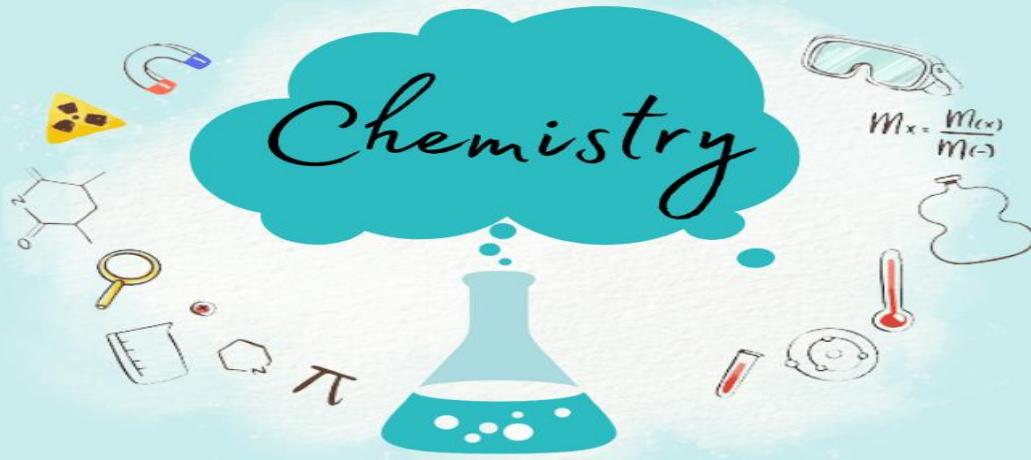


+1 CHEMISTRY NOTES

(FOR THE ACADEMIC YEAR 2024 - 25)



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1. SOME BASIC CONCEPTS OF CHEMISTRY

Chemistry is the branch of Science that deals with the preparation, properties, structure and reactions of material substances.

Some important branches of Chemistry are:

1. Inorganic Chemistry
2. Organic Chemistry
3. Physical Chemistry
4. Analytical Chemistry
5. Polymer Chemistry
6. Biochemistry
7. Medicinal Chemistry
8. Industrial Chemistry
9. Hydrochemistry
10. Electrochemistry
11. Green Chemistry etc.

Matter: Matter is anything that occupies space and has a definite mass. Based on the physical state we can divide matter into different categories.

1. Solid state
2. Liquid state
3. Gaseous state
4. Plasma state
5. Bose-Einstein condensate
6. Fermionic condensate
7. Quark-Gluon Plasma



In earth crust, matter mainly exists in three physical states – solid state, liquid state and gaseous state.

In solids, the particles are orderly arranged and they are very close to each other. The particles cannot move freely. So solids have definite shape and definite volume.

In liquids, the particles are close to each other but they can move around. So, liquids have definite volume but do not have definite shape.

In gases, the particles are far apart as compared to those present in solid or liquid state and their movement is easy and fast. So they do not have definite shape and volume. They take the shape of the container in which they are placed. Also they occupy the complete space of the container in which they are placed.

The three states of matter are interconvertible by changing the conditions of temperature and pressure.



Classification of matter

Based on the chemical composition, matter can be divided into two categories – pure substances and mixtures.

Pure substances contain only one type of particles. E.g. Sodium (Na), Potassium (K), Hydrogen (H), Oxygen (O), Helium (He), carbon dioxide (CO_2), water (H_2O), ammonia (NH_3), cane sugar ($\text{C}_{12}\text{H}_{22}\text{O}_{11}$) etc.

Pure substances are classified into two – **elements and compounds**.

Elements are pure substances which contain only one type of atom. The term element was first introduced by Robert Boyle, the father of ancient Chemistry. Now there are 118 elements starting from hydrogen (${}_1\text{H}$) and ending in Oganesson (${}_{118}\text{Og}$). Some elements exist as monoatomic, some are diatomic and some others are polyatomic. E.g. all metals (Sodium, Potassium, Calcium etc) and noble gases (Helium, Neon etc.) are monoatomic. Hydrogen, Nitrogen, Oxygen etc are diatomic. Phosphorus (P_4) and Sulphur (S_8) are polyatomic.

Compounds are pure substances which contain more than one type of atoms. They are formed by the combination of two or more atoms of different elements in a definite ratio. Their constituents cannot be separated by physical methods, but they can be separated by chemical methods.

E.g. CO_2 , H_2O , NH_3 , H_2SO_4 etc.

Mixtures contain more than one type of particles. The components of a mixture can be separated by using physical methods like filtration, crystallisation, distillation etc.

E.g. all types of solutions, gold ornaments, sea water, muddy water, air etc.

There are two types of mixtures – homogeneous and heterogeneous mixtures.

Mixtures having uniform composition throughout are called **homogeneous mixtures**. Here the components are completely mixed with each other. E.g. all type of solutions, air etc.

Mixtures having different compositions at different parts are called **heterogeneous mixtures**.

E.g. sea water, soil. Muddy water etc.

Physical and chemical properties

The properties or characteristics of matter can be classified into two types — **physical properties and chemical properties**.

Properties which can be measured or observed without changing the composition or identity of the substance are called physical properties. Measurement of physical properties does not require the occurrence of a chemical change.

E.g. colour, odour, melting point, boiling point, density, mass etc.

Properties which can be measured only with the occurrence of a chemical change are called chemical properties. E.g. composition, combustibility, reactivity with acids and bases, etc.

Measurement of physical properties

Any quantitative observation or measurement is represented by a number followed by units in which it is measured. Earlier, two different systems of measurement were used: the English System and the Metric System.

Now a days, a common standard system known as International System of Units (SI) is used. This system has **seven base units** and they are length, mass, time, electric current, thermodynamic temperature, amount of substance and luminous intensity. Their SI units are as follows:

Physical Quantity	SI unit & its symbol
Length	metre (m)
Mass	kilogram (kg)
Time	second (s)

Electric current	ampere (A)
Thermodynamic temperature	kelvin (K)
Amount of substance	mole (mol)
Luminous intensity	candela (cd)

Mass and Weight

Mass is the amount of matter present in a body. It is a constant quantity. Its SI unit is kilogram (kg).

Weight is the gravitational force acting on a body. It is a variable quantity. i.e. it changes with place. Its SI unit is newton (N).

Volume (V)

It is the amount of space occupied by a body. Its SI unit is m^3 . In Chemistry, smaller volumes are used.

Hence, volume is often denoted in cm^3 , dm^3 , mL, L etc.

$$1 m^3 = 10^6 cm^3 \quad 1 L = 10^3 cm^3 (mL) \quad 1 cm^3 = 1 mL$$

$$1 dm^3 = 10^3 cm^3 \quad 1 dm^3 = 1 L$$

Density (d)

It is the amount of mass per unit volume.

i.e. density = mass/volume. Its SI unit is kg/m^3 . But it is commonly expressed in g/cm^3 .

Temperature (T)

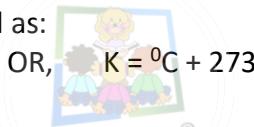
It is the degree of hotness or coldness of a body. It is commonly expressed in degree celsius ($^{\circ}C$). Other units are degree fahrenheit ($^{\circ}F$), kelvin (K) etc. Its SI unit is kelvin (K).

Degree celsius and degree fahrenheit are related as:

$$^{\circ}F = \frac{9}{5} (^{\circ}C) + 32$$

Degree celsius and kelvin are related as:

$$K = ^{\circ}C + 273.15$$



$$\text{OR, } K = ^{\circ}C + 273$$

Precision and Accuracy

Precision refers to the closeness of various measurements for the same quantity. But, accuracy is the agreement of a particular value to the true value of the result.

Scientific Notation

It is an exponential notation in which a number is represented in the form $N \times 10^n$, where n is an exponent having positive or negative values and N is a number (called digit term) which varies between 1.000... and 9.999.....

While writing scientific notation, the value of the exponent 'n' becomes positive, when the decimal is shifted to left and it becomes negative, when the decimal is shifted to right.

E.g. the scientific notation of 368.9 is 3.689×10^2 and that of 0.000563 is 5.63×10^{-4} .

Significant Figures

Every experimental measurement has some amount of uncertainty associated with it. The uncertainty in the experimental or the calculated values is indicated by mentioning the number of significant figures. **Significant figures are meaningful digits which are known with certainty.** The uncertainty is indicated by writing the certain digits and the last uncertain digit.

There are certain rules for determining the number of significant figures. These are:

1. All non-zero digits are significant. For example in 285 cm, there are three significant figures and in 0.25 mL, there are two significant figures.
2. Zeros preceding to first non-zero digit are not significant. Such zero indicates the position of the decimal point. Thus, 0.03 has one significant figure and 0.0052 has two significant figures.
3. Zeros between two non-zero digits are significant. Thus, 2.005 has four significant figures.

4. Zeros at the end or right of a number are significant if they are on the right side of the decimal point; otherwise, they are not significant. For example, 0.200 g has three significant figures.
5. Exact numbers have an infinite number of significant figures. For example, in 2 balls or 20 eggs, there are infinite significant figures since these are exact numbers and can be represented by writing infinite number of zeros after placing a decimal i.e., 2 = 2.000000 or 20 = 20.000000
6. In numbers written in scientific notation, all digits are significant. E.g. 4.01×10^2 has three significant figures, and 8.256×10^{-3} has four significant figures.

Rounding off a number to the required number of significant figures

The rules related to rounding off a number are:

- 1) If the rightmost digit to be removed is more than 5, the preceding number is increased by one. E.g. 1.386 can be round off to three significant figures, by removing 6. So it becomes 1.39.
- 2) If the rightmost digit to be removed is less than 5, the preceding number is not changed. E.g. In 4.334, if 4 is to be removed, then the result is rounded upto 4.33.
- 3) If the rightmost digit to be removed is 5, then the preceding number is not changed if it is an even number but it is increased by one if it is an odd number.

For example, if 6.35 is to be rounded by removing 5, we have to increase 3 to 4 giving 6.4 as the result. But if 6.25 is to be rounded off, it becomes 6.2.

LAWS OF CHEMICAL COMBINATIONS

The combination of elements to form compounds is governed by the following five basic laws:

1. **Law of Conservation of Mass (Law of indestructibility of matter)**: This law was proposed by Antoine Lavoisier. It states that matter can neither be created nor destroyed. Or, in a chemical reaction, the total mass of reactants is equal to the total mass of products. Chemical equations are balanced according to this law.

Illustration

Consider the reaction $2\text{H}_2 + \text{O}_2 \longrightarrow 2\text{H}_2\text{O}$

Here 4 g of H_2 combines with 32 g of O_2 to form 36 g of water.

Total mass of reactants = 4 + 32 = 36g

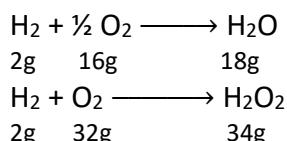
Total mass of products = 36 g

2. **Law of Definite Proportions (Law of definite composition)**: This law was proposed by Joseph Proust. It states that a given compound always contains exactly the same proportion of elements by weight. Or, the same compound always contains the same elements combined in a fixed ratio by mass.

Illustration: Carbon dioxide can be formed in the atmosphere by various methods like respiration, burning of fuels, reaction of metal carbonates and bicarbonates with acid etc. All these samples of CO_2 contain only two elements Carbon and Oxygen combined in a mass ratio 3:8.

3. **Law of Multiple Proportions**: This law was proposed by John Dalton. It states that if two elements can combine to form more than one compound, the different masses of one of the elements that combine with a fixed mass of the other element, are in small whole number ratio.

Illustration: Hydrogen combines with oxygen to form two compounds – water and hydrogen peroxide.



Here, the masses of oxygen (i.e. 16 g and 32 g) which combine with a fixed mass of hydrogen (2g) bear a simple ratio, i.e. 16:32 or 1: 2.

4. Gay Lussac's Law of Gaseous Volumes: This law was proposed by **Gay Lussac**. It states that when gases combine to form gaseous products, their volumes are in simple whole number ratio at constant temperature and pressure.

Illustration: H_2 combines with O_2 to form water vapour according to the equation $2\text{H}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{H}_2\text{O}(\text{g})$. If 100 mL of hydrogen combine with 50 mL of oxygen, we get 100 mL of water vapour. Thus, the volumes of hydrogen and oxygen which combine together (i.e. 100 mL and 50 mL) bear a simple ratio of 2:1.

5. Avogadro's Law: This law was proposed by Amedeo Avogadro. It states that equal volumes of all gases at the same temperature and pressure should contain equal number of moles or molecules.

Illustration: If we take 10L each of NH_3 , N_2 , O_2 and CO_2 at the same temperature and pressure, all of them contain the same number of moles and molecules.

DALTON'S ATOMIC THEORY

The term atom was first used by John Dalton from the Greek word a-tomio (means indivisible). He proposed the first atomic theory. The **important postulates** of this theory are:

1. Matter is made up of minute and indivisible particles called atoms.
2. Atoms can neither be created nor be destroyed.
3. Atoms of same element are identical in their properties and mass. While atoms of different elements have different properties and mass.
4. Atoms combined to form compound atoms called molecules.
5. When atoms combine, they do so in a fixed ratio by mass.

Dalton's theory could explain the laws of chemical combination.

Atoms and Molecules



Atom is the smallest particle of an element. Molecules are the smallest particle of a substance. A molecule has all the properties of that substance.

Types of molecules

Based on the type of atoms, molecules are divided into two: **homonuclear molecule and heteronuclear molecule**.

A molecule containing only one type of atom is called **homonuclear molecule**. E.g. H_2 , O_2 , N_2 , O_3 (ozone) etc.

Heteronuclear molecules contain different types of atoms. E.g. CO_2 , H_2O , $\text{C}_6\text{H}_{12}\text{O}_6$, NH_3 etc.

Based on the no. of atoms there are three types of molecules: **monoatomic, diatomic and polyatomic molecules**.

Monoatomic molecules contain only one atom. E.g. all metals, noble gases like He, Ne, Ar etc.

Diatomic molecules contain 2 atoms. E.g. H_2 , O_2 , N_2 , halogens (F_2 , Cl_2 , Br_2 and I_2)

Polyatomic molecules contain more than two atoms. E.g. ozone (O_3), Phosphorus (P_4), Sulphur (S_8) etc.

Atomic mass

Atomic mass (Relative atomic mass) of an element is a number that expresses how many times the mass of an atom of the element is greater than $1/12^{\text{th}}$ the mass of a C^{12} atom.

For e.g. atomic mass of Nitrogen is 14, which means that mass of one N atom is 14 times greater than $1/12^{\text{th}}$ the mass of a C^{12} atom.

Atomic mass unit (amu): $1/12^{\text{th}}$ the mass of a C^{12} atom is called atomic mass unit (amu).

$$\begin{aligned} \text{i.e. } 1 \text{ amu} &= \frac{1}{12} \times \text{mass of a } \text{C}^{12} \text{ atom} \\ &= 1.66 \times 10^{-24} \text{ g} = 1.66 \times 10^{-27} \text{ kg} \end{aligned}$$

Nowadays, 'amu' has been replaced by 'u' which is known as ***unified mass***.

Average atomic mass:

Most of the elements have isotopes. So we can calculate an average atomic mass of an element by considering the atomic mass of the isotopes and their relative abundance. For e.g. chlorine has two isotopes ^{35}Cl and ^{37}Cl in the ratio 3:1. So the average atomic mass Cl = $(3 \times 35 + 1 \times 37) / 4 = 35.5$

Molecular mass:

Molecular mass is the sum of atomic masses of the elements present in a molecule. It is obtained by multiplying the atomic mass of each element by the number of its atoms and adding them together.

For e.g. molecular mass of H_2SO_4 is calculated as: $2 \times 1 + 32 + 4 \times 16 = 98 \text{ u.}$

Formula mass:

In the case of ionic compounds (like NaCl), there is no discrete (separate) molecules. Here the positive ions and the negative ions are arranged in a three-dimensional structure. So we can calculate only formula mass by taking molecular formula of the compound.

Mole concept

Mole is the unit of amount of substance. It is defined as the amount of substance that contains as many particles as there are atoms in exactly 12 g C^{12} isotope.

1 mole of any substance contains 6.022×10^{23} atoms [602213670000000000000000 atoms]. This number is known as ***Avogadro number or Avogadro constant*** (N_A or N_0).

1 mol of hydrogen atoms = 6.022×10^{23} atoms

1 mol of water molecules = 6.022×10^{23} water molecules

1 mol of sodium chloride = 6.022×10^{23} formula units of sodium chloride

$$\text{No. of moles (n)} = \frac{\text{Given mass in gram (w)}}{\text{Molar mass (M)}}$$

$$\text{No. of molecules} = \text{no. of moles} \times 6.022 \times 10^{23}$$

Molar mass: The mass of one mole of a substance in gram is called its molar mass (gram molecular mass). The molar mass in grams is numerically equal to molecular mass in u.

Molar mass of oxygen = 32g

Molar mass of hydrogen = 2g etc.

Molar volume: It is the volume of 1 mole of any substance. At standard temperature and pressure (STP), molar volume of any gas = 22.4 L (or, 22400 mL). i.e. 22.4 L of any gas at STP contains 1 mole of the gas or 6.022×10^{23} molecules of the gas and its mass = molar mass.

For e.g. 22.4 L of hydrogen gas = 1 mole of H_2 = 6.022×10^{23} molecules of hydrogen = 2 g of H_2

Q1) How many moles of water molecules are present in 180 g of water?

$$\text{Ans: No. of moles} = \frac{\text{Given mass in gram}}{\text{Molar mass}} = \frac{180}{18} = \underline{\underline{10 \text{ mol}}}$$

Percentage composition

It is the percentage of each element present in 100g of sample of a substance.

$$\text{i.e. Percentage composition of an element} = \frac{\text{Mass of that element in the compound} \times 100}{\text{Molar mass of the compound}}$$

Applications: We can check the purity of a given sample of a substance. Also by knowing the percentage composition, we can calculate the empirical and molecular formula of a compound.

Empirical and Molecular formulae

Empirical formula is the simplest formula of a compound, which gives only the ratio of different elements present in that compound. But molecular formula is the actual formula of the compound, that gives the exact number of different elements present in the sample. For e.g. the empirical formula of glucose is CH_2O but its molecular formula is $\text{C}_6\text{H}_{12}\text{O}_6$.

Molecular formula is related to empirical formula by the equation:

$$\text{Molecular formula (M.F)} = \text{Empirical formula (E.F)} \times n$$

$$\text{Where } n = \frac{\text{Molecular mass (MM)}}{\text{Empirical formula mass (EFM)}}$$

By knowing the percentage composition, we can calculate the empirical and molecular formula of a compound as follows:

Q2) An organic compound on analysis gave the following composition. Carbon = 40%, Hydrogen = 6.66% and oxygen = 53.34%. Calculate its molecular formula if its molecular mass is 180.

Ans:

Element	Percentage	Atomic mass	Percentage Atomic mass	Simple ratio	Simplest whole no. ratio
C	40	12	40/12 = 3.33	3.33/3.33 = 1	1
H	6.66	1	6.66/1 = 6.66	6.66/3.33 = 2	2
O	53.34	16	53.34/16 = 3.33	3.33/3.33 = 1	1

$$\text{Empirical Formula} = \text{CH}_2\text{O}$$

$$\text{Empirical Formula Mass (EFM)} = 12+2+16 = 30$$

$$\text{Molar mass (MM)} = 180$$

$$n = \text{MM}/\text{EFM} = 180/30 = 6$$

$$\text{Molecular formula} = \text{Empirical formula} \times n = (\text{CH}_2\text{O}) \times 6 = \text{C}_6\text{H}_{12}\text{O}_6$$

Stoichiometry and Stoichiometric calculations

The word 'stoichiometry' is derived from two Greek words – stoicheion (meaning element) and metron (meaning measure). Thus stoichiometry deals with the calculations involving the masses or the volumes of reactants and the products.

Chemical Equation

It is the representation of a chemical reaction by symbols and formulae. Here the reactants are written in the left-hand side and the products, on the right-hand side. (The substances which participate in a chemical reaction are called **reactants** and the substances which are formed as a result of a reaction are called **products**).

A chemical equation should be balanced and the physical states of reactants and products are written in brackets.

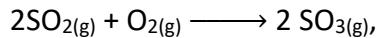
The following information are obtained from a chemical equation.

1. An idea about the reactants and products and their physical states.
2. An idea about the masses of reactants and products.
3. An idea about the number moles and molecules of reactants and products.
4. An idea about the volumes of reactants and products at STP.

Limiting reagent (Limiting reactant)

The reagent which limits a reaction or the reagent which is completely consumed in a chemical reaction is called limiting reagent or limiting reactant.

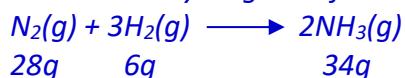
For e.g. in the reaction:



2 moles of SO_2 reacts completely with 1 mole of O_2 to form 2 moles of SO_3 . If we take 10 moles each of SO_2 and O_2 , we get only 10 moles of SO_3 because 10 moles of SO_2 requires only 5 moles of O_2 for the complete reaction. So here SO_2 is the limiting reagent and 5 moles of O_2 remains unreacted.

Q3) A reaction mixture for the production of NH_3 gas contains 250 g of N_2 gas and 50 g of H_2 gas under suitable conditions. Identify the limiting reactant if any and calculate the mass of NH_3 gas produced.

Ans: Nitrogen reacts with Hydrogen to form ammonia according to the equation,



28g N_2 requires 6g H_2 for the complete reaction.

So, 250g N_2 requires, $6 \times 250/28 = 53.57\text{g H}_2$.

But here there is only 50g H_2 .

So we have to consider the reverse case.

i.e. 6g H_2 requires 28g N_2 .

So, 50g H_2 requires $28 \times 50/6 = 233.33\text{g N}_2$

Here H_2 is completely consumed. So it is the limiting reagent.

Amount of ammonia formed = $50 + 233.33 = 283.33\text{ g}$

Reactions in solutions

Solutions are homogeneous mixture containing 2 or more components. The component which is present in larger quantity is called solvent and the other components are called solutes. Or, the substance which is dissolved is called solute and the substance in which solute is dissolved is called solvent.

For e.g. in NaCl solution, NaCl is the solute and water is the solvent.

A solution containing only 2 components are called **binary solution**. If the solvent is water, it is called **aqueous solution**.

The composition of a solution is expressed in terms of concentration. It is defined as the amount of solute present in a given volume of solution. Concentration can be expressed in the following ways:

1. **Mass percent (w/w or m/m):** It is defined as the number of parts solute present in 100 parts by mass of solution.

$$\text{i.e. Mass \% of a component} = \frac{\text{Mass of solute} \times 100}{\text{Mass of solution}}$$

2. **Mole fraction:** It is defined as the ratio of the number of moles of a particular component to the total number of moles of solution.

$$\text{i.e. Mole fraction of a component} = \frac{\text{Number of moles of the component}}{\text{Total number of moles of all the components}}$$

For example, in a binary solution, if the number of moles of A and B are n_A and n_B respectively, then mole fraction of the component A (χ_A) = $\frac{n_A}{n_A + n_B}$

$$\text{and mole fraction of the component B} (\chi_B) = \frac{n_B}{n_A + n_B}$$

$$\chi_A + \chi_B = \frac{n_A}{n_A + n_B} + \frac{n_B}{n_A + n_B} = 1$$

i.e. the sum of the mole fractions of all the components in a solution is always equal to 1.

If there are 1,2,3, i components, then $\chi_1 + \chi_2 + \chi_3 + \dots + \chi_i = 1$

3. **Molarity (M):** It is the number of moles of solute dissolved per litre of solution.

$$\text{i.e. Molarity (M)} = \frac{\text{Number of moles of solute (n)}}{\text{Volume of solution in litre (V)}}$$

1 M NaOH solution means 1 mole (40 g) of NaOH is present in 1 L of solution.

When a solution is diluted from one concentration to another, its new concentration can be calculated by the equation: $M_1V_1 = M_2V_2$.

Where M_1 - initial molarity, M_2 - final molarity, V_1 - initial volume and V_2 - final volume.

4. Molality (m): It is defined as the number of moles of solute present per kilogram (kg) of the solvent.

$$\text{i.e. Molality (m)} = \frac{\text{Number of moles of solute}}{\text{Mass of solvent in kg}}$$

Among the concentration terms, molarity depends on temperature because it is related to volume, which changes with temperature. All the others are temperature independent.

Q4) Calculate the molarity of a solution containing 8 g of NaOH in 500 mL of water.

Ans: Here mass of solute (NaOH) = 8 g and volume of solution = 500 mL = 0.5 L

Molar mass of NaOH = 40 g mol⁻¹

$$\text{No. of moles of NaOH} = \frac{\text{mass of NaOH in gram}}{\text{Molar mass of NaOH}} = \frac{8}{40} = 0.2 \text{ mol}$$

$$\text{Molarity} = \frac{\text{Number of moles of solute (n)}}{\text{Volume of solution in litre (V)}} = \frac{0.2}{0.5} = 0.4 \text{ M}$$

Q5) Calculate the mass of oxalic acid dihydrate ($\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$) required to prepare 0.1M, 250 mL of its aqueous solution.

Ans: Here molarity of solution = 0.1M and volume of solution = 250 mL = 0.25 L

No. of moles of oxalic acid = Molarity x volume of solution in litre = 0.1 x 0.25 = 0.025 mol

Molar mass of Oxalic acid dihydrate = 126 g/mol

Mass of oxalic acid = No. of moles x Molar mass of oxalic acid = 0.025 x 126 = 3.15 g

Q6) Calculate the amount of $\text{CO}_2(\text{g})$ produced by the reaction of 32g of $\text{CH}_4(\text{g})$ and 32g of $\text{O}_2(\text{g})$.



16g 64g 44g 36g

64g O_2 requires 16g CH_4 for the complete reaction.

So, 32g O_2 requires 8g CH_4 .

16g CH_4 combines with 64g O_2 to form 44g CO_2 .

Therefore, 8g CH_4 combines with 32g Oxygen to form 22g CO_2

Q7) If the density of methanol is 0.793 kg L⁻¹, what is its volume needed for making 2.5 L of its 0.25 M solution?

Ans: Density of methanol = 0.793 kg L⁻¹

i.e. mass of 1 L of methanol = 0.793 kg = 793 g

$$\text{No. of moles of methanol (CH}_3\text{OH}) = \frac{\text{Mass in gram}}{\text{Molar mass}} = \frac{793}{32} = 24.78 \text{ mol}$$

Molarity = no. of moles of solute per L of solution = 24.78 M

Here we have to prepare 2.5L (V₂) of 0.25M (M₂) methanol solution from 24.78M (M₁) methanol.

So we can use the equation $M_1V_1 = M_2V_2$

$$24.78 \times V_1 = 0.25 \times 2.5 = 0.025 \text{ L} = 25 \text{ mL}$$

Volume of methanol required = 25 mL

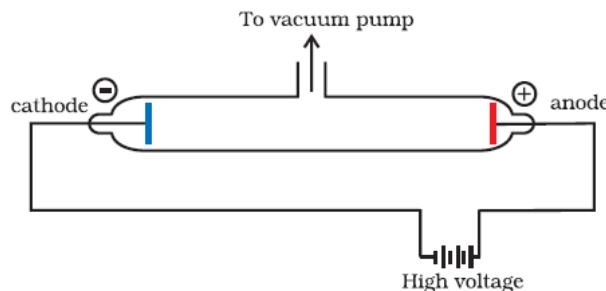
2. STRUCTURE OF ATOM

The word 'atom' has been derived from the Greek word 'a-tomio' means 'uncuttable' or 'non-divisible'. The first atomic theory of matter was proposed by John Dalton in 1808. Dalton's atomic theory was able to explain the law of conservation of mass, law of constant proportion and law of multiple proportion very successfully. However, it failed to explain many experimental results.

Discovery of Sub-atomic particles

1. Discovery of Electron

Electron was discovered by J J Thomson through *Cathode ray discharge tube experiment*. A cathode ray tube is made of glass containing two thin metal pieces (called electrodes) sealed in it. The electrical discharge through the gases could be observed only at very low pressures and at very high voltages.



When a very high voltage (about 10,000 volts) is applied between the two electrodes, no electric discharge occurs at normal pressure. When the pressure of the gas inside the tube is less than 1 mm of mercury, a dark space appears near the cathode. When the pressure is reduced to 0.01 mm Hg, it fills the whole tube. When the pressure is further reduced (10^{-4} mm Hg), the electric discharge passes between the electrodes and the tube begins to glow. This is due to the striking of some invisible rays from the cathode. These *rays which start from the cathode and move away from it, in straight lines are called cathode rays or cathode ray particles*.

