CHEMISTRY

CHAPTER 5: STATES OF MATTER

STATES OF MATTER

Introduction

Gas is the state of matter in which molecules are always in random motion. Intermolecular interactions are extremely small (almost negligible) as compared to other states like solid and liquid. Gases are highly compressible state of matter and its state of diffusion is maximum. Gases have their own importance in living world. Air is a gaseous mixture of oxygen, nitrogen, CO2, Ar, etc.

Intermolecular Forces

Intermolecular forces are the forces of attraction and repulsion between interacting particles. This term does not include the electrostatic forces that exist between the two oppositely charged ions.

Van der Waal's Forces

These are the weak forces of attraction between two molecules with or without any strong bond. These are electrostatic in nature. Types of van der Waal's forces are as follow:

1. **Dipole-dipole interaction:** These forces exist between two molecules which are polar in nature. Opposite charges of two dipoles attract each other and produce interactions called keesom forces. In HCl, dipole-dipole interactions exist.
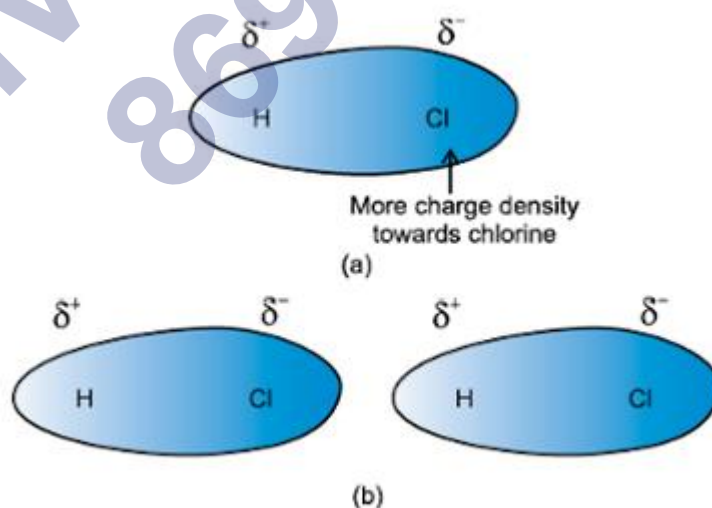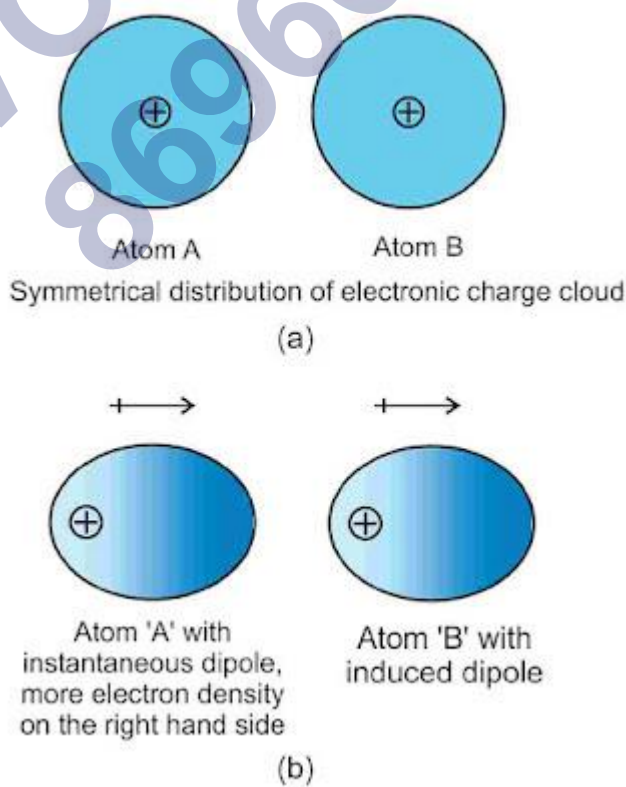

Dipole-dipole interaction energy is inversely proportional to the sixth power of the distance between the rotating polar molecules.

interaction energy $\propto \dfrac{\pi}{r^6}$

2. **Dipole-induced dipole interaction:** When a polar molecule comes closer to a non-polar molecule it induces weak polarity (dipole) in that molecule. Now, weak interactions develop between polar molecule and molecule in which polarity is induced. These interactions are known as Debye interactions.

Permanent dipole
(a polar molecule)

non-polar molecule

Permanent dipole
(a polar molecule)

Induced dipole in
a non-polar molecule
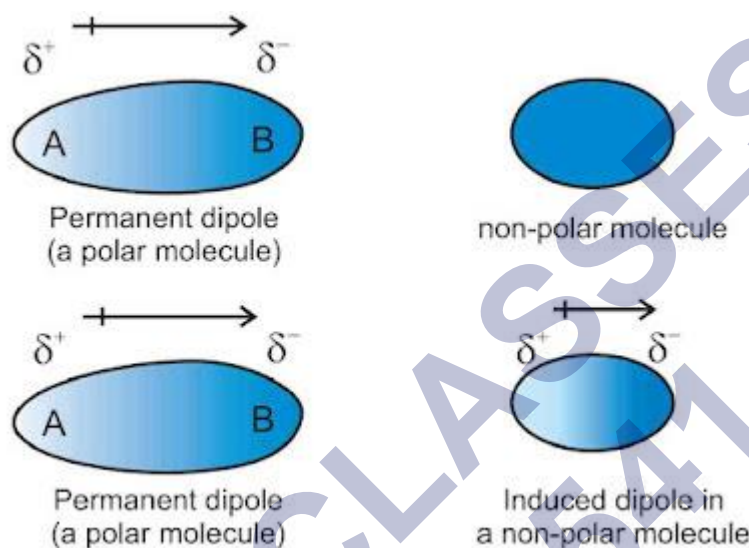
3. **London dispersion forces:** This polar molecule produces polarity in other molecule. Weak interaction arises between instantaneous dipoles. These interactions are known as Dispersion forces or London forces.

Atom A

Atom B

Symmetrical distribution of electronic charge cloud

(a)

Atom 'A' with
instantaneous dipole,
more electron density
on the right hand side

Atom 'B' with
induced dipole

(b)

Measurable Properties of Gases

1. **Temperature:** Temperature is a relative measure, or indication of hotness or coldness. At absolute zero on Kelvin scale is equivalent to −273.15°C on the Celsius scale. Both the Celsius and the Kelvin scales have units of equal magnitude that is one degree celsius equivalent to one kelvin.

   Thus T(K) = T(°C) + 273.15

2. **Pressure of a gas:** According to laws of motion, pressure is defined as force applied per unit area of surface. It is denoted by P and SI unit of it is pascal (Pa). It is a scalar quantity.

$$P = \frac{F}{A}$$

3. **Atmospheric Pressure:** The atmospheric pressure at a point is equal to the weight of a column of air of unit cross-sectional area extending from that point to the top of the atmosphere. Its value is 1.013×10^5 Pa at sea level. Atmospheric pressure is measured using an instrument called barometer.

Gaseous Laws

Boyle's Law (Volume-Pressure Relation)

According to this, "The volume of a given mass of gas is inversely proportional to pressure at constant temperature." This law is given by Robert Boyle.

$$P \propto \frac{1}{v} \dots \dots \text{(at Constant T and n)}$$

$$P = k\frac{1}{v}$$

where k is the proportionality constant.

If a fixed amount of gas at constant temperature T occupying volume V_1 at pressure P_1 undergoes expansion, so that volume becomes V_2 and pressure becomes P_2, then according to Boyle's law:

$P_1V_1 = p_2V_2$ = constant

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

Charle's Law (Volume-Temperature Relation)

According to this, "The volume of a given mass of gas is directly proportional to its absolute temperature at constant pressure." This law is given by Jacques Charles.

$V \propto T$ ……. (at constant P)

$V = kT$

where k is the proportionality constant.

If a fixed amount of gas at constant pressure P occupying volume V_1 at temperature T_1 undergoes expansion, so that volume becomes V_2 and temperature becomes T_2, then according to Charle's Law:

$$\frac{V}{T} = \cdots \ldots \ldots . \text{constant}$$

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

Gay Lussac's Law (Pressure-Temperature Relation)

It states that at constant volume, the pressure of a fixed mass of a gas is directly proportional to the Kelvin temperature. The law may be expressed mathematically as

$P \propto T$ …….. (at constant V)

$P = kT$

where k is the proportionality constant.

If a fixed amount of gas at constant volume V occupying pressure P_1 at temperature T_1 undergoes expansion, so that pressure becomes P_2 and temperature becomes T_2, then according to Gay Lussac's Law:

$$\frac{P}{T} = \text{constant}$$

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

Avogadro's Law ((Volume - Amount Relationship)

According to this, "Equal volumes of all gases at same temperature and pressure contain equal numbers of molecules".

$V \propto n$

$V = kn$

where k is the proportionality constant.

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

Ideal Gas Equation

On combining the Boyle's law, Charles law and Avogadro's law we get an equation known as ideal gas equation which correlate P, V, T of a gas.

$V \propto \frac{1}{P}$ (according to Boyle's law at constant T)

$V \propto T$ (according to Charle's law at constant P)

$V \propto n$ (according to Avogadro's law at constant P and T)

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

$PV \propto nT$

$PV = nRT$

Where R is proportionality constant known as universal gas constant.

Numerical value of R:

➢ $R = 0.0821$ litre atm K^{-1} mol^{-1}

➢ $R = 0.0831$ litre bar K^{-1} mol^{-1}

➢ $R = 8.314$ J K^{-1} mol^{-1}

➢ $R = 1.987 \approx 2$ cal K^{-1} mol^{-1}

➢ $R = 8.314 \times 107$ erg K^{-1} mol^{-1}

If temperature, volume and pressure of a fixed amount of gas vary from T_1, V_1 and p_1 to T_2, V_2 and p_2 then we can write

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

This equation is also known as Combined gas law.

