

CHEMISTRY

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*(1) State and explain the types of van. der waals forces.

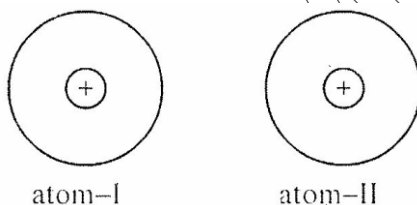
Ans: There are three types of van der waals forces,

- (i) Dispersion forces or London forces.
- (ii) Dipole–dipole forces
- (iii) Dipole–induced dipole forces.

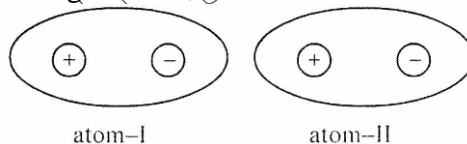
(i) **Dispersion forces or London forces:**

➤ This force of attraction was proposed by German scientist Fritz London, so it is known as London forces. Scientist Fritz London. So it is known as London forces.

➤ Generally, in atoms of non–polar molecules, their electronic charge cloud is distributed symmetrically. In such atoms or molecules the temporary dipolarity is developed which can be explained as below. As shown in two atoms (atom–I and atom–II), the electron cloud is distributed symmetrically.

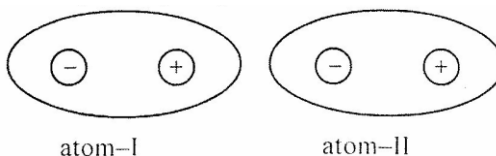


➤ When two such atoms come close to each other, in one atom the electronic charge density undergoes the dispersion. Hence electron density will move towards the right hand side pole. So the left hand side pole will be in shortage of that, therefore atom–I become temporarily dipolar.



➤ Now the other atom atom–II comes in contact and realises its effect and the dispersion in symmetrical electron density and dipole character is induced in it.

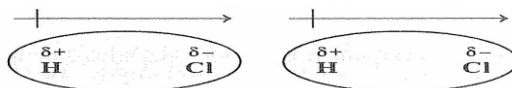
➤ The opposite pole of atom–I and II comes in contact that develops temporary force of attraction.



➤ The force of attraction in atoms or molecules in which there is a temporary dispersion in electron density that affects the electron density of nearby atom or molecules, this is known as dispersion force.

(ii) Dipole–dipole forces:

- The molecules are made up of the atoms having more difference in their electro negativities are always dipolar.
- In such molecules, which are permanently dipolar, the atom having higher electronegativity becomes partially negatively charged and atom having less electronegativity become partially positively charged.
- The value of partial charges is always less than unit electronic charge $1.6 \times 10^{-19} \text{ C}$
- In such dipolar molecules there is a force of attraction between the poles of atoms having partially opposite charges,



- 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 force between such molecules so the cumulative effect of both the forces is observed. In these molecules these forces are stronger than London forces.

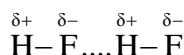
(iii) Dipole–induced dipole forces:

- When dipolar molecules come closer to non–polar molecules, then this type of force of attraction is observed.
- In dipole 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 below.
- The non–polar molecule comes in contact with B⁻ pole of the 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.
- These types of molecules also have interactive London forces and hence, in such molecules the cumulative effect of both forces can be observed.

(2) Discuss the relation of hydrogen bond and states of matter?

Ans: Hydrogen bond is found in the molecules in which highly polar N–H, O–H or H–F bonds are present.

- Although hydrogen bonding is regarded as being limited to N, O and F; but species such as Cl may also participate in hydrogen bonding,
- energy of hydrogen bond varies between 10 to 100 kJ mol⁻¹. This is quite a significant amount of energy; therefore, hydrogen bonds are powerful force in determining the structure and properties of many compounds, for example proteins and nucleic acids.
- Strength of the hydrogen bond is determined by the coulombic interaction between the lone–pair electrons of the electronegative atom of one molecule and the hydrogen atom of other molecule.
- Following diagram shows the formation of hydrogen bond.



(3) State and explain Boyle's law.