These rays can be further checked by making a hole in the anode and coating the tube behind anode with phosphorescent material like zinc sulphide. When these rays strike the zinc sulphide coating, a bright spot on the coating is developed.

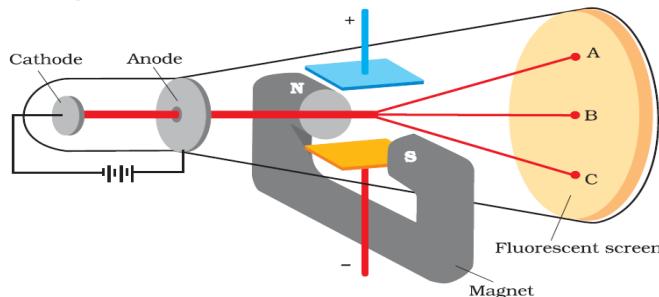
Properties of Cathode Rays

- i. The cathode rays start from cathode and move towards the anode.
- ii. They are invisible, but their behaviour can be observed with the help of fluorescent or phosphorescent materials.
- iii. In the absence of electrical or magnetic field, these rays travel in straight lines.
- iv. In the presence of electrical or magnetic field, the cathode rays behave similar to that of negatively charged particles. From this, it is clear that the cathode rays consist of negatively charged particles called electrons.
- v. The characteristics of cathode rays (electrons) do not depend upon the material of electrodes and the nature of the gas present in the cathode ray tube.
- vi. These rays possess kinetic energy and hence can do mechanical work.
- vii. They can produce x-rays when incident on metals with high atomic mass.

Charge to Mass (e/m_e) Ratio of Electron

J.J. Thomson measured the ratio of electrical charge (e) to the mass of electron (m_e) by using cathode ray tube and applying electrical and magnetic field perpendicular to each other as well as to the

path of electrons. There is a fluorescent screen on one side of the discharge tube. When these rays strike the fluorescent screen, a bright spot is developed.



In the absence of electric or magnetic field, the cathode rays hit the screen at point B. When only electrical field is applied, the electrons deviate from their path and hit the cathode ray tube at point A. Similarly, when only magnetic field is applied, electron strikes the cathode ray tube at point C. By carefully balancing the electrical and magnetic field strength, it is possible to bring back the electron beam to the point B. From the strength of electrical and magnetic field, Thomson was able to calculate the value of e/m_e as:

$$e/m_e = 1.7588 \times 10^{11} \text{ C kg}^{-1}$$

Where, m_e is the mass of the electron in kg and e is the magnitude of the charge on the electron in coulomb (C).

Charge on the Electron (e)

R.A. Millikan determined the charge on the electrons by a method known as 'oil drop experiment'. He found that the charge on the electron to be $-1.6022 \times 10^{-19} \text{ C}$.

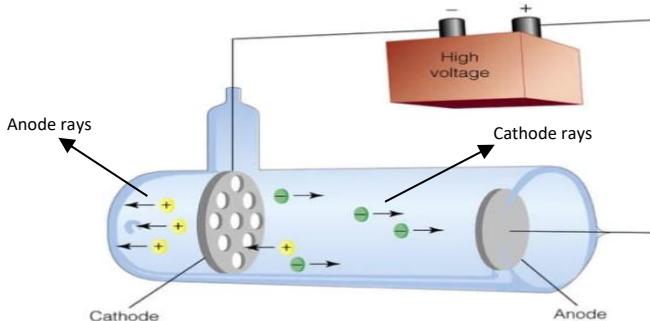
Mass of electron (m_e)

The mass of the electron (m_e) was determined as follows:

$$\begin{aligned} \text{Mass of electron } (m_e) &= \frac{e}{e/m_e} = \frac{1.6022 \times 10^{-19}}{1.7588 \times 10^{11}} \\ &= 9.1 \times 10^{-31} \text{ kg} \end{aligned}$$

2. Discovery of Protons

E. Goldstein modified the discharge tube experiment by perforated (with small holes) cathode. After evacuating the tube and on applying high voltage, he found that some rays were emitting behind the cathode and moving in the opposite direction of cathode rays. These rays deflect to the negative plate of electric field. So they carry positive charge and were called **anode rays or canal rays**.



Properties of Canal rays

The characteristics of canal rays are:

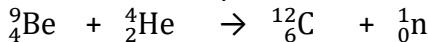
- They depend on the nature of gas present in the cathode ray tube. These are positively charged gaseous ions.
- The charge to mass ratio of anode rays depends on the nature of the gas.
- Some of the positively charged particles carry a multiple of the fundamental unit of electrical charge.

- iv. They also travel in straight lines, in the absence of electrical or magnetic field.
- v. The behaviour of these particles in the magnetic or electrical field is opposite to that observed for cathode rays.
- vi. They can produce heating effect and can do mechanical work.
- vii. They are invisible and can be observed with the help of fluorescent or phosphorescent materials.

The smallest and lightest positive ion was obtained from hydrogen and was called proton.

3. Discovery of Neutrons

Neutrons were discovered by James Chadwick by bombarding a thin sheet of beryllium by α -particles.



They are electrically neutral particles having mass slightly greater than that of the protons.

Characteristics of sub-atomic particles

Sub-atomic particle	Symbol	Discoverer	Absolute Charge (in Coulomb)	Relative charge	Mass (in kg)
Electron	e	J J Thomson	-1.6022×10^{-19}	-1	9.01×10^{-31}
Proton	p	E Goldstein	$+1.6022 \times 10^{-19}$	+1	1.6726×10^{-27}
Neutron	n	James Chadwick	0	0	1.675×10^{-27}

Some important terms relating to Atomic structure

Atomic Number: It is the number of protons present in the nucleus or number of electrons present outside the nucleus.



It is denoted by the symbol 'Z'.

Atomic number (Z) = nuclear charge or number of protons (p)
= number of electrons (e)

Mass Number: It is the total number of protons and neutrons in atom. Or, it is the total number of nucleons in an atom. [Protons and neutrons are together called nucleons].

It is denoted by 'A'.

i.e. Mass number (A) = no. of protons (p) + no. of neutrons (n)

or, $A = p + n$

By knowing the atomic number and mass number, we can calculate the number of neutrons as: $n = A - Z$

If an element 'X' has the atomic number Z and the mass number A, it is denoted as: ${}^A_Z\text{X}$ or ${}^Z\text{X}^A$

Isotopes, Isobars and Isotones

Isotopes are atoms with same atomic number but different mass number. That is, they contain same number of protons but different number of neutrons.

Hydrogen has three isotopes: Protium (${}^1_1\text{H}$), Deuterium (${}^2_1\text{H}$ or ${}^2_1\text{D}$) and Tritium (${}^3_1\text{H}$ or ${}^3_1\text{T}$). Among these, Protium is the ordinary hydrogen and Tritium is the radioactive isotope of Hydrogen.

The number of protons, neutrons and electrons present in the 3 types of hydrogen are:

Isotope	Number of protons	Number of electrons	Number of neutrons
Protium	1	1	0
Deuterium	1	1	1
Tritium	1	1	2

Almost all the elements have isotopes. All the isotopes of a given element have same chemical properties, but they differ in their physical properties.

Isobars are atoms of different elements having same mass number but different atomic number. i.e. they have different number of protons but have equal sum of the protons and neutrons (nucleons).

e.g. $^{14}_6\text{C}$ and $^{14}_7\text{N}$ $^{40}_{18}\text{Ar}$ and $^{40}_{20}\text{Ca}$

Isotones are atoms having same number of neutrons but have different atomic numbers. Some examples are:

Isotones	p	e	N
$^{14}_6\text{C}$	6	6	8
$^{15}_7\text{N}$	7	7	8
$^{16}_8\text{O}$	8	8	8

ATOM MODELS

1. Thomson's Model of Atom

J. J. Thomson proposed the first atom model, which is known as **the plum pudding or raisin pudding or watermelon model.**

According to this model:

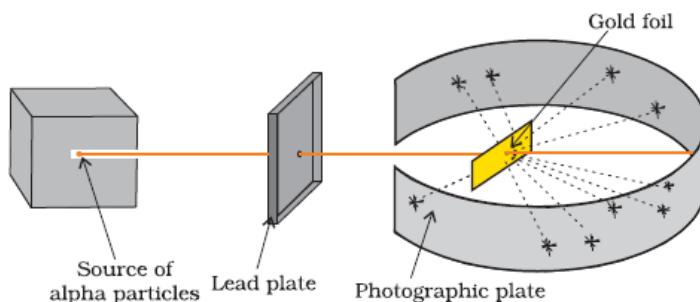
- an atom has a spherical shape in which the positive charge is uniformly distributed.
- The electrons are distributed in it, just like the seeds are distributed in a water melon or plums are distributed in a pudding.
- The mass of the atom is uniformly distributed over the atom.
- The total positive charge in an atom is equal to the total negative charge and hence the atom is electrically neutral.

This model was able to explain the electrical neutrality of the atom. But it failed to explain the experimental observations made by Rutherford and others.

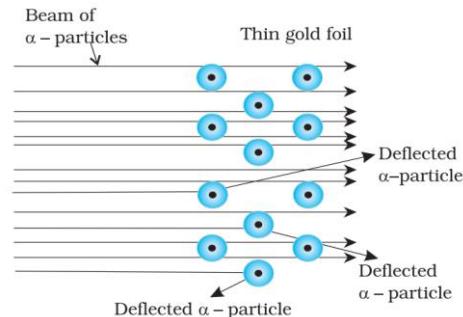
2. Rutherford's Nuclear Model of Atom

Earnest Rutherford proposed an atom model based on α -particle scattering experiment. He bombarded a very thin gold foil [approximately 10^{-7}m or 100 nm thickness] with α -particles.

The Experiment: A stream of high energy α -particles from a radioactive source was directed at a thin gold foil. The thin gold foil had a circular fluorescent zinc sulphide screen (photographic plate) around it. Whenever α -particles struck the screen, a tiny flash of light was produced at that point.



[Rutherford's scattering experiment]



[Schematic molecular view of the gold foil]

Observations and conclusions of α -particle scattering experiment are:

Observations	Conclusions
<ol style="list-style-type: none"> Most of the α-particles passed through the gold foil without any deviation. A small fraction of the α-particles was deflected by small angles. 	<ol style="list-style-type: none"> Most space in the atom is empty. The positive charge of the atom is concentrated in a very small volume at the centre called nucleus.

<p>3. A very few α- particles (approximately 1 out of 20,000) bounced back [i.e. deflected by nearly 180°].</p>	<p>3. The volume occupied by the nucleus is negligibly small as compared to the total volume of the atom. [The radius of the atom is about 10^{-10} m, while that of the nucleus is 10^{-15} m].</p>
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On the basis of above observations and conclusions, Rutherford proposed ***the nuclear model of atom*** or ***Planetary model of atom***. According to this model:

1. The positive charge and most of the mass of the atom are concentrated in an extremely small region called nucleus.
2. Electrons are revolving round the nucleus with a very high speed in circular paths called orbits.
3. Electrons and the nucleus are held together by electrostatic forces of attraction.

Drawbacks or Limitations of Rutherford's atom model

1. Rutherford's model could not explain the stability of the atom.
2. It could not explain the electronic structure of atom.

Wave nature of Electromagnetic Radiation

James Clerk Maxwell suggested that when electrically charged particle moves under acceleration, alternating electrical and magnetic fields are produced and transmitted. These fields are transmitted in the forms of waves called ***electromagnetic waves or electromagnetic radiation (emr)***. These are the radiations associated with electrical and magnetic fields.

The important characteristics of these radiations are:

1. The oscillating electrical and magnetic fields are perpendicular to each other and both are perpendicular to the direction of propagation of the wave.
2. The electromagnetic waves do not require a medium for propagation and can move in vacuum.
3. There are many types of electromagnetic radiations, which differ from one another in wavelength (or frequency). These constitute electromagnetic spectrum. The important electromagnetic radiations in the increasing order of wavelength are:
Cosmic rays, Gamma rays, X-rays, Ultra-violet rays, Visible light, Infra-red rays, Microwaves, Radio waves.
4. All electromagnetic radiations travel with a constant speed of 3×10^8 m/s through vacuum.

Some important terms relating to electromagnetic radiations

1. **Frequency (v):** It is defined as the number of waves that pass through a given point in one second. The SI unit for frequency is hertz (Hz) or s^{-1} .
2. **Wavelength (λ) :** It is the distance between two adjacent crests or troughs. Its unit is m or cm. Commonly the wavelength of electromagnetic radiations are expressed in nanometer (nm) or Angstrom unit (\AA^0). $1\text{nm} = 10^{-9}\text{ m} = 10^{-7}\text{ cm}$ $1\text{\AA}^0 = 10^{-10}\text{ m} = 10^{-8}\text{ cm}$.
3. **Speed of light (c):** It is the distance travelled by an electromagnetic radiation in one second. $c = 3 \times 10^8$ m/s in vacuum.

The frequency (v), speed of light (c) and the wave length (λ) are related to each other as: $c = v\lambda$

$$\text{Or, } v = \frac{c}{\lambda}$$

4. **Wave number (\bar{v}):** It is defined as the number of wavelengths per unit length. Or, it is the reciprocal of wavelength. i.e. $\bar{v} = 1/\lambda$. Its SI unit is m^{-1} . But it is commonly expressed in cm^{-1} .

Particle Nature of Electromagnetic Radiation: Planck's Quantum Theory

Some of the experimental phenomenon like diffraction and interference can be explained by the wave nature of the electromagnetic radiation. But some phenomena like black body radiation, photoelectric effect, variation of heat capacity of solids with temperature, line spectra of atoms etc. could not be explained by the wave nature of electromagnetic radiation.

Black body radiation

An ideal body which emits and absorbs all frequencies of radiations is called a *black body* and the radiation emitted by such a body is called *black body radiation*.

A perfect black body is rare. But carbon black behaves nearly like a black body.

The amount of light emitted (intensity of radiation) from a black body and its spectral distribution depends only on its temperature. At a given temperature, intensity of radiation emitted increases with the increase of wavelength, reaches a maximum value and then decreases.

The phenomenon of black body radiation was first explained by **Max Planck** by his **Quantum theory**. According to this theory:

1. Atoms and molecules could emit (or absorb) energy not in a continuous manner, but discontinuously in small packets of energy called quanta or photons.
2. The energy (E) of a quantum of radiation is proportional to its frequency (ν). i.e. $E = h\nu$. Where 'h' is known as Planck's constant ($h = 6.626 \times 10^{-34} \text{ Js}$).

Photoelectric effect

It is the phenomenon of ejection of electrons by certain metals (like potassium, rubidium, caesium etc.) when light of suitable frequency incident on them. The electrons ejected are called photoelectrons.



This phenomenon was first observed by Heinrich Hertz.

The important results observed in photoelectric effect are:

1. The electrons are ejected from the metal surface as soon as the beam of light strikes the surface. i.e., there is no time lag between the striking of light beam and the ejection of electrons from the metal surface.
2. The number of electrons ejected is proportional to the intensity or brightness of light.
3. For each metal, there is a minimum frequency (known as threshold frequency [ν_0]) below which photoelectric effect is not observed.
4. The kinetic energy of the ejected electrons is directly proportional to the frequency of the incident light.

Explanation of photoelectric effect by Einstein

A satisfactory explanation to photoelectric effect was first given by **Albert Einstein** using **Planck's quantum theory**.

According to him, when a photon of sufficient energy strikes the metal surface, it suddenly transfers its energy to the electron of the metal atom and the electron is ejected without any time lag. A part of this energy is used to eject the electron from the metal surface (i.e. to overcome the attractive force of the nucleus). This energy is called work function [$h\nu_0$]. The other part of this energy is given to the ejected electron in the form of kinetic energy. Greater the energy possessed by the photon, greater will be transfer of energy to the electron and greater the kinetic energy of the ejected electron.

Since the striking photon has energy equal to $h\nu$ and the minimum energy required to eject the electron is $h\nu_0$ (also called work function, W_0) then the difference in energy ($h\nu - h\nu_0$) is transferred as

the kinetic energy of the photoelectron.

Applying the law of conservation of energy principle, the kinetic energy of the ejected electron is given by $K.E = h\nu - h\nu_0$

$$\text{Or, } h\nu = h\nu_0 + \frac{1}{2} m_e v^2$$

Where m_e is the mass of the electron and v is the velocity of the ejected electron.

A more intense beam of light contains larger number of photons, so the number of electrons ejected is also larger.

Q1) The threshold frequency for a metal is $7.0 \times 10^{14} \text{ s}^{-1}$. Calculate the kinetic energy of an emitted electron when radiation of frequency (ν) $1.0 \times 10^{15} \text{ s}^{-1}$ hits the metal.

Ans: Here threshold frequency (ν_0) = $7.0 \times 10^{14} \text{ s}^{-1}$ and frequency of radiation (ν) = $1.0 \times 10^{15} \text{ s}^{-1}$

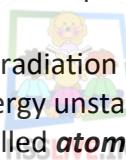
$$K.E \text{ of emitted electron} = h\nu - h\nu_0 = h(\nu - \nu_0) = 6.626 \times 10^{-34} (1.0 \times 10^{15} - 7.0 \times 10^{14}) = 19.878 \times 10^{-20} \text{ J}$$

Dual Behaviour of Electromagnetic Radiation

Some phenomena of electromagnetic radiations can be explained by the wave nature of emr, but some others can be explained by its particle nature. So electromagnetic radiations possess both particle and wave nature. This is known as dual nature of Electromagnetic Radiation. When radiation interacts with matter, it shows particle like nature.

Atomic spectrum

When a ray of white light is passed through a prism, we get a series of coloured bands called spectrum. This spectrum is called continuous spectrum, because here violet merges into blue, blue into green and so on.



Similarly, when electromagnetic radiation interacts with matter, atoms and molecules may absorb energy and reach to a higher energy unstable state. To attain stability, they emit radiations in the form of spectrum. Such a spectrum is called **atomic spectrum**.

Emission and Absorption Spectra

The spectrum of radiation emitted by a substance that has absorbed energy is called an **emission spectrum**. Atoms, molecules or ions that have absorbed radiation are said to be "excited". To produce an emission spectrum, energy is supplied to a sample by heating it or irradiating it and the wavelength (or frequency) of the radiation emitted is recorded.

An **absorption spectrum** is like the photographic negative of an emission spectrum. Here a continuum of radiation (like white light) is passed through a sample which absorbs radiation of certain wavelengths. The missing wavelengths leave dark spaces in the bright continuous spectrum.

The study of emission or absorption spectra is referred to as **spectroscopy**.

The emission spectra of atoms in the gas phase do not form a continuous spectrum. The excited atoms emit light only at specific wavelengths with dark spaces between them. Such spectra are called **line spectra or atomic spectra**.

Line emission spectra are very useful in the study of electronic structure of atoms. Each element has a unique line emission spectrum. The characteristic lines in atomic spectra can be used in chemical analysis to identify unknown atoms in the same way as finger prints are used to identify people. So line emission spectra are also called **finger print of atoms**.

Line Spectrum of Hydrogen

When an electric discharge is passed through gaseous hydrogen, the H_2 molecules dissociate and the energetically excited hydrogen atoms produced emit electromagnetic radiation of discrete

frequencies. The hydrogen spectrum consists of several series of lines named after their discoverers. The first five series of lines are **Lyman, Balmer, Paschen, Brackett and Pfund series**. Among these lines, the **Balmer series is the only series that we can see** (since it lies in the visible region of emr).

Johannes Rydberg proposed an equation for finding the wave number of the different lines in Hydrogen spectrum. The expression is: $\tilde{V} = \frac{1}{\lambda} = 109677 \left\{ \frac{1}{n_1^2} - \frac{1}{n_2^2} \right\} \text{ cm}^{-1}$

Where $n_1 = 1, 2, 3, \dots$ and $n_2 = n_1 + 1, n_1 + 2, \dots$

The different spectral lines, their spectral region and their n_1 and n_2 values are as follows:

Series	Spectral region	n_1	n_2
Lyman series	Ultra violet	1	2,3,4,....
Balmer series	Visible	2	3,4,5,....
Paschen series	Infra-red	3	4,5,6,....
Brackett series	Infra-red	4	5,6,7,....
Pfund series	Infra-red	5	6,7,8,....

3. BOHR'S MODEL FOR HYDROGEN ATOM

The general features of the structure of hydrogen atom and its spectrum were first explained by Niels Bohr. The important postulates of his theory are:

1. The electron in the hydrogen atom can move around the nucleus in circular paths of fixed radius and energy. These paths are called orbits or stationary states or allowed energy states. These energy levels are numbered as 1,2,3 etc or as K, L, M, N, etc. These numbers are known as **Principal quantum numbers**.
2. The energy of an electron in an orbit does not change with time. However, when an electron absorbs energy, it will move away from the nucleus (i.e. to a higher energy level) and when it loses energy, it will move towards the nucleus (i.e. to a lower energy level).
3. The radius of orbits can be given by the equation: $r_n = a_0 n^2$ where $a_0 = 52.9 \text{ pm}$. Thus the radius of the first stationary state is 52.9 pm (called the Bohr radius). As n increases, the value of r will increase.
4. The energy of electron in an orbit is given by the expression: $E_n = -R_H \frac{1}{n^2}$, where $n = 1,2,3, \dots$ and R_H is a constant called Rydberg constant. Its value is $2.18 \times 10^{-18} \text{ J}$. The energy of the lowest state (the ground state) is given by $E_1 = -2.18 \times 10^{-18} \text{ J}$. As the value of n increases, the energy of the electron also increases.
5. The frequency of radiation absorbed or emitted when transition occurs between two stationary states that differ in energy by ΔE , is given by: $v = \frac{\Delta E}{h} = \frac{E_2 - E_1}{h}$

Where E_1 and E_2 are the energies of lower and higher energy levels respectively. This expression is commonly known as *Bohr's frequency rule*.

6. The angular momentum of an electron is quantized. i.e. it is an integer multiple of $h/2\pi$.

$$\text{Or, Angular momentum, } m_e v r = \frac{n h}{2\pi}$$

Where m_e is the mass of electron, v is the velocity of electron and r is the radius of Bohr orbit. $n = 1,2,3, \dots$ Thus an electron can move only in those orbits whose angular momentum is an integral multiple of $h/2\pi$. So only certain fixed orbits are allowed.

Significance of negative energy of electron

When the electron is free from the influence of nucleus, its energy is taken as zero. In this situation, the electron is at the orbit with $n = \infty$. When the electron is attracted by the nucleus and is present in orbit n , the energy is emitted and its energy is lowered. That is the reason for the presence of negative sign in equation.

Explanation of Line Spectrum of Hydrogen

According to Bohr atom model, radiation is absorbed if the electron moves from lower energy to higher energy level and radiation is emitted if the electron moves from higher orbit to lower orbit. The energy gap between the two orbits is given by equation:

$$\Delta E = E_2 - E_1$$

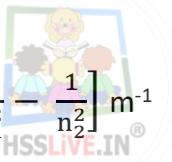
$$\text{But } E_1 = \frac{R_H}{n_1^2} \text{ and } E_2 = \frac{R_H}{n_2^2}$$

$$\begin{aligned}\text{Therefore, } \Delta E &= R_H \left[\frac{1}{n_1^2} - \frac{1}{n_2^2} \right] \\ &= 2.18 \times 10^{-18} \left[\frac{1}{n_1^2} - \frac{1}{n_2^2} \right]\end{aligned}$$

The frequency associated with the absorption and emission of the photon can be given as:

$$\begin{aligned}v &= \frac{\Delta E}{h} = \frac{R_H}{h} \left[\frac{1}{n_1^2} - \frac{1}{n_2^2} \right] \text{ Hz} \\ &= \frac{2.18 \times 10^{-18} \text{ J}}{6.626 \times 10^{-34} \text{ Js}} \left[\frac{1}{n_1^2} - \frac{1}{n_2^2} \right] \text{ Hz} \\ &= 3.29 \times 10^{15} \left[\frac{1}{n_1^2} - \frac{1}{n_2^2} \right] \text{ Hz}\end{aligned}$$

$$\text{The wave number } (\tilde{V}) = \frac{1}{\lambda} = \frac{v}{c} = \frac{R_H}{hc} \left[\frac{1}{n_1^2} - \frac{1}{n_2^2} \right] \text{ m}^{-1}$$



$$\begin{aligned}&= \frac{3.29 \times 10^{15}}{3 \times 10^8} \left[\frac{1}{n_1^2} - \frac{1}{n_2^2} \right] \text{ m}^{-1} \\ &= 1.09677 \times 10^7 \times \left[\frac{1}{n_1^2} - \frac{1}{n_2^2} \right] \text{ m}^{-1} \\ &= 109677 \times \left[\frac{1}{n_1^2} - \frac{1}{n_2^2} \right] \text{ cm}^{-1}\end{aligned}$$

In case of absorption spectrum, $n_2 > n_1$ and the term in the bracket is positive and energy is absorbed. On the other hand, in case of emission spectrum $n_1 > n_2$, ΔE is negative and energy is released.

Limitations of Bohr Atom Model:

Bohr atom model could explain the stability and line spectra of hydrogen atom and hydrogen like ions (e.g. He^+ , Li^{2+} , Be^{3+} etc). But it has the following limitations:

1. It could not explain the fine spectrum of hydrogen atom.
2. It could not explain the spectrum of atoms other than hydrogen.
3. It was unable to explain the splitting of spectral lines in the presence of electric field (Stark effect) and in magnetic field (Zeeman effect).
4. It could not explain the ability of atoms to form molecules by chemical bonds.
5. It did not consider the wave character of matter and Heisenberg's uncertainty principle.

Dual Behaviour of Matter – de Broglie's equation

de Broglie proposed that like radiation, matter also exhibit dual behaviour i.e., both particle and wave like properties. This means that electrons should also have momentum as well as wavelength. He gave the following relation between wavelength (λ) and momentum (p) of a material particle.

$$\lambda = \frac{h}{p} = \frac{h}{mv}$$

Where m is the mass of the particle, v is the velocity and p is the momentum. The above equation is known as **de Broglie's equation**.

Like electromagnetic radiations, an electron beam also undergoes diffraction. This is an evidence for the wave nature of electrons. An electron microscope works on the principle of wave nature of electron.

According to de Broglie, every moving object has a wave character. The wavelengths associated with ordinary objects are so short (because of their large masses) that their wave properties cannot be detected. The wavelengths associated with electrons and other subatomic particles (with very small mass) can be detected experimentally.

Heisenberg's Uncertainty Principle

Werner Heisenberg proposed the uncertainty principle which is the consequence of dual behaviour of matter and radiation. It states that "*it is impossible to determine simultaneously, the exact position and exact momentum (or velocity) of a moving microscopic particle like electron*".

Mathematically, it can be given as in equation:

$$\Delta x \cdot \Delta p \geq \frac{h}{4\pi}$$

Or, $\Delta x \cdot m \Delta v \geq \frac{h}{4\pi}$

Or, $\Delta x \cdot \Delta v \geq \frac{h}{4\pi m}$



Where Δx is the uncertainty in position and Δp (or, Δv) is the uncertainty in momentum (or velocity) of the particle.

If the position of the electron is known with high degree of accuracy (Δx is small), then the velocity of the electron will be uncertain [Δv is large] and vice versa.

Significance of Uncertainty Principle

Heisenberg Uncertainty Principle is significant only for motion of microscopic objects and is not applicable to macroscopic objects. According to this Principle, we cannot determine the exact position and momentum of an electron. Thus it rules out the existence of definite paths or orbits of electrons. We can only say the probability of finding an electron at a given point.

Reasons for the Failure of the Bohr Model

In Bohr model, electrons are moving in well-defined circular orbits about the nucleus. The wave character of the electron is not considered in Bohr model. Further, an orbit is a clearly defined path and this path can completely be defined only if both the position and the velocity of the electron are known exactly at the same time. This is not possible according to the Heisenberg uncertainty principle. Therefore, Bohr model of the hydrogen atom not only ignores dual behaviour of matter but also contradicts Heisenberg uncertainty principle.

QUANTUM MECHANICAL MODEL OF ATOM

On the basis of dual nature of matter and the uncertainty principle, Erwin Schrodinger and Werner Heisenberg proposed a new model of atom called Quantum mechanics. The fundamental equation of quantum mechanics was developed by Schrödinger and is known as Schrödinger equation. It is written as:

$$\hat{H} \psi = E \psi$$

where \hat{H} is a mathematical operator called *Hamiltonian operator*, E is the total energy of the system (K.E + P.E) and ψ is called the wave function. On solving the above equation, we get different values for E and ψ .

When Schrödinger equation is solved for hydrogen atom, the solution gives the possible energy levels the electron can occupy and the corresponding wave function (ψ). These quantized energy states and corresponding wave functions are characterized by a set of three quantum numbers.