Dalton's Law of Partial Pressure

Dalton's law of partial pressure and states that "the total pressure exerted by a mixture of non reacting gases is equal to the sum of partial pressure of each gas present in the mixture".

Total = $p_1 + p_2 + p_3 +$ ......(at constant T, V)

Kinetic Theory of Gases

The postulates of kinetic theory of gases are as follows:

1. The gaseous molecules are considered to be point masses.
2. The volume of a molecule is negligible as compared to total volume of the gas.
3. The molecules neither attract nor repel each other.
4. The collisions are perfectly elastic i.e. there is no loss of energy during the molecular collisions.
5. The average kinetic energy of molecules is directly proportional to the absolute temperature of the gas.
6. The effect of gravity on molecular motion is negligible.

The Kinetic Gas Equation

where P = Pressure of the gas

$$PV = \frac{1}{3}mv^2$$

V = Volume of the gas

m = Mass of one molecule of a gas

n = number of molecules of gas

u = root mean square speed of the molecule

m × n = M = molecular weight of the gas.

$$PV = \frac{1}{3}Mu^2$$

Graham's Law of Diffusion

According to Graham's Law "at constant pressure and temperature, the rate of diffusion or effusion of a gas is inversely proportional to the square root of its vapour density or molecular

mass".

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

Behaviour of Real gases

Ideal gas: A gas which obeys the gas laws and the gas equation PV = nRT strictly at all temperatures and pressures is said to be an ideal gas. But actually the concept of ideal gas is hypothetical as there is no gas which practically is ideal. So, the non-ideal gases are the real gases which are the actually existing gases which obey gas equation approximately only under two conditions.

(i) Low pressure.

(ii) High temperature.

Causes of Deviation

There are two hypothetical postulates in the kinetic theory of gases. These are as follows:

1. The volume of a molecule is negligible as compared to total volume of the gas. Actually, gas molecules do possess some volume which account for the deviation.

2. There is no intermolecular forces of attraction between gaseous molecules.

By correcting these two postulates, we get an equation which can be applied to the gases which deviate from ideal behaviour. This deviation of a gas from ideal behaviour can also be expressed in terms of compressiblity factor (Z).

$$Z = \frac{PV}{RT}$$

Van der Waal's Equation

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

Where a and b are van der waal's constant.

Liquifaction of Gases

Gases can be liquefied by applying high pressure or by cooling.

Critical Temperature: It is the temperature above which gas cannot be liquefied, no matter how

high be pressure.

$$T_c = \frac{8a}{27Rb}$$

Critical Pressure: It is the minimum pressure that is required to liquefy a gas at critical temperature.

$$P_c = \frac{a}{27b^2}$$

Critical Volume: It is the volume occupied by gas at critical temperature and critical pressure.

$Vc = 3b$

1. **Liquid State:**

It is the intermediate state between gaseous and solid states. Liquids possess fluidity like gases but incompressibility like solids.

Properties of liquid are:

   a. A liquid is made up of molecules. Only $Hg(l)$ is in atomic state.
   b. The intermolecular forces of attraction in a liquid are quite large.
   c. Liquids have no definite shape but have definite volume as the cohesive forces are strong.
   d. Liquids diffuses slowly in comparison to gas.
   e. They have definite volume but irregular shapes or we can say that they can take the shape of the container.
2. **Evaporation:** The process of change of liquid into vapour state at any given temperature is evaporation. Evaporation is accompanied by cooling as average kinetic energy of remaining molecules decreases. Example: Ether evaporates faster than alcohol.
3. **Vapour Pressure:** In a closed vessel when the rate of evaporation become equal to rate of condensation, i.e. equilibrium is established, the pressure exerted by the vapours of liquid on its on surface is known as vapour pressure.
4. **Boiling Point:** Boiling point of the liquid is the temperature at which the vapour pressure of the liquid is equal to the atmospheric pressure. Ex- Boiling point of pure water is 100 ℃.
5. **Surface tension:** "It is the force acting on the surface at right angles to any line of unit length". The property of surface tension may also be described in terms of the tendency of a liquid to decrease its surface area. It's SI unit is N/m.

   Surface tension, $S = \frac{F}{l}$
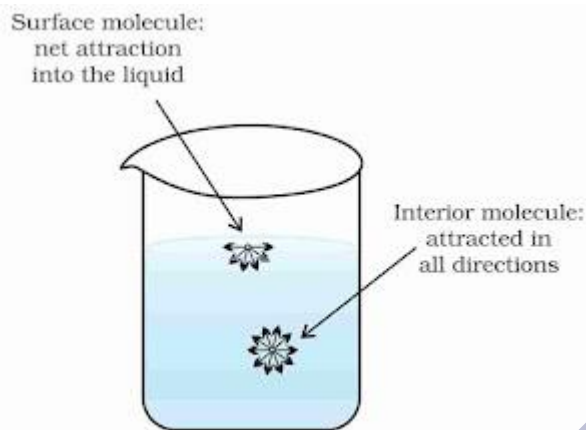
6. **Viscosity:** The property of the liquids which determines their resistance to flow, is called viscosity. The forces between the layers which oppose the relative motion between them are known as the forces of viscosity. Thus viscosity may be thought of as the internal function of a fluid in motion.
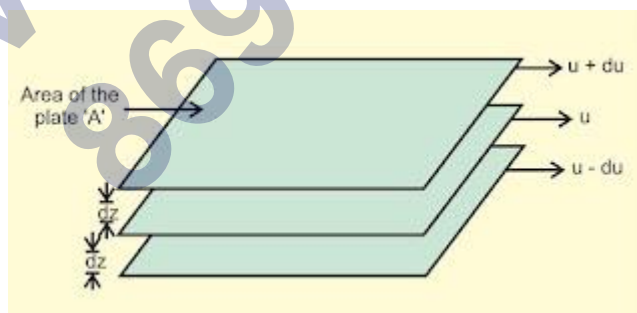
$F \propto \dfrac{dv}{dz}$ is called velocity gradient]

$F \propto A$

$$F = nA\dfrac{dv}{dz}$$

η is the coefficient of viscosity. It is expressed in $Nm^{-2}s$ or poise

1 poise = 0.1 $Nm^{-2}s$

7. **Fluidity(Φ):** The reciprocal of the coefficient of viscosity is called Fluidity.

$$\Phi = \dfrac{1}{\eta}$$

1. **Three different states of matter (solid, liquid and gas):** Solid is that state of matter which has a definite shape and a definite volume, liquid has a definite volume but no definite shape whereas gas has neither definite shape nor definite volume.

2. **Two more states of matter:**

    i. Plasma state which consists of a mixture of electrons and positively charged ions formed due to super heating of gases, e.g., in sun or stars.

    ii. Super cooled solid state in which atoms lose their identity to form a single super atom.

3. **Triple point:** It is the temperature at which all the three states of matter or phases of the same substance exist together, e.g., ice, water and water vapour exist together at 0.01°C (273.16 K) and 4.58 mm pressure.

4. **Ideal and Real gases:** A gas which obeys ideal gas equation under all conditions of temperature and pressure is called an ideal gas. However, the concept of ideal gas is only hypothetical. The gases obey gas laws only if pressure is low or temperature is high. Such gases are called real gases.

5. **Significance of van der Waal's constants:** 'a' is a measure of the magnitude of attractive forces whereas 'b' is a measure of the effective size of the gas molecules. b = 4v where v is actual volume of gas molecules. 'b' is called excluded volume or co-volume.

6. **Boiling point:** It is the temperature at which vapour pressure of the liquid becomes equal to external pressure. When external pressure = 1 atm = 760 mm, it is called normal boiling point.

7. **Surface tension of liquids:** It is the force acting at right angles to the surface along one centimeter length of the surface. Its units are dynes cm–1 or Nm–1.

8. **Vapour pressure of a liquid:** It is the pressure exerted by the vapour present in equilibrium with a liquid in a closed vessel at a particular temperature. Cooling is caused by evaporation because more energetic molecules leave the liquid.

9. **Viscosity of liquids:** It is the internal resistance of a liquid to flow or it is the force of friction which one part of the liquid offers to another part of the liquid.

10. **Factors affecting viscosity:**

    i. **Nature of the liquid :** Greater the inter-molecular forces, higher is the viscosity.

    ii. **Temperature:** Viscosity of a liquid decreases with increase of temperature because kinetic energy increases and hence inter-molecular forces of attraction decrease.

11. **Boyle's law:** Temperature remaining constant, volume of a given mass of a gas is inversely proportional to its pressure, i.e., $V \propto \frac{1}{P}$ at constant T or PV = constant.

12. **Dalton's law of partial pressures:** If two or more gases which do not react chemically with

each other are enclosed in a vessel, then total pressure exerted by the gaseous mixture is the sum of their partial pressure.

13. **Graham's law of diffusion/effusion:** Under similar conditions of temperature and pressure, rates of diffusion/effusion of different gases are inversely proportional to the square root of their densities.

14. **Compressibility factor (Z):** The extent of deviation of a real gas from ideal behaviour is expressed in terms of compressibility factor (Z) viz. $Z = P\dfrac{V}{n}RT$.

Characteristics of Gases

Characteristics of Gases

1) Gases have neither definite shape nor definite volume. They take up the shape and volume of the container.

2) They have lower density than liquids and solids.