Ans: "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:

$$P \propto \frac{1}{V} \quad \therefore P = K \times \frac{1}{V}$$

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

$$\therefore PV = K$$

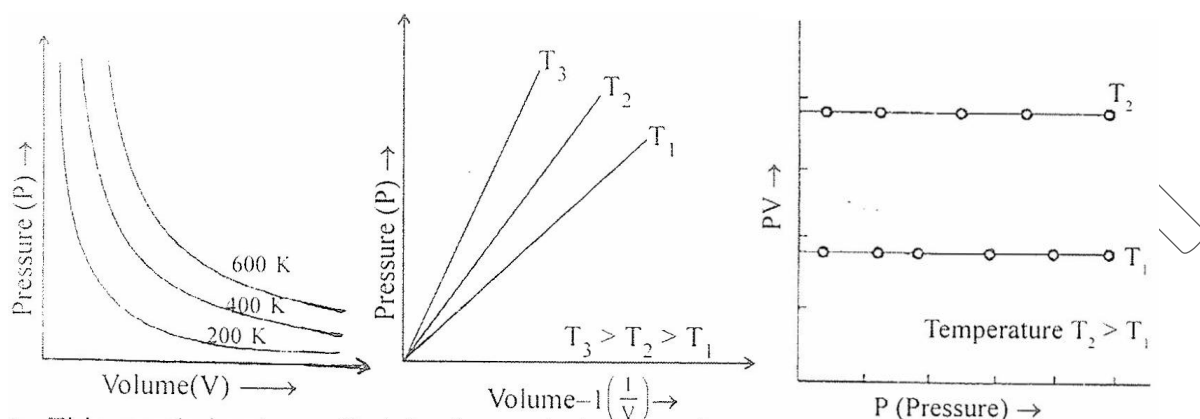
- So from Boyle's law it is said that "At constant temperature for fixed amount of gas the product of its pressure and volume is constant."
- Now, suppose at the initial stage, at constant temperature the fixed amount of gas has its pressure and volume as P_1 and V_1 respectively and at final stage they become P_2 and V_2 then according to Boyle's law

$$P_1V_1 = K \quad \dots (1)$$

$$P_2V_2 = K \quad \dots (2)$$

From equations (1) and (2) $P_1V_1 = P_2V_2$ (at constant temperature and fixed amount)

➤ Boyle's law can be shown by following graph which indicates the relation between pressure and volume of gas at different constant temperature and fixed



➤ 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.

(7) **Derive a relation between the density and pressure of gas. State its application.**

Ans: According to Boyle's law

$$PV = K \quad \dots (1)$$

$$\text{Now, density } d = \frac{m}{V}$$

$$\therefore V = \frac{m}{d} \quad \dots (2)$$

Hence from equation (1) and (2) we get

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

$$\therefore d = \frac{m}{K} \times P$$

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'

$$\therefore d = k'P$$

$$\therefore d \propto P$$

$$\therefore \frac{d}{P} = K'$$

$$\text{So, } \frac{d_1}{P_1} = \frac{d_2}{P_2}$$

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."

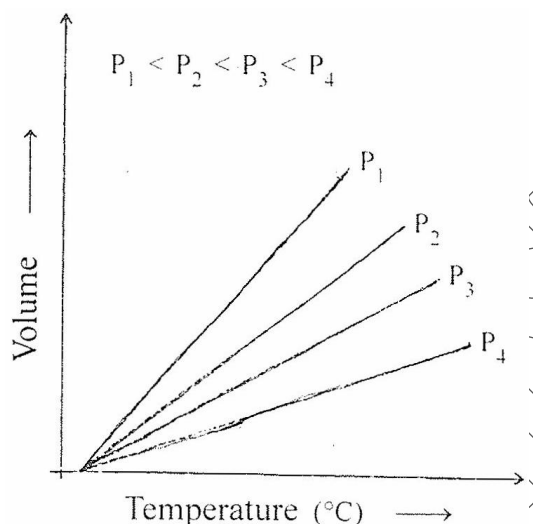
The application of this relation is useful to understand the practical illustration. The pressure of air decreases on Mount Abu (nearly 0.5 bar). So, as the pressure of air decreases the density also decreases. This means that the density of O_2 in air also decreases and it becomes difficult to breath. 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. Even though by chance if any difficulty arises in breathing, then the facilities of O_2 is also available.