Significance of ψ

The wave function (ψ) is a mathematical function and it has no physical meaning. Wave functions of hydrogen or hydrogen like species with one electron are called atomic orbitals. All the information about the electron in an atom is stored in its orbital wave function ψ . It may be positive or negative.

But ψ^2 has some physical significance. It gives the probability of finding an electron at a point within an atom. So ψ^2 is known as **probability density** and is always positive. From the value of ψ^2 , it is possible to predict the probability of finding the electron around the nucleus.

Quantum Numbers

These are certain numbers used to explain the size, shape and orientation of orbitals. Or, Quantum numbers are the address of an electron. There are four quantum numbers which describe the electron in an atom. They are Principal Quantum number (n), Azimuthal Quantum number (l), Magnetic Quantum number (m or m_l) and Spin Quantum number (s).

1. Principal Quantum Number (n)

The following information are obtained from n.

1. It gives the size of the orbit.
2. It gives the energy of electron in an orbit.
3. It gives the shell in which the electron is found.
4. It also gives the average distance between the electron and the nucleus. As the value of n increases, the distance between the electron and the nucleus also increases.

The possible values of n are 1, 2, 3, 4, 5 etc.

If $n = 1$ the electron is in K shell

$n = 2$ the electron is in L shell

$n = 3$ the electron is in M shell and so on.

2. Azimuthal Quantum Number [Subsidiary or orbital angular momentum Quantum number] (l)

The following information are obtained from l .

1. It gives the shape of the orbital.
2. It gives the sub shell or sub level in which the electron is located.
3. It also gives the orbital angular momentum of the electron.

For a given value of n, l can have n values ranging from 0 to $n - 1$. That is, for a given value of n, the possible value of l are : $l = 0, 1, 2, \dots, (n-1)$.

For example, when $n = 1$, value of l is only 0. For $n = 2$, the possible value of l can be 0 and 1. For $n = 3$, the possible l values are 0,1 and 2.

$l=0$ represents s orbital, $l=1$ represents p orbital, $l=2$ represents d orbital and $l=3$ represents f orbital

The number of sub shells in a principal shell is equal to the value of n. For example,

When $n = 1$, $l=0$. i.e. K shell contains only one sub shell - s sub shell

when $n = 2$, $l=0$ and 1. i.e. L shell contains two sub shells - s and p sub shells

when $n = 3$, $l=0, 1$ and 2. i.e. M shell contains three sub shells – s, p and d sub shells

when $n = 4$, $l=0, 1, 2$ and 3. i.e. N shell contains four sub shells – s, p,d and f sub shells

3. Magnetic Quantum Number (m or m_l)

It gives information about the orientation of orbitals in space. For a given ' l ' value, there are $(2l+1)$ possible values for m and these values are given by : $m = -l$ to 0 to $+l$

Thus for $l = 0$, $m_l = 0$ [$2 \times 0 + 1 = 1$]. i.e. s sub shell contains only one orbital called s orbital.

For $l = 1$, $m_l = -1, 0$ and $+1$ [$2 \times 1 + 1 = 3$]. i.e. p subshell contains three orbitals called p orbitals (p_x, p_y and p_z).

For $l = 2$, $m_l = -2, -1, 0, +1$ and $+2$ [$2 \times 2 + 1 = 5$]. i.e. d subshell contains five orbitals called d orbitals ($d_{xy}, d_{xz}, d_{yz}, d_{x^2-y^2}$ and d_{z^2})

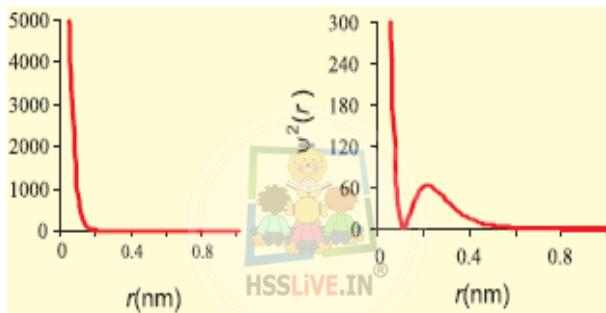
4. Spin Quantum Number (s or m_s)

It is the only experimental quantum number and it gives the spin orientation of electrons. This spin may be either clockwise or anticlockwise. So the values for s may be $+\frac{1}{2}$ or $-\frac{1}{2}$. $+\frac{1}{2}$ represents clock-wise spin and $-\frac{1}{2}$ represents anticlock-wise spin.

Shapes of orbitals

1. s-orbitals

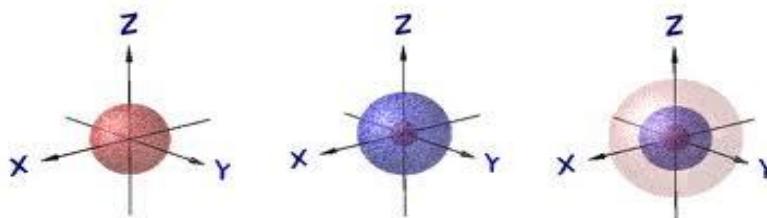
For s-orbitals, $l = 0$ and hence $m_l = 0$. So there is only one possible orientation for s orbitals. They are **spherically symmetrical**. The plots of probability density (ψ^2) against distance from the nucleus (r) for 1s and 2s atomic orbitals are as follows:



For 1s orbital the probability density is maximum at the nucleus and it decreases with increase in r . But for 2s orbital the probability density first decreases sharply to zero and again starts increasing. After reaching a small maximum it decreases again and approaches zero as the value of r increases. The region where the probability density (ψ^2) reduces to zero is called **nodal surface** or **node**.

For 1s orbital, there is no node, for 2s orbital there is only one node, for 3s orbital there are 2 nodes and so on. In general, for an ns-orbital there are $(n - 1)$ nodes.

All the s-orbitals are spherically symmetrical and their size increases with increase in n . The boundary surface diagrams for 1s, 2s and 3s orbitals are as follows:



2. p-orbitals

For p-orbitals, $l = 1$ and $m_l = -1, 0, +1$. i.e., there are three possible orientations for p orbitals. So there are 3 types of p-orbitals – p_x, p_y and p_z . Each p orbital consists of two lobes. The probability density function is zero on the plane where the two lobes touch each other.

The size, shape and energy of the three orbitals are identical. They differ only in the orientation of the lobes. For p_x orbital, the lobes are along the x-axis, for p_y , they are along the y-axis and for p_z , they are along the z-axis. All the p-orbitals have dumb-bell shape.

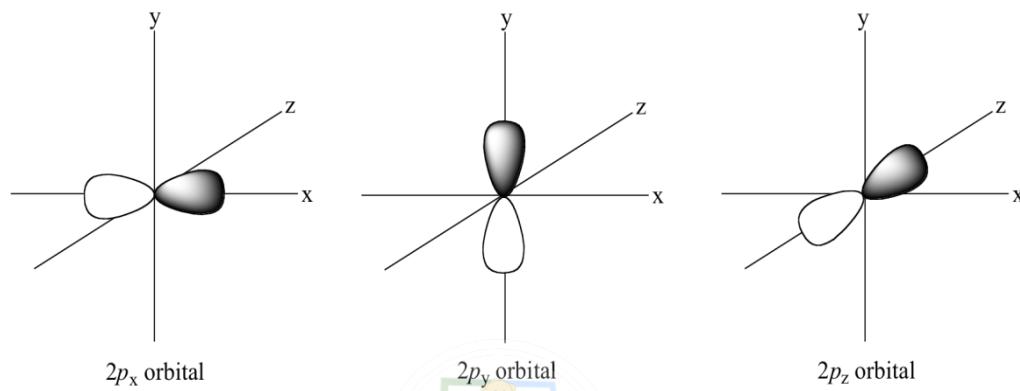
The number of radial nodes for p-orbitals are given by $(n - 2)$, that is number of radial node is 1 for 3p orbital, two for 4p orbital and so on. Besides the radial nodes, the probability density functions for the np orbitals are zero at the plane, passing through the nucleus (origin). For example, in the case of p_z orbital, xy-plane is a nodal plane. These are called angular nodes and number of angular nodes is given by ' l '.

$$\text{Number of radial nodes} = n - l - 1$$

$$\text{Number of angular nodes} = l$$

$$\text{Total number of nodes} = n - 1$$

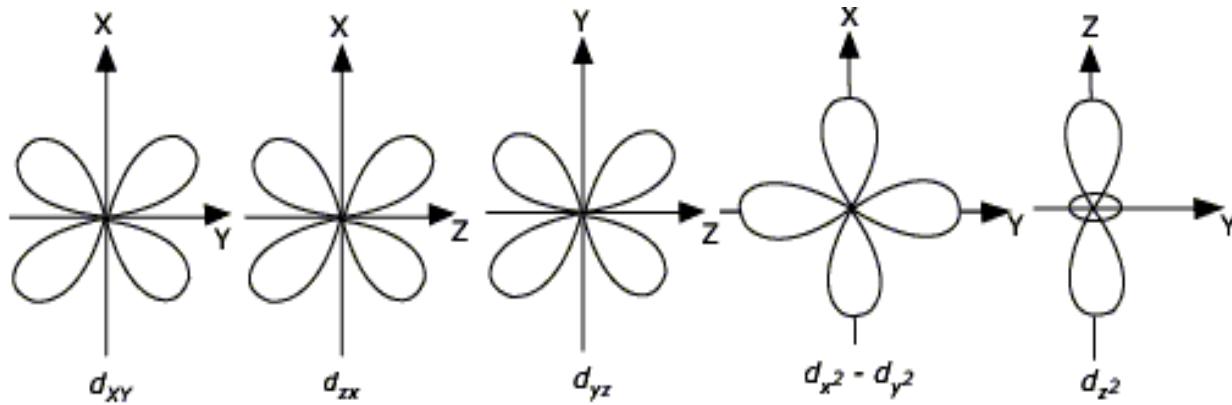
The boundary surface diagrams for three 2p orbitals are as follows:



3. d-orbitals

For d-orbitals, $l = 2$ and $m_l = -2, -1, 0, +1$ and $+2$, i.e., there are five possible orientations for d orbitals. So there are 5 types of d-orbitals. They are d_{xy} , d_{xz} , d_{yz} , $d_{x^2-y^2}$ and d_{z^2} .

The shapes of the first four d-orbitals are double dumb-bell and that of the fifth one, d_{z^2} , is dumb-bell having a circular collar in the xy-plane. The five d-orbitals have equivalent energies. For d-orbitals the number of radial nodes is 2 and the total number of nodes is $n-2$. Boundary surface diagrams for d-orbitals are as follows:



4. f-orbitals

For f-orbitals, $l = 3$ and $m_l = -3, -2, -1, 0, +1, +2$ and $+3$. i.e., there are seven possible orientations for f orbitals. So there are 7 types of f-orbitals.

They are f_{x^3} , f_{y^3} , f_{z^3} , $f_x(y^2-z^2)$, $f_y(z^2-x^2)$, $f_z(x^2-y^2)$ and f_{xyz} . They have diffused shapes.

Rules for Filling of electrons in various orbitals

The filling of electrons into the orbitals of different atoms takes place according to the 3 rules - aufbau principle, Pauli's exclusion principle and the Hund's rule of maximum multiplicity.

1. Aufbau principle:

The German word aufbau means 'build up'. The building up of orbitals means the filling up of orbitals with electrons.

The principle states that *the orbitals are filled in the increasing order of their energies*. In other words, electrons first occupy the lowest energy orbital and then to higher energy orbitals.

This rule has two sub rules:

- The various orbitals are filled in the increasing order of their ($n+l$) value.*
- If two orbitals have the same ($n+l$) values, the orbital with the lower n value is filled first.*

The increasing order of orbitals is as follows:

1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p, 5s, 4d, 5p, 6s, 4f, 5d, 6p, 7s...

2. Pauli's Exclusion Principle

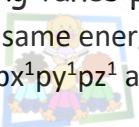
It states that no two electrons in an atom can have the same set of four quantum numbers. i.e. an orbital can accommodate a maximum of only 2 electrons with opposite spin.

If 2 electrons have same values for n, l and m, they should have different values for s. i.e. if s = +½ for the first electron, it should be -½ for the second electron.

3. Hund's rule of maximum multiplicity

It states that electron pairing takes place only after partially filling all the degenerate orbitals. [Orbitals having same energies are called degenerate orbitals]. For example the electronic configuration of N is $1s^2 2s^2 2p_x^1 p_y^1 p_z^1$ and not $1s^2 2s^2 2p_x^2 p_y^1$.

Electronic Configuration of Atoms



The distribution of electrons into various orbitals of an atom is called its *electronic configuration*.

The electronic configuration of different atoms can be represented in two ways.

(i) $s^a p^b d^c \dots$ notation

(ii) Orbital diagram

The electrons in the completely filled shells are known as *core electrons* and the electrons in the outer most shell are called *valence electrons*.

Stability of Completely Filled and Half Filled Subshells

Atoms having *half filled or completely filled electronic configurations have extra stability* compared to other atoms. This is *due to their symmetrical distribution of electrons and greater exchange energy*.

For example, the electronic configuration of Cr is [Ar] $3d^5 4s^1$ and not $3d^4 4s^2$. This is because d^5 represents a half filled configuration and has extra stability. Similarly for Cu, the electronic configuration is [Ar] $3d^{10} 4s^1$ and not $3d^9 4s^2$. This is due to the greater stability of completely filled d^{10} configuration.

3. CLASSIFICATION OF ELEMENTS AND PERIODICITY IN PROPERTIES

Earlier classifications

1) Dobereiner's classification:

Johann Dobereiner classified elements into small groups each containing three elements. These small groups were called *triads*.

E.g. for triads are:

i)	^7Li	^{23}Na	^{39}K
ii)	^{40}Ca	^{88}Sr	^{137}Ba

In triads, the atomic mass of the middle element is approximately the average of the other two elements. This is known as **Law of Triads**. This classification was rejected, since the law of triad is applicable only to a very few elements.

2) Newlands classification:

Newland arranged elements in the increasing order of their atomic masses. He noted that the properties of every eighth element, starting from a given element, are similar to that of the first element. The relationship is just like the resemblance of first and eighth musical notes. He named this as **law of octaves**.

But his classification was rejected since the law of octaves was applicable to elements upto calcium.

A.E.B. de Chancourtois arranged elements in increasing order of atomic weights and made a *cylindrical table of elements* to display the regular repetition of properties.

3) Lothar Meyer's classification: Lothar Meyer plotted the physical properties of elements like *atomic volume, melting point and boiling point* against *atomic weight* and obtained a periodically repeated pattern. Based on this, he developed a periodic table similar to that of Mendeleev's.

4) Mendeleev's classification:

Dmitri Mendeleev (a Russian chemist) classified the elements in the increasing order of their atomic weights. He found that the properties of elements repeat after a regular interval. Based on this observation, he proposed a **periodic law** which states that "The properties of elements are the periodic functions of their atomic weights." That is, when elements are arranged in the increasing order of their atomic weights, their properties repeat after a regular interval.

Mendeleev's periodic table contains horizontal rows called series (periods) and vertical columns called groups. Elements with similar properties are placed in the same group. He mainly depends on the similarities in the empirical formulae and the properties of the compounds formed by the elements. So he did not strictly obey the increasing order of atomic weights. Also he corrected the wrong atomic masses of some elements.

When Mendeleev proposed his periodic table, some of the elements were not discovered. He left some vacant places (gaps) for them in the periodic table and predicted some of their properties. For e.g. both **Gallium and Germanium** were not discovered at that time. He named these elements as **Eka-Aluminium and Eka-Silicon** respectively and predicted their properties. These elements were discovered later and found that Mendeleev's predictions were correct.

Merits of Mendeleev's periodic table

- 1) It was the first comprehensive classification of elements.
- 2) He corrected the wrong atomic weights of some elements and placed them in correct position in the periodic table.
- 3) He left vacant places for undiscovered elements and predicted some of their properties.
- 4) Elements with similar properties are placed in the same group.

Demerits of Mendeleev's periodic table

- 1) Elements with dissimilar properties are found in same group.
- 2) He could not give an exact position for hydrogen.
- 3) He could not give exact position for Lanthanoids and Actinoids and also for isotopes.
- 4) Mendeleev's periodic table did not strictly obey the increasing order of atomic weights.

Modern Periodic table

Henry Moseley's work on the X-ray spectra of elements proved that atomic number is a more fundamental property than atomic mass. Based on this observation, he modified the Mendeleev's periodic law as "*the physical and chemical properties of elements are the periodic functions of their atomic numbers*". This is known as **Modern Periodic law**.

Based on the modern periodic law, numerous forms of periodic tables have been proposed. The most commonly used is **the long form of periodic table**.

In this periodic table, the elements are arranged in the increasing order of their atomic number. It contains **7** horizontal rows called **periods** and **18** vertical columns called **groups or families**.

In the long form of modern periodic table, hydrogen has given a particular position at the top centre.

PERIODS

There are 7 periods in Modern periodic table. The period number corresponds to the highest principal quantum number of the elements.

Period No.	Elements	No. of Elements	Subshells filled	Description
I	${}_1\text{H}$ & ${}_2\text{He}$	2	1s	Very short period
II	${}_3\text{Li}$ to ${}_{10}\text{Ne}$	8	2s & 2p	
III	${}_{11}\text{Na}$ to ${}_{18}\text{Ar}$	8	3s & 3p	
IV	${}_{19}\text{K}$ to ${}_{36}\text{Kr}$	18	4s, 3d & 4p	Long periods
V	${}_{37}\text{Rb}$ to ${}_{54}\text{Xe}$	18	5s, 4d & 5p	
VI	${}_{55}\text{Cs}$ to ${}_{86}\text{Rn}$	32	6s, 4f, 5d & 6p	Longest periods
VII	${}_{87}\text{Fr}$ to ${}_{118}\text{Og}$	32	7s, 5f, 6d & 7p	

The 14 elements each of sixth and seventh periods are placed in separate rows below the main body of the periodic table. These are together called **inner transition elements**. The 14 elements of sixth period [from ${}_{57}\text{Ce}$ (cerium) to ${}_{71}\text{Lu}$ (lutetium)] are called *Lanthanides or Lanthanones or Lanthanoids or rare earths*. The 14 elements of seventh period [from ${}_{90}\text{Th}$ (thorium) to ${}_{103}\text{Lr}$ (lawrencium)] are called *Actinides or Actinones or Actinoids*.

GROUPS

Vertical columns in Long form of Modern periodic table are called groups or families. There are 18 groups and these are numbered from 1 to 18. Due to the similar outer electronic configuration and same valency, the elements present in the same group have similar properties.

Group No.	Elements	General outer Electronic configuration	Family name
1	Li, Na, K, Rb, Cs & Fr	ns^1	Alkali metals
2	Be, Mg, Ca, Sr, Ba & Ra	ns^2	Alkaline earth metals
3 to 12	4 rows of elements	$(\text{n}-1)\text{d}^{1 \text{ to } 10} \text{ns}^{0 \text{ to } 2}$	Transition elements
13	B, Al, Ga, In, Tl & Nh	$\text{ns}^2 \text{np}^1$	Boron Family
14	C, Si, Ge, Sn, Pb & Fl	$\text{ns}^2 \text{np}^2$	Carbon Family
15	N, P, As, Sb, Bi & Mc	$\text{ns}^2 \text{np}^3$	Nitrogen Family
16	O, S, Se, Te, Po & Lv	$\text{ns}^2 \text{np}^4$	Oxygen Family
17	F, Cl, Br, I, At, Ts	$\text{ns}^2 \text{np}^5$	Halogen Family
18	He, Ne, Ar, Kr, Xe, Rn, Og	$\text{ns}^2 \text{np}^6$	Noble gases

The Blocks in the Modern periodic table

The Modern periodic table is divided into 4 blocks based on the subshell in which the last electron enters. They are s block, p block, d block and f block.

1. The s-block elements

These are elements in which the last electron enters in the outer most s sub shell. They include elements of the groups 1 and 2. Their general outer electronic configuration is ns^1 or ns^2 . They are all reactive metals with low ionization enthalpies. They lose their outer most electrons readily to form +1 and +2 ions. Their metallic character and reactivity increases down the group. They mainly form ionic compounds (except Li and Be).

2. The p-block elements

These are elements in which the last electron enters in the outer most p sub shell. They include elements of the groups 13 to 18. Their general outer electronic configuration is $ns^2 np^{1 \text{ to } 6}$. Their non-metallic character increases from left to right in a period and metallic character increases from top to bottom in a group.

The 18th group elements are called Noble gases or inert gases. They have completely filled orbitals and so they do not undergo chemical reactions at ordinary conditions.

s and p block elements are together called **Representative elements**, because these are the only elements which show the general trends in the periodic table and also they contain metals, non-metals and metalloids.

3. The d-block elements

These are elements in which the last electron enters in the penultimate d sub shell. They include elements of the groups 3 to 12. They are also called **Transition elements (Transition metals)**, since they show a regular transition (change) from the most electropositive s block elements to the least electropositive p block elements. Their general outer electronic configuration is $(n-1)d^{1 \text{ to } 10} ns^{0 \text{ to } 2}$.

Some properties of transition elements are:

- a) They are all metals.
- b) They form coloured compounds or ions in aqueous solution.
- c) They show variable oxidation states and valencies.
- d) They are generally paramagnetic.
- e) They show catalytic properties.

4. The f-block elements

These are elements in which the last electron enters in the anti-penultimate f sub shell. They include **lanthanides** of 6th period and **actinides** of 7th period. They are also called **Inner transition elements**. Their general outer electronic configuration is $(n-2)f^{1 \text{ to } 14}(n-1)d^{0 \text{ to } 1} ns^2$. They are all metals. Within each series the properties of these elements are similar. Actinoid elements are radioactive. Elements after Uranium ($Z=92$) in the actinide series are called **trans-uranium elements** or **trans-uranic elements** or **artificial elements**. [Neptunium ($_{93}\text{Np}$) and Plutonium ($_{94}\text{Pu}$) are also found naturally in Pitch blende, an ore of Uranium].

Electronic configuration of an element and its position in the periodic table

From the electronic configuration of an element, we can assign its period, group and block in the periodic table.

Block: The subshell in which the last electron enters.

Period number = the highest principal quantum number in its electronic configuration.

Group number: For s-block elements = no. of valence s electrons

For p-block elements = no. of valence s electrons + valence p electrons + 10

For d-block elements = no. of valence s electrons + no. of penultimate d electrons.

Nomenclature of elements with atomic numbers > 100

For naming elements with atomic number > 100, IUPAC has made some recommendations. A systematic nomenclature be derived directly from the atomic number of the element using the numerical roots for 0 and numbers 1-9.

Digit	0	1	2	3	4	5	6	7	8	9
Root name	nil	un	bi	tri	quad	pent	hex	sept	oct	enn
Abbreviation	n	u	b	t	q	p	h	s	o	e

The roots are put together in order of digits which make up the atomic number and "ium" is added at the end.

Atomic Number	Name according to IUPAC nomenclature	Symbol	IUPAC Official Name and Symbol
101	Unnilunium	Unu	Mendelevium (Md)
102	Unnilbium	Unb	Nobelium (No)
103	Unniltrium	Unt	Lawrencium (Lr)
104	Unnilquadium	Unq	Rutherfordium (Rf)
105	Unnilpentium	Unp	Dubnium (Db)
106	Unnilhexium	Unh	Seaborgium (Sg)
107	Unnilseptium	Uns	Bohrium (Bh)
108	Unniloctium	Uno	Hassium (Hs)
109	Unnilennium	Une	Meitnerium (Mt)
110	Ununnilium	Uun	Darmstadtium (Ds)
111	Unununium	Uuu	Rontgenium (Rg)
112	Ununbium	Uub	Copernicium (Cp)
113	Ununtrium	Uut	Nihonium (Nh)
114	Ununquadium	Uuq	Flerovium (Fl)
115	Ununpentium	Uup	Moscovium (Mc)
116	Ununhexium	Uuh	Livermorium (Lv)
117	Ununseptium	Uus	Tennessee (Ts)
118	Ununoctium	Uuo	Oganesson (Og)
119	Ununennium	Uue	
120	Unbinilium	Ubn	

Periodic properties of Elements

The properties which repeat after a regular interval are called periodic properties. Some of the important periodic properties of elements are atomic and ionic radii, ionization enthalpy, electron gain enthalpy, electropositivity, electronegativity etc.

1. Atomic Radius

It is defined as the distance from the centre of the nucleus to the outermost shell having electrons. Atomic radius of individual atoms cannot be determined. So it is expressed in any of the following methods:

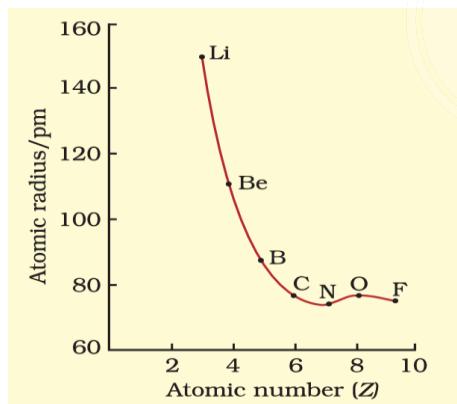
- Covalent radius*: It is half of the inter nuclear distance between two covalently bonded (single bonded) atoms. It is used to express the atomic radius of non-metal atoms. For e.g. the bond distance of Cl_2 molecule is 198 pm. So the covalent radius is 99 pm.
- Metallic radius*: It is the half of the inter nuclear distance between two metallic ions in a metal crystal.
- van der Waal's radius*: It is defined as the half of the inter nuclear distance between two non-bonded atoms of separate molecules in the solid state.

Atomic radius is commonly expressed in picometre (pm) or angstrom (\AA^0) unit. [1 pm = 10^{-12} m and 1 $\text{\AA}^0 = 10^{-10}$ m]. It is measured by x-ray diffraction method or by spectroscopic method.

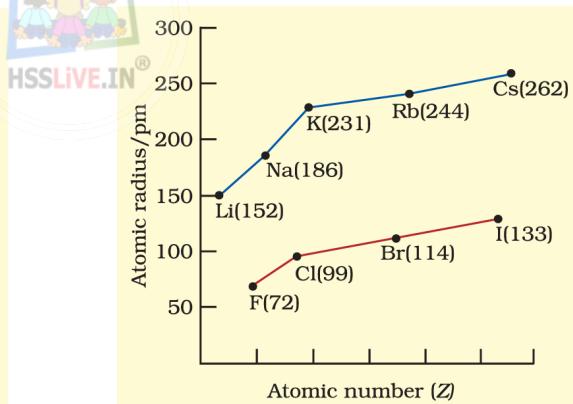
Variation of atomic radius along a group and a period

The atomic size decreases from left to right in a period. This is because in a period, the electrons are added to the same valence shell. Thus the number of shells remains the same, but the effective nuclear charge increases. So the atomic radius decreases. In a given period, alkali metals (group 1) have the maximum size and halogens (group 17) have the minimum size.

In a group, the atomic radius increases from top to bottom. This is because of the increase in no. of shells and shielding effect. (In atoms with higher atomic number, the inner electrons partially shield the attractive force of the nucleus. So the outer electrons do not experience the full attraction of the nucleus and this is known as shielding effect or screening effect).



Variation of atomic radii along 2nd period



Variation of atomic radii along 1st and 17th groups.

Atomic radius of noble gases is larger than that of halogens. This is because noble gases are monoatomic. So van der Waal's radius is used to express their atomic radius which is greater than covalent radius or metallic radius.

2. Ionic radius

It is defined as the half of the inter nuclear distance between cations and anions of an ionic crystal. The variation of ionic radius is same as that of atomic radius.

Generally a cation is smaller than its parent atom (e.g. Na^+ is smaller than Na atom). This is because a cation has fewer electrons, but its nuclear charge remains the same as that of the parent atom.

An anion is larger than its parent atom (e.g. Cl^- is larger than Cl atom). This is because the addition of one or more electrons would result in an increased electronic repulsion and a decrease in effective nuclear charge.

Isoelectronic species:

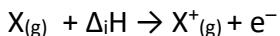
Species (atoms and ions) having the same number of electrons are called isoelectronic species. E.g. N^{3-} , O^{2-} , F^- , Ne , Na^+ , Mg^{2+} , Al^{3+} etc. (All these contain 10 electrons).

Among isoelectronic species, the cation with greater positive charge will have the smaller radius. This is because of the greater attraction of electrons to the nucleus. The anion with greater negative charge will have the larger radius. Here the repulsion between electrons is greater than the attraction of the nucleus. So the ion will expand in size.