3) They are highly compressible

4) Gases intermix completely in all proportion without any mechanical aid.

5) They exert pressure equally in all direction.

Measurement of mass

The mass of a gas can be easily determined by weighing the container containing the gas, and then emptying the container by taking out the gas and weighing the empty container again. The difference between the two masses gives the mass of the gas.

$$number\ of\ moles\ (n) = \frac{mass\ of\ substance\ of\ substance\ (g)}{molar\ mass\ of\ substance}$$

$$n = \frac{m}{M}$$

1 mole = 6.022 × 1023

Measurement of volume

As a gas fills the whole of the vessel in which it is put, hence the volume of the gas is equal to the volume of its container which in turn can be calculated from the dimensions of the container.
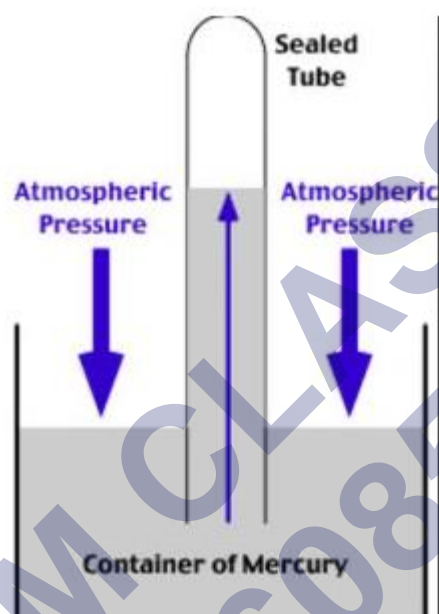
The S.I. unit of volume is m^3.

$1 m^3 = 10^3 dm^3 = 10^6 cm^3$

$1 ml = 1 cm^3$

$1 L = 10^3 cm^3 = 1 dm^3 = 10^{-3} m^3$

Measurement of pressure

The instrument used for the measurement of atmospheric pressure is called a barometer.

It consists of inverting a tube filled with mercury in a dish of mercury. The height of the mercury column above the level of mercury in the dish is a measure atmospheric pressure at that place.

Mercury is used as a barometric liquid because

1) The height of the column in a barometer is inversely proportional to the density of the liquid. As Mercury has very high density, the height of the column setup is very convenient for study.

2) Mercury is non-volatile at room temperature. Hence, the vapour pressure due to Mercury vapour is negligible.

The instrument used for the measurement of the pressure of a gas is called manometer. It simply consists of a U- shaped tube containing mercury usually.

Two types of manometers are:

1)Those in which the longer limb is closed. Closed limb manometer is used only for gases at pressure less than the atmospheric pressure.

$$P_{gas} = P_{atm} + hpg$$
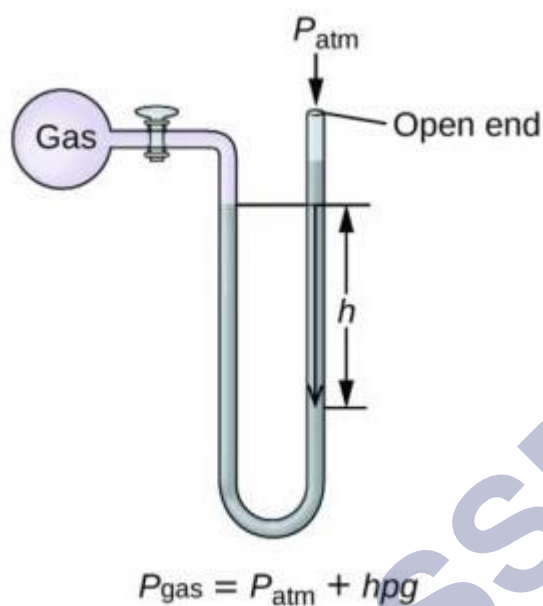
2)Those in which the longer limit is open.Open limb manometer is used for all.
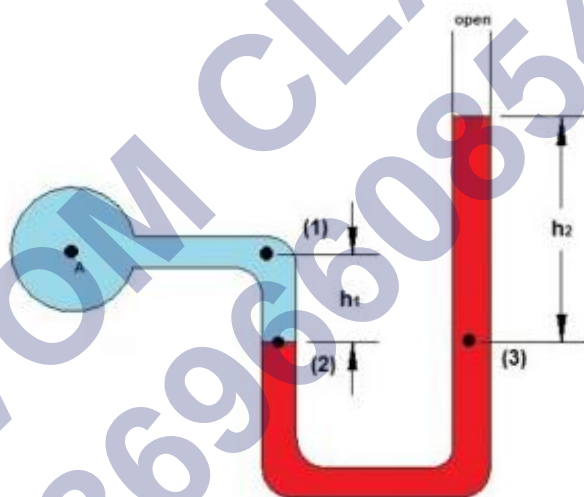
Suppose height of the mercury column= h cm

Area of cross section of the tube= A cm^2

Volume of the mercury column= A × h cm^3

Density of mercury at room temperature= ρ g cm^{-3}

mass of mercury column=A × h × ρ grams

weight of mercury column= (A × h × ρ) × g gram

Weight of mercury column is the force acting on A cm3.Hence

Pressure= h × ρ × g

A standard or normal atmospheric pressure is defined as the pressure exerted by a mercury column of exactly 76 cm at 0°C. This is the pressure exerted by the atmosphere at the sea level.

1 atm= 76 cm = 760 mm = 760 torr

1 atm= 1.01325 bar

1atm= 0.987 atm

The S.I. unit of pressure is pascal(Pa)

1 Pa= 1 Nm^{-2} = 1kg m^{-1} s^{-2}

1atm= 1.0132^5 × 105 Nm^{-2}

1 bar= 10^2 kPa

Measurement of temperature

Temperature is a measure of the extent of hotness or coldness of a body.

It is based on the principle that substances expands on heating.

Substance used in the measurement of temperature is mercury.

There are three different scales on which the temperature are measured

1)Fahrenheit scale

2)Kelvin scale

3)Celsius scale

$$T_k = T_C + 273.15 \quad T_C = \frac{5}{9}(T_F - 32) \quad T_F = \frac{9}{5}T_C + 32$$

Maxwell-Boltzmann Distribution

Maxwell-Boltzmann distribution of Molecular speed

At a particular temperatures, different molecules of a gas possess different speeds. Due to continues collision among the molecules themselves and against the walls of the container ,their speed keep on changing.

As a result of collision, some others are speeded up, some others are slowed down and hence the fashions of molecules possessing particular speed remain constant at constant temperature.

If fractions of molecules possessing particular speed are plotted against their corresponding speeds at a particular temperature, a curve is obtained. This distribution of speed is called **maxwell-Boltzmann distribution.**

The white area shows the proportion of particles in the sample that do not have enough energy to react.

activation energy E_a

The blue area shows the proportion of particles in the sample that have enough energy to react.
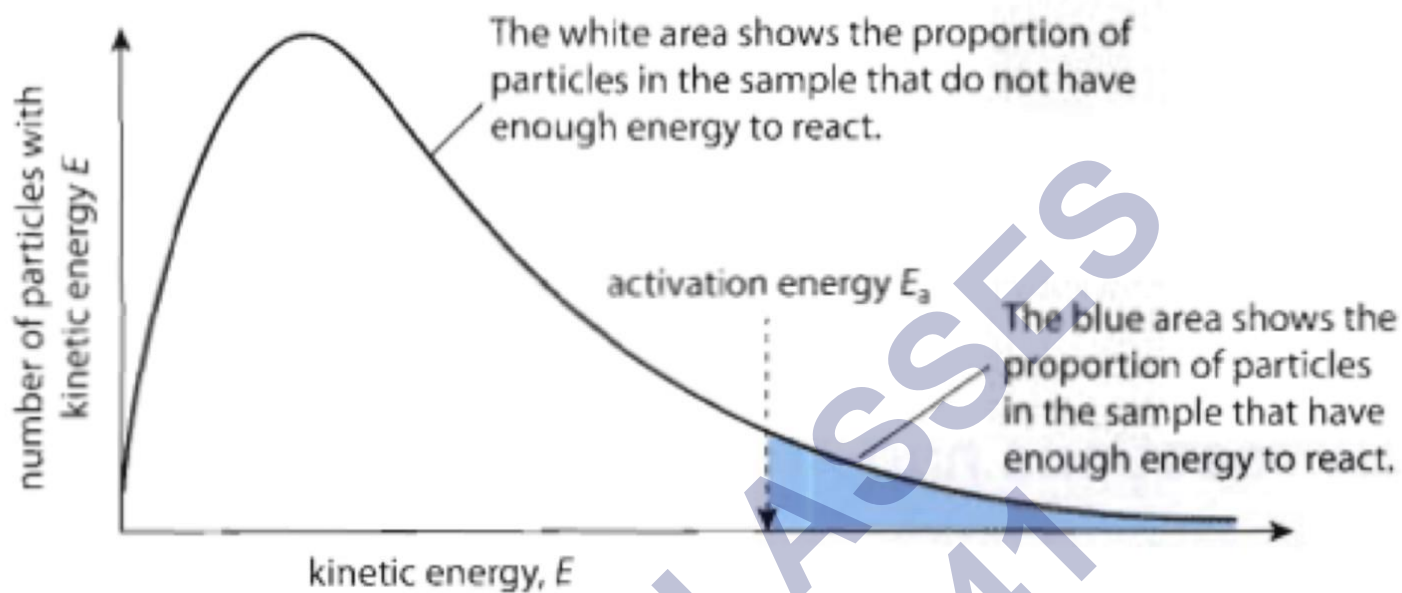
From this curve, it may observed that,

(1) Fraction of molecules having too low or too high-speed are very small.