(8) What is absolute zero temperature? Explain.

Ans: 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 graph.



➤ For the fixed 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,

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

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

➤ 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.

(9) State and explain Charles law.

Ans: "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 $\left(V_0 \times \frac{1}{273}\right)$. Now if the temperature increased by t °C, then the

change in volume is $\left(V_0 \times \frac{t}{273}\right)$. So at t °C temperature the

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

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

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

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

but $t + 273 = T_t$ K and for 273 is T_0 . putting this value in above equation we get,

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

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

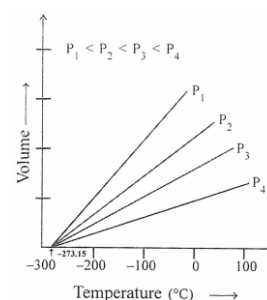
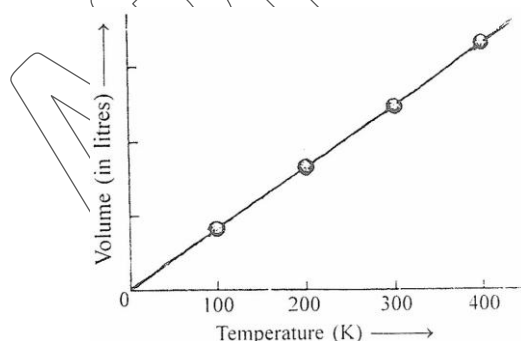
$$\therefore \frac{V_t}{V_0} = \frac{T_t}{T_0} = K \text{ or } \frac{V_t}{V_0} = \frac{V_t}{T_t} = K$$

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

$$\therefore V = KT \text{ or } V \propto T$$

Charles law:

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



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 $\frac{V}{T} = K$.

(10) State and explain Gay-Lussac's law.

Ans: "For constant volume, the pressure of a fixed amount of gas varies directly with its absolute, temperature."

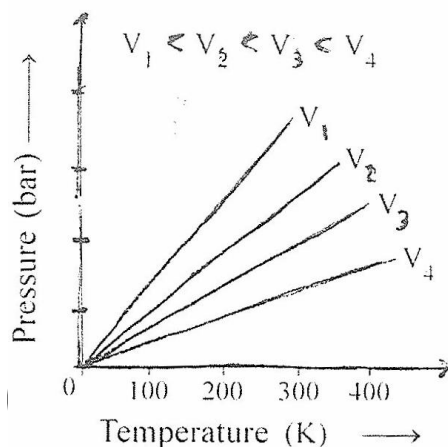
Gay-Lussac's law is written mathematically as $P \propto T$, (constant volume of gas, fixed amount)

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

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 P_2 and T_2 , then according to Gay-Lussac's law

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

Gay-Lussac's law can also be explained by graph. The relation between pressure and absolute temperature is obtained as shown in Figure. Now, at constant volume and fixed amount of gas, the values of y obtained are constant at different temperatures i.e. $\frac{P}{T} = K$. The constant K is different at different constant values $V_1 < V_2, < V_3 < V_4$.



(11) What is standard temperature and pressure [STP]?

Ans: The volume of a fixed amount of gas depends upon its temperature and pressure. So 0°C or 273 K temperature and 1 bar pressure (105 Pa) are 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 $22.71\text{ }^\circ\text{98 litre.mole}^{-1}$) at standard temperature (STP) and the volume at STP is known as molar volume. So, normally at STP, 22.413996 liter 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 liter of gas contains 6.022×10^{23} molecules.

(12) Derive the ideal gas equation.

Ans: 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,

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

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

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

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

$$\therefore PV = nRT \text{ (where R is proportionality constant)}$$

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 event though R has different values related to different unit systems.

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

Ideal gas equation $PV = nRT$, where n is the number of moles

But, $n = \frac{m}{M}$, where m is mass of gas and M = molecular mass.

Putting this value in above equation we get.