Thus among the isoelectronic species N^{3-} , O^{2-} , F^- , Ne , Na^+ , Mg^{2+} and Al^{3+} , the largest ion is N^{3-} and the smallest ion is Al^{3+} .

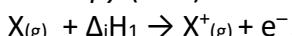
3. Ionisation enthalpy (Δ_iH)

It is defined as the energy required to remove an electron from the outer most shell of an isolated gaseous atom in its ground state. Or, it is the energy required to convert a gaseous neutral atom to a gaseous unipositive ion. It may be represented as:

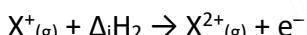


Its unit is kJ/mol or J/mol.

The energy required to remove the first electron from the outer most shell of a neutral atom is called *first ionisation enthalpy (Δ_iH_1)*.



Second ionisation enthalpy (Δ_iH_2) is the amount of energy required to remove an electron from a unipositive ion.



Energy is always required to remove an electron from an atom or ion. So Δ_iH is always positive.

The second ionisation enthalpy is always higher than first ionization enthalpy. This is because it is more difficult to remove an electron from a positively charged ion than from a neutral atom.

Similarly third ionisation enthalpy is higher than second ionisation enthalpy and so on.

i.e. $\Delta_iH_1 < \Delta_iH_2 < \Delta_iH_3 \dots \dots \dots$

As the ease of removal of electron increases, the ionisation enthalpy decreases.

Factors affecting ionisation enthalpy

The important factors which affect ionisation enthalpy are:

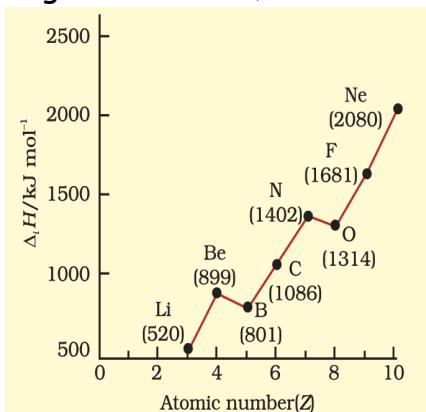
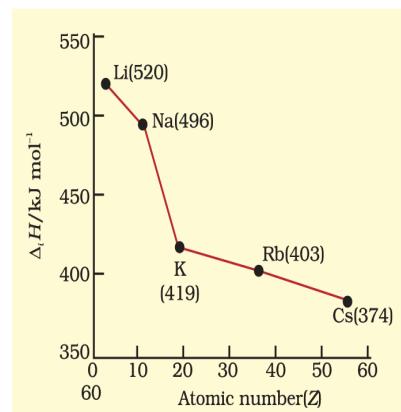
- Atomic size:* Greater the atomic size (atomic radius), smaller will be the ionisation enthalpy.
- Nuclear charge:* The value of ionisation enthalpy increases with nuclear charge.
- Shielding effect:* As the shielding effect increases, the electrons can easily be removed and so the ionisation enthalpy decreases.
- Presence of half-filled or completely filled orbitals* increases ionisation enthalpy.

[As the ease of removal of electron increases, ionisation enthalpy decreases].

Variation of Δ_iH along a period and a group

Along a period, ionisation enthalpy increases from left to right. This is because of the decrease in atomic radius and increase in nuclear charge. Thus alkali metals have the least Δ_iH and noble gases have the most.

Down a group, Δ_iH decreases due to increase in atomic radius and shielding effect. Thus among alkali metals, lithium has the highest Δ_iH and francium has the lowest.

Variation of ionisation enthalpy along 2nd periodVariation of ionisation enthalpy along 1st group

In the second period of modern periodic table, the first ionisation enthalpy of Boron is slightly less than that of Beryllium. This is because after the removal of one electron from boron, it gets the stable configuration ($1s^2 2s^2$). So B loses one electron faster.

Similarly the first ionisation enthalpy of nitrogen is greater than that of oxygen. This is because N has half filled electronic configuration ($1s^2 2s^2 2p^3$), which is more stable and so more energy is required to remove an electron.

4. Electron gain enthalpy ($\Delta_{eg}H$)

It is the heat change (enthalpy change) when an electron is added to the outer most shell of an isolated gaseous atom. It can be represented as $X_{(g)} + e^- \rightarrow X^{-}_{(g)}$

Its unit is kJ/mol. It may be positive or negative depending on the nature of the element. For most of the elements, energy is released when electron is added to their atoms. So $\Delta_{eg}H$ is negative.

Noble gases have large positive electron gain enthalpy because of their stable completely filled electronic configuration.

Electron gain enthalpy also depends on atomic size, nuclear charge, shielding effect etc. As the atomic size increases, $\Delta_{eg}H$ becomes less negative. When nuclear charge increases, electron gain enthalpy becomes more negative. As shielding effect increases, $\Delta_{eg}H$ becomes less negative. Presence of half-filled or completely filled orbitals make $\Delta_{eg}H$ less negative.

[As the ease of addition of electron increases, electron gain enthalpy becomes more negative].

Periodic variation of $\Delta_{eg}H$

From left to right across a period, $\Delta_{eg}H$ become more negative. This is because of decrease in atomic radius and increase in nuclear charge. So the ease of addition of electron increases.

Down a group, $\Delta_{eg}H$ becomes less negative. This is due to increase in atomic radius and shielding effect.

Electron gain enthalpy of fluorine is less negative than chlorine. This is because, when an electron is added to F, it enters into the smaller 2nd shell. Due to the smaller size, the electron suffers more repulsion from the other electrons. But for Cl, the incoming electron goes to the larger 3rd shell. So the electronic repulsion is low and hence Cl adds electron more easily than F. [OR, Due to the compactness of the 2p subshell of F, electronic repulsion is greater in F and hence it does not easily add electron]. Due to the same reason $\Delta_{eg}H$ of oxygen is less negative than sulphur.

Thus in modern periodic table, alkali metals have the least negative $\Delta_{eg}H$ and halogens have the most negative $\Delta_{eg}H$. Among halogens, $\Delta_{eg}H$ becomes less negative in the order: Cl > F > Br > I [The negative electron gain enthalpy is also called electron affinity].

5. Electronegativity

Electronegativity of an atom in a compound is the ability of the atom to attract shared pair of electron of electrons. It is not a measurable quantity and so it has no unit. There are different scales for measuring the Electronegativity of elements. The most commonly used one is the **Pauling Electronegativity scale** developed by Linus Pauling. The other electronegativity scales are Mulliken-Jaffe scale, Allred-Rochow scale etc.

Electronegativity depends on atomic size and nuclear charge. As the atomic radius increases, electronegativity decreases. Greater the nuclear charge, greater will be the electronegativity.

Generally electronegativity increases across a period and decreases along a group. So in modern periodic table, Fluorine is the most electronegative element and Francium is the least electronegative element. Since francium is radioactive, caesium is the least electronegative stable element. *In Pauling Scale, electronegativity of Fluorine is 4.0 and that of Oxygen is 3.5.*

The electronegativity of an element is *not constant*. It varies depending on the element to which it is bound. It is directly related to the non-metallic character of elements. *An increase in electronegativity across a period indicates an increase in non-metallic character and decrease in metallic character.*

6. Electropositivity

It is the tendency of an atom to lose the most loosely bound electron (valence electron). It is directly related to the metallic character of elements. It depends on atomic size and nuclear charge. As the atomic radius increases, electropositivity increases.

Along a period, electropositivity decreases from left to right. But down a group, it increases. So francium is the most electropositive element and fluorine is the least electropositive element.

7. Valency

It is the combining capacity of an element. Or, it is the number of electrons lost or gained by an atom during a chemical reaction.

Along a period, valency first increases upto the middle and then decreases (for s and p block elements only). In a group, valency remains constant. Transition elements can show variable valency.

Valency is numerically equal to oxidation number of the element. The difference is that oxidation number has a positive or negative sign but the valency doesn't.

Anomalous Properties of Second Period Elements

The first element in groups 1 (lithium) and 2 (beryllium) and groups 13 to 17 (boron to fluorine) differs from the other members of their respective group in their properties. This is known as anomalous properties. *This is due to their small size, large charge to radius ratio, high electronegativity and absence of vacant d-orbitals.*

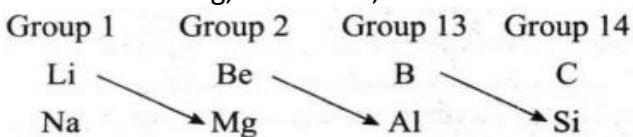
Some of the anomalous properties are:

- They can form multiple bonds with themselves (e.g. C = C, N ≡ N etc.) and with other elements of the second period (e.g. C = O, C ≡ N etc.).
- Their maximum co-valency is 4, due to the absence of vacant d-orbitals. But other elements of the respective groups can expand their covalency beyond 4 (due to the presence of vacant d-orbitals). For this reason, Aluminium forms $[AlF_6]^{3-}$ whereas boron cannot form $[BF_6]^{3-}$ but forms only $[BF_4]^-$. Similarly, Phosphorus forms PCl_5 while nitrogen cannot form NCl_5 .

Diagonal relationship

The similarities in properties shown by the diagonally placed elements of the 2nd and 3rd periods in the Modern periodic table are called Diagonal relationship. This is due to their similar atomic radii, ionisation enthalpy, electronegativity etc.

E.g. Lithium shows similarities with Mg, Be with Al, B with Si etc.

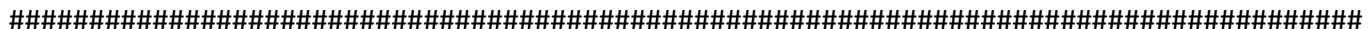


Periodic Trends and Chemical Reactivity

The periodicity in properties of elements is related to electronic configuration. That is, elements having similar outer electronic configuration show similarities in chemical and physical properties.

The atomic and ionic radii, generally decrease in a period from left to right. As a consequence, the ionization enthalpies generally increase and electron gain enthalpies become more negative across a period. This results into high chemical reactivity at the two extremes and the lowest in the centre. Thus, the maximum chemical reactivity at the extreme left (among alkali metals) is exhibited by the loss of an electron leading to the formation of a cation and at the extreme right (among halogens) shown by the gain of an electron forming an anion. This property can be related with the reducing and oxidizing behaviour of the elements. i.e. Elements at the extreme left (alkali metals) of the periodic table are good reducing agents and those at the extreme right (halogens) are good oxidising agents.

The chemical reactivity of an element can be explained by its reactions with oxygen. Elements on two extremes of a period (1st and 17th groups) easily combine with oxygen to form oxides. The normal oxide formed by the element on extreme left (1st group) is the most basic (e.g. Na₂O), whereas that formed by the element on extreme right (17th group) is the most acidic (e.g. Cl₂O₇). Oxides of elements in the centre are amphoteric (e.g. Al₂O₃, As₂O₃) or neutral (e.g. CO, NO, N₂O). Amphoteric oxides behave both as acidic (with bases) and basic (with acids), while neutral oxides have no acidic or basic properties.



4. CHEMICAL BONDING AND MOLECULAR STRUCTURE

The attractive force that binds the atoms together in a molecule is called a chemical bond. It is formed either by the transfer of electrons or by the sharing of electrons.

Lewis symbols

In the formation of a chemical bond, only the outermost electrons participate and these electrons are called valence electrons. The inner electrons are well protected and they are called core electrons.

G.N Lewis introduced simple notations to represent valence electrons in an atom. These notations are called Lewis symbols or Lewis notations. Here the nucleus and the inner electrons are represented by the symbol of the element and the valence electrons by dots or crosses.

E.g. for sodium [₁₁Na -2,8,1], the Lewis symbol is $\cdot\text{Na}$ and for chlorine [₁₇Cl -2,8,7] is $\ddot{\cdot}\text{Cl}\cdot$

Lewis symbols are informative. It gives the valency of an atom, which is either equal to the number of dots or crosses or equal to 8 – no. of dots or crosses.

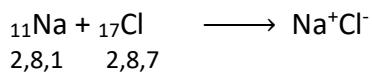
Octet rule

This rule was proposed by Lewis and Kossel. According to this rule, atoms undergo chemical reaction in order to attain an octet of electrons in the valence shell. Or, atoms containing 8 electrons in their valence shell are stable.

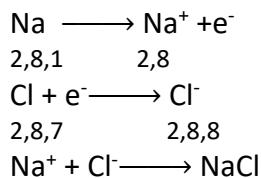
Ionic or Electrovalent Bond

A bond formed by the transfer of electron between 2 atoms is called ionic or electrovalent bond. Or, it is the force of attraction between two oppositely charged ions.

E.g. formation of NaCl



In Na atom, there is only one electron in the valence shell and in Cl, there are 7 electrons in the valence shell. In order to attain octet state, Na atom loses one electron and form Na^+ ion and Cl atom gains one electron and form Cl^- ion. These two ions attract each other by electrostatic force called ionic bond.



Energy changes during the formation of an ionic bond

An ionic bond formation involves the following steps:

- 1) The formation of a positive ion (cation) from the electropositive atom. The amount of energy required for this process is called ionisation enthalpy ($\Delta_i\text{H}$).

$$\text{M(g)} + \Delta_i\text{H} \longrightarrow \text{M}^+(\text{g}) + \text{e}^-$$
- 2) Formation of negative ion from the electronegative atom. The energy involved in this process is called electron gain enthalpy ($\Delta_{eg}\text{H}$).

$$\text{X(g)} + \text{e}^- \longrightarrow \text{X}^-(\text{g}) + \Delta_{eg}\text{H}$$
- 3) The packing of the cation and anion to form an ionic compound. The energy change in this process is called lattice enthalpy ($\Delta_{lattice}\text{H}$)

$$\text{M}^+ + \text{X}^- \longrightarrow \text{MX(s)} + \Delta_{lattice}\text{H}$$

So the factors favouring the ionic bond formation are:

- i) Low ionisation enthalpy of the electropositive atom (metal atom)

- ii) High negative electron gain enthalpy of the electronegative atom (non-metal atom)
- iii) High lattice enthalpy of the ionic compound formed.

Lattice Enthalpy

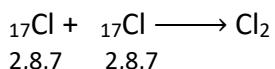
It is the energy required to completely separate one mole of an ionic compound into corresponding gaseous ions. Or, it is the energy released when one mole of an ionic compound is formed from gaseous ions.

The stability of an ionic compound is determined by its Lattice Enthalpy. Generally greater the Lattice Enthalpy, stabler will be the compound.

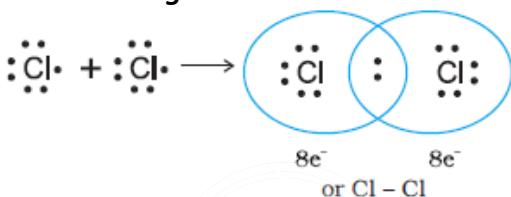
Covalent bond

A bond formed by the mutual sharing of electrons between two or more atoms is called covalent bond.

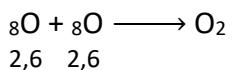
e.g. 1) The formation of Chlorine molecule (Cl_2)



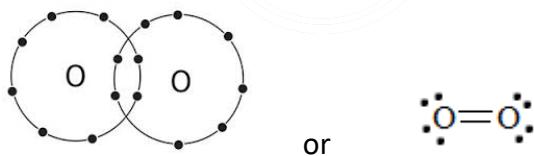
Both the chlorine atoms have 7 electrons in their outermost shell. So here the exchange of electrons is not possible. For the formation of Cl_2 molecule, each Cl atom shares one pair of electron. The bond thus formed is called a **single covalent bond**.



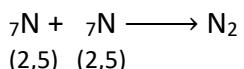
2) The formation of O_2 molecule



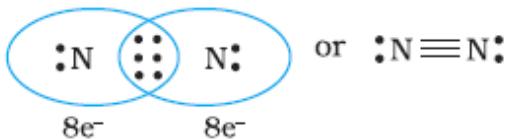
To attain octet, each oxygen atom shares 2 pairs of electrons. Thus a **double covalent bond** is formed.



3) The formation of N_2 molecule



To attain the octet configuration, the nitrogen atoms share 3 pairs of electrons. Thus a **triple bond** is formed.



In the formation of a covalent bond, each combining atoms contribute at least one electron to the shared pair. **The number of electrons contributed by an atom to the shared pair (bonded pair) during the formation of a covalent bond is called covalency.** In the formation of Cl_2 molecule, the covalency of each Cl atoms is one, in O_2 molecule, the covalency of O atom is 2 and in N_2 , it is 3.

A covalent bond formed by the sharing of one pair of electron is called a single bond. A double bond is formed when 2 pairs of electrons are shared between 2 atoms and a triple bond is formed when 3 pairs of electrons are shared between two atoms. The double and triple bonds are together called **multiple bonds**.

Limitations of Octet rule

- 1) It could not explain the stability of compounds with incomplete octet (containing less than 8 electrons around the central atom). E.g. LiCl, BeH₂, BCl₃ etc.
- 2) It could not explain the stability of molecules containing odd number of electrons like NO, NO₂ etc.
- 3) It could not explain the stability of molecules containing more than 8 electrons around the central atom (i.e. expanded octet). E.g. PF₅, SF₆, H₂SO₄, IF₇ etc.
- 4) octet rule is based upon the chemical inertness of noble gases. But some noble gases like xenon and krypton form compounds with F and O.
- 5) This theory does not account for the shape of molecules.
- 6) It does not explain the relative stability of the molecules.

Bond Parameters

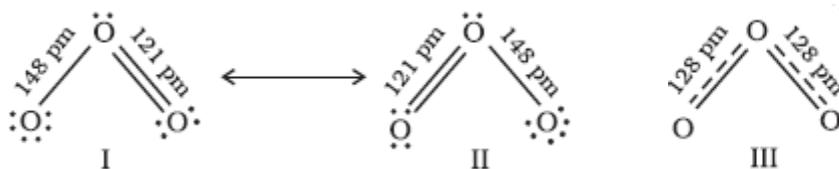
- 1) **Bond Length:** It is defined as the average equilibrium distance between the nuclei of two bonded atoms in a molecule. It is measured by spectroscopic, X-ray diffraction and electron diffraction techniques. It is expressed in pico-metre (pm) or in angstrom unit (Å).
- 2) **Bond Angle:** It is defined as the angle between the orbitals containing bonding electron pairs around the central atom in a molecule. It can be experimentally determined by spectroscopic methods. It is expressed in degree.
- 3) **Bond Enthalpy:** It is defined as the amount of energy required to break one mole of a particular bond between 2 atoms in gaseous state. Its unit is kJ/mol.
For diatomic molecules, bond enthalpy is equal to bond dissociation enthalpy. Larger the bond dissociation enthalpy, stronger will be the bond formed. For poly atomic molecules, the bond enthalpy is the average of the bond dissociation enthalpies.
- 4) **Bond order:** It is defined as the number of bonds between 2 atoms in a molecule. For H₂, bond order = 1, for O₂, bond order = 2 and for N₂, bond order = 3. Isoelectronic molecules and ions have identical bond orders.

Generally with increase in bond order, bond enthalpy increases and bond length decreases.

Resonance Structures

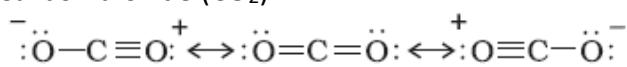
In the case of some compounds, all the observed properties cannot be explained by a single structure. Here we use more than one structures of the compound. These different structures are called **resonance structures** or **canonical structures** or **contributing structures**. The phenomenon is known as **resonance**. Resonating structures are separated by double headed arrows.

e.g. i) Ozone (O₃)

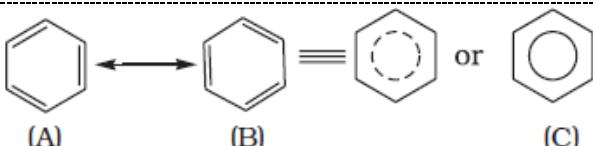


The actual structure of ozone is not I or II. It is a resonance hybrid of the structures I and II which can be represented as structure III.

ii) Carbon dioxide (CO₂)



iii) Benzene (C₆H₆)



Characteristics of resonance

- a) Resonance stabilizes the molecule. As the number of resonating structures increases, the stability also increases.
 - b) Resonance changes the bond length.
 - c) The difference in energy between the actual structure and the most stable canonical structure is called resonance energy. Greater the resonance energy, stabler will be the molecule

Polarity of bonds – Dipole moment

When a covalent bond is formed between 2 similar atoms, the shared pair of electrons is equally attracted by the two atoms. So the electron pair is exactly between the two nuclei. The bond so formed is called a non-polar covalent bond.

But when the covalent bond is formed between 2 dissimilar atoms, the shared electron pairs are more attracted by one of the atoms. So one atom gets a slight negative charge (δ^-) and the other gets a slight positive charge (δ^+). Such molecules are called polar molecules. E.g. HCl, HF, H_2O , HI etc.

The polarity of a molecule is expressed in terms of *dipole moment* (μ). It is defined as the product of the magnitude of charge at one end (Q) and distance between the charges (r).

Mathematically, $\mu = Q \times r$.

The unit of dipole moment is Coulomb metre (Cm). But it is usually expressed in the unit **Debye (D)**.

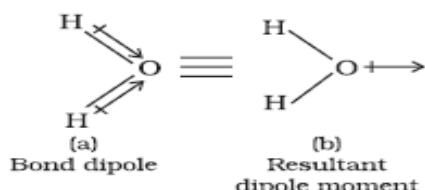
1D = 3.336×10^{-30} Cm.
 dipole moment is a vector quantity with tail on the positive end.
 e.g.: HF 

Dipole moment is a vector quantity. i.e. it has both magnitude and direction. It is denoted by a small arrow with tail on the positive centre and head pointing towards the negative centre.

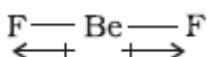
e.g.: HF

In the case of poly atomic molecules, dipole moment depends on the individual bond dipoles and the spatial arrangement of bonds. Here the dipole moment of the molecule is the vector sum of the bond dipoles of various bonds.

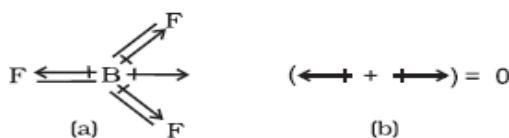
e.g., H_2O



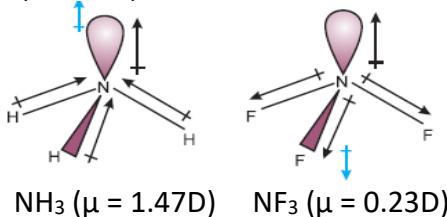
For BeF_2 , the net dipole moment is zero, since the two equal bond dipoles are in opposite directions and cancel each other.



In BF_3 , the net dipole moment is zero. Here the resultant of any 2 bond dipoles is equal and opposite to the third.



Both ammonia (NH_3) and nitrogen fluoride (NF_3) are pyramidal in shape. Even though F is more electro negative than H, the net dipole moment of NF_3 is smaller than that of NH_3 . This is because in the case of NH_3 , the orbital dipole due to lone pair is in the same direction as the resultant dipole moment of the three N - H bonds. But in NF_3 , the orbital dipole is in the opposite direction to the resultant dipole moment of the three N-F bonds. So the dipole moments get partially cancelled.



Covalent character in ionic bonds – Fajans Rules

The partial covalent character of ionic bonds was explained by Fajans in terms of the following rules:

- 1) The smaller the size of the cation and the larger the size of the anion, the greater the covalent character of an ionic bond.
- 2) The greater the charge on the cation, the greater the covalent character of the ionic bond.
- 3) For cations of the same size and charge, the ion with electronic configuration $(n-1)d^m n s^0$ is more polarising than the ion with a noble gas configuration $(n s^2 n p^6)$.

THE SHAPES OF MOLECULES

Covalent bonds are directional in nature. i.e. they are directed to some specified positions in space. So covalent compounds have definite shapes.

The Valence Shell Electron Pair Repulsion [VSEPR] Theory

This theory was proposed by Sidgwick and Powell and later modified by Nyholm and Gillespie. The important postulates of this theory are:

- 1) The shape of the molecule depends on the number of valence shell electron pairs (VSEPRs) around the central atom.
- 2) The valence shell electron pairs repel each other.
- 3) In order to reduce the repulsion, the electron pairs stay at maximum distance.
- 4) The valence shell is taken as a sphere with the electron pairs localising on the spherical surface at maximum distance from one another.
- 5) A multiple bond is treated as if it is a single electron pair and the two or three electron pairs of a multiple bond are treated as a single super pair.
- 6) If a molecule has resonance structures, the VSEPR model is applicable to any such structure.
- 7) Presence of lone pairs of electron causes distortion in the expected geometry of the molecule.
- 8) The repulsion between two lone pairs of electrons is different from those between two bond pairs or between a lone pair and bond pair. The repulsion decreases in the order lone pair - lone pair > lone pair - bond pair > bond pair - bond pair.
- 9) As the angle between the electron pairs increases, the repulsion decreases.

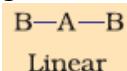
Prediction of geometry of molecules using VSEPR theory

I) Molecules containing only bond pairs of electrons:

1) **AB₂ type** (where A is the central atom and B is the no. of bond pairs)

Here there are 2 VSEPs. In order to reduce the repulsion, these electron pairs are arranged at an angle of 180°. Thus the shape of the molecule is linear with bond angle 180°.

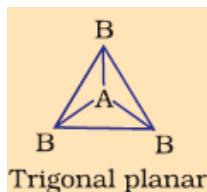
E.g. BeCl₂, HgCl₂ etc.



2) **AB₃ type**

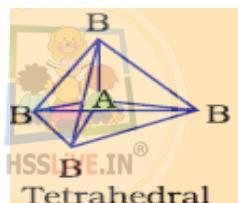
Here there are 3 VSEPs. In order to reduce the repulsion, these electron pairs are arranged at an angle of 120°. Thus the shape of the molecule is planar triangular (trigonal planar) with bond angle 120°.

e.g. BF₃, BCl₃ etc.



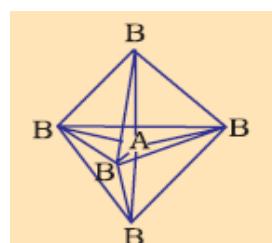
3) **AB₄ type**

Here there are 4 VSEPs. These are arranged at the four corners of a tetrahedron and hence the shape of the molecule is tetrahedral with bond angle 109°28'. e.g.: CH₄, NH₄⁺ etc.



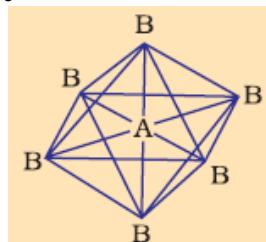
4) **AB₅ type**

Here there are 5 VSEPs. To reduce the repulsion, they are arranged at the five corners of a trigonal bipyramidal with bond angles 120° and 90°. E.g. PCl₅



5) **AB₆ type**

Here there are 6 VSEPs. To reduce the repulsion, they are arranged at the six corners of an octahedron with bond angles 90°. E.g.: SF₆



II) Molecules containing both bond pairs and lone pairs:

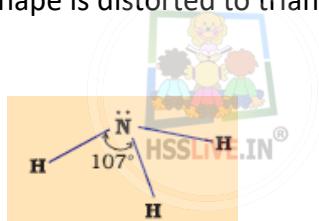
The presence of lone pairs of electron causes distortion in the shape of the molecules.

Type of molecule	Total no. of VSEPs	No. of b.ps	No. of l.ps	Shape	E.g.
AB ₂ E	3	2	1	Bent	SO ₂ , O ₃
AB ₃ E	4	3	1	Trigonal Pyramid	NH ₃
AB ₂ E ₂	4	2	2	Bent	H ₂ O
AB ₄ E	5	4	1	See-saw	SF ₄
AB ₃ E ₂	5	3	2	T-Shape	ClF ₃
AB ₅ E	6	5	1	Square Pyramid	BrF ₅
AB ₄ E ₂	6	4	2	Square Planar	XeF ₄

Explanation of shapes of ammonia and water molecules by VSEPR theory

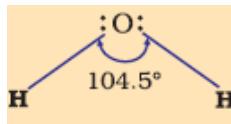
1. NH₃

In ammonia, the central atom N has 5 valence electrons ($\gamma N = 2,5$). Among these electrons, three are used for the formation of bonds with hydrogen atoms and the remaining 2 electrons stay as lone pairs. So there are 4 VSEPs. Hence the expected shape of the molecule is tetrahedral. But due to the presence of lone pairs, the shape is distorted to triangular pyramid and the bond angle changes from $109^{\circ}28'$ to 107° .