(2) The peak of the curve corresponds to a speed possessed by the maximum fraction or maximum number of molecules. This speed is called most probable speed and is represented by c*

Effect of nature of the gas

At the same temperature, lighter gas will have higher value of most probable speed i.e. move faster than heavier gases.

For example : Distribution curve for chlorine and nitrogen gases are:

Effect of temperature

Maxwell – Boltzmann distribution curve for a gas at three different temperatures is
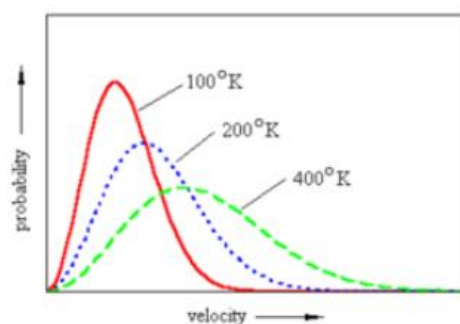
(1) The peak shift forward showing that the most probable velocity increases.

(2) The peak shift downwards showing that fraction of molecules or number of molecules possessing most probable velocity decreases.

(3) The curve is flattened in the middle showing that more molecules have speeds near to the most probable speed.

(4) The fraction of molecules having higher speed increases.

(5) The fraction of molecules having lower speed decreases.

Relationship between different types of speed
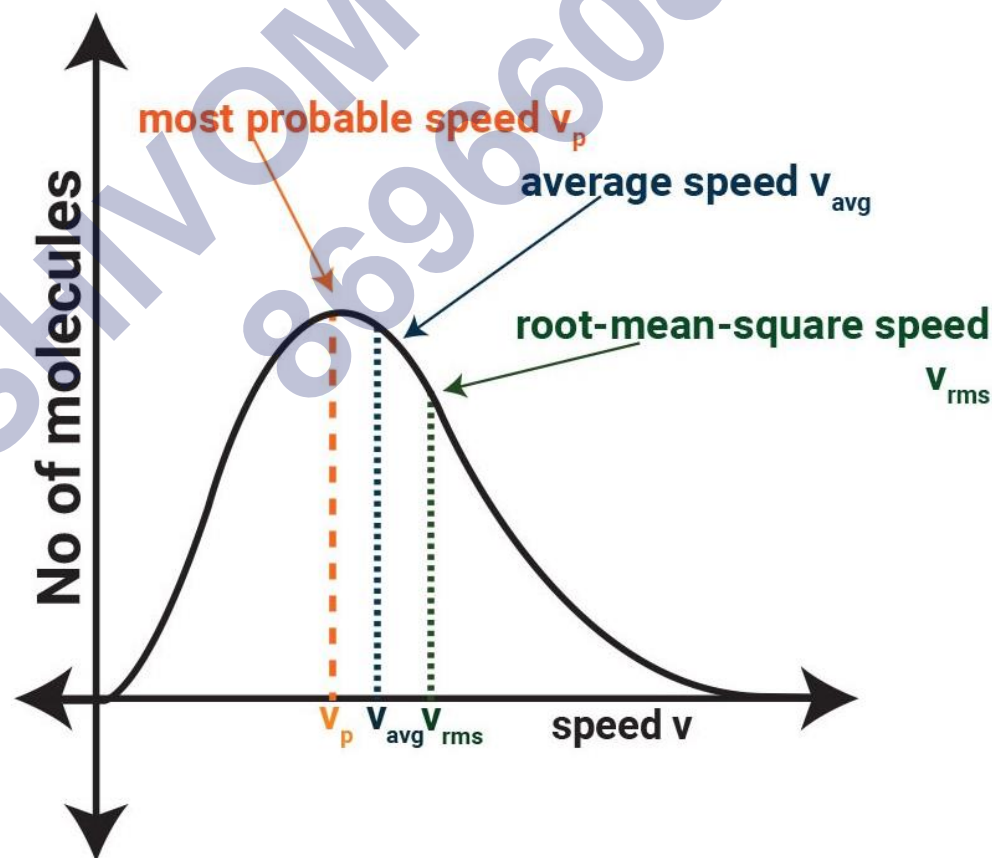
Liquefaction of Gases And Critical Temperature

The liquefaction of a gas takes place when the intermolecular forces of attraction become so high that they bind the gas molecules together to form the liquid state.

The intermolecular forces of attraction can be increased either by increasing the pressure so that the molecules come close together or by cooling the gas so that the kinetic energy of the molecules decreases and they become slower.

The effect of temperature on the liquefaction of gases is found to be very important as higher the temperature of the gas ,more difficult it is to liquefy it and higher is the pressure required.

Gas like hydrogen ,helium, oxygen, nitrogen could not be liquefied at room temperature by application of pressure alone. Each of these gases could also be liquefied provided first it is cooled down to or below a particular temperature. For each gas, there is a particular temperature above which it cannot be liquefied, howsoever, high pressure may be applied on the gas. This temperature is called critical temperature.

Critical temperature of a gas may be defined as that temperature above which it cannot be liquefied however high pressure may be applied on the gas.

The pressure required to liquefy the gas at the critical temperature is called critical pressure .

The volume occupied by 1 mole of the gas at critical temperature and critical pressure is called critical volume.

All the three are called critical constants of the gas and are represented by Tc, Tp, Tv.

Andrews experiment on critical phenomena
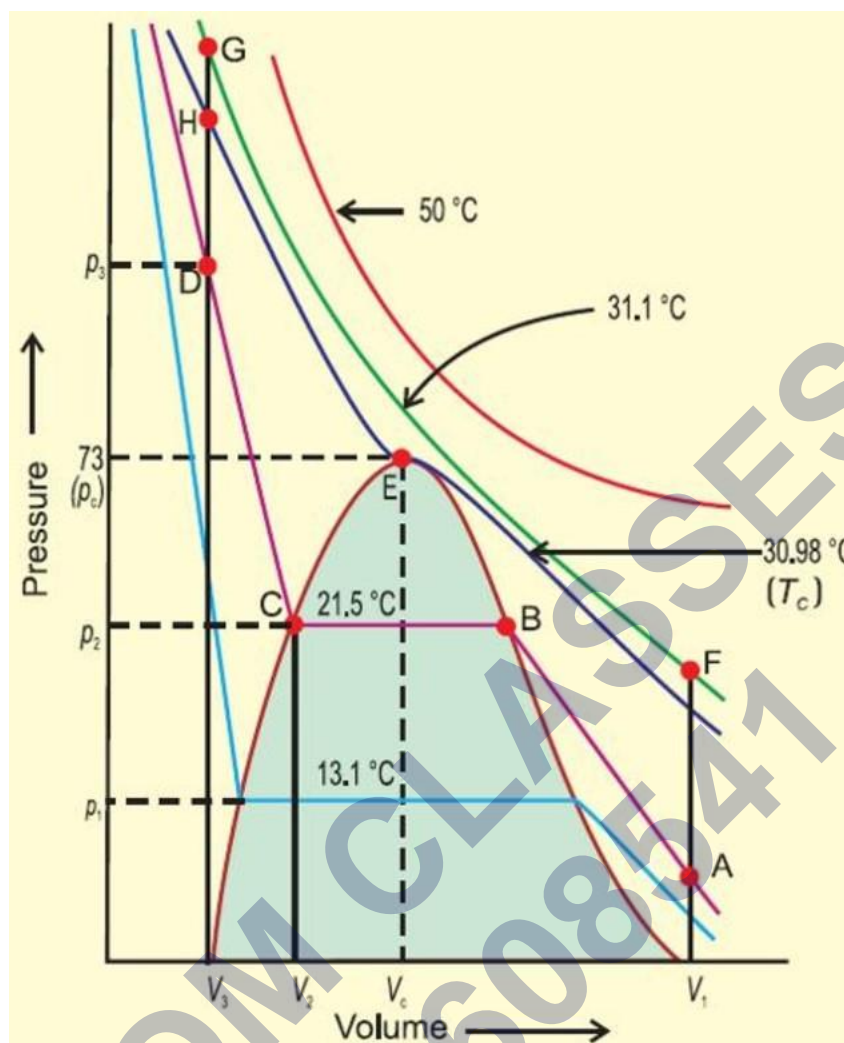
Andrews in 1861 was the first to study the critical phenomena experimentally using carbon dioxide gas.

He studied the effect of pressure on the volume of carbon dioxide at different constant temperature. The plots obtained are called isotherms.

At the lowest temperature employed i.e. 13.1° C , at low pressure, carbon dioxide exist as a gas, as shown at the point A.

As the pressure is increased, the volume of the gas decreases along the curve.

The point at which liquefaction of the gas starts, volume decreases rapidly because liquid has much less volume than the gas.

Once the liquification is complete, the increase in pressure has very little effect upon volume because liquids are very little compressible. Hence a steep curve is obtained.

As the temperature is increased, horizontal portion becomes smaller and smaller and at 30.98 °C , it is reduced to a point E.

Above 30.98°C ,the gas cannot be liquefied at all, however high pressure may be applied. Thus 30.98°C is the critical temperature.

We get a dome shaped curve.

A point like A represent gaseous state.

A point Like D represents a liquid state.

A point within the dome shaped area represents existence of liquid and gaseous carbon dioxide in equilibrium.

Importance of critical temperature

The critical temperature of a gas is a measure of the strength of the intermolecular forces of attraction.

Weaker are the intermolecular forces ,more difficult it is to liquefy that gas and hence lower would be the critical temperature of that gas.

Helium and hydrogen have weak intermolecular forces, thus they are difficult to liquefy and hence have low critical temperature.