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

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

$$\therefore P = \frac{dRT}{M}$$

(13) Discuss the different forms of gas constant R. Also derive its different value in different units.

Ans: 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 different in different systems.

From ideal gas equation, $PV = nRT$

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

But, pressure = force / area

$$\therefore R = \frac{(\text{force/area}) \times \text{volume}}{\text{mole} \times \text{temperature}}$$

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

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

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

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.

$$\therefore R = \frac{PV}{nT} = \frac{1 \text{ atmosphere} \times 22.4 \text{ L}}{1 \text{ mole} \times 273 \text{ K}} = 0.0821 \text{ litre atmosphere mole}^{-1} \text{ K}^{-1}$$

(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.

$$\begin{aligned} \therefore R &= \frac{PV}{nT} = \frac{1 \text{ atmosphere} \times 22400 \text{ cm}^3}{1 \text{ mole} \times 273 \text{ K}} \\ &= 82.1 \text{ atmosphere cm}^3 \text{ mole}^{-1} \text{ K}^{-1} \end{aligned}$$

(3) If the unit of pressure and volume are dyne cm² and cm³ respectively, then the unit R will be erg mole⁻¹ K⁻¹.

$$\therefore R = \frac{PV}{nT} = \frac{76 \text{ cm of hg height} \times 22400 \text{ cm}^3}{1 \text{ mole} \times 273 \text{ K}} = \frac{76 \times 13.6 \times 981 \times 22400 \text{ cm}^3}{1 \times 273 \text{ K}}$$

where 13.6 is the density of Hg and $g = 981 \text{ dyne} = 8.314 \times 10^{-7} \text{ erg mole}^{-1} \text{ K}^{-1} = 8.314 \text{ J K}^{-1} \text{ mole}^{-1}$

(4) Now, 4.184 J = 1 calorie

$$\begin{aligned} \therefore R &= 8.314 / 4.184 = 1.987 \text{ calorie K}^{-1} \text{ mole}^{-1} \approx 2 \text{ calorie K}^{-1} \text{ mole}^{-1} \\ &= 2 \times 10^{-3} \text{ Kilocalorie K}^{-1} \text{ mole}^{-1} \end{aligned}$$

(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

$$\therefore R = \frac{PV}{nT} = \frac{1 \text{ bar} \times 22.71 \text{ litre}}{1 \text{ mole} \times 273.15 \text{ K}} = 8.314 \times 10^{-2}$$

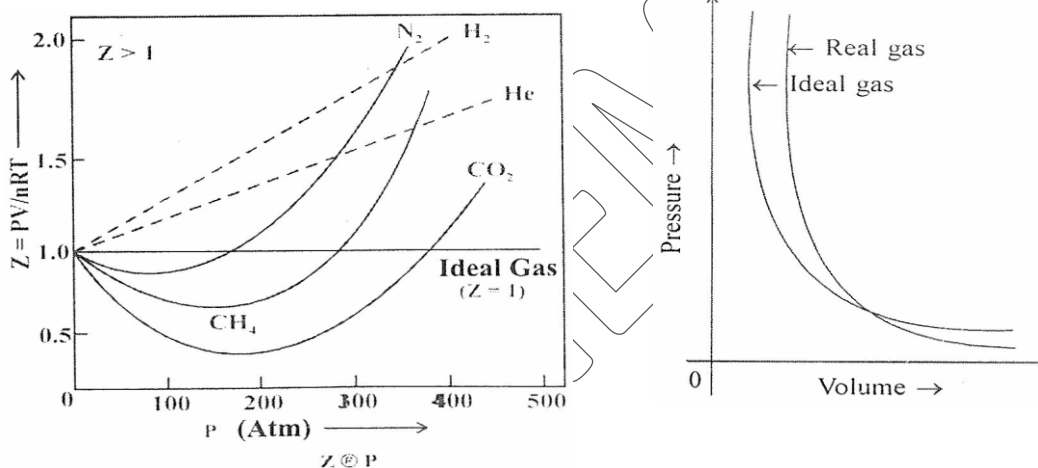
$$\text{bar lit mol}^{-1} \text{ K}^{-1} = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$$

(14) Explain the effect of pressure on the deviation from ideal gas behaviour.