2. H₂O

In water, the central atom O has 6 valence electrons ($\gamma O = 2,6$). Two of them are used for the formation of bonds with hydrogen atoms and the remaining 4 electrons stay as lone pairs. So there are 4 VSEPs. Hence the expected shape of the molecule is tetrahedral. But due to the presence of 2 lone pairs, the shape is distorted to bent or angular or inverted v shape and the bond angle changes from $109^{\circ}28'$ to 104.5° .



Orbital overlap concept

Orbital overlapping is the process of partial interpenetration of atomic orbitals. The important characteristics of orbital overlapping are:

1. A covalent bond is formed by the overlapping of half-filled atomic orbitals present in the valence shell of atoms.
2. The overlapping orbitals should contain electron with opposite spin.
3. As a result of overlapping, the electrons get paired and a stable covalent bond is formed.
4. The strength of a covalent bond depends on the extent of overlapping. The greater the extent of overlapping, the stronger will be the covalent bond formed.

Types of overlapping

There are two types of orbital overlapping.

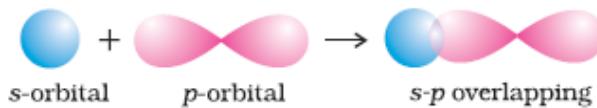
1. Axial overlapping:

If the overlapping of atomic orbitals take place along inter nuclear axis, it is called axial overlapping or end to end overlapping. A bond formed by axial overlapping is called **sigma (σ) bond**. The electrons present in sigma bond are called sigma electrons. All single bonds are sigma bonds. A sigma bond can be formed by the following ways:

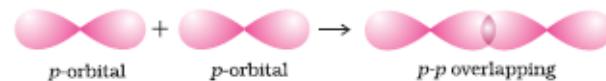
- s-s overlapping:** Here the overlapping of two half-filled s-orbitals take place along the inter nuclear axis.



- s-p overlapping:** It occurs with the overlapping of one half filled s-orbital and one half filled p-orbital.

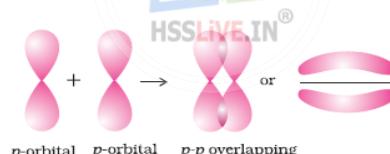


- p-p overlapping:** Here two half-filled p- orbitals of two atoms overlap.



2. Lateral overlapping:

Here the overlapping take place perpendicular to the inter nuclear axis. The bond formed as a result of lateral overlapping is called pi (π) bond. The electrons in pi bond are called π electrons.



A π bond is always present along with σ bonds. A double bond contains one σ bond and one π bond. A triple bond contains one sigma bond and two pi bonds.

A sigma bond is stronger than a pi bond. This is because the extent of overlapping is greater in a sigma bond.

Hybridisation

It is the process of inter mixing atomic orbitals having slightly different energies to form new orbitals having equivalent energy and identical shape. The new orbitals formed are called hybrid orbitals.

Characteristics of hybridisation

- The number of hybrid orbitals formed is equal to the number of atomic orbitals undergo hybridization.
- The hybrid orbitals are always equivalent in energy and in identical shape.
- The hybrid orbitals are more effective in forming stable bonds than the pure atomic orbitals.
- The hybrid orbitals are directed to some fixed positions in space. So the type of hybridization gives the shape of the molecule.

Important conditions of hybridisation

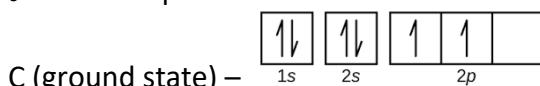
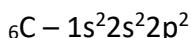
- The orbitals present in the valence shell of the atom are hybridized.
- The orbitals undergoing hybridization should have almost equal energy.
- Promotion of electrons is not an essential condition before hybridisation.
- Completely filled orbitals of valence shell can also take part in hybridisation.

Types of hybridisation

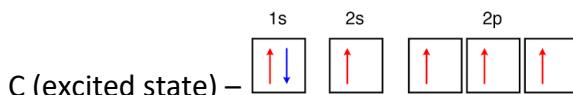
1. sp^3 hybridisation: It is the process of inter mixing of one s-orbital and three p-orbitals to form four new orbitals having equivalent energy and shape. The 4 new orbitals formed are called sp^3 hybrid orbitals. They are directed to the four corners of a regular tetrahedron with bond angle $109^{\circ}28'$. Each sp^3 hybrid orbital has 25% s-character and 75% p-character.

E.g. i) Formation of methane (CH_4)

In CH_4 , the central atom C has the electronic configuration



In order to explain the tetra valency of C, it is suggested that one of the electrons of 2s orbital is promoted to 2p orbital.

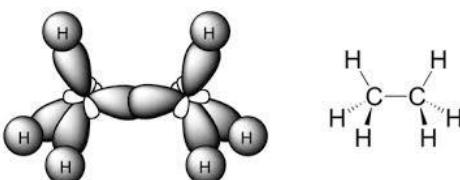


Now, one s-orbital and three p-orbitals undergo sp^3 hybridisation. These sp^3 hybrid orbitals are directed to the four corners of a regular tetrahedron with bond angle $109^{\circ}28'$. Each of these sp^3 hybrid orbitals overlap with 1s orbital of H to form four C-H σ bonds.



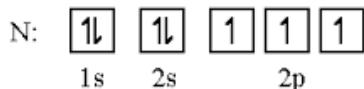
ii) Formation of ethane (C_2H_6)

In ethane, each C atom undergoes sp^3 hybridisation. Out of the 4 sp^3 hybrid orbitals, one of each C atom overlaps axially to form a C-C σ bond. The remaining 3 sp^3 hybrid orbitals of each C atom overlap with 1s orbital of H atom to form 6 C-H σ bonds.



iii) Formation of Ammonia (NH_3) molecule

In NH_3 , the central atom N has the electronic configuration $1s^2 2s^2 2p^3$.

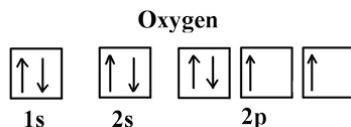


The one s-orbital and three p-orbitals of N undergo sp^3 hybridisation to form 4 sp^3 hybrid orbitals. One of this sp^3 hybrid orbitals is occupied by a lone pair and the other three sp^3 hybrid orbitals overlap with 1s orbital of hydrogen to form 3 N-H bonds. Due to the greater repulsion between lone pair and bond pairs, the shape is distorted to pyramidal and the bond angle becomes 107° .



iv) Formation of water (H_2O) molecule

In H_2O , the central atom O has the electronic configuration $1s^2 2s^2 2p^4$.



Now the one s-orbital and three p-orbitals of O undergo sp^3 hybridisation to form 4 sp^3 hybrid orbitals. Two of these sp^3 hybrid orbitals are occupied by lone pairs and the other two sp^3 hybrid orbitals overlap with 1s orbital of hydrogen to form 2 O-H bonds. Due to the greater repulsion between lone pairs, the shape is distorted to angular shape or bent structure or inverted 'v' shape and the bond angle becomes 104.5° .

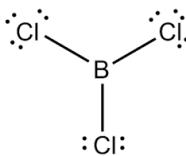


2. sp^2 hybridisation: It is the process of inter mixing of one s-orbital and two p-orbitals to form three new orbitals having equivalent energy and shape. The 3 new orbitals formed are called sp^2 hybrid orbitals. They are directed to the three corners of an equilateral triangle. So the shape of the molecule is planar triangular or trigonal planar with bond angle 120° . Each sp^2 hybrid orbitals has 33% s-character and 66% p-character.

E.g. i) Formation of BCl_3

Here the central atom B has the electronic configuration $1s^2 2s^2 2p^1$. In the excited state, one of the 2s electrons is promoted to vacant 2p orbital. So the configuration becomes $2s^1 2p^2$.

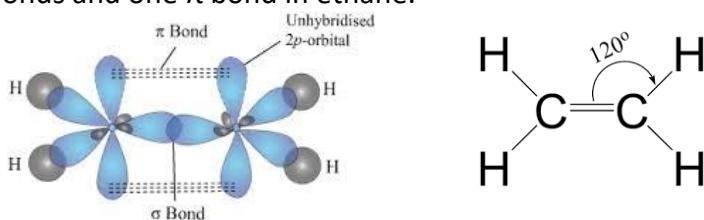
Now one s-orbital and two p-orbitals undergo hybridisation. The 3 hybrid orbitals formed overlap with 2p orbitals of Cl to form 3 B-Cl σ bonds. Since the hybridisation is sp^2 , the shape of the molecule is planar triangular with bond angle 120° .



ii) Formation of ethane or ethylene (C_2H_6)

In ethane, each C atom undergoes sp^2 hybridisation. Out of the 3 sp^2 hybrid orbitals, one of each C overlaps axially to form a C-C σ bond. The remaining two sp^2 hybrid orbitals of each C overlap with the 1s orbital of H to form 4 C-H σ bonds.

Now each C atom has one unhybridized p-orbital, which overlaps laterally to form a π bond. Thus there are 5 σ bonds and one π bond in ethane.

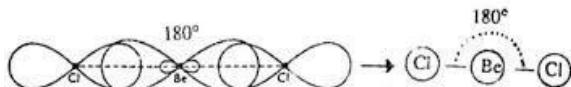


3. sp hybridisation: It is the process of inter mixing of one s-orbital and one p-orbital to form two new orbitals having equivalent energy and shape. The 2 new orbitals formed are called sp hybrid orbitals. They are directed in a line. So the shape is linear with bond angle 180° . Each sp hybrid orbital has 50% s-character and 50% p-character.

e.g. i) **Formation of BeCl_2**

In BeCl_2 , the central atom Be has the electronic configuration $1s^2 2s^2$. In the excited state, one of the 2s electrons is promoted to 2p level. So the configuration becomes $1s^2 2s^1 2p^1$.

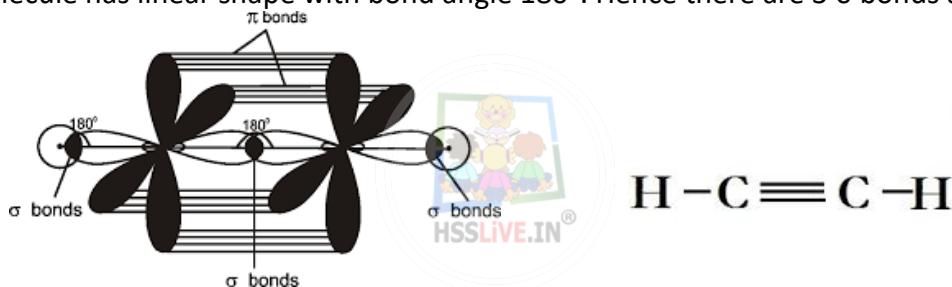
Now one s-orbital and one p-orbital undergo sp hybridisation to form 2 new sp hybrid orbitals. Each of these hybrid orbitals overlaps with the 2p orbitals of Cl to form 2 Be-Cl bonds. So the shape of the molecule is linear with bond angle 180° .



ii) **Formation of ethyne or acetylene (C_2H_2)**

In acetylene, each C atom undergoes sp hybridisation. Out of the 2 sp hybrid orbitals, one of the sp hybridized orbitals of each carbon, overlaps axially to form a C-C σ bond. The remaining one sp hybrid orbital of each carbon overlap with the 1s orbital of hydrogen atoms to form 2 C-H σ bonds.

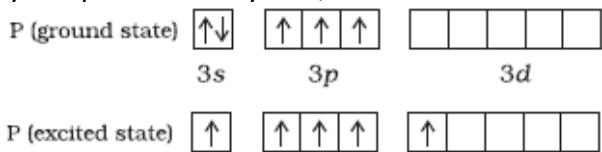
Now each C atom has 2 unhybridized p-orbitals, which overlap laterally to form 2 π bonds. Thus the molecule has linear shape with bond angle 180° . Hence there are 3 σ bonds and 2 π bonds in ethyne.



4. sp^3d hybridisation: It is the process of inter mixing of one s-orbital, three p-orbitals and one d-orbital to form five new orbitals having equivalent energy and shape. The 5 new orbitals formed are called sp^3d hybrid orbitals. These are directed to the five corners of a regular trigonal bipyramidal with bond angles 120° and 90° .

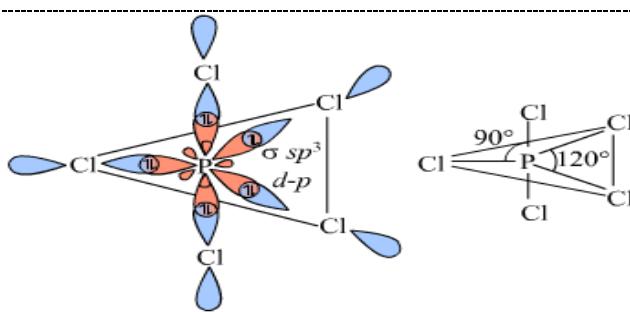
E.g. **Formation of PCl_5**

In PCl_5 , the central atom P has the electronic configuration ${}_{15}\text{P} - [\text{Ne}] 3s^2 3p^3 3d^0$. To satisfy the penta valency of P, one of the 3s electrons is promoted to 3d level.



Now, one s-orbital, three p-orbitals and one d-orbital undergo sp^3d hybridisation. These 5 sp^3d hybrid orbitals are directed to the five corners of a regular **trigonal bipyramidal with bond angles 120° and 90°** .

In PCl_5 , three P-Cl bonds lie in one plane, at an angle of 120° . These three bonds are called equatorial bonds. The other two P-Cl bonds lie one above and one below this plane. They are called axial bonds. The axial bond pairs suffer more repulsion from the equatorial bond pairs. So the axial bond length is greater than the equatorial bond length. So PCl_5 is highly unstable and is very reactive.



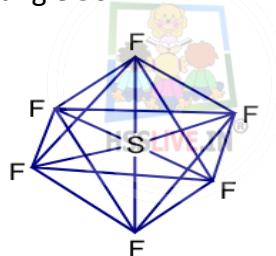
5. sp^3d^2 hybridisation: It is the process of inter mixing of one s-orbital, three p-orbitals and two d-orbitals to form six new orbitals having equivalent energy and shape. The 6 new orbitals formed are called sp^3d^2 hybrid orbitals. These are directed to the six corners of a regular octahedron with bond angle 90° .

e.g. **Formation of SF_6**

In SF_6 the central sulphur atom has the ground state outer electronic configuration $3s^23p^4$. In the excited state one electron each from $3s$ and $3p$ orbitals are promoted to $3d$ level.

(ground state)			
	3s	3p	3d
(excited state)			

Now one s-orbital, three p-orbitals and two d-orbitals undergo sp^3d hybridisation. These hybrid orbitals overlap with p- orbitals of fluorine atoms to form 6 S-F sigma bonds. Thus SF_6 molecule has a regular octahedral geometry with bond angle 90° .



VALENCE BOND THEORY

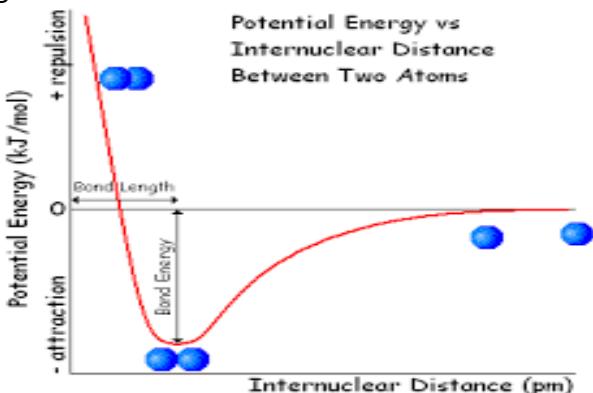
This theory was introduced by Heitler and London and later developed by Linus Pauling in order to explain the shape of molecules theoretically. VBT can be explained by considering the formation of H_2 molecule.

Consider 2 hydrogen atoms A and B with nuclei N_A and N_B and electrons e_A and e_B respectively. When the two atoms are at large distance from each other, there is no interaction between them. So their potential energy is zero. When the two atoms approach each other, new attractive and repulsive forces begin to operate.

Attractive forces arise between nucleus of one atom and electron of other atom i.e., $N_A - e_B$ and $N_B - e_A$. Repulsive forces arise between electrons of two atoms, i.e. $e_A - e_B$, and the nuclei of two atoms $N_A - N_B$. Attractive forces bring the two atoms close to each other whereas repulsive forces push them away.

Experimentally, it has been found that the magnitude of new attractive force is more than the new repulsive forces. So the two atoms approach each other and potential energy decreases. At a particular stage, the net attractive force balances the net repulsive forces and the energy becomes minimum. At this stage, the hydrogen atoms are said to be bonded together to form a stable molecule. The distance between the two atoms at this stage is called **bond length** (74 pm). The amount of energy liberated at this stage is called **bond enthalpy** (435.8 kJ/mol).

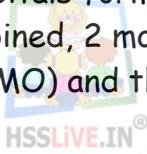
The potential energy diagram for the formation of H₂ molecule is as shown below:



Molecular Orbital Theory

This theory was developed by F.Hund and R.S Mulliken. The **important postulates** of this theory are:

- 1) In molecules, the electrons are present in some special type of orbitals called molecular orbitals (M.Os).
- 2) The atomic orbitals (A.Os) of comparable energy and proper symmetry combine to form molecular orbitals.
- 3) Atomic orbitals are monocentric, while molecular orbitals are polycentric. i.e. electrons present in atomic orbitals are attracted by only one nucleus. While the electrons present in molecular orbitals are attracted by more than one nuclei.
- 4) The number of molecular orbitals formed = the number of atomic orbitals combined. i.e. if 2 atomic orbitals combined, 2 molecular orbitals are formed. One is called bonding molecular orbital (BMO) and the other is called anti-bonding molecular orbitals (ABMO)
- 5) The BMO has lower energy and greater stability than the corresponding ABMO.
- 6) The molecular orbitals give the electron probability distribution around a group of nuclei.
- 7) The molecular orbitals are filled according to 3 rules - Aufbau principle, Pauli's exclusion principle and Hund's rule.



Formation of molecular orbitals – Linear Combination of Atomic Orbitals (LCAO) method

Molecular orbitals are formed by the combination of atomic orbitals by an approximate method known as Linear Combination of Atomic Orbitals (LCAO). According to this theory, the combinations of atomic orbitals take place by addition and subtraction of wave functions of atomic orbitals. The M.O formed by the addition of A.Os is called the bonding molecular orbital (BMO) and by the subtraction of A.Os is called the anti-bonding molecular orbitals (ABMO).

The electron density in a BMO is located between the nuclei of the bonded atoms. So the repulsion between the nuclei is very low. Therefore a BMO always possess lower energy than the combining A.Os. While in the case of an ABMO, most of the electron density is located away from the space between the nuclei. There is a nodal plane between the nuclei and hence the repulsion between the nuclei is high. So an ABMO possess higher energy than the combining A.Os. ABMO is denoted by using an asterisk (*) mark.

Conditions for the combination of atomic orbitals

The combination of A.Os to form M.Os takes place only if the following conditions are satisfied:

1. The combining A.Os must have the same or nearly the same energy.
2. The combining A.Os must have the same symmetry about the molecular axis.
3. The combining A.Os must overlap to the maximum extent.

Types of molecular orbitals

M.Os of diatomic molecules are designated as σ (sigma), π (Pi), δ (delta) etc. the sigma M.Os are symmetrical about the bond axis, while the pi M.Os are not symmetrical.

Linear combination of two 1s atomic orbitals produces two M.Os – a BMO σ 1s and an ABMO σ^* 1s.

Similarly linear combination of two 2s atomic orbitals produces two M.Os – σ 2s and σ^* 2s.

If z-axis is taken as the inter nuclear axis, linear combination of two $2p_z$ orbitals produces two sigma M.Os σ 2p_z and σ^* 2p_z.

While the combination of $2p_x$ and $2p_y$ orbitals produce M.Os which are not symmetrical about the bond axis. So two $2p_x$ orbitals produce 2 sigma M.Os – π 2p_x and π^* 2p_x and two $2p_y$ orbitals produce 2 M.Os – π 2p_y and π^* 2p_y.

Energies of various M.Os

The various M.Os are filled in the increasing order of their energies (Aufbau Principle).

The increasing order of energy is:

$$\sigma 1s < \sigma^* 1s < \sigma 2s < \sigma^* 2s < (\pi 2p_x = \pi 2p_y) < \sigma 2p_z < (\pi^* 2p_x = \pi^* 2p_y) < \sigma^* 2p_z$$

For O₂, F₂ and Ne₂, the order is:

$$\sigma 1s < \sigma^* 1s < \sigma 2s < \sigma^* 2s < \sigma 2p_z < (\pi 2p_x = \pi 2p_y) < (\pi^* 2p_x = \pi^* 2p_y) < \sigma^* 2p_z$$

Bond Order

It is defined as the half of the difference between the number of bonding electrons (N_b) and the number of anti-bonding electrons (N_a).

$$\text{i.e. Bond order (B.O)} = \frac{1}{2} [N_b - N_a]$$

A molecule is stable only if the bond order is positive. (i.e. N_b > N_a). A negative or zero bond order (i.e. N_b < N_a or N_b = N_a) means an unstable molecule.

For a single bond, B.O = 1, for a double bond B.O = 2 and so on. Bond order gives an approximate measure of the bond length. In general, **as the bond order increases, bond length decreases and bond enthalpy increases**.

Molecular orbital configuration and Bond order of some Homonuclear diatomic molecules

Molecule	M.O configuration	Total no. of electrons	No. of Bonding Electrons (N _b)	No. of Anti-bonding electrons (N _a)	Bond Order = $\frac{1}{2} [N_b - N_a]$
H ₂	$\sigma 1s^2$	2	2	0	= $\frac{1}{2} [2 - 0] = \frac{1}{2} \times 2 = 1$
He ₂	$\sigma 1s^2 \sigma^* 1s^2$	4	2	2	= $\frac{1}{2} [2 - 2] = \frac{1}{2} \times 0 = 0$
Li ₂	$\sigma 1s^2 \sigma^* 1s^2 \sigma 2s^2$	6	4	2	= $\frac{1}{2} [4 - 2] = \frac{1}{2} \times 2 = 1$
Be ₂	$\sigma 1s^2 \sigma^* 1s^2 \sigma 2s^2 \sigma^* 2s^2$	8	4	4	= $\frac{1}{2} [4 - 4] = \frac{1}{2} \times 0 = 0$
B ₂	$\sigma 1s^2 \sigma^* 1s^2 \sigma 2s^2 \sigma^* 2s^2 \pi 2p_x^1 \pi 2p_y^1$	10	6	4	= $\frac{1}{2} [6 - 4] = \frac{1}{2} \times 2 = 1$
C ₂	$\sigma 1s^2 \sigma^* 1s^2 \sigma 2s^2 \sigma^* 2s^2 \pi 2p_x^2 \pi 2p_y^2$	12	8	4	= $\frac{1}{2} [8 - 4] = \frac{1}{2} \times 4 = 2$
N ₂	$\sigma 1s^2 \sigma^* 1s^2 \sigma 2s^2 \sigma^* 2s^2 \pi 2p_x^2 \pi 2p_y^2 \sigma 2p_z^2$	14	10	4	= $\frac{1}{2} [10 - 4] = \frac{1}{2} \times 6 = 3$

O ₂	$\sigma 1s^2 \sigma^*1s^2 \sigma 2s^2 \sigma^*2s^2$ $\sigma 2p_z^2 \pi 2p_x^2 \pi 2p_y^2$ $\pi^*2p_x^1 \pi^*2p_y^1$	16	10	6	$= \frac{1}{2} [10 - 6] = \frac{1}{2} \times 4 = 2$
F ₂	$\sigma 1s^2 \sigma^*1s^2 \sigma 2s^2 \sigma^*2s^2$ $\sigma 2p_z^2 \pi 2p_x^2 \pi 2p_y^2$ $\pi^*2p_x^2 \pi^*2p_y^2$	18	10	8	$= \frac{1}{2} [10 - 8] = \frac{1}{2} \times 2 = 1$
Ne ₂	$\sigma 1s^2 \sigma^*1s^2 \sigma 2s^2 \sigma^*2s^2$ $\sigma 2p_z^2 \pi 2p_x^2 \pi 2p_y^2$ $\pi^*2p_x^2 \pi^*2p_y^2 \sigma^*2p_z^2$	20	10	10	$= \frac{1}{2} [10 - 10] = \frac{1}{2} \times 0 = 0$

He₂, Be₂ and Ne₂ molecules do not exist, since their Bond orders are zero. H₂, Li₂, B₂ and F₂ molecules contain a single bond, since their bond order = 1, C₂ and O₂ molecules contain a double bond, since their B.O = 2 and for N₂, there is a triple bond since its bond order = 3.

Magnetic nature

If all the M.Os in a molecule are doubly occupied, the substance is diamagnetic. i.e. that substance is repelled by an external magnetic field. If one or more M.Os are singly occupied, it is paramagnetic. i.e. it is attracted by an external magnetic field. E.g. O₂ molecule.

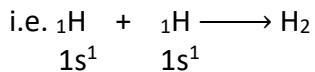
Molecular orbital Diagrams

The representation of various M.Os in the increasing order of energy is called M.O diagram.

Bonding in Some Homonuclear Diatomic Molecules

1. Hydrogen (H₂) Molecule

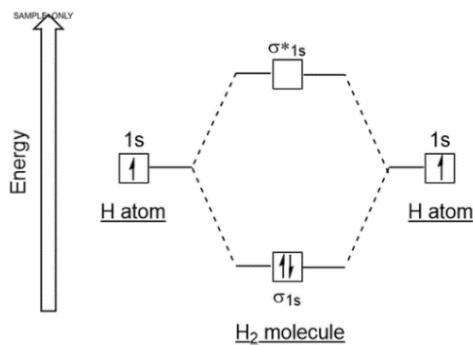
H₂ molecule is formed by the combination of two Hydrogen atoms.



Total no. of electrons in H₂ molecule = 2

So its M.O configuration is $\sigma 1s^2$

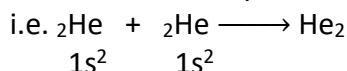
M.O diagram for H₂ molecule is:



Due to the absence of unpaired electrons in M.Os, H₂ molecule is diamagnetic.

2. Helium (He₂) Molecule

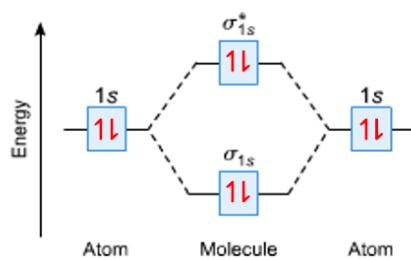
He₂ molecule is formed by the combination of two Helium atoms.



Total no. of electrons in He₂ molecule = 4

So its M.O configuration is $\sigma 1s^2 \sigma^*1s^2$

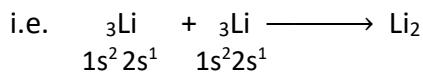
Its M.O diagram is:



Since N_b = N_a, B.O = 0 and hence He₂ molecule does not exist.

3. Lithium (Li₂) Molecule

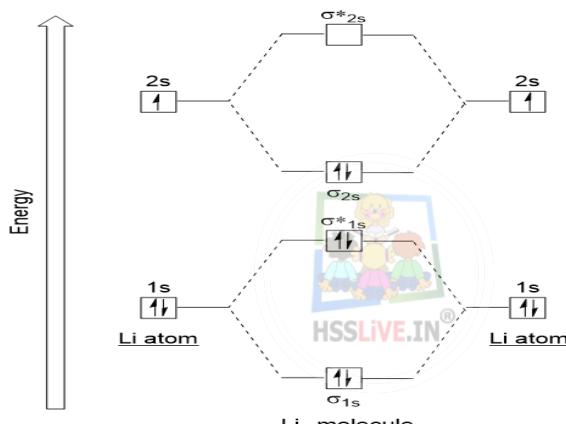
Li₂ molecule is formed by the combination of two Lithium atoms.



Total no. of electrons in Li₂ molecule = 6

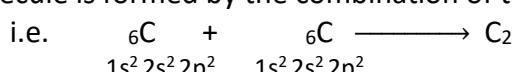
So its M.O configuration is = σ1s² σ*1s² σ2s²

Its M.O diagram is:



4. Carbon (C₂) Molecule

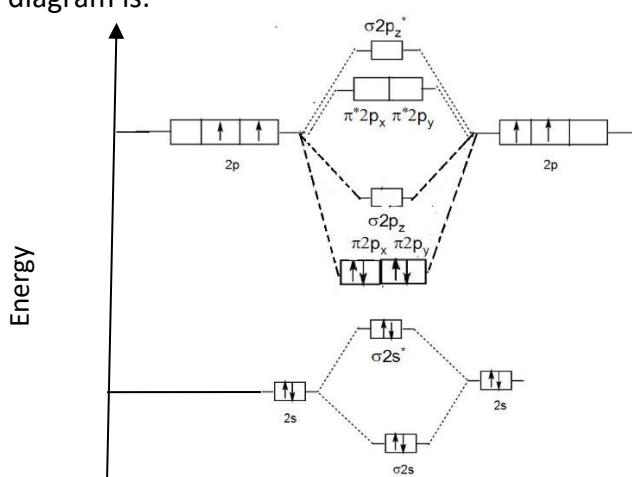
C₂ molecule is formed by the combination of two Carbon atoms.