Carbon dioxide and ammonia have strong intramolecular forces of attraction, they can be easily liquefied and their critical temperature are high which are above room temperature.

Van der waals constant a is also a measure of intermolecular forces of attraction. Hence it is found that the values of constant a increase in the same order as the critical temperature.

As a gas can be liquefied below the critical temperature by applying pressure. Therefore above the critical temperature ,it is a gas but below the critical temperature it is a vapour.

For ex: Carbon dioxide below its critical temperature is called carbon dioxide vapour.

Filed Under: States of Matter, Chemistry, Class 11

Tagged With: Andrews experiment on critical phenomenon, carbon dioxide vapour, critical constants, critical pressure, Critical temperature, critical volume, Importance of critical temperature, isotherms, liquefaction of a gas

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Vapour Pressure

In a liquid, the molecules are quite close together so that there are considerable forces of attraction between them and hence they are held together in a definite volume.

The liquids possess fluidity like gases but incompressibility like solid.

Properties of Liquid

(1) Liquids have no definite shape: They take up the shape of the vessel in which they are put. This is because the molecules in a liquid are in a state of constant rapid motion.

(2) Liquids have a definite volume: This is because the intermolecular forces of attraction in a liquid are quite strong and unlike gas molecules, the liquid molecules are not completely free to move.

(3) Liquids have much higher density than gases:This is because the molecules in a liquid are quiet close together. Thus the molecules are much more closely packed than those of the gases.

(4) Compressibility :liquids are much less compressible than gases.This is because the intermolecular distances of separation are much smaller in liquid than that in gases.

(5) Diffusion: liquids diffuse like gases but the diffusion is much slower because the liquid molecules are quite close, they undergo a much larger number of collisions with each other.

Vapour Pressure
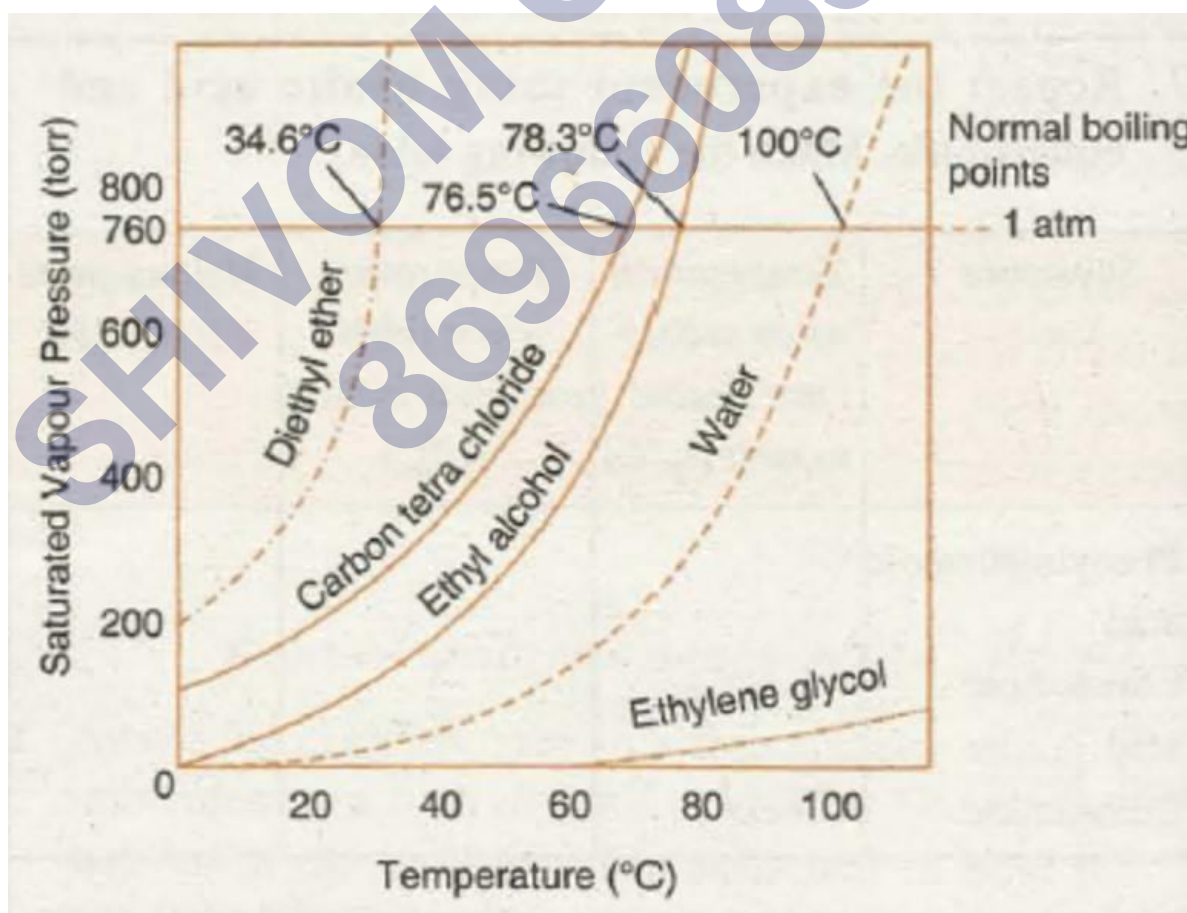
Suppose some liquid is placed in an evacuated vessel connected to a manometer. According to

kinetic theory of liquids, the molecules of the liquid are constantly moving in different directions with different speeds. As these molecules are moving with different speeds, they possess different kinetic energy.

At any particular temperature ,the energy of some of the molecules may be so high that they may overcome the forces of attraction by the neighbouring molecules and may leave the liquid and come in the space above the liquid. This process is called evaporation

As the time passes, more and more molecules of the liquid leave the liquid and come in space above the liquid. The molecules thus present above the liquid are called vapour. The molecules in the vapour phase are also constantly moving and some of them strike the surface of the liquid and maybe recaptured by the liquid. The process is called condensation.

If the liquid is added into the evacuated vessel ,then initially, as there are no molecules of vapour, the rate of condensation is zero.

If the temperature is kept constant, the evaporation continues at constant rate as shown by the straight line plot. With the passage of time ,as a number of molecules in the vapour phase becomes more and more ,the rate of condensation also increases.

A stage is reached when rate of condensation becomes equal to rate of evaporation i.e. as many molecules re-enter into a liquid as leave the liquid in the same time.This state is called state of equilibrium .

The pressure exerted by the vapours at this stage is called vapour pressure or saturated vapour pressure as the vapour phase is saturated with vapours at this stage.

Vapour pressure of a liquid at any temperature may be defined as the pressure exerted by the vapour present above the liquid in equilibrium with the liquid at that temperature.

Important results related with process of evaporation

(1) Cooling caused by Evaporation

When a liquid evaporates ,the more energetic molecules leave the liquid. As a result the average kinetic energy of the remaining liquid decreases and hence the temperature falls.

(2) Factors affecting Vapour Pressure

(i) Nature of the liquid : If the intermolecular forces of attraction in the liquid are weak ,the molecules can easily leave the liquid and come into vapour phase and hence the vapour pressure is higher.

For example: The vapour pressure of acetone, benzene is higher than that of water at same temperature.

(ii) Effect of temperature: As the temperature of a liquid is increased, the vapour pressure of liquid increases.

(3) Boiling point

The vapour pressure of a liquid increases as the temperature is increased. The vapour escaping are only from the surface of the liquid. If the temperature is further increased till the vapour pressure becomes equal to atmospheric pressure, the vapour in the form of bubbles from below the surface start rising to the surface and escape into the air. The temperature at which this happens is called boiling point.

Boiling

Boiling point of a liquid is defined as the temperature at which the vapour pressure of the liquid becomes equals to external pressure.

When the external pressure is normal atmospheric pressure, the boiling point is called normal boiling point.

When the external pressure is equal to 1 bar, the boiling point is called standard boiling point of the liquid.

Standard boiling point of a liquid is slightly less than the normal boiling point because one bar is slightly less than 1 atmosphere pressure.

Application of effect of external pressure on boiling point

(1) If the external pressure is higher, more heat will be required to make the vapour pressure equal to external pressure and hence higher will be the boiling point. That is why in hospitals ,the surgical instruments are sterilised in autoclaves in which boiling point of water is raised by using a weigh to cover the vent.

(2) If the external pressure is decreased, the boiling point is lowered. This is the reason that a liquid boils at a lower temperature on the top of the mountain than on the sea shore. That is why at hills, use of pressure cooker is essential for cooking food.

(3) It is used for purifying the unstable liquids by distillation under reduced pressure.