Ans: To study the deviation in the behaviour of real gas from that of ideal gas, its idea can be obtained by

plotting that of ideal $\frac{PV}{nRT} \rightarrow P \cdot \frac{PV}{nRT}$ is called compressibility factor, which is indicated by Z.

- For ideal gas value of $Z = 1$. because $PV = nRT$ for ideal gas equation. $PV = nRT$
- 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, for H, and He gases always $Z > 1$ so it is called positive deviation and it indicates that at all values of pressure they are less compressive than real gas, while for N, and CO gases at low. pressure $Z < 1$ is called negative deviation. It indicates that, they are more compressive than real gas and at high pressure $Z > 1$ is called positive deviation which indicates that at high pressure, they are less compressive than real gases shown in figure.

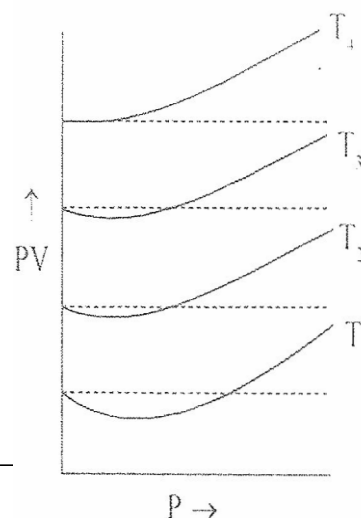


- For all gases the pressure is reduced and when it becomes zero, at that time $Z = 1$ means at zero pressure all gases behave as an ideal gas.
- To study the deviation, the experimental data obtained for volumes of real gas at different pressures and theoretical data obtained for volumes of an ideal gas by calculation on the basis of Boyle's law at different pressures can be plotted against volume as shown in Figure.
- 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 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.

(15) Explain the effect of temperature on deviation from ideal gas behaviour.

Ans: The effect of temperature can be explained by comparing the real behaviour of N, gas and its ideal behaviour at different temperatures.

- As shown in Figure at different temperatures for N, 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 the deviation of real gas compared to ideal gas behaviour goes on decreasing.
- 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 , 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 , gas it is 332 K and for H_2 , gas it is 108 K.

(16) Derive van der waal's equation. OR Explain the corrections made in the ideal gas equation for applying it to the real gases.

Ans: According to the following assumptions made from the kinetic molecular theory of gases:

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

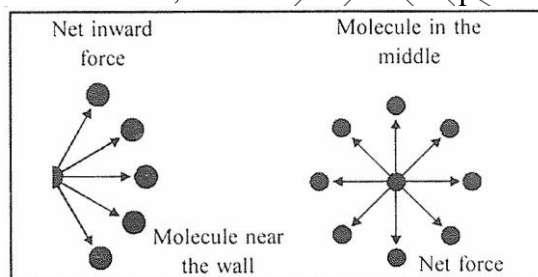
(2) The volume of a molecule is negligible (which can be avoided) compared to total volume of gas.

➤ 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 graph of volume and pressure will be same, but in fact, 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, 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, i.e. they are ready to touch the wall of container, at that time, as shown in Figure, 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 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 sum of real pressure and $\frac{an^2}{V}$.

Ideal pressure of gas $\frac{an^2}{V}$.

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:

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

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.

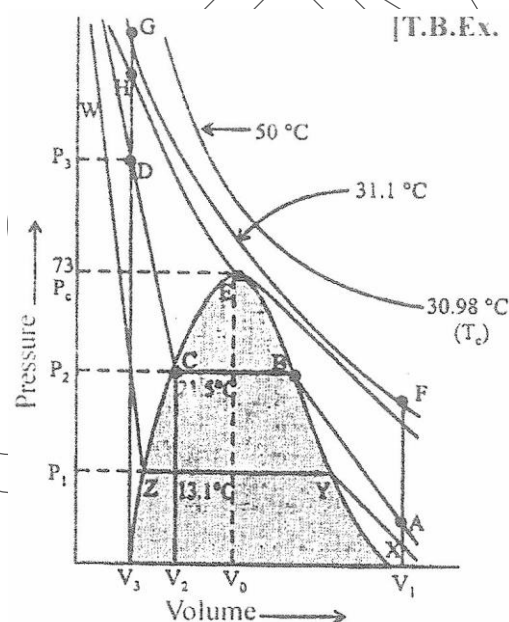
(17) Explain liquefaction of gases. OR Define: Critical temperature, critical pressure. Critical volume.