Total no. of electrons in C₂ molecule = 12

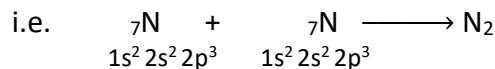
So its M.O configuration is = σ1s² σ*1s² σ2s² σ*2s² π2p_x² π2p_y²

Its M.O diagram is:



5. Nitrogen (N_2) Molecule

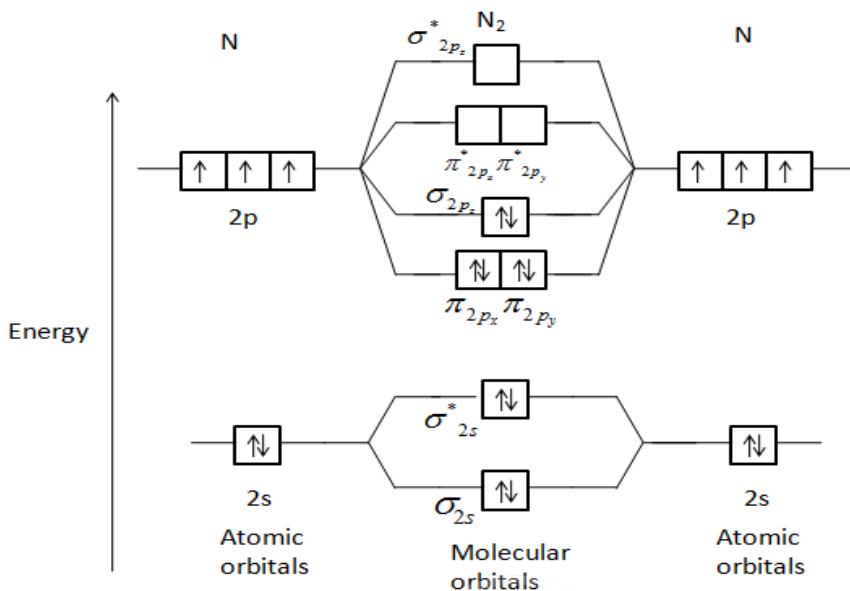
N_2 molecule is formed by the combination of two Nitrogen atoms.



Total no. of electrons in N_2 molecule = 14

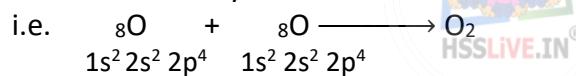
So its M.O configuration is = $\sigma 1s^2 \sigma^* 1s^2 \sigma 2s^2 \sigma^* 2s^2 \pi 2p_x^2 \pi 2p_y^2 \sigma 2p_z^2$

Its M.O diagram is:



6. Oxygen (O_2) molecule

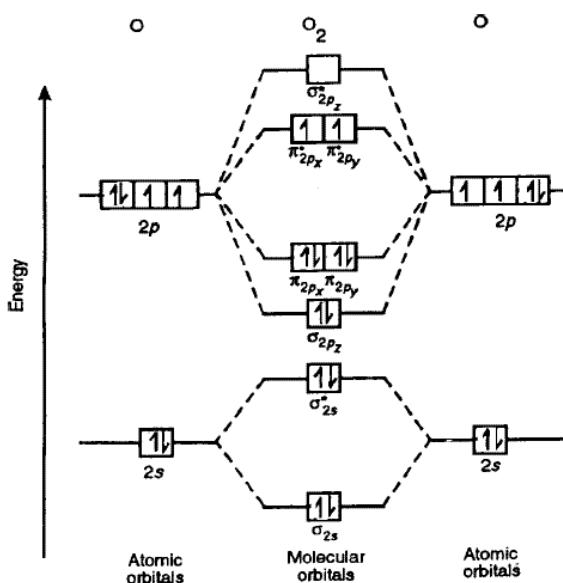
O_2 molecule is formed by the combination of two Oxygen atoms.



Total no. of electrons in O_2 molecule = 16

So its M.O configuration is = $\sigma 1s^2 \sigma^* 1s^2 \sigma 2s^2 \sigma^* 2s^2 \sigma 2p_z^2 \pi 2p_x^2 \pi 2p_y^2 \pi^* 2p_x^1 \pi^* 2p_y^1$

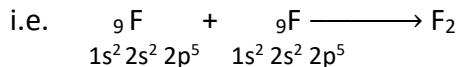
Its M.O diagram is:



Due to the presence of unpaired electrons, O_2 molecule is paramagnetic.

7. Fluorine (F_2) molecule

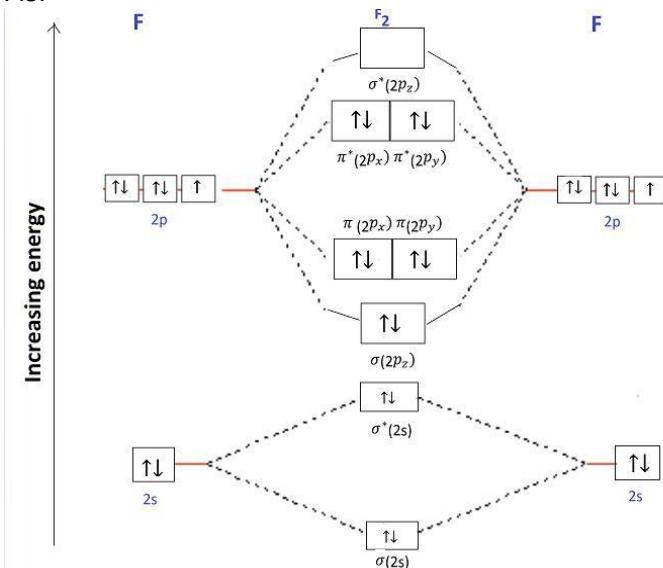
F_2 molecule is formed by the combination of two Fluorine atoms.



Total no. of electrons in F_2 molecule = 18

So its M.O configuration is = $\sigma 1s^2$ $\sigma^* 1s^2$ $\sigma 2s^2$ $\sigma^* 2s^2$ $\sigma 2p_z^2$ $\pi 2p_{x^2}$ $\pi 2p_{y^2}$ $\pi^* 2p_{x^2}$ $\pi^* 2p_{y^2}$

Its M.O diagram is:

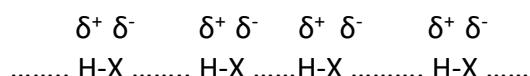


Due to the absence of unpaired electrons, F_2 molecule is diamagnetic.

Hydrogen Bonding

The weak attractive force between Hydrogen atom of one molecule and electronegative atom (like F, O or N) of the same or different molecule is termed as Hydrogen bond. It is weaker than a covalent bond but stronger than van der Waal's force. It is represented by dotted line (.....).

Cause of Hydrogen bonding: When hydrogen is bonded to a strongly electronegative atom X, the shared electron pair is shifted more towards X. So Hydrogen atom gets a slight positive charge (δ^+) and the electronegative atom gets a slight negative charge (δ^-). This results in the formation of a polar molecule. The electrostatic force of attraction between these polar molecules is termed as H-bonding.



Types of Hydrogen bonding

There are two types of H bonds- inter molecular hydrogen bonding and intra molecular hydrogen bonding.

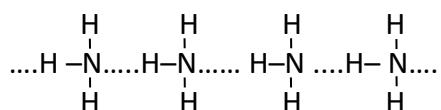
- 1) **Inter molecular Hydrogen bonding:** It is the hydrogen bond formed by H atom of one molecule and the electronegative atom of another molecule.

e.g. i) Hydrogen bonding in HF



ii) H_2O $\text{H}-\underset{\text{H}}{\text{O}} \dots \text{H}-\underset{\text{H}}{\text{O}} \dots \text{H}-\underset{\text{H}}{\text{O}} \dots \text{H}-\underset{\text{H}}{\text{O}} \dots$

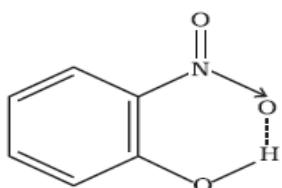
iii) NH₃



Inter molecular H bonding influences the physical properties of the compounds. For example water (H₂O) is a liquid with high boiling point but hydrogen sulphide (H₂S) is a gas. This is because in water inter molecular H bonding is possible which is not possible in H₂S.

2) **Intra molecular Hydrogen bonding:** It is the hydrogen bond formed between H atom and the electronegative atom of the same molecule.

e.g. Hydrogen bonding in ortho-nitrophenol



5. THERMODYNAMICS

It is a branch of science that deals with the relation between heat and work. *Chemical thermodynamics is a branch of chemistry that deals with the heat changes associated with chemical reactions.*

System and Surroundings

System is the part of the universe which is under observation or investigation. The part of the universe except system is called surroundings. The system and surroundings are separated by a boundary which may be real or imaginary.

$$\text{System} + \text{surroundings} \rightarrow \text{Universe}$$

Types of systems

Depending on the ability to exchange energy and matter with the surroundings, systems are classified into three types:

1. **Open system:** It is a system that can exchange both energy and matter with the surroundings. E.g. Hot water taken in an open vessel.
2. **Closed system:** It is a system that can exchange only energy and not matter with the surroundings. E.g. Hot water taken in a closed vessel.
3. **Isolated system:** It is a system that cannot exchange both energy and matter with the surroundings. E.g. Hot water taken in a thermos flask.

Depending on the number of particles, systems are of two types:

1. **Microscopic system:** It is a system that contains a few number of particles.
2. **Macroscopic system:** It is a system that contains a large number of particles.

The properties of a macroscopic system are called **macroscopic properties**. The important macroscopic properties are: temperature (T), pressure (p), volume (V), length (l), breadth (b), height (h), internal energy (U), enthalpy (H), entropy (S), Gibb's energy (G) etc.

Macroscopic properties can be divided into two:

1. **Extensive properties:** These are properties which depend on the amount of matter present in the system. Or, these are the properties which change when a system is divided.

E.g.: Volume (V), length (l), breadth (b), height (h), internal energy (U), enthalpy (H), entropy (S), Gibb's energy (G), heat capacity (C) etc.

2. **Intensive properties:** These are properties which are independent of the amount of matter present in the system. Or, these are the properties which do not change when a system is divided.

E.g. : Temperature (T), pressure (p), molar volume (V_m), density, refractive index, molar heat capacity, viscosity, surface tension etc.

State and Path functions:

A function or a property that depends only on the initial and final state of a system and not on the path followed is called a state function.

E.g. for state functions: temperature (T), pressure (p), volume (V), internal energy (U), enthalpy (H), entropy (S), Gibb's energy (G) etc.

Path functions: These are properties which depend on the path followed also.

E.g. heat (q) and work (w).

Thermodynamic process

A thermodynamic process is the method (path) by which a state change occurs in a system. The different types of thermodynamic process are:

1. **Isothermal process:** It is a process that occurs at constant temperature. For this process, $\Delta T = 0$ but $q \neq 0$. Here the system exchanges heat energy with the surroundings, in order to keep the temperature constant.
 2. **Isobaric process:** It is a process that occurs at constant Pressure. For such a process, $\Delta p = 0$
 3. **Isochoric process:** It is a process that occurs at constant volume. For such a process, $\Delta V = 0$
 4. **Adiabatic process:** It is a process that occurs at constant heat energy. Here no heat enters into or leaves from the system. For such a process, $q = 0$ but $\Delta T \neq 0$
 5. **Cyclic process:** It is a process that takes place in a cyclic manner. Here the system undergoes a series of changes and finally returns to its initial state. For such a process, $\Delta U=0$ and $\Delta H = 0$
 6. **Reversible process:** Every process is associated with two types of forces – driving force and opposing force. Driving force favours the process while opposing force opposes it. *If the driving and opposing forces are differed by an infinitesimally small quantity the process takes place in both directions. Such a process is called reversible process.*
- A reversible process proceeds infinitely slowly by a series of equilibrium states such that the system and the surroundings are always in equilibrium with each other.
7. **Irreversible process:** If the driving and opposing forces are differed by a large quantity, then the process takes place in only one direction. Such a process is called irreversible process.

Heat and Work

Heat: It is a form of energy. Heat flows from a hot body to a cold body, when there is a thermal contact between the two. When a body absorbs heat, its energy increases and when it evolves heat, its energy decreases. Thus by international convention, when heat is absorbed by a system, q becomes +ve and when heat is evolved by a system q becomes -ve.

Work: In thermodynamics, there are two types of work – expansion work and non-expansion work.

1. **Expansion work (w_{exp}):** It is related to gaseous systems. It is the product of pressure (p) and change in volume (ΔV). i.e., expansion work (w_{exp}) = $-p\Delta V$
For irreversible process, (w_{exp}) = $-p\Delta V$ and
For reversible process, (w_{exp}) = $-2.303nRT \log \frac{V_2}{V_1}$
2. **Non-expansion work ($w_{non-exp}$):** It is related to electrochemical cells. It is the product of potential difference (E) and charge (Q). i.e., $w_{non-exp} = E \times Q$

By international convention, w becomes +ve, when work is done *on* the system and w becomes -ve, when work is done *by* the system.

Expression for pressure-volume work

Consider a cylinder fitted with a frictionless piston and contains one mole of an ideal gas.

Let the total volume of the gas is V_1 and pressure of the gas inside is p .

If external pressure is p_{ex} which is greater than p , piston is moved inward till the pressure inside becomes equal to p_{ex} . Let this change took place in a single step and the final volume be V_2 .

During this compression, let the piston moves a distance l and its cross-sectional area is A .

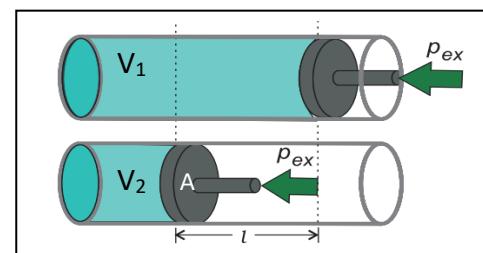
Then, volume change, $\Delta V = l \times A = (V_2 - V_1)$.

We know that pressure = Force/Area

Therefore, force on the piston = $p_{ex} \cdot A$

If w is the work done on the system by movement of the piston,
then $w = \text{force} \times \text{distance} = p_{ex} \cdot A \cdot l$

$$= p_{ex} (-\Delta V) = -p_{ex} \Delta V = -p_{ex} (V_2 - V_1)$$



Here the negative sign is to make the work done positive, since $(V_2 - V_1)$ is negative.

If the pressure is not constant, but changes during the process such that it is always infinitesimally greater than the pressure of the gas, then, at each stage of compression, the volume decreases by an infinitesimal amount, dV .

Then we can calculate the work done on the gas, $w = - \int_{V_1}^{V_2} (p_{\text{ex}} \cdot dV)$

Here, p_{ex} at each stage is equal to $(p_{in} + dp)$ in case of compression and $(p_{in} - dp)$ in case of expansion.

Generally, $p_{ex} = (p_{in} \pm dp)$. Such processes are called reversible processes.

Therefore, $w_{rev} = - \int_{V_1}^{V_2} (p_{in} \pm dp) \cdot dV$

Since $dP \times dV$ is very small, we can write $w_{rev} = - \int_{V_1}^{V_2} p_{in} \cdot dV$

But $p_{in} = p$, the pressure of the gas inside the cylinder.

$$W_{rev} = - \int_{V_1}^{V_2} p.dV$$

For n mol of an ideal gas i.e., $pV = nRT$. So $p = \frac{nRT}{V}$

$$\text{Thus } w_{\text{rev}} = - \int_{V1}^{V2} \frac{nRT}{V} \cdot dV$$

On integrating this equation, we get, $w_{rev} = -nRT \ln \frac{V_2}{V_1}$ [since $\int \frac{1}{V} dV = \ln V$]

On changing the base of logarithm, we can write: $w_{rev} = -2.303 nRT \log \frac{V_2}{V_1}$

Where n – no. of moles of the gas, R – Universal gas constant ($R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$), T – Absolute temperature, V_1 – initial volume of the gas and V_2 – the final volume)

{Note: Here ln is the natural logarithm. To convert natural logarithm (base e) to common logarithm (base 10), multiply by 2.303}.

Free expansion: Expansion of a gas into vacuum (external pressure = 0) is called free expansion. No work is done during free expansion of an ideal gas whether the process is reversible or irreversible.

Internal Energy (U)

Every body is associated with a definite amount of energy. This energy is called internal or intrinsic energy. It is the energy possessed by a body. It is the sum of different types of molecular energies like translational kinetic energy, rotational kinetic energy, vibrational kinetic energy, electronic energy, nuclear energy etc.

Internal energy of a body is an extensive property and state function. We cannot calculate the exact value of internal energy, but we can calculate the change in internal energy (ΔU) during a process by using an apparatus called *Bomb Calorimeter*.

The change in internal energy (ΔU) = $U_2 - U_1$, where U_1 and U_2 are the initial and final internal energies respectively. The unit of internal energy is kJ/mol.

The internal energy of a system can be changed in the following ways:

1. by the transfer of heat into or out of the system
 2. by work done on or by the system
 3. by the transfer of matter into or out of the system.

First law of thermodynamics:

It is same as law of conservation of energy. It states that energy can neither be created nor be destroyed. Or, the total energy in the universe is always a constant. Or, the total energy of an isolated system is always a constant.

Mathematically, $\Delta U = q + w$ (1)

So equation (3) becomes, $\Delta H = \Delta U + \Delta nRT$

where $\Delta n = n_{p(g)} - n_{R(g)}$

i.e., Δn = no. of moles of gaseous products – no. of moles of gaseous reactants

If $\Delta n = 0$, then $\Delta H = \Delta U$

If $\Delta n > 0$, then $\Delta H > \Delta U$

and if $\Delta n < 0$, then $\Delta H < \Delta U$.

Significance of ΔH

We know that $\Delta H = \Delta U + P\Delta V$ (at constant pressure)

From first law of thermodynamics, $\Delta U = q - P\Delta V$

So, $q = \Delta U + P\Delta V$

From the above equations, we can write, $\Delta H = q_p$

i.e. enthalpy change in a chemical reaction is equal to the amount of heat evolved or absorbed at constant pressure. This is the significance of ΔH .

Heat capacity (C)

It is the amount of heat required to raise the temperature of a body through 1°C or 1K . If q amount of heat is required to raise the temperature of a body through ΔT , then heat capacity (C) = $\frac{q}{\Delta T}$.

Specific heat capacity is the amount of heat required to raise the temperature of unit mass of a body through 1°C or 1K .

Molar heat capacity is the amount of heat required to raise the temperature of 1 mole of a substance through 1°C or 1K .

Relation between C_p and C_v

At constant volume, the heat capacity, C is denoted by C_v and at constant pressure, it is denoted by C_p .

We know that heat, $q = C \Delta T$

At constant volume, the heat $q_v = \Delta U = C_v \cdot \Delta T$

At constant pressure, $q_p = \Delta H = C_p \cdot \Delta T$

We know that $H = U + pV$

For 1 mole of an ideal gas, $\Delta H = \Delta U + \Delta(pV)$

From ideal gas equation $pV = nRT$, for 1 mol of an ideal gas, $pV = RT$

So, $\Delta H = \Delta U + \Delta(RT)$

Or, $\Delta H = \Delta U + R\Delta T$

On putting the values of ΔH and ΔU , we get

$$C_p \Delta T = C_v \Delta T + R \Delta T$$

$$\text{Or, } C_p = C_v + R$$

$$\text{Or, } C_p - C_v = R \quad [\text{This is known as Meyer's relation}]$$



Measurement of ΔU and ΔH - Calorimetry

We can measure energy changes associated with chemical or physical processes by an experimental technique called calorimetry. In calorimetry, the process is carried out in a vessel called calorimeter, which is immersed in a known volume of a liquid.

Measurement of ΔU

ΔU is measured in a bomb calorimeter. Here, a steel vessel (the bomb) is immersed in a water bath. A combustible substance is burnt in pure dioxygen supplied in the steel bomb. Heat evolved during the reaction is transferred to the water around the bomb. The increase in temperature is measured by using a thermometer.

Since the bomb calorimeter is sealed, its volume does not change.

i.e., the energy changes associated with the reaction is measured at constant volume.

Under these conditions, no work is done as the reaction is carried out at constant volume (i.e. $\Delta V = 0$) in the bomb calorimeter. By knowing the heat capacity of the calorimeter and the temperature change during the reaction, we can calculate ΔU by the equation:

$$\Delta U = q_v = C_v \cdot \Delta T$$

Measurement of ΔH

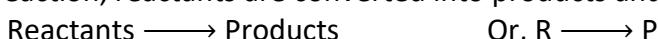
Measurement of heat change at constant pressure (generally under atmospheric pressure) can be done in a calorimeter. Here the reaction is carried out at normal pressure and the temperature change is measured by using a thermometer. By knowing the heat capacity of the calorimeter, we can calculate ΔH by the equation:

$$\Delta H = q_p = C_p \cdot \Delta T$$

ΔH obtained here is also called the heat of reaction or enthalpy of reaction, $\Delta_r H$.

ENTHALPY CHANGE OF A REACTION – REACTION ENTHALPY ($\Delta_r H$)

In a chemical reaction, reactants are converted into products and is represented by,



The enthalpy change during a chemical reaction is called the reaction enthalpy. It is given by the symbol $\Delta_r H$.

$\Delta_r H = (\text{sum of enthalpies of products}) - (\text{sum of enthalpies of reactants})$

$$\text{i.e. } \Delta_r H = \sum H_p - \sum H_R$$

Standard enthalpy of reactions ($\Delta_r H^\ominus$)

The standard enthalpy of reaction is the enthalpy change for a reaction when all the substances are in their standard states. In thermodynamics, the standard state refers to the existence of a substance in its pure form at 1 bar pressure and 298 K temperature.

Standard enthalpy of formation ($\Delta_f H^\ominus$)

It is the standard enthalpy change for the formation of one mole of a compound from its elements in their most stable state of aggregation (or, reference state). It is denoted by the symbol $\Delta_f H^\ominus$. For e.g. the std. enthalpy of formation of CO_2 is the enthalpy change when 1 mole of CO_2 is formed from C and O_2 at 298K temperature, 1 bar pressure and all the substances are in their stable state.

The reference state of an element is its most stable state at 25°C and 1 bar pressure. The reference state of dihydrogen is H_2 gas and those of dioxygen, carbon and sulphur are O_2 gas, $\text{C}_{\text{graphite}}$ and $\text{S}_{\text{Rhombic}}$ respectively. The enthalpy of formation may be positive or negative.

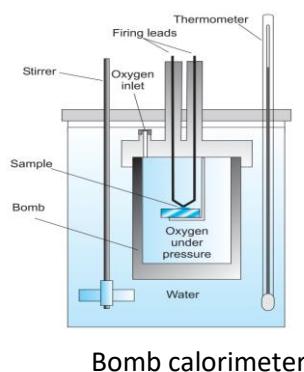
By convention, standard enthalpy of formation ($\Delta_f H^\ominus$) of an element in reference state (i.e., its most stable state of aggregation) is taken as zero.

By knowing the std. enthalpies of formation of reactants and products, we can determine the std. enthalpy of reaction by the equation: $\Delta_r H^\ominus = \sum \Delta_f H^\ominus_{(P)} - \sum \Delta_f H^\ominus_{(R)}$

i.e. std. enthalpy of reaction = sum of the standard enthalpies of formation of products – sum of the std. enthalpies of formation of reactants.

Enthalpies of phase transition

It is the enthalpy change when one mole of a substance changes from one phase to another phase at a particular temperature. The important types of Enthalpies of phase transition are:



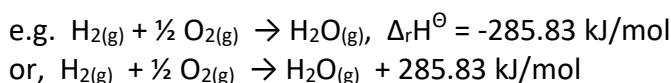
Bomb calorimeter

- 1) Molar Enthalpy of fusion ($\Delta_{\text{fus}}H^\ominus$):** It is the enthalpy change when one mole of a solid substance changes to liquid state at its melting point.
- 2) Molar Enthalpy of vaporization ($\Delta_{\text{vap}}H^\ominus$):** It is the enthalpy change when one mole of a liquid substance changes to its vapour state at its boiling point.
- 3) Molar Enthalpy of sublimation ($\Delta_{\text{sub}}H^\ominus$):** It is the enthalpy change when one mole of a solid substance is directly converted to gaseous state at a particular temperature below its m.p.

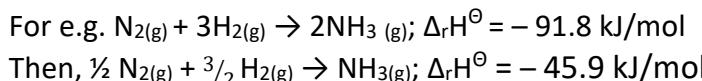
Enthalpies of fusion, vaporization and sublimation are positive, since heat is absorbed during these process. The magnitude of the enthalpy change depends on the strength of the intermolecular forces in the substance.

Thermochemical equations

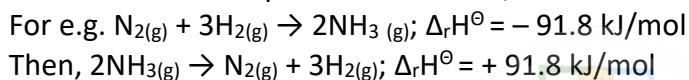
A balanced chemical equation together with the value of enthalpy of reaction is called a thermochemical equation. Here the physical state of the each of the reactants and products is also shown in bracket.



When we multiply or divide a thermochemical equation with a number, then Δ_rH^\ominus is also multiplied or divided with the same number.



When a chemical equation is reversed, the value of Δ_rH^\ominus is reversed in sign.



Hess's Law of Constant Heat Summation

The law states that the total enthalpy change for a physical or chemical process is the same whether the reaction taking place in a single step or in several steps.

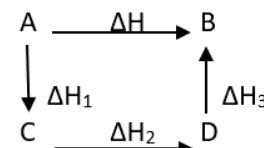
Or, the total enthalpy change for a process is independent of the path followed.

Thus according to Hess's law, if a reaction takes place in several steps, then its standard reaction enthalpy is the sum of the standard enthalpies of the intermediate reactions.

Illustration:

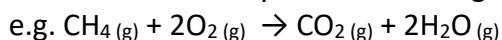
Consider a process in which the reactant A is converted to product B in a single step by involving heat change ΔH . Let the same reactant A is first converted to C, then to D and finally to B involving heat changes ΔH_1 , ΔH_2 and ΔH_3 respectively.

Then according to Hess's law: $\Delta H = \Delta H_1 + \Delta H_2 + \Delta H_3$



Standard enthalpy of combustion (Δ_cH^\ominus)

It is defined as the enthalpy change when 1mole of a substance is completely burnt in presence of excess of air or oxygen and all the reactants and products being in their standard states. It is always negative since heat is always evolved during combustion.



Enthalpy of atomization (Δ_aH^\ominus)

It is the enthalpy change on breaking one mole of bonds completely to obtain atoms in the gas phase. In the case of diatomic molecules the enthalpy of atomization is same as the bond dissociation enthalpy.



Bond Enthalpy ($\Delta_{\text{bond}}H^\ominus$)

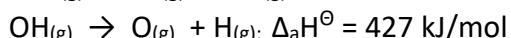
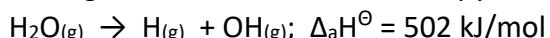
Chemical reactions involve the breaking and making of chemical bonds. Energy is required to break a bond and energy is released when a bond is formed. So enthalpy of bond dissociation is positive and enthalpy of bond formation is negative.

*The amount of heat required to break one mole of covalent bonds to form products in the gas phase is called the **bond dissociation enthalpy**.* For diatomic molecules, bond dissociation enthalpy and bond enthalpy are same.



In the case of polyatomic molecules, bond dissociation enthalpy is different for different bonds within the same molecule. So here **bond enthalpy is the average of bond dissociation enthalpies of various similar bonds**.

For e.g. for water, the bond enthalpy is calculated as follows:



Here the bond enthalpy of O-H bond is taken as the average of the two bond dissociation enthalpies.

$$\text{i.e. bond enthalpy of O-H bond} = \frac{502+427}{2} = 464.5 \text{ kJ/mol}$$

The standard enthalpy of reaction, $\Delta_r H^\ominus$ is related to bond enthalpies of the reactants and products in gas phase reactions as:

$$\Delta_r H^\ominus = \sum \text{bond enthalpies of reactants} - \sum \text{bond enthalpies of products}$$

This equation is valid when all the reactants and products in the reaction are in gaseous state.

Enthalpy of Solution ($\Delta_{\text{sol}}H^\ominus$)

Enthalpy of solution is the enthalpy change when one mole of a substance is dissolved in a specified amount of solvent.