(4) Heat of Vaporisation

When the liquid starts boiling ,if extra heat is supplied to the liquid, it is used up not in increasing the temperature of the liquid but to overcome the intermolecular forces of attraction, existing in the liquid and thus changing the liquid into vapour. Hence the temperature remain constant till whole of the liquid changes into vapour.
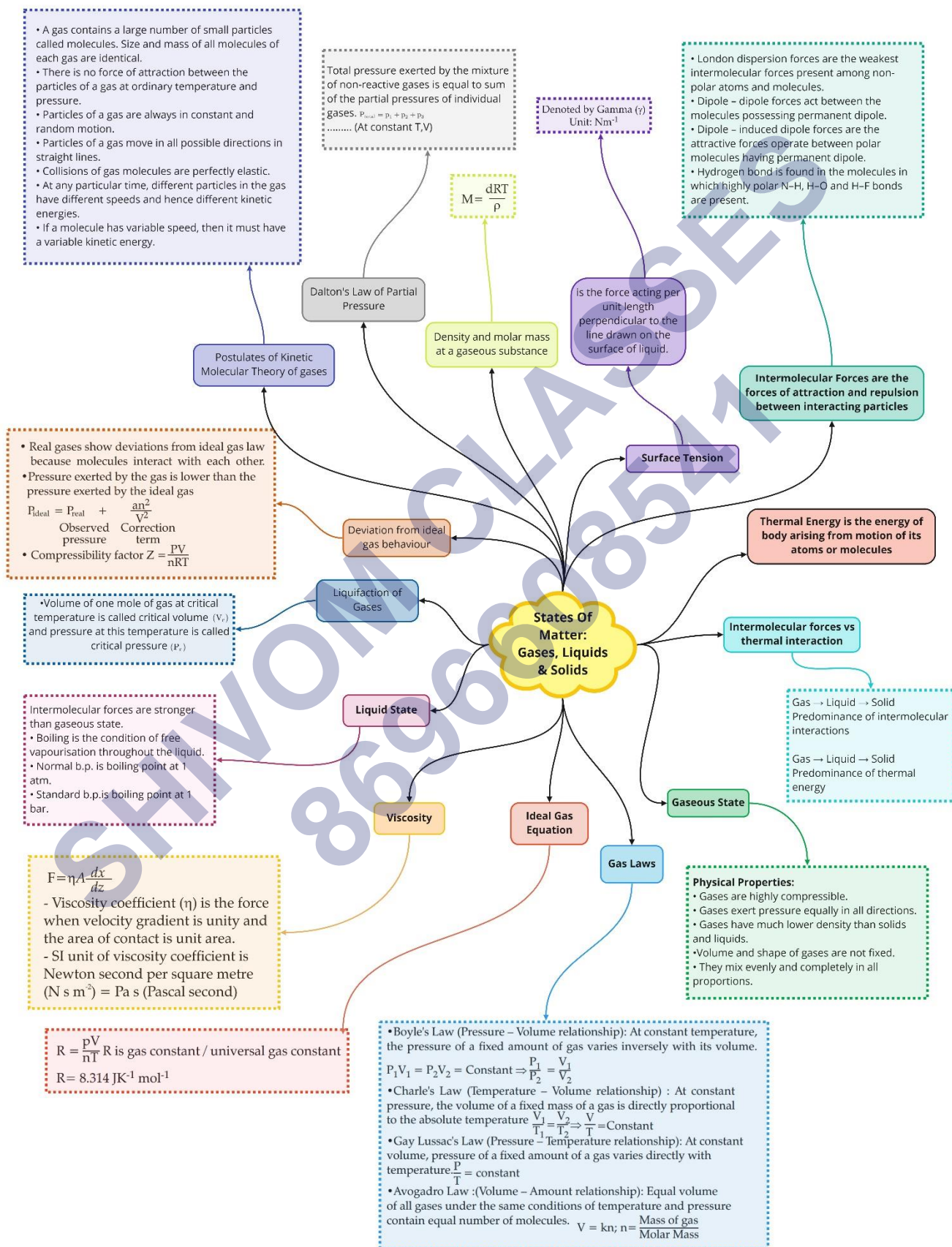
The amount of heat required to change 1 mole of the liquid into its vapour at the boiling point is called the heat of vaporisation of the liquid.

Greater the intermolecular forces of attraction present in a liquid, greater is the heat of vaporisation and higher is the boiling point.

Class : 11th Chemistry
Chapter- 5: States Of Matter: Gases, Liquids & Solids

• A gas contains a large number of small particles called molecules. Size and mass of all molecules of each gas are identical.
• There is no force of attraction between the particles of a gas at ordinary temperature and pressure.
• Particles of a gas are always in constant and random motion.
• Particles of a gas move in all possible directions in straight lines.
• Collisions of gas molecules are perfectly elastic.
• At any particular time, different particles in the gas have different speeds and hence different kinetic energies.
• If a molecule has variable speed, then it must have a variable kinetic energy.

Total pressure exerted by the mixture of non-reactive gases is equal to sum of the partial pressures of individual gases. $P_{total} = p_1 + p_2 + p_3$ .... (At constant T,V)

Denoted by Gamma (γ) Unit: Nm^{-1}

• London dispersion forces are the weakest intermolecular forces present among non-polar atoms and molecules.
• Dipole – dipole forces act between the molecules possessing permanent dipole.
• Dipole – induced dipole forces are the attractive forces operate between polar molecules having permanent dipole.
• Hydrogen bond is found in the molecules in which highly polar N–H, H–O and H–F bonds are present.

$$M = \frac{dRT}{\rho}$$

Dalton's Law of Partial Pressure

Density and molar mass at a gaseous substance

is the force acting per unit length perpendicular to the line drawn on the surface of liquid.

Postulates of Kinetic Molecular Theory of gases

Intermolecular Forces are the forces of attraction and repulsion between interacting particles

• Real gases show deviations from ideal gas law because molecules interact with each other.
• Pressure exerted by the gas is lower than the pressure exerted by the ideal gas

$$P_{ideal} = P_{real} + \frac{an^2}{V^2}$$
Observed pressure   Correction term
• Compressibility factor $Z = \frac{PV}{nRT}$

Surface Tension

Deviation from ideal gas behaviour

Thermal Energy is the energy of body arising from motion of its atoms or molecules

•Volume of one mole of gas at critical temperature is called critical volume (V_c) and pressure at this temperature is called critical pressure (P_c)

Liquifaction of Gases

States Of Matter: Gases, Liquids & Solids

Intermolecular forces vs thermal interaction

Intermolecular forces are stronger than gaseous state.
• Boiling is the condition of free vapourisation throughout the liquid.
• Normal b.p. is boiling point at 1 atm.
• Standard b.p.is boiling point at 1 bar.

Liquid State

Gas → Liquid → Solid Predominance of intermolecular interactions

Gas → Liquid → Solid Predominance of thermal energy

Viscosity

Ideal Gas Equation

Gaseous State

$$F = \eta A \frac{dx}{dz}$$
- Viscosity coefficient (η) is the force when velocity gradient is unity and the area of contact is unit area.
- SI unit of viscosity coefficient is Newton second per square metre ($N\,s\,m^{-2}$) = Pa s (Pascal second)

Gas Laws

Physical Properties:
• Gases are highly compressible.
• Gases exert pressure equally in all directions.
• Gases have much lower density than solids and liquids.
•Volume and shape of gases are not fixed.
• They mix evenly and completely in all proportions.

$$R = \frac{pV}{nT} \quad R \text{ is gas constant / universal gas constant}$$
$$R = 8.314\ JK^{-1}\ mol^{-1}$$

•Boyle's Law (Pressure – Volume relationship): At constant temperature, the pressure of a fixed amount of gas varies inversely with its volume.
$$P_1V_1 = P_2V_2 = \text{Constant} \Rightarrow \frac{P_1}{P_2} = \frac{V_1}{V_2}$$
•Charle's Law (Temperature – Volume relationship) : At constant pressure, the volume of a fixed mass of a gas is directly proportional to the absolute temperature $\frac{V_1}{T_1} = \frac{V_2}{T_2} \Rightarrow \frac{V}{T} = \text{Constant}$
•Gay Lussac's Law (Pressure – Temperature relationship): At constant volume, pressure of a fixed amount of a gas varies directly with temperature. $\frac{P}{T} = \text{constant}$
•Avogadro Law :(Volume – Amount relationship): Equal volume of all gases under the same conditions of temperature and pressure contain equal number of molecules. $V = kn; \ n = \frac{\text{Mass of gas}}{\text{Molar Mass}}$

Important Questions

Multiple Choice questions-

Question 1. Three containers A, B, C of equal volume contain oxygen, neon and methane respectively at same temperature and pressure. The increasing order of their masses is

(a) A < B < C

(b) B < C < A

(c) C < A < B

(d) C < B < A

Question 2. A gas will approach ideal behaviour at

(a) Low temperature, low pressure

(b) Low temperature, high pressure

(c) High temperature, low pressure

(d) High temperature, high pressure

Question 3. Containers A and B have same gas. Pressure, volume and temperature of A are all twice those of B. The ratio of number of molecules of A and B is

(a) 1 : 2

(b) 2 : 1

(c) 1 : 4

(d) 4 : 1

Question 4. According to kinetic theory of gases,in an ideal gas,between two successive collisions a gas molecule travels

(a) In a circular path

(b) In a wavy path

(c) In a straight line path

(d) With an accelerated velocity

Question 5. When did substances exist in different crystalline forms the phenomenon is called:

(a) Allotropy

(b) Polymorphism

(c) Polymerization

(d) Isomorphism

Question 6. Sl unit of pressure is :

(a) Pascal

(b) torr

(c) mm of Hg

(d) none of the above

Question 7. If the pressure of a gas is increased then its mean free path becomes:

(a) 0

(b) Less

(c) More

(d) Infinity

Question 8. 1 atmosphere is equal to:

(a) 1 torr

(b) 760 cm

(c) 760 mm

(d) 76 torr

Question 9. Grahams law refers to :

(a) Boiling point of water

(b) Gaseous Diffusion

(c) Gas Compression

(d) Volume changes of gases

Question 10. The rise or fall of a liquid within a tube of small bore is called :

(a) Surface Tension

(b) Capillary Action

(c) Viscosity

(d) Formation of Curvature

Question 11. The rates of diffusion of gases are inversely proportional to square root of their densities . This statement refers to :

(a) Daltons Law

(b) Grahams Law

(c) Avogadros Law

(d) None of the Above

Question 12. Cooling is caused by :

(a) Evaporation

(b) Convection

(c) Conduction

(d) none of the above

Question 13. If helium and methane are allowed to diffuse out of the container under the similar conditions of temperature and pressure, then the ratio of rate of diffusion of helium to methane is:

(a) 2 : 1

(b) 1 : 2

(c) 3 : 5

(d) 4 : 1

Question 14. Equal masses of ethane and hydrogen are mixed in an empty container at 25°C . The fraction of total pressure exerted by hydrogen is

(a) 1 : 2

(b) 1 : 1

(c) 01 : 16

(d) 15 : 16

Question 15. The volume of 2.8 g of carbon monoxide at 27°C and 0.0821 atm is

(a) 30 L

(b) 3 L

(c) 0.3 L

(d) 1.5 L

Very Short:

1. What change in energy takes place when a molecule is formed from its atoms?

2. Arrange the following in order of increasing bond strengths.

3. Name the shapes of the following molecules: CH_4, C_2H_2, CO_2.

4. Arrange the following in order of increasing strengths of hydrogen bonding O, F, S, Cl, N

5. Identify the compound/compounds in the following in which S does not obey the Octet rule: SO_2, SF_2, SF_4, SF_6.

6. Name one compound each involving sp^3, sp^2, sp hybridization.

7. s-s, s-p, p-p form a bond, and only p-p form π bond.