Ans: 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; 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.

(18) Explain the isotherm curve for liquefaction of gases.

Ans:



- 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 strong 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.
- At lower temperature i.e. 13.1°C temperature and lower pressure, at point X the 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°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 CO₂ 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 CO₂ gas. Above this temperature, however, the pressure is applied, still the liquefaction of CO₂ is not possible but at 30.98°C or less than that temperature liquefaction is possible under pressure.

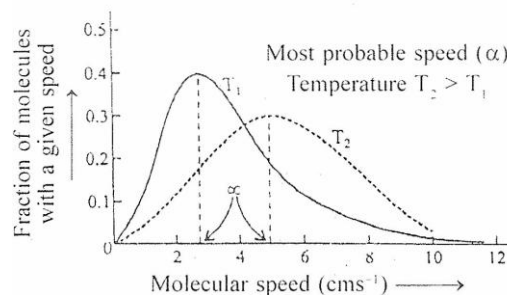
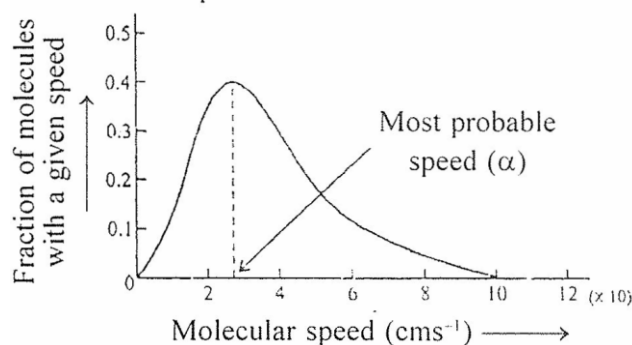
➤ According to kinetic molecular theory of gases on lowering the temperature the kinetic energy of the molecules decreases and as a result slow moving molecules come closer to each other. At sufficiently low temperature some of the slow moving molecules cannot resist the force of attraction and they 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 increases in pressure 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 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 H₂ gas starts liquefying first and at that time He gas is not liquefied.

(19) Write a note on kinetic energy and molecular speeds.

Ans: 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. The feature of molecular speed is shown below.



- (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. 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.

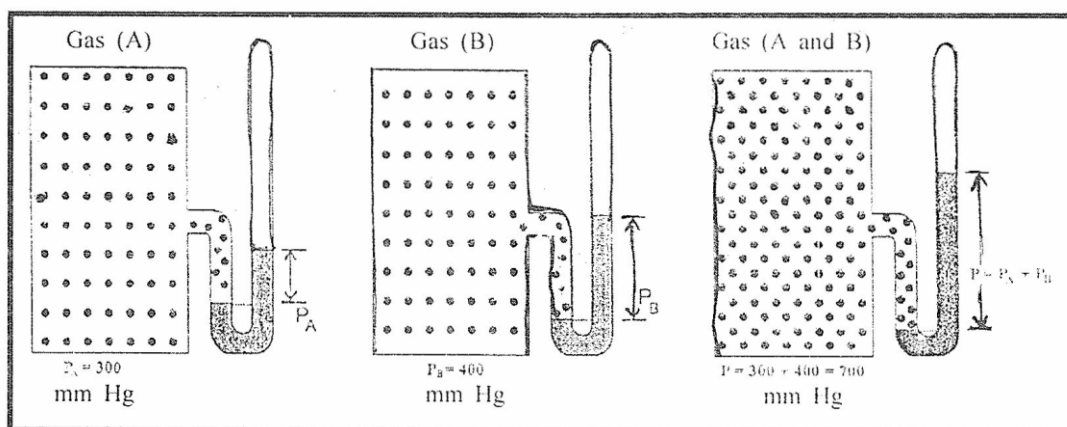
- (1) most probable speed (2) average speed (3) root mean square speed.

