit. The relation $T = (t + 273.15)$ K is obtained. On the basis of experimental observations a relation between absolute temperature and volume is obtained,

which is known as Charles' law. Mathematically it is written as $\frac{V}{T} = K$ or $\frac{V_1}{T_1} = \frac{V_2}{T_2}$.

The relation between pressure and absolute temperature (T) is obtained on the basis of experimental observations by scientist Gay Lussac and is known as Gay Lussac's law.

Mathematically it is written as $\frac{P}{T} = K$ or $\frac{P_1}{T_1} = \frac{P_2}{T_2}$. The relation between volume of a gas and number of molecules was given by Avogadro, which is known as Avogadro's law. The mathematical form of it is $V = K \cdot n$. The 0°C or 273 K temperature and 1 bar pressure is accepted as a standard value by SI system and hence these values are known as standard temperature and pressure (STP). 1 mole of gas at STP is having volume 22.4 litre and number of molecules equal to 6.022×10^{23} known as molar volume and Avogadro's number respectively. Combining Boyle's law and Charles' law, the relation

obtained $\frac{PV}{T} = K$ or $\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$ is known as combined gas equation. The ideal gas equation, $PV = nRT$ is also known as equation of state and R is called universal gas constant which has different values in different units. The real gas behaves as ideal gas

- (6) The temperature of O_2 gas is changed from $25^\circ C$ to $50^\circ C$, then the change in volume is...
- (A) twice (B) less than twice (C) half (D) more than twice
- (7) What is the value of compression factor Z for the gas ?
- (A) 1 (B) >1 (C) <1 (D) Zero
- (8) At what temperature does the gas start liquefying ?
- (A) T_C (B) $> T_C$ (C) $< T_C$ (D) T_C or $< T_C$
- (9) Which change is observed during evaporation of liquid in atmosphere ?
- (A) heat increases (B) cooling starts
(C) heat becomes zero (D) all of above
- (10) How many number of hydrogen atoms are in 1 gram H_2 ?
- (A) 6.022×10^{23} (B) 3.011×10^{23} (C) 6.022×10^{-23} (D) 6.022×10^{24}
- (11) Higher the critical temperature is liquefaction.
- (A) slow (B) fast (C) slow or fast (D) all the above
- (12) Which relation is true for 4 gms of He gas ?
- (A) the number of atoms are double than molecules
(B) the number of atoms are four times that of molecules
(C) the number of atoms are sixteen times that of molecules
(D) the number of atoms and molecules are same
- (13) If the temperature is increased the viscosity is
- (A) increased (B) decreased (C) not changed (D) becomes zero
- (14) Which two liquids on mixing starts diffusion ?
- (A) water-kerosene (B) water-benzene
(C) water-petrol (D) water-alcohol

2. Write answers to the following questions :

- (1) Write types of van der Waals forces.
- (2) In which type of atoms or molecules London forces are observed ?
- (3) Which type of molecules possess hydrogen bonding ?

- (4) Which combined forces decide the physical state of substances ?
- (5) Write Boyle's law.
- (6) What is the absolute temperature ?
- (7) Give value of standard temperature and pressure.
- (8) Write Charles' law.
- (9) Write Avogadro's law.
- (10) State Gay-Lussac's law.
- (11) Write combined gas equation.
- (12) State the variables in ideal gas equation.
- (13) What is a real gas ?
- (14) In which condition the real gas behaves as an ideal gas ?
- (15) What is an ideal gas ?
- (16) State the equation of compression constant Z .
- (17) Write van der Waals' equation.
- (18) What is critical temperature ?
- (19) What is critical mass ?
- (20) Write Graham's law.
- (21) Write Avogadro's hypothesis.
- (22) Define viscosity, diffusion, vapour pressure.
- (23) State different critical constants.
- (24) State the factors affecting vapour pressure.

3. Write answers to the following questions :

- (1) Give the different types of van der Waals' forces.
- (2) Explain dipole-dipole forces.
- (3) Explain London forces.
- (4) Explain dipole-induced dipole forces.
- (5) What is Kelvin scale ?
- (6) Write Avogadro's law and explain.

- (7) Derive combined gas equation.
- (8) Derive unit of R from ideal gas equation.
- (9) Explain liquid state and write its properties.
- (10) Explain kinetic energy of molecules.
- (11) Explain positive and negative deviation for real gas.

4. Write answers to the following questions :

- (1) Write a short note on hydrogen bonding.
- (2) Explain characteristics of gaseous state.
- (3) State gas laws and derive ideal gas equation.
- (4) Obtain values of R from different unit systems
- (5) Explain deviation from ideal gas.
- (6) Explain liquefaction of gas.
- (7) Explain isotherm curve for liquefaction of gas.
- (8) Explain Graham's law of gaseous diffusion.
- (9) Explain Dalton's law of partial pressures.
- (10) Describe the experiment of diffusion of NH_3 and HCl.

5. Solve the following examples :

- (1) Find the volume of 6.022×10^{21} molecules of CO_2 gas at 27°C temperature and 2 bar pressure.
- (2) Find the number of molecules, atoms and total number of molecules, atoms and 350 K temperature and 10^3 Pa pressure.
- (3) 2×10^6 molecules of N_2 gas enter into the vessel having volume 400 ml at 127°C temperature. Find the pressure of N_2 gas.
- (4) The % composition by volume of Cl_2 , H_2 and N_2 are in 1:2:7 by proportion. If the total pressure is 40 bar, find the partial pressures of each gas.
- (5) At 25°C temperature 4 gram H_2 is filled in 500 ml vessel. Due to small hole in vessel, after sometime, the pressure in vessel became 50 bar. Find the number of molecules which have escaped from the vessel.
- (6) The O_2 gas is collected over water at 127°C temperature in 2 litre vessel. If the pressure of dry O_2 gas is 32.20 bar then find the vapour pressure of water under the same conditions.