Short Questions:

1. Which out of CH_3F and CH_3Cl has a higher dipole moment and why?

2. Define the term chemical bond. What are its different types?

3. Why covalent bonds are called directional bonds whereas ionic bonds are called non-directional?

4. AlF_3 is a high melting solid whereas SiF4 is a gas. Explain why?

5. Using the VSEPR theory identifies the type of hybridization and draw the structure of OF_2 What are oxidation states of O and F?

6. Account for the following: The experimentally determined N-F bond length in NF_3 is greater than the sum of the single covalent radii of N and F.

Long Questions:

1. State with reasons, which is more polar CO_2 or N_2O?

2. Out of peroxide ion (O_2) and superoxide ion (O_2) which has larger bond length and why?

3. Explain the formation of the following molecules according to the orbital concept, F2, HF, O_2, H_2O, N_2, NH_3 molecules.

4. What is a hydrogen bond, what are its causes, and give the conditions for hydrogen bonding? What is the strength of hydrogen bonding? Describe the two types of hydrogen bonding.

Assertion Reason Questions:

1. In the following questions, a statement of Assertion (A) followed by a statement of Reason (R) is given. Choose the correct option out of the choices given below each question.

   Assertion (A): Three states of matter are the result of balance between intermolecular forces and thermal energy of the molecules.

   Reason (R): Intermolecular forces tend to keep the molecules together but thermal energy of molecules tends to keep them apart.

   (i) Both A and R are true and R is the correct explanation of A.

   (ii) Both A and R are true but R is not the correct explanation of A.

   (iii) A is true but R is false.

   (iv) A is false but R is true.

2. In the following questions, a statement of Assertion (A) followed by a statement of Reason

(R) is given. Choose the correct option out of the choices given below each question.

Assertion (A): At constant temperature, pV vs V plot for real gases is not a straight line.

Reason (R) : At high pressure all gases have Z > 1 but at intermediate pressure most gases have Z < 1.

(i) Both A and R are true and R is the correct explanation of A.

(ii) Both A and R are true but R is not the correct explanation of A.

(iii) A is true but R is false.

(iv) A is false but R is true.

Case Study Based Question:

1. Intermolecular forces are the forces of attraction and repulsion that exist between molecules of a compound. These cause the compound to exist in a certain state of matter – solid, liquid or gas and affect the melting and boiling points of compounds as well as the solubilities of one substance in another. Attractive intermolecular forces are also called van der Waals' forces. These are weak forces.

(1) Dipole-dipole forces act between the molecules possessing permanent dipole. Ends of dipoles possess 'partial charges'. The partial charge is:

    (a) More than unit electronic charge

    (b) Equal to unit electronic charge

    (c) Less than unit electronic charge

    (d) Double the unit electronic charge

(2) The nature of inter-particle forces in benzene is:

    (a) Dipole-dipole interaction

    (b) Dispersion force

    (c) Ion-dipole interaction

    (d) H-bonding.

(3) The interaction energy between two temporary dipoles is proportional to (where r is the distance between the two particles)

    (a) $1/r^4$

    (b) $1/r^2$

    (c) $1/r^5$

    (d) $1/r^6$

(4) Attractive intermolecular forces known as van der Waals forces do not include which of

the following types of interactions?

   (a) London forces

   (b) Dipole-dipole forces

   (c) Ion-dipole forces

   (d) Dipole-induced dipole forces

(5) In which of the following molecules, the van der Waals forces are likely to be the most important in determining the m.pt. and b.pt?

   (a) CO

   (b) H_2S

   (c) Br_2

   (d) HCl

2. If a hydrogen atom is bonded to a highly electronegative element such as fluorine, oxygen, nitrogen, then the shared pair of electrons lies more towards the electronegative element. This leads to a polarity in the bond in such a way that a slight positive charge gets developed on H-atom, viz

$$H^{\delta+} : O^{\delta-} \qquad H^{\delta+} : F^{\delta-} \qquad H^{\delta+} : N^{\delta-}$$

Such a bond between the hydrogen atom of one molecule and the more electronegative atom of the same or another molecule is called a hydrogen bond.

(1) Which of the following compounds can form hydrogen bond?

   (a) CH_4

   (b) H_2O

   (c) NaCl

   (d) $CHCl_3$

(2) The boiling point is not affected due to hydrogen bonding in:

   (a) Water

   (b) Ammonia

   (c) Methyl alcohol

   (d) Hydrogen chloride

(3) Unusual high b.p. of water is result of:

   (a) Intermolecular hydrogen bonding

   (b) Intramolecular hydrogen bonding

(c) Both intra and intermolecular hydrogen bonding

(d) High specific heat

(4) Which of the following statements is not true?

(a) Intermolecular hydrogen bonds are formed between two different molecules of compounds.

(b) Intramolecular hydrogen bonds are formed between two different molecules of the same compound.

(c) Intramolecular hydrogen bonds are formed within the same molecule.

(d) Hydrogen bonds have a strong influence on the physical properties of a compound.

Answer Key:

MCQ

1. (a) 0

2. (a) Sp^2

3. (b) Sp and sp^2

4. (c) sp^3, 0

5. (d) $K^+ < Ca^{2+} < Mg^{2+} < Be^{2+}$

6. (c) Acetonitrile

7. (c) O_2^-

8. (c) Triangular

9. (b) $A_2 B_3$

10. (b) SF_4

11. (c) NaCl

12. (d) Ice

13. (d) NO^+ and CN^+

14. (c) HCl and He atoms

15. (b) sp and sp^2

Very Short Answer:

1. There is a fall in energy.

2. $F_2 < Cl_2 < O_2 < N_2$

3. CH_4: Tetrahedral; C_2H_2: Cylindrical; CO_2: linear

4. $Cl < S < N < O < F$.

5. SF_4, SF_6.

6. sp^3: CH_4: sp^2: C_2H_4: sp: C_2H_2

7. s-s, s-p, p-p form a bond, and only p-p form π bond.

Short Answer:

Ans: 1. The dipole moment of CH_3Cl is greater than that of CH_3F. The C-F bond length in CH_3F is smaller than the C-Cl bond length in CH_3Cl. The charge separation in the C-F bond is more than in the Cl-C bond- fluoride being more electronegative than chlorine. The bond length has a greater effect than the charge separation. Hence the dipole moment of CH_3C1 is greater than that of CH_3F.

Ans: 2. The attractive forces which hold the constituent atoms in molecules or species in lattices etc. are called a chemical bond.
They are of the following types:

1. Electrovalent or ionic bond
2. Covalent bond
3. Coordinate or dative bond
4. metallic bond
5. hydrogen bond
6. van der Waals forces.

Ans: 3. A covalent bond is formed by the overlap of half-filled atomic orbitals which have definite directions. Hence covalent bond is directional. In ionic compounds, each ion is surrounded by a number of oppositely charged ions and hence there is no definite direction.

Ans: 4. AlF_3 is an ionic solid due to the large difference in electronegativities of Al and F whereas SiF_4 is a covalent compound and hence there are only weak van der Waal's forces among its molecules.

Ans: 5. The electron dot structure of OF_2 is

:$\ddot{F}$:$\ddot{O}$::$\ddot{F}$:   Or
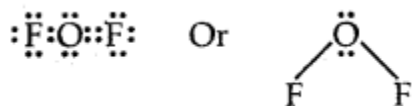
Thus, the central atom (O-atom) has 4 pairs of electrons (2 bond pairs and 2 lone pairs). Hence oxygen in OF_2 is sp^3 hybridized and the molecule is V-shaped oxidation state of F = – 1, oxidation state of O = + 2.

Ans: 6. This is because both N and F are small and hence have high-electron density. So they repel the bond pairs thereby making the N-F bond length larger.

Long Answer:

Ans: 1. N_2O is more polar than CO_2 which is a linear molecule and thus symmetrical. Its net dipole moment is zero.

$$\overset{\leftarrow+}{O} = C = \overset{+\rightarrow}{O}$$
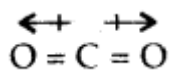
N_2O is linear but unsymmetrical. It is a resonance hybrid of the following canonical structures:

:$\ddot{N}$ = N = $\ddot{O}$: $\longleftrightarrow$:N ≡ N – $\ddot{O}$:
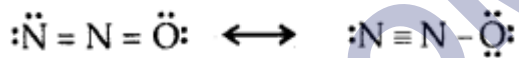
It has a net dipole moment of 0.116 D.