The enthalpy of solution in water is determined by the values of the lattice enthalpy, $\Delta_{\text{lattice}}H^\ominus$ and enthalpy of hydration of ions, $\Delta_{\text{hyd}}H^\ominus$.

$$\text{i.e. } \Delta_{\text{sol}}H^\ominus = \Delta_{\text{lattice}}H^\ominus + \Delta_{\text{hyd}}H^\ominus$$

For most of the ionic compounds, $\Delta_{\text{sol}}H^\ominus$ is positive and the dissolution process is endothermic. Therefore the solubility of most salts in water increases with rise of temperature.

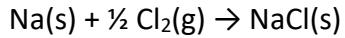
If the lattice enthalpy is very high, the dissolution of the compound may not take place at all. Fluorides of many metals are less soluble than the corresponding chlorides, because of their higher lattice enthalpies.

Lattice Enthalpy ($\Delta_{\text{lattice}}H^\ominus$)

The lattice enthalpy of an ionic compound is the enthalpy change when one mole of an ionic compound dissociates into gaseous ions.

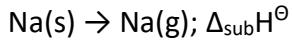
We cannot determine lattice enthalpies directly by experiment. So an indirect method called **Born-Haber Cycle** is used to calculate lattice enthalpy of a compound.

This can be explained by consider the formation of NaCl.

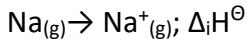


This involves the following steps:

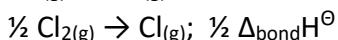
1. Conversion of solid sodium atom to gaseous sodium atom. The energy change involved in this process is called sublimation energy.



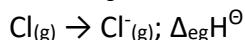
2. Conversion gaseous sodium atom to gaseous sodium ion. The energy change in this process is called ionisation enthalpy.



3. Conversion of gaseous chlorine molecule to gaseous chlorine atom. The energy change during this process is called bond dissociation enthalpy.



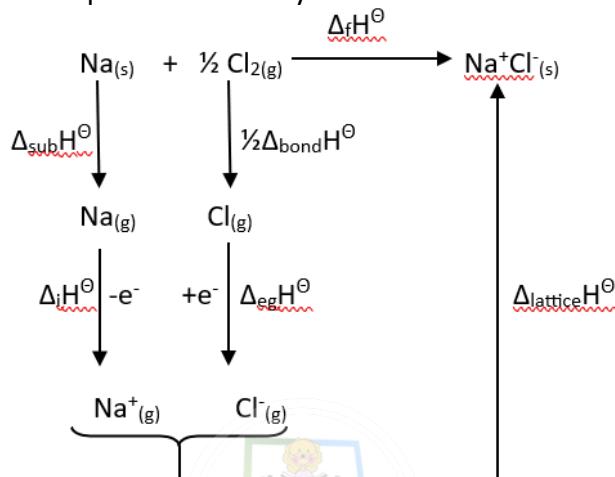
4. Conversion of chlorine atom to chloride ion. The energy change involved in this process is called electron gain enthalpy ($\Delta_{\text{eg}}H^\ominus$).



5. Packing of $\text{Na}^+_{(g)}$ and $\text{Cl}^-_{(g)}$ to form $\text{NaCl}_{(s)}$. the energy change in this process is called lattice enthalpy ($\Delta_{\text{lattice}}H^\ominus$)



The different steps can be represented in a cyclic form as follows:



By applying Hess's law we can write: $\Delta_f H^\ominus = \Delta_{\text{sub}}H^\ominus + \Delta_i H^\ominus + \frac{1}{2} \Delta_{\text{bond}}H^\ominus + \Delta_{\text{eg}}H^\ominus + \Delta_{\text{lattice}}H^\ominus$

From this lattice enthalpy can be determined as:

$$\Delta_{\text{lattice}}H^\ominus = \Delta_f H^\ominus - [\Delta_{\text{sub}}H^\ominus + \Delta_i H^\ominus + \frac{1}{2} \Delta_{\text{bond}}H^\ominus + \Delta_{\text{eg}}H^\ominus]$$

Enthalpy of Dilution ($\Delta_{\text{dil}}H^\ominus$):

It is the enthalpy change when a solution is diluted (i.e. more solvent is added to the solution. It depends on the original concentration of the solution and the amount of solvent added.

Spontaneous Process

It is a process that takes place without the help of any external agency. All natural processes are spontaneous. E.g. flow of water from high level to low level, flow of heat from hot body to cold body, inter mixing of gases, burning of fuels, melting of ice, evaporation of water etc. A spontaneous process cannot reverse its direction by its own.

Spontaneous chemical reactions are also called *feasible or probable or irreversible reactions*.



A process that takes place with the help of an external agency is called *non-spontaneous process*. E.g. flow of water from low level to high level.

Criteria for spontaneity

During spontaneous processes like burning of fuels, flow of heat from hot body to cold body, flow of water from high level to low level etc, energy of the system decreases. So **one of the criteria for spontaneity is decrease in energy**.

But for some spontaneous processes like melting of ice, evaporation of water etc, heat is absorbed. i.e. the energy of the system increases during the process. The above processes are

accompanied with increase in disorder (entropy) of the system. Thus another criterion for spontaneity is increase in disorderness or randomness of the system.

Entropy (S)

It is a measure of degree of disorderness or randomness of a system. As the disorderness increases, entropy also increases. It is an extensive property and state function.

If S_1 is the initial entropy of a system and S_2 is its final value, then the change in entropy $\Delta S = S_2 - S_1$.

For a given substance, the solid state has the least entropy and the gaseous state has the most. When temperature increases entropy also increases. The unit of entropy and entropy change is J/K/mol.

If a system absorbs 'q' amount of heat reversibly at a temperature T, then the change in entropy, $\Delta S = \frac{q_{rev}}{T}$, where q_{rev} . is the amount of heat absorbed reversibly.

Entropy and spontaneity

During a spontaneous process, disorderness of the system increases. Thus entropy increases and hence ΔS becomes positive.

The total entropy change for the system and surroundings is given by $\Delta S_{Total} = \Delta S_{syst.} + \Delta S_{surr.}$

For a spontaneous process, $\Delta S_{Total} > 0$

When a system attains equilibrium, the entropy becomes maximum and there is no further change in entropy. So $\Delta S_{Total} = 0$

If $\Delta S_{Total} < 0$, the process is non-spontaneous.

Second Law of Thermodynamics:

It can be stated as the entropy of the universe always increases during every spontaneous process.



Third law of Thermodynamics:

It states that the entropy of any perfectly crystalline substance is zero at absolute zero of temperature. By using this law, we can calculate the absolute value of entropy of pure substances from their thermodynamic data.

Gibb's energy (G)

It is defined as the maximum amount of available energy that can be converted to useful work. It is given by the equation, $G = H - TS$

It is an extensive property and a state function.

If G_1 is the initial Gibb's energy and G_2 is its final value, then the change in Gibb's energy (ΔG) = $G_2 - G_1$.
The unit of Gibb's energy is kJ/mol.

Relation between ΔG , ΔH and ΔS (Gibb's Equation)

We know that $G = H - TS$

$$\begin{aligned} \text{So, } \Delta G &= \Delta H - \Delta(TS) \\ &= \Delta H - (T\Delta S + S\Delta T) \end{aligned}$$

At constant temperature, $\Delta T = 0$.

So, $\Delta G = \Delta H - T\Delta S$. This equation is known as *Gibb's equation*.

At standard state, $\Delta G^\ominus = \Delta H^\ominus - T\Delta S^\ominus$

The change in Gibb's energy for a system can be written as

$$\Delta G_{syst.} = \Delta H_{syst.} - T\Delta S_{syst.}$$

Gibb's energy and Spontaneity

We know that $\Delta S_{\text{Total}} = \Delta S_{\text{syst.}} + \Delta S_{\text{surr.}}$ (1)

Consider a system which absorbs 'q' amount of heat reversibly at a constant temperature T and constant pressure p.

$$\text{Then, } \Delta S_{\text{surr.}} = \frac{q_p}{T}$$

But $q_p = \Delta H_{\text{surr.}}$ and $\Delta H_{\text{surr.}} = -\Delta H_{\text{syst.}}$

$$\text{So, } \Delta S_{\text{surr.}} = \frac{-\Delta H_{\text{syst.}}}{T}$$

So equation (1) becomes, $\Delta S_{\text{Total}} = \Delta S_{\text{syst.}} - \frac{\Delta H_{\text{syst.}}}{T}$

On multiplying by $-T$, we get

$$-T\Delta S_{\text{Total}} = -T\Delta S_{\text{syst.}} + \Delta H_{\text{syst.}}$$

Or, $-T\Delta S_{\text{Total}} = \Delta G_{\text{syst.}}$ (Since, $\Delta H_{\text{syst.}} - T\Delta S_{\text{syst.}} = \Delta G_{\text{syst.}}$)

For a spontaneous process, ΔS_{Total} is positive. So $\Delta G_{\text{syst.}}$ is negative. (or, $\Delta G_{\text{syst.}} < 0$)

For a non-spontaneous process, ΔS_{Total} is negative, so $\Delta G_{\text{syst.}}$ is positive. (or, $\Delta G_{\text{syst.}} > 0$)

For a process at equilibrium, $\Delta S_{\text{Total}} = 0$. So $\Delta G_{\text{syst.}} = 0$

Conditions for ΔG to be negative

We know that for a spontaneous process, $\Delta G_{\text{syst.}}$ is negative. Also $\Delta G = \Delta H - T\Delta S$.

- 1) If ΔH is negative and ΔS is +ve, ΔG is always –ve and the process is always spontaneous.
- 2) If both ΔH and ΔS are positive, ΔG will be –ve when $T\Delta S > \Delta H$. This is possible at high temperature. i.e. the process will be spontaneous at higher temperature. E.g. melting of ice.
- 3) If both ΔH and ΔS are negative, ΔG will be –ve when $T\Delta S < \Delta H$. This is possible at low temperature. i.e. the process will be spontaneous at lower temperature. E.g. Condensation of water-vapour.

Note: If ΔH is +ve and ΔS – ve, then ΔG will be always +ve and the process will be always non-spontaneous.

Gibb's energy change (ΔG) and Equilibrium constant (K)

Consider a reversible reaction: $A + B \rightleftharpoons C + D$

The Gibb's energy change of this reaction is $\Delta_r G = \Delta_r G^\ominus + RT \ln K$

At equilibrium, $\Delta_r G = 0$

So, $0 = \Delta_r G^\ominus + RT \ln K$

Or, $\Delta_r G^\ominus = -RT \ln K$

Or, $\Delta_r G^\ominus = -2.303RT \log K$

Where R is the universal gas constant and T is the absolute temperature. [R = 8.314 J K⁻¹mol⁻¹]

So for a spontaneous process, the value of K should be positive.

Q1) The equilibrium constant for a reaction is 5. What will be the value of ΔG° ? Given that R = 8.314 J K⁻¹mol⁻¹ and T = 300K.

Ans: $\Delta G^\circ = -2.303RT \log K$

$$= -2.303 \times 8.314 \times 300 \times \log 5 = -4014.58 \text{ J mol}^{-1}$$

Q2) For the reaction, $4Fe(s) + 3O_2(g) \rightarrow 2 Fe_2O_3(s)$, the entropy change is - 549.4 J K⁻¹ mol⁻¹ at 298 K. Inspite of the negative entropy change, why is the reaction spontaneous? Given $\Delta H^\circ = -1648 \text{ kJ mol}^{-1}$.

Ans: We know that $\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ}$

Here $\Delta H^{\circ} = -1648 \text{ kJ mol}^{-1} = -1648 \times 10^3 \text{ J/mol}$. $\Delta S^{\circ} = -549.4 \text{ J K mol}^{-1}$ and $T = 298 \text{ K}$

So, $\Delta G^{\circ} = -1648 \times 10^3 - 298 \times -549.4 = -1484.28 \times 10^3 \text{ J mol}^{-1} = -1484.28 \text{ kJ mol}^{-1}$

Q3) Calculate the work done for the reversible isothermal expansion of 1 mole of an ideal gas at 27°C , from a volume of 10 dm^3 to a volume of 20 dm^3 .

Ans: Here $n = 1 \text{ mol}$, $R = 8.314 \text{ J/K/mol}$, $V_1 = 10 \text{ dm}^3$, $V_2 = 20 \text{ dm}^3$ and $T = 25 + 273 = 298 \text{ K}$

For isothermal reversible expansion, work done, $w_{exp} = -2.303nRT \log \frac{V_2}{V_1}$

$$= -2.303 \times 1 \times 8.314 \times 298 \times \log \frac{20}{10}$$

$$= -1717.46 \text{ J}$$

Q4) Find the temperature above which the reaction $\text{MgO}_{(s)} + \text{C}_{(s)} \rightarrow \text{Mg}_{(s)} + \text{CO}_{(g)}$ becomes spontaneous. (Given $\Delta_rH^{\circ} = 490 \text{ kJ mol}^{-1}$ and $\Delta_rS^{\circ} = 198 \text{ JKmol}^{-1}$).

Ans: At equilibrium, $\Delta_rG^{\circ} = 0$

So the Gibbs's equation, $\Delta_rG^{\circ} = \Delta_rH^{\circ} - T\Delta_rS^{\circ}$ becomes:

$$0 = \Delta_rH^{\circ} - T\Delta_rS^{\circ}$$

$$\text{Or, } \Delta_rH^{\circ} = T\Delta_rS^{\circ}$$

$$\text{So, } T = \Delta_rH^{\circ}/\Delta_rS^{\circ} = 490 \times 10^3 / 198 = 2474.74 \text{ K}$$

So at 2474.74 K , the reaction is at equilibrium.

Above this temperature, the reaction becomes spontaneous. [Here both Δ_rH° and Δ_rS° are +ve. So Δ_rG° becomes -ve only when $T\Delta_rS^{\circ} > \Delta_rH^{\circ}$. This is possible at high temperature.]

Q5) The enthalpy of combustion of $\text{CH}_{4(g)}$, $\text{C}_{(\text{graphite})}$ and $\text{H}_{2(g)}$ at 298 K are $-890.3 \text{ kJ mol}^{-1}$, $-393.5 \text{ kJ mol}^{-1}$ and $-285.8 \text{ kJ mol}^{-1}$ respectively. Calculate the enthalpy of formation of $\text{CH}_{4(g)}$.



Ans: The required equation is: $\text{C}_{(\text{graphite})} + 2\text{H}_{2(g)} \rightarrow \text{CH}_{4(g)}$

The given data are: $\text{CH}_{4(g)} + 2\text{O}_{2(g)} \rightarrow \text{CO}_{2(g)} + 2\text{H}_2\text{O}_{(l)}$; $\Delta H = -890.3 \text{ kJ/mol}$ (i)

$\text{C}_{(\text{graphite})} + \text{O}_{2(g)} \rightarrow \text{CO}_{2(g)}$; $\Delta H = -393.5 \text{ kJ/mol}$ (ii)

$\text{H}_{2(g)} + \frac{1}{2}\text{O}_{2(g)} \rightarrow \text{H}_2\text{O}_{(l)}$; $\Delta H = -285.8 \text{ kJ/mol}$ (iii)

Multiply equation (iii) x 2: $2\text{H}_{2(g)} + \text{O}_{2(g)} \rightarrow 2\text{H}_2\text{O}_{(l)}$; $\Delta H = -285.8 \times 2 = -571.6 \text{ kJ/mol}$ (iv)

Reverse equation (i): $\text{CO}_{2(g)} + 2\text{H}_2\text{O}_{(l)} \rightarrow \text{CH}_{4(g)} + 2\text{O}_{2(g)}$; $\Delta H = 890.3 \text{ kJ/mol}$ (v)

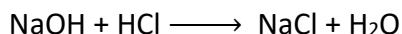
Now add the equations (ii) + (iv) + (v) we get $\text{C}_{(\text{graphite})} + 2\text{H}_{2(g)} \rightarrow \text{CH}_{4(g)}$; $\Delta H = -393.5 + -571.6 + 890.3 = -74.8 \text{ kJ/mol}$

6. EQUILIBRIUM

Reversible and irreversible reactions

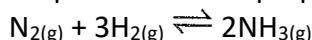
A reaction that takes place in only one direction is called an **irreversible reaction**.

e.g. Reaction between NaOH and HCl



Reversible reactions are those which take place in both directions. i.e. here reactants combined to form products and the products recombine to form reactants.

E.g. Haber process for the preparation of ammonia.



The process by which reactants are converted to products is called **forward reaction** and the process by which products recombine to form reactants is called **backward reaction**. After sometimes, the rate of forward reaction becomes equal to the rate of backward reaction and the reaction attains equilibrium. Thus *equilibrium is a state in which the rates of forward and backward reactions are equal*.

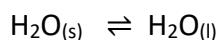
Equilibrium is dynamic in nature. i.e. at equilibrium the reaction does not stop. The reactant molecules collide to form products and the product molecules collide to form the reactants and the rates of these reactions are equal.

Physical equilibrium

Equilibrium involving physical process is called physical equilibrium. E.g. melting of ice, evaporation of water, sublimation, dissolution of solids or gases in liquids etc.

1. Solid-Liquid Equilibrium

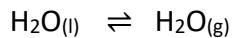
When ice and water are kept in a perfectly insulated thermos flask at 273K and 1 atm pressure, there exist an equilibrium between ice and water. i.e. ice is converted to water (melting or fusion) and water is converted to ice (freezing) at the same rate. At this stage, there is no change in the mass of ice and water.



Ice and water are in equilibrium only at particular temperature and pressure. For any pure substance at atmospheric pressure, the temperature at which the solid and liquid phases are at equilibrium is called **the normal melting point or normal freezing point** of the substance.

2. Liquid-Vapour Equilibrium

Water and water vapour are in equilibrium position at atmospheric pressure (1.013 bar) and at 100°C in a closed vessel. At this stage, the conversion of water to water-vapour [evaporation] and the reverse process [condensation] takes place in equal rates.



For any pure liquid, the temperature at which the liquid and vapours are at equilibrium at one atmospheric pressure (1.013 bar), is called **normal boiling point of the liquid**. The normal boiling point of water is 100°C.

Boiling point of the liquid depends on the atmospheric pressure. It also depends on the altitude of the place. At high altitude the boiling point decreases.

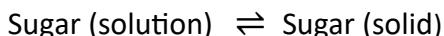
3. Solid – Vapour Equilibrium

If we place solid iodine in a closed vessel, after sometimes the vessel gets filled up with violet vapour and the intensity of colour increases with time. After certain time the intensity of colour becomes constant and at this stage, equilibrium is attained. $\text{I}_{2(\text{solid})} \rightleftharpoons \text{I}_{2(\text{vapour})}$

4. Dissolution of Solid in Liquids

Consider the dissolution of sugar in a fixed amount of water. When we add sugar into water, at first, we can dissolve more amount of sugar, since the solution is unsaturated. But after sometime, the

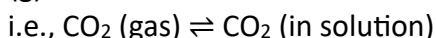
rate of dissolution of sugar decreases and rate of its crystallisation increases. i.e. the sugar molecules in the solution separate out as solid sugar. At equilibrium state, the rate of dissolution becomes equal to the rate of crystallisation. At this stage, the solution is called saturated solution. It is a solution in which no more solute can be dissolved at a given temperature. The concentration of the solute in a saturated solution depends upon the temperature.



5. Dissolution of Gases in Liquids

The solubility of a gas in a liquid depends on nature of the gas, pressure of the gas and temperature. When pressure of the gas increases, its solubility also increases. A quantitative relation between pressure and solubility was proposed by Henry and is known as **Henry's law**. The law states that the mass of a gas dissolved in a given mass of a solvent is proportional to the pressure of the gas above the solvent, at a constant temperature.

In soda water, CO_2 gas is dissolved in water at high pressure. There is an equilibrium between the $\text{CO}_2(\text{g})$ in the solution and that in the free state above the solution.



When the bottle is opened, some of the dissolved carbon dioxide gas, escapes out with a fizzing sound and a new equilibrium at low pressure is attained.

The solubility of a gas in a liquid decreases with increase in temperature.

General Characteristics of Physical Equilibrium

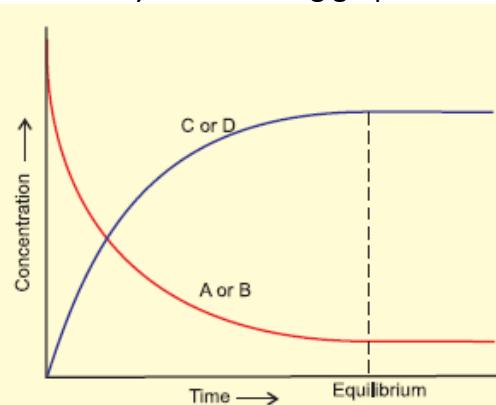
- (i) Equilibrium is possible only in a closed system at a given temperature.
- (ii) Both the opposing processes (forward and backward processes) occur at the same rate and there is a dynamic but stable condition.
- (iii) All measurable properties of the system remain constant at equilibrium.
- (iv) When equilibrium is attained for a physical process, it is characterised by constant value of one of its parameters at a given temperature.
- (v) The magnitude of such quantities at any stage indicates the extent to which the physical process has proceeded before reaching equilibrium.

Chemical Equilibrium

Equilibrium associated with chemical reactions is called chemical equilibrium. At equilibrium, the concentrations of reactants and products are constant.

Consider a hypothetical reaction, $\text{A} + \text{B} \rightleftharpoons \text{C} + \text{D}$

As the reaction proceeds, the concentration of the reactants decreases and that of the products increases. After sometimes, the two reactions occur at the same rates and an equilibrium state is reached. This can be illustrated by the following graph.

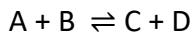


After the equilibrium is attained, the concentration of the reactants and products become constant. At equilibrium, the rate of forward reaction (r_f) = the rate of backward reaction (r_b).

Law of Chemical Equilibrium and Equilibrium Constant

This law was proposed by Guldberg and Waage. It states that *at constant temperature, the ratio of the product of concentration of the products to that of the reactants, in which each concentration terms is raised to a power which is equal to the stoichiometric coefficients in the balanced chemical equation, has a constant value.*

For a general reversible reaction:



According to the equilibrium law, $\frac{[C][D]}{[A][B]} = K_c$

Where K_c is called the equilibrium constant.

For a general reaction, $aA + bB \rightleftharpoons cC + dD$,

$$K_c = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

For the reaction $H_2 + I_2 \rightleftharpoons 2HI$; $K_c = \frac{[HI]^2}{[H_2][I_2]}$

For the reaction $N_2 + 3H_2 \rightleftharpoons 2NH_3$; $K_c = \frac{[NH_3]^2}{[N_2][H_2]^3}$

Equilibrium constant for the reverse reaction is the inverse of that for the forward reaction.

i.e. if the equilibrium constant for the reaction: $H_2 + I_2 \rightleftharpoons 2HI$ is K_c ,

then that for the reverse reaction: $2HI \rightleftharpoons H_2 + I_2$ is $\frac{1}{K_c}$.

Equilibrium constant for gaseous reactions

For a reaction involving gases, the concentration terms are replaced by partial pressures.

For example, $H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)}$; $K_p = \frac{p_{HI}^2}{p_{H_2} p_{I_2}}$

Where K_p is called equilibrium constant in terms of partial pressure, p_{HI} , p_{H_2} and p_{I_2} are the partial pressures of HI, H₂ and I₂ respectively.

Relation between K_c and K_p

Consider a general reaction, $aA + bB \rightleftharpoons cC + dD$

The equilibrium constant in terms of concentration for this reaction is $K_c = \frac{[C]^c[D]^d}{[A]^a[B]^b}$ (1)

And the equilibrium constant in terms of partial pressures is $K_p = \frac{p_C^c p_D^d}{p_A^a p_B^b}$ (2)

From ideal gas equation, $pV = nRT$, $p = \frac{nRT}{V} = CRT$ (since $n/V = C$, the concentration)

Therefore, $p_A = C_A RT$, $p_B = C_B RT$, $p_C = C_C RT$ and $p_D = C_D RT$

Substitute these values in equation (2), we get

$$K_p = \frac{(C_C RT)^c (C_D RT)^d}{(C_A RT)^a (C_B RT)^b}$$

$$\text{Or, } K_p = \frac{C_C^c C_D^d}{C_A^a C_B^b} \frac{(RT)^{c+d}}{(RT)^{a+b}}$$

$$\text{Or, } K_p = \frac{C_C^c C_D^d}{C_A^a C_B^b} (RT)^{(c+d)-(a+b)}$$

$$\text{Or, } K_p = K_c \cdot (RT)^{\Delta n}, \text{ where } K_c = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

And Δn is the change in no. of moles of gaseous species.

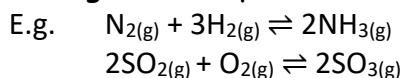
i.e. $\Delta n = \text{no. of moles of gaseous products} - \text{no. of moles of gaseous reactants}$.

Special cases:

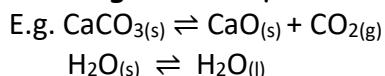
- i) If $\Delta n = 0$, then $K_p = K_c$
- ii) If $\Delta n > 0$, then $K_p > K_c$ and
- iii) If $\Delta n < 0$, then $K_p < K_c$

Homogeneous and heterogeneous equilibria

Equilibrium reaction in which all the reactants and products are in the same phase is called homogeneous equilibrium.



Equilibrium reaction in which the reactants and products are in different phases is called heterogeneous equilibrium.



Characteristics of Equilibrium constant

The important characteristics of equilibrium constant are:

1. Equilibrium constant is applicable only when the concentrations of the reactants and products have attained their equilibrium state.
2. The value of equilibrium constant is independent of the initial concentrations of reactants and products.
3. The value of equilibrium constant depends on temperature.
4. The equilibrium constant for the reverse reaction is the reciprocal of that of the forward reaction.
5. If for the reaction $A \rightleftharpoons B$, the value of equilibrium constant is K_c , then for the reaction $nA \rightleftharpoons nB$, its value is K_c^n .

Applications of Equilibrium constant

The important applications of equilibrium constant are:

1. Prediction of the extent of a reaction

- Greater the value of equilibrium constant, greater will be the concentration of products. In general,
- a) If $K_c > 10^3$ (i.e. K_c is very large), the reaction proceeds nearly to completion.
 - b) If $K_c < 10^{-3}$ (i.e. if K_c is very small), the reaction proceeds rarely.
 - c) If the value of K_c is in between 10^3 and 10^{-3} appreciable concentrations of both reactants and products are present at equilibrium.

2. Prediction of the direction of a reaction

By knowing the values of K_c and Q_c , we can predict the direction of a reaction. The reaction quotient (Q_c) is defined in the same way as the equilibrium constant (K_c) except that the concentrations in Q_c are not necessarily the equilibrium values.

For a general reaction, $aA + bB \rightleftharpoons cC + dD$, the reaction quotient, $Q_c = \frac{[C]^c[D]^d}{[A]^a[B]^b}$

If $Q_c > K_c$, the reaction will proceed in the direction of reactants (reverse direction).

If $Q_c < K_c$, the reaction will proceed in the direction of products (forward direction).

If $Q_c = K_c$, the reaction mixture is at equilibrium.

3. Calculation of equilibrium concentrations

By knowing the value of equilibrium constant, we can calculate the equilibrium concentrations of reactants and products.

RELATIONSHIP BETWEEN EQUILIBRIUM CONSTANT (K_c), REACTION QUOTIENT (Q_c) AND GIBBS ENERGY CHANGE (ΔG)

The Gibb's energy change of a reaction is related to the reaction quotient (Q_c) by the equation:

$$\Delta G = \Delta G^\ominus + RT \ln Q_c$$

where, ΔG^\ominus is standard Gibbs energy change.

At equilibrium, $\Delta G = 0$ and $Q_c = K_c$, so the equation becomes,

$$0 = \Delta G^\ominus + RT \ln K_c$$

$$\text{Or, } \Delta G^\ominus = -RT \ln K_c$$

On changing the base, we get $\Delta G^\ominus = -2.303RT \log K_c$

We know that for a spontaneous process ΔG should be negative. So the value of K_c should be positive.

Factors affecting equilibrium

The important factors affecting equilibrium are temperature, pressure, concentration and catalyst.

The effect of these factors on equilibrium state can be explained by using **Le Chatier's Principle**.

It states that whenever there is a change in concentration, pressure or temperature of a system at equilibrium, the system will try to readjust in such a way so as to cancel the effect of that change.

1. Effect of concentration change

If we change the concentration of reactants or products in an equilibrium process, then according to Le Chatelier's principle, the system will try to reduce the effect of that change. For this the rate of either forward or backward reaction changes.