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

(20) State and explain Dalton's law of partial pressure.

Ans: In 1801, Dalton stated the law of partial pressure which can be written as "The total pressure exerted by the mixture of non-reactive gases is equal to the sum of the partial pressures of individual gas."

Partial pressure 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, take three vessels having same volume at 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 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

$$P_{total} = P_A + P_B$$

➤ 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 (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.

$$P_{O_2} = P_{total} - P_{H_2O}$$

➤ 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.

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

$$\text{But, } P_1 = \frac{n_1RT}{V}, P_2 = \frac{n_2RT}{V} \text{ and } P_3 = \frac{n_3RT}{V}$$

Putting values in above equation we get,

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

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

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

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

$$\text{Taking ratio of } P_1 \text{ and } P_{\text{total}} \quad \frac{P_1}{P_{\text{total}}} = \frac{n_1 RT}{V} \times \frac{V}{\text{total mole} \times RT} = \frac{n_1}{\text{total mole}}$$

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

$$\therefore \frac{P_1}{P_{\text{total}}} = X_1$$

$$\therefore P_1 = X_1 \cdot P_{\text{total}}$$

$$\text{Similarly, } P_2 = X_2 \cdot P_{\text{total}}$$

$$\text{and } P_3 = X_3 \cdot P_{\text{total}}$$

➤ 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.

$$\text{The partial pressure of gas } (P_A) = \frac{\% \text{ by volume of gas A} \times \text{total pressure}}{100}$$

(21) Explain the Graham's law of gaseous diffusion.

Ans: In 1928, Graham 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, $r \propto \frac{1}{\sqrt{M}}$

$$\text{➤ Now, for two different gases, comparing the rates of diffusion, } \frac{r_1}{r_2} = \sqrt{\frac{d_2}{d_1}} = \sqrt{\frac{M_2}{M_1}}$$

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

➤ 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.

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

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

➤ For convenience during the experiment the time taken by two gases for diffusion of equal volume are measured or the volume of two 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:

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

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

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

(22) State the importance of Graham's law of gaseous diffusion.

Ans: 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.

(23) Explain Avogadro's hypothesis.

Ans: 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 favorable 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.

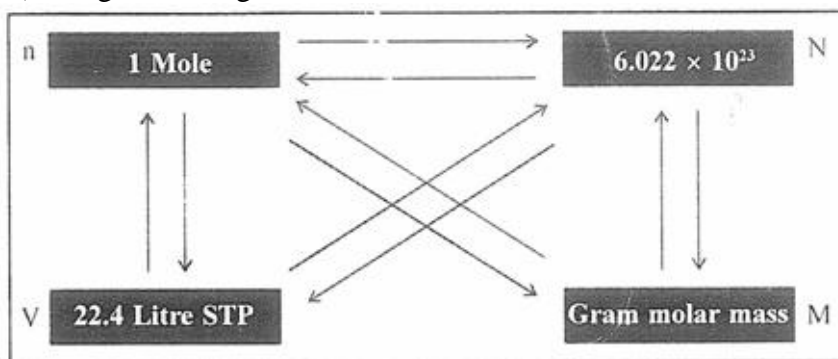
➤ "In 22.4 litre of any gas at 273 K temperature and 1 bar pressure (STP) contain 1 mole molecules."

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



(24) Explain liquid state of matter. Discuss the physical properties of liquid in detail.

Ans: 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. .

(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 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 some time, 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 closer 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 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 speeds 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 force, higher is the vapour pressure. Higher the temperature of liquid more is the vapour pressure.

(vii) Surface tension:

➤ The molecules of a liquid on any hypothetical unit length line on free surface of liquid exerts the force parallel to the surface and perpendicular to the molecules, 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 inter-molecular forces. As the intermolecular forces increase the viscosity also increases. Viscosity decreases with increase in the temperature.

(25) Explain how evaporation creates cooling?

Ans: 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 speeds of all liquid molecules are not the same as some molecules have maximum speed; some have medium speed and some have minimum.

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