Ans: 2. The bond order of O_2^- is 1.5 while that of O_2^{2-} is 1.0.

The lesser the bond order, the greater is the bond length as the bond order is inversely proportional to bond length. (Hence O_2^{2-} has a larger bond length than O_2^{2-}.

Ans: 3. 1. Formation of F2 molecule. Atomic number (Z) of fluorine is 9 and its orbital electronic configuration is $1s^2\ 2s^2\ 2p^2x,\ 2p^2y,\ 2p^1z$. Thus, a fluorine atom has one half-filled atomic orbital. Therefore, two atoms of fluorine combine to form the fluorine molecule as a result of the combination for their half-filled atomic orbitals shown in Fig. The two atoms get linked by a single covalent bond
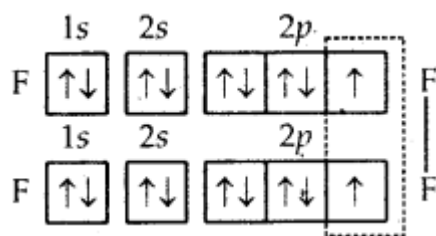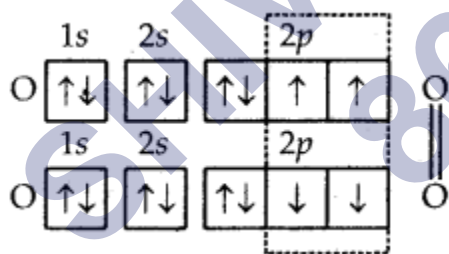
Formation of F_2 molecule

2. **Formation of HF molecule.** Fluorine atom, as stated above, has one half-filled atomic orbital. Hydrogen atom (Z = 1) has only one electron in Is orbital. Thus, the hydrogen fluoride (HF) molecule. is formed as a result of the combination (or overlap) of the half-filled orbitals belonging to the participating atoms.
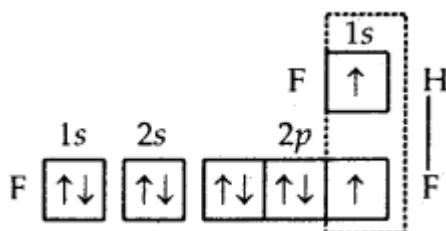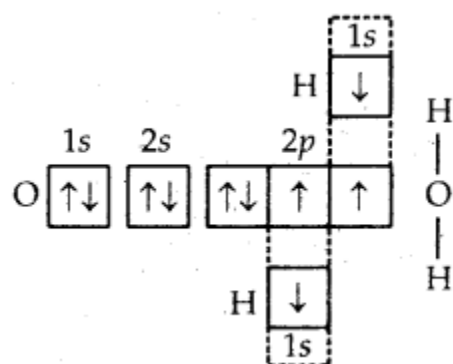

3. **Formation of O_2 molecules.** The atomic number (Z) of oxygen is 8 and its orbital electronic configuration is $1s^2\ 2s^2\ 2p^2x\ 2p^1x\ 2p^1z$. This means that an oxygen atom has two half-filled orbitals with one electron each. Two such atoms will combine to form a molecule of oxygen as a result of the overlap of the half-filled orbitals with opposite spins of electrons.
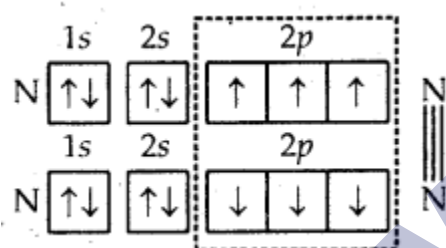

Formation of O_2 molecule

Thus, the two atoms of oxygen are bonded to each other by two covalent bonds or double bonds (O = O).

4. **Formation of H_2O molecule.** In the formation of the H_2O molecule, the two half-filled orbitals of the oxygen atom combine with the half-filled orbitals (1s) of the hydrogen atoms. Thus, the oxygen atom gets linked to the two hydrogen atoms by single covalent bonds as shown in
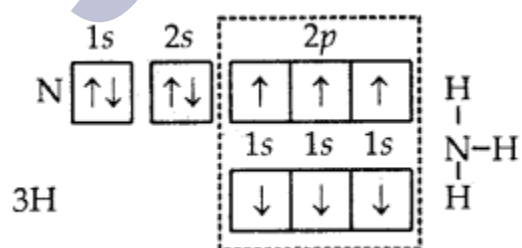
Formation of H_2O molecule

5. Formation of N_2 molecule. The atomic number of nitrogen is 7 and its orbital electronic configuration is $1s^2 2s^2 2p^1x 2p^1y 2p^1 z$. This shows that the nitrogen atom has three half-filled atomic orbitals. Two such atoms combine as a result of the overlap of the three half-filled orbitals and a triple bond gets formed (N = N)


Formation of N_2 molecule

6. Formation of NH_3 molecule. In the formation of ammonia (NH_3) molecule, three half-filled orbitals present in the valence shell of nitrogen atom combine with 1s orbital of three hydrogen atoms with one electron each. As a result, the nitrogen atom completes its octet and a molecule of NH_3 is formed in which the nitrogen atom is linked to three hydrogen atoms by covalent bonds.

Formation of NH_3 molecule

Ans: 4. When hydrogen is connected to small highly electronegative atoms such as F, O, and N in such cases hydrogen forms an electrostatic weak bond with an electronegative atom of

the second molecule, this type of bond binds the hydrogen atom of one molecule and the electronegative atom of the 2nd molecule is called as hydrogen bond. It is a weak bond and it is denoted by dotted lines e.g., in HF, hydrogen forms a weak bond with the electronegative F atom of the 2nd molecule neighboring HF.

$$\overset{\delta+}{H}-\overset{\delta-}{F}.....\overset{\delta+}{H}-\overset{\delta-}{F}.....\overset{\delta+}{H}-\overset{\delta-}{F}$$
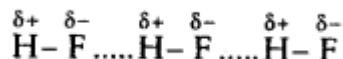
So it means hydrogen is acting as a bridge between two molecules by one covalent bond and the other by a hydrogen bond. Due to this hydrogen bonding, HF will not exist as a single molecule but it will exist as an associated molecule (HF)n. So hydrogen bond may be defined as a weak electrostatic bond that binds the hydrogen atom of one molecule and electronegative bond atoms (F, O, N) of the second neighboring molecule.

Cause of hydrogen bonding: When a hydrogen atom is bonded to an electronegative atom (say F, O, N) through a covalent bond, due to electronegativity difference, the electronegative atom attracts the shared pair of electrons towards its side with a great force as a result of which the shared pair of electrons will be displaced toward electronegative atom and away from a hydrogen atom.

Due to which hydrogen atom will acquire a slightly negative charge and if another molecule is brought nearer to it in such a way that electronegative atom of the second molecule faces hydrogen atom of the 1st molecule, due to opposite charges present on the atoms, an electrostatic bond will be formed between the hydrogen atom of one molecule and electronegative atom of 2nd molecule and this is called as hydrogen bond.

$$\overset{\delta+}{H}-\overset{\delta-}{F}.....\overset{\delta+}{H}-\overset{\delta-}{F}.....\overset{\delta+}{H}-\overset{\delta-}{F}$$
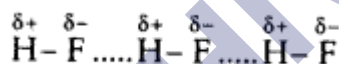
Conditions for hydrogen bonding. The following two necessary conditions for hydrogen bonding are:

1. Hydrogen atom should be connected to highly electronegative atom say F, O, or N.

2. The electronegative atom of which the hydrogen atom is connected should be the same in size.

The smaller the size of the electronegative atom greater will be the attraction of that atom for shared pair of electrons and hence that pair will be displaced more nearer to that atom and hence that atom will develop greater negative charge and the hydrogen atom will develop a greater positive charge and hence hydrogen atom of this molecule will easily attract negative atom of the Ian molecule and hence a hydrogen bond will be

easily formed.

As both these conditions are satisfied only by F, O, N atoms so only three atoms show hydrogen bond.

Strength of Hydrogen Bond: A hydrogen bond is a very weak bond. It is weaker than an ionic or a covalent bond. Its strength ranges from 13 kJ mol-1 to 42 kJ mol^{-1}. The strength of the hydrogen bond for some of the molecules is the order H-F H (40 kJ mol-1) > O-H...... O (28 kJ mol^{-1}) > H-N...... H (13 kJ mol^{-1}) whereas the strength of a covalent bond is quite high. For example, the bond strength of the H-H bond in H_2 is 433 kJ mol^{-1}

Types of H-bonding

There are two types of hydrogen-bonds

1. Intermolecular hydrogen bond. It is formed between two different molecules of the same or different compounds. For example H-bond in case of HF, alcohol, or water.

2. Intramolecular Hydrogen bond. It is formed when a hydrogen atom is in between the two highly electronegative (F, O, N) atoms present within the same molecule. For example, in o-nitrophenol, hydrogen is in between the two oxygen atoms.
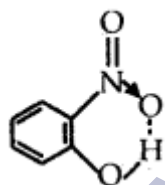
Assertion Reason Answer:

1. (i) Both A and R are true and R is the correct explanation of A.

2. (ii) Both A and R are true but R is not the correct explanation of A.

Case Study Answer:

1. **Answer:**

   (1) (c) Less than unit electronic charge

   (2) (b) Dispersion force

   (3) (d) $1/r^6$

(4) (c) Ion-dipole forces

(5) (c) Br_2

2. **Answer:**

(1) (b) H_2O

(2) (d) Hydrogen chloride

(3) (a) Intermolecular hydrogen bonding

(4) (b) Intramolecular hydrogen bonds are formed between two different molecules of the same compound.