In general, an increase in concentration of reactants increases the rate of forward reaction (i.e. the equilibrium is shifted to the products side) and an increase in concentration of products increase the rate of backward reaction (i.e. the equilibrium is shifted to the reactants side).

For example in the reaction $2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)}$, if we increase the concentration of SO_2 or O_2 , the system will try to reduce the concentration by shifting the equilibrium to the forward direction. If we remove SO_3 from the reaction mixture, its concentration decreases. To increase the concentration, the equilibrium is shifted to the forward direction.

In Haber process for the preparation of ammonia, the amount of ammonia formed can be increased by increasing the concentration of N_2 or H_2 or by removing NH_3 from the reaction mixture.

2. Effect of temperature change

According to Le Chatelier's principle, increase in temperature favours endothermic process and decrease in temperature favours exothermic process. In a reversible reaction, if the forward reaction is endothermic, the backward reaction will be exothermic.

E.g.: $N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2 NH_{3(g)}$; $\Delta H = -92.38 \text{ kJ/mol}$

Here since ΔH is negative, the forward reaction is exothermic. So to increase the production of NH_3 , temperature should decrease. At higher temperature, the rate of backward reaction increases. i.e. the ammonia formed is decomposed to N_2 and H_2 .

3. Effect of pressure change

Pressure has its effect only in gaseous reactions. In general, an increase in pressure favours the reaction in which number of moles decreases and vice versa.

Thus in the reaction, $N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2 NH_{3(g)}$, when the pressure increases, the system will try to reduce the pressure. This can be achieved by shifting the reaction into the direction in which no. of moles decreases (since pressure is directly proportional to the number of moles). So in this reaction, the equilibrium will shift to the forward direction.

If the volume of the reaction mixture is halved, the concentration and the partial pressure become doubled. So the reaction is shifted to the direction in which the number of moles or volume decreases.

4. Effect of catalyst

A catalyst is a substance that increases the rate or speed of a chemical reaction.

In an equilibrium reaction, a catalyst increases the rate of both forward and backward reactions simultaneously and helps to attain the equilibrium faster. It lowers the activation energy for the forward and backward reactions by exactly the same amount. It does not affect the equilibrium composition of the reaction mixture.

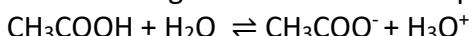
Thus in Haber process for the manufacture of ammonia, spongy iron (Fe) acts as the catalyst. In contact process for the manufacture of sulphuric acid, V_2O_5 (Vanadium pentoxide) is used as the catalyst.

5. Effect of inert gas addition

If an inert gas (which does not take part in the reaction) is added to an equilibrium mixture at constant volume (or, at constant pressure), there is no change to the equilibrium. It is because the addition of inert gas at constant volume (or, at constant pressure) does not change the partial pressure or the concentration of the reactants and the products.

Ionic equilibrium in solution

Equilibrium involving ions is called ionic equilibrium. E.g. dissociation of acetic acid in water.



Electrolytes and non-electrolytes

Based on the ability to conduct electricity, Michael Faraday divided substances into two – electrolytes and non-electrolytes.

Electrolytes are substances which conduct electricity in molten state or in solution state.

E.g. All acids, bases and almost all salts

Non-electrolytes are substances which do not conduct electricity in molten state or in solution state.

E.g. sugar, urea etc.

Electrolytes are further classified into two - strong electrolytes and weak electrolytes.

Strong electrolytes are electrolytes which dissociate almost completely in aqueous solution.

E.g. strong acids like HCl , HNO_3 , H_2SO_4 etc., strong bases like $NaOH$, KOH etc. and salts like $NaCl$, KCl , Na_2SO_4 , K_2SO_4 , KNO_3 , $NaNO_3$ etc.

Electrolytes which dissociate only partially in aqueous solution are called *weak electrolytes*. E.g. weak acids like acetic acid [CH_3COOH], formic acid [$HCOOH$] etc., weak bases like $Mg(OH)_2$, $Ca(OH)_2$, NH_4OH etc. and some salts like $CaSO_4$, $BaSO_4$ etc.

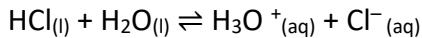
A weak electrolyte dissociates only partially in aqueous solution and so an equilibrium is formed between the ions and the unionised molecules. This type of equilibrium, which involve ions in aqueous solution is called ionic equilibrium.

Acids, Bases and Salts

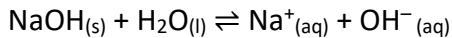
Acid – base concepts:

1. **Arrhenius concept:** According to this concept, acids are substances which give hydrogen ion (H^+) or hydronium ion (H_3O^+) in aqueous solution and bases are substances which give hydroxyl ion (OH^-) in aqueous solution.

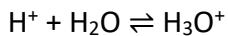
E.g. HCl is an acid since it produces H_3O^+ in aqueous solution.



E.g. for base is $NaOH$



Note: H^+ ions exist in water as hydronium ions (H_3O^+)



Limitations: This concept is applicable only to aqueous solutions.

2. The Bronsted – Lowry concept:

According to this concept acids are proton (H^+) donors and bases are (H^+) acceptors.

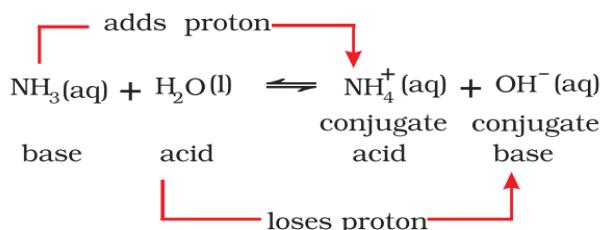
For example in the reaction $NH_3(l) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$

Here NH_3 is a base since it accepts an H^+ ion to form NH_4^+ and H_2O is an acid since it donates an H^+ ion to form OH^- . In the reverse reaction, NH_4^+ is an acid and OH^- is a base.

The acid-base pair that differs by only one proton is called a conjugate acid–base pair.

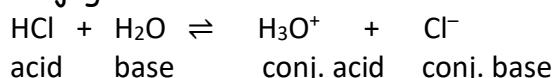
An acid formed from a base is called conjugate acid and a base formed from an acid is called conjugate base.

For example



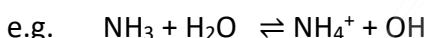
In general, Conjugate base = Acid - H^+

Conjugate acid = Base + H^+

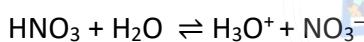


If the acid is strong, its conjugate base is weak and vice versa. So in the above example Cl^- is a weak conjugate base of the strong acid HCl.

Water can act both as acid and base. So it is an amphoteric substance.



acid



base



3. Lewis concept:

According to this concept acids are electron pair acceptors and bases are electron pair donors. Substances which donate electron pair are called Lewis bases and substances which accept electron pair are called Lewis acids.

Example for Lewis acids are BF_3 , $AlCl_3$, H^+ , Co^{3+} , Mg^{2+} etc.

Example for Lewis bases are NH_3 , H_2O , OH^- , Cl^- , Br^- etc.

For a substance to act as Lewis acid, it should contain vacant orbitals and for a substance to act as Lewis base, it should contain lone pairs of electrons.

E.g. for acid – base reaction is $BF_3 + :NH_3 \longrightarrow BF_3\leftarrow :NH_3$

All cations are Lewis acids and all anions are Lewis bases.

The ionization constant of water (The ionic product of water)

Water is a weak electrolyte and hence it ionizes only partially as:



$$\text{The dissociation constant, } K = \frac{[H^+][OH^-]}{[H_2O]} \quad \text{Or, } K = \frac{[H_3O^+][OH^-]}{[H_2O]^2}$$

$$\text{Or, } K \cdot [H_2O] = [H^+][OH^-] \quad \text{Or, } K \cdot [H_2O]^2 = [H_3O^+][OH^-]$$

$$\text{Or, } K_w = [H^+][OH^-] \quad \text{Or, } K_w = [H_3O^+][OH^-]$$

Where K_w is called the ionization constant of water or ionic product of water. It is defined as the product of the molar concentration of hydrogen ion (hydronium ion) and hydroxyl ion in water or in any aqueous solution.

For pure water at 298K, $[H^+] = [OH^-] = 10^{-7} M$.

$$\text{Therefore, } K_w = [H^+][OH^-] = 10^{-7} \times 10^{-7} = 10^{-14} M^2$$

The value of K_w is temperature dependent.

By knowing the concentrations of H_3O^+ and OH^- ions, we can predict the nature of an aqueous solution.

If $[H_3O^+] > [OH^-]$, the solution is acidic

If $[H_3O^+] < [OH^-]$, the solution is basic

If $[H_3O^+] = [OH^-]$, the solution is neutral

The p^H scale

p^H is defined as the negative logarithm of the hydrogen ion or hydronium ion concentration in moles per litre (i.e. molarity).

$$\text{i.e. } p^H = -\log[H^+] \text{ or } p^H = -\log[H_3O^+]$$

Negative logarithm of hydroxyl ion concentration in mol/L is called p^{OH} .

$$\text{i.e. } p^{OH} = -\log[OH^-]$$

For pure water, at 298K ($25^\circ C$), $[H^+] = 10^{-7}$. Therefore p^H of pure water is 7.

The p^H scale was introduced by Sorenson. It contains numbers from 0 to 14. If the p^H is less than 7, the solution is acidic, if it is greater than 7, it is basic and if it is 7, the solution is neutral.

If the p^H is 0, 1, 2 etc., the solution is a strongly acidic and if it is 12, 13, 14 etc., it is strongly basic. The p^H of our blood is 7.4 and that of our saliva is 6.4. So blood is slightly basic and saliva is slightly acidic.

Relation between p^H and p^{OH}

$$\text{We know that } K_w = [H^+][OH^-] = 10^{-14} \text{ at } 298K$$

Taking negative logarithm on both sides:

$$-\log K_w = -\log[H^+] + -\log[OH^-] = -\log 10^{-14}$$

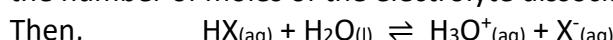
$$\text{Or, } p^{Kw} = p^H + p^{OH} = 14$$

Thus by knowing the p^H , we can calculate p^{OH} as $p^{OH} = 14 - p^H$

Ionisation constant of weak acids (K_a)

Consider a weak acid HX, which ionizes only partially as: $HX + H_2O \rightleftharpoons H_3O^+ + X^-$

Let 'c' be the initial concentration of HX and 'α' is the degree (extent) of dissociation. (It is the ratio of the number of moles of the electrolyte dissociated to the total number of moles).



$$\begin{array}{ccc} \text{Initial concn.} & c & 0 & 0 \\ \text{Eqm. concn.} & c(1-\alpha) & \alpha & \alpha \end{array}$$

$$\text{The dissociation constant, } K_a = \frac{[H_3O^+][X^-]}{[HX]}$$

Where K_a is the dissociation constant of the weak acid.

$$\text{Or, } K_a = \frac{c\alpha \cdot c\alpha}{c(1-\alpha)} = \frac{c\alpha^2}{1-\alpha}$$

Larger the value of K_a , stronger is the acid. The negative logarithm of K_a is called p^{K_a} .

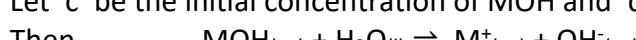
$$\text{i.e. } p^{K_a} = -\log K_a$$

Greater the value of K_a , smaller will be the value of p^{K_a} and stronger will be the acid.

Ionisation constant of weak bases (K_b)

Consider a weak base MOH, which ionizes partially as: $MOH \rightleftharpoons M^+ + OH^-$

Let 'c' be the initial concentration of MOH and 'α' is the degree of dissociation.



$$\begin{array}{ccc} \text{Initial concn.} & c & 0 & 0 \\ \text{Eqm. concn.} & c(1-\alpha) & \alpha & \alpha \end{array}$$

$$\begin{array}{ccc} & & \\ & & \end{array}$$

The dissociation constant of weak base, $K_b = \frac{[M^+][OH^-]}{[MOH]}$

$$\text{Or, } K_b = \frac{c\alpha \cdot c\alpha}{c(1-\alpha)} = \frac{c\alpha^2}{1-\alpha}$$

The negative logarithm of K_b is called p^{K_b} .

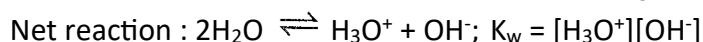
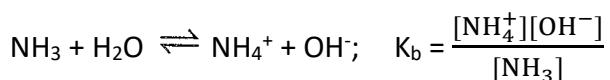
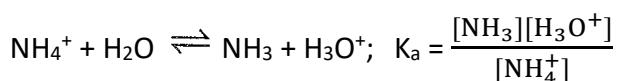
$$\text{i.e. } p^{K_b} = -\log K_b.$$

As the value of K_b increases, p^{K_b} decreases and the basic strength increases.

Relation between K_a , K_b and K_w

For conjugate acid – base pair K_a and K_b are related as: $K_a \times K_b = K_w$

This can be deduced as follows:



$$K_a \times K_b = \frac{[\text{NH}_3][\text{H}_3\text{O}^+]}{[\text{NH}_4^+]} \times \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]} = [\text{H}_3\text{O}^+][\text{OH}^-] = K_w$$

$$\text{i.e. } K_a \times K_b = K_w = 10^{-14}$$

$$\text{or, } p^{K_a} + p^{K_b} = p^{K_w} = 14$$

Factors Affecting Acid Strength

The extent of dissociation of an acid and its acidic strength depend on the strength and polarity of the H-A bond. Weaker the H-A bond, more easily it dissociates to give H^+ ion and hence stronger is the acid. Also, greater the polarity of the H – A bond (when the electronegativity difference between the atoms H and A increases) the more easily it dissociates and hence greater is the acidity.

In a group, acidity is mainly determined by bond strength. From top to bottom in a group, as the size of A increases, H-A bond strength decreases and so the acid strength increases. Thus acidic strength of hydrohalic acids increases in the order: $\text{HF} < \text{HCl} < \text{HBr} < \text{HI}$.

In a period, acidity is mainly determined by polarity of the bond. As the electronegativity of A increases from left to right in a period, the strength of the acid also increases. So the acidity of hydrides of second period elements increases in the order: $\text{CH}_4 < \text{NH}_3 < \text{H}_2\text{O} < \text{HF}$.

Hydrolysis of Salts and the p^H of their Solutions

The interaction of anion or cation or both of a salt with water is known as salt hydrolysis. The cations (e.g., Na^+ , K^+ , Ca^{2+} , Ba^{2+} , etc.) of strong bases and anions (e.g., Cl^- , Br^- , NO_3^- , ClO_4^- etc.) of strong acids do not get hydrolysed. So the solutions of salts formed from strong acids and bases (e.g. NaCl , KCl , NaNO_3 , KNO_3 , Na_2SO_4 , K_2SO_4 etc.) are neutral. i.e., their p^H is 7.

- Hydrolysis of salt of strong base and weak acid:** Sodium acetate (CH_3COONa), sodium carbonate (Na_2CO_3), potassium cyanide (KCN) etc. are examples for such type of salts. Here only the anion of the weak acid undergoes hydrolysis (since cation of the strong base does not hydrolyse). So the solution of such salts will be basic. i.e. $p^H > 7$.

p^H of such salt solution is given by $p^H = 7 + \frac{1}{2} (\text{p}K_a + \log C)$ where C is the concentration of salt.

- Hydrolysis of salt of weak base and strong acid:** NH_4Cl , NH_4NO_3 , CuSO_4 etc. are examples for such type of solutions. Here only cation of weak base undergoes hydrolysis. So the solution is acidic. p^H of such a solution is given by $p^H = 7 - \frac{1}{2} (\text{p}K_b + \log C)$.

3. Hydrolysis of salt of weak base and weak acid: Ammonium acetate ($\text{CH}_3\text{COONH}_4$), ammonium carbonate ($(\text{NH}_4)_2\text{CO}_3$) etc. are examples for such type of salts. Here both cation and anion undergo hydrolysis and hence weak acid and weak base are produced in solution. So the solution may be neutral, acidic or basic depending upon the relative strength of acid and base formed. pH of such a solution is given by $\text{pH} = 7 + \frac{1}{2} (\text{pK}_a - \text{pK}_b)$.

Common Ion Effect

It is the suppression of the dissociation of a weak electrolyte by the addition of a strong electrolyte containing a common ion.

For e.g. consider the dissociation of acetic acid (a weak electrolyte).



If we add some sodium acetate (CH_3COONa) to the above equilibrium reaction, the concentration of acetate ion increases. Then according to Le-Chatelier's principle, the equilibrium will be shifted towards left or, the rate of forward reaction decreases. i.e. the dissociation rate of acetic acid decreases. This is known as common ion effect.

Another example is the dissociation of the weak base ammonium hydroxide (NH_4OH)



If we add some NH_4Cl to the above equilibrium process, the concentration of NH_4^+ increases and hence the equilibrium is shifted to the left. i.e. the dissociation rate of NH_4OH decreases.

Buffer Solutions

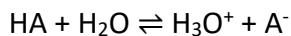
Solution which resists the change in pH on dilution or with the addition of small amount of acid or alkali is called Buffer solution. There are two types of buffer solutions – acidic buffer and basic buffer.

Acidic buffer is a mixture of a weak acid and its salt with a strong base. E.g. a mixture of acetic acid and sodium acetate acts as an acidic buffer around pH 4.75.

Basic buffer is a mixture of a weak base and its salt with a strong acid. E.g. a mixture of NH_4OH and NH_4Cl acts as a basic buffer around pH 9.25.

pH of a Buffer solution – Henderson - Hasselbalch Equation

Consider an acidic buffer prepared by mixing a weak acid HA and its conjugate base A^- . The weak acid HA ionises in water as:



The dissociation constant of weak acid, $K_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]}$

Taking $-\text{ve}$ logarithm on both sides:

$$-\log K_a = -\log[\text{H}_3\text{O}^+] + -\log[\text{A}^-] - -\log[\text{HA}]$$

$$\text{Or, } -\log[\text{H}_3\text{O}^+] = -\log K_a + \log[\text{A}^-] - \log[\text{HA}]$$

$$\text{Or, } \text{pH} = \text{p}K_a + \log \frac{[\text{A}^-]}{[\text{HA}]}$$

This equation is known as **Henderson-Hasselbalch equation**.

The equation can be written in general form as: $\text{pH} = \text{p}K_a + \log \frac{[\text{Salt}]}{[\text{Acid}]}$

For a basic buffer, $\text{pOH} = \text{p}K_b + \log \frac{[\text{Salt}]}{[\text{Base}]}$

or, $\text{pH} = 14 - \left[\text{p}K_b + \log \frac{[\text{Salt}]}{[\text{Base}]} \right]$

Solubility Equilibrium

The solubility of a salt in solvent mainly depends on the lattice enthalpy and solvation enthalpy. As a general rule, for a salt to be able to dissolve in a particular solvent its solvation enthalpy must be greater than its lattice enthalpy.

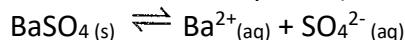
Each salt has its characteristic solubility which depends on temperature. We can classify salts on the basis of their solubility in the following three categories.

Category I	Soluble	Solubility > 0.1M
Category II	Slightly Soluble	Solubility in between 0.01M and 0.1M
Category III	Sparingly Soluble	Solubility < 0.01M

Solubility Product Constant

Consider the dissociation of a sparingly soluble salt in water. Since it dissolves only partially, there exists an equilibrium between the undissolved solid and the ions.

e.g. Solution of barium sulphate (BaSO_4)



$$\text{The equilibrium constant, } K = \frac{[\text{Ba}^{2+}][\text{SO}_4^{2-}]}{[\text{BaSO}_4]}$$

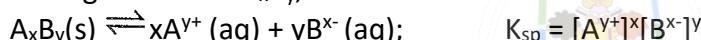
For a pure solid, the concentration remains constant.

$$\text{Therefore, } K \cdot [\text{BaSO}_4] = [\text{Ba}^{2+}][\text{SO}_4^{2-}] \quad \text{Or, } K_{sp} = [\text{Ba}^{2+}][\text{SO}_4^{2-}]$$

Where K_{sp} is called the *solubility product constant* or simply the *solubility product*. It is defined as the product of the molar concentration of ions of a sparingly soluble salt or in a saturated solution.

If S is the molar solubility of BaSO_4 , then $K_{sp} = S \times S = S^2$

For a general salt A_xB_y , its dissociation can be denoted as:



If the concentration in the above equation is not the equilibrium concentration, then K_{sp} is given by Q_{sp} .

At equilibrium, $K_{sp} = Q_{sp}$.

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If $K_{sp} > Q_{sp}$, the dissolution process occurs and if $K_{sp} < Q_{sp}$, the precipitation of the salt occurs.

Solubility product and common ion effect found application in the purification of NaCl . If we take a saturated solution of NaCl and pass HCl gas through it, then NaCl gets precipitated due to the increased concentration of Cl^- ions. NaCl thus obtained has very high purity.

Q1) If the concentration of hydrogen ion in a soft drink is $3 \times 10^{-3} \text{ M}$, calculate its pH.

Ans: Here $[\text{H}^+] = 3 \times 10^{-3}$

We know that $pH = -\log[\text{H}^+]$

$$= -\log(3 \times 10^{-3}) = 2.523$$

Q2) Calculate the solubility (S) of CaSO_4 at 298 K , if its solubility product constant (K_{sp}) at this temperature is 9×10^{-6} .

Ans: $\text{CaSO}_4(s) \rightleftharpoons \text{Ca}^{2+}(aq) + \text{SO}_4^{2-}(aq)$

$$K_{sp} = S^2. \text{ Here } K_{sp} = 9 \times 10^{-6}$$

$$\text{So, } S = \sqrt{K_{sp}} = \sqrt{(9 \times 10^{-6})} = 3 \times 10^{-3} \text{ M}$$

Q3) Find the value of K_c for the following equilibrium if the value of K_p is $1.8 \times 10^{-2} \text{ atm}$ at 600 K . ($R = 0.0821 \text{ L atm K}^{-1}\text{mol}^{-1}$): $2\text{NOCl}_{(g)} \rightleftharpoons 2\text{NO}_{(g)} + \text{Cl}_{2(g)}$

Ans: Here $K_p = 1.8 \times 10^{-2}$, $R = 0.0821 \text{ atm/K/mol}$

$$\Delta n = n_{P(g)} - n_{R(g)} = 3 - 2 = 1 \text{ and } T = 600 \text{ K}$$

$$K_p = K_c (RT)^{\Delta n}$$

$$1.8 \times 10^{-2} = K_c (0.0821 \times 600)^1$$

$$K_c = \frac{1.8 \times 10^2}{0.0821 \times 600} = 3.65 \times 10^{-4}$$

Q4) Calculate the pH of a 0.01 M acetic acid solution with the degree of ionization 0.045 .

Ans: Degree of ionisation, $\alpha = 0.045$

$$[H_3O^+] = c\alpha = 0.01 \times 0.045 = 4.5 \times 10^{-4}$$

$$pH = -\log[H_3O^+] = -\log(4.5 \times 10^{-4}) = 3.3468$$

Q5) Calculate the pH of an acidic buffer containing 0.1 M CH_3COOH and 0.5 M CH_3COONa . [K_a for CH_3COOH is 1.8×10^{-5}].

Ans: For an acidic buffer Henderson - Hasselbalch equation, $pH = pK_a + \log \frac{[\text{salt}]}{[\text{acid}]}$

$$\text{Here } [\text{acid}] = 0.1\text{M}, [\text{salt}] = 0.5\text{M} \text{ and } K_a = 1.8 \times 10^{-5}$$

$$pK_a = -\log K_a = -\log(1.8 \times 10^{-5}) = 5.7447$$

$$pH = pK_a + \log \frac{[\text{salt}]}{[\text{acid}]}$$

$$= 5.7447 + \log \frac{[0.5]}{[0.1]} = 6.444$$

Q6) The solubility of Mg(OH)_2 at 298K is 1.5×10^{-4} . Calculate the solubility product.

Ans: Let the solubility of Mg(OH)_2 is S . The dissociation of Mg(OH)_2 can be represented as:



$$\text{Eqm. Concn: } S \quad S \quad 2S$$

$$K_{SP} = [\text{Mg}^{2+}][\text{OH}^-]^2 = S \times (2S)^2$$

$$\text{i.e. } K_{SP} = 4S^3$$

$$\text{Here } S = 1.5 \times 10^{-4}$$

$$\text{So, } K_{SP} = 4 \times (1.5 \times 10^{-4})^3 = 1.35 \times 10^{-11}$$

Q7) The ionization constant of nitrous acid is 4.5×10^{-4} . Calculate the pH of 0.04 M solution of nitrous acid in water. (Hint: $\text{HNO}_2 + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{NO}_2^-$; $K_a = C\alpha^2$)

Ans: $K_a = 4.5 \times 10^{-4}$, $C = 0.04\text{M}$

$$K_a = C\alpha^2$$

$$\alpha = \sqrt{\frac{K_a}{C}} = \sqrt{\frac{4.5 \times 10^{-4}}{0.04}} = 0.106$$

$$[H_3O^+] = c\alpha = 0.04 \times 0.106 = 0.00424$$

$$pH = -\log[H_3O^+] = -\log(0.00424) = 2.373$$

Q8) Calculate the pH of a 0.1 M solution of NaOH .

Ans: $\text{NaOH} \rightarrow \text{Na}^+ + \text{OH}^-$

$$\begin{array}{cc} 0.1\text{M} & 0.1\text{M} \\ [OH^-] = 0.1\text{M} & \\ pOH = -\log[OH^-] = -\log(0.1) = 1 & \\ pH = 14 - pOH = 14 - 1 = 13 & \end{array}$$

7. REDOX REACTIONS

Redox reactions involve oxidation and reduction. The important concepts relating to redox reactions are:

I. Classical Concept: According to this concept, *oxidation is the process of addition of oxygen/electronegative element to a substance or removal of hydrogen/electropositive element from a substance.*

Reduction is the process of removal of oxygen/electronegative element from a substance or addition of hydrogen/electropositive element to a substance.

Substance which is oxidised is called reducing agent and the substance which is reduced is called oxidising agent.

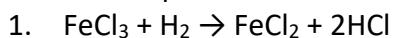
If oxidation and reduction take place simultaneously, the process is called *Redox reaction*.

i.e. Reduction + Oxidation → Redox reactions

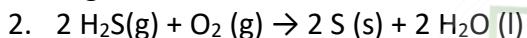


Here Zn is converted to ZnO. i.e oxygen is added to Zn. So it is oxidised and hence the reducing agent. CuO is converted to Cu. i.e. oxygen is removed from Cu. So it is reduced and hence it is the oxidising agent.

Other examples are:



Here the electronegative Cl atom is removed from FeCl_3 . So it is reduced. H_2 is oxidised since an electronegative Cl atom is added to it. FeCl_3 is the oxidising agent and H_2 is the reducing agent.



Here H_2S is oxidised and O_2 is reduced.

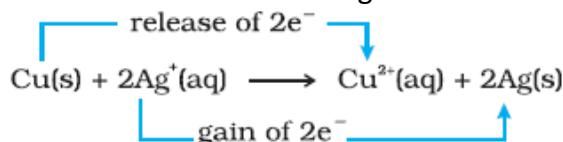


II. Electronic Concept: According to this concept *oxidation is the process of removal (losing) of electron and reduction is the process of addition (gaining) of electron*. A redox reaction is the process of exchange of electrons between two or more substances.

A substance that accepts electron is called oxidising agent and a substance that donates electron is called a reducing agent.

E.g. In the reaction $\text{Zn} + \text{Cu}^{2+} \rightarrow \text{Zn}^{2+} + \text{Cu}$, Zn loses two electrons and forms Zn^{2+} . So it is oxidised. Cu^{2+} gains two electrons and forms Cu. So it is reduced. Here Zn is the reducing agent and Cu^{2+} is the oxidising agent.

Other examples are:

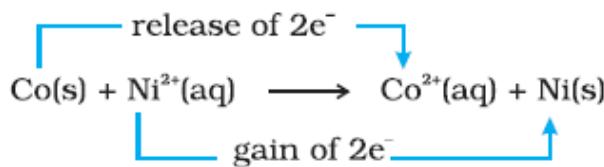


Here Cu loses two electrons. So it is oxidised and is the reducing agent. Ag^+ accepts an electron. So it is reduced and is the oxidising agent.

In the first example, Cu is reduced while in the second reaction it is oxidised. So the oxidation or reduction of a metal depends on the nature of the metal to which it is combined.

*The series in which the different metals are arranged in the decreasing order of their reactivity is called **electrochemical series or reactivity series**. Generally, a metal lying above in the reactivity series can displace another metal from its salt solution.* For example Zn can displace copper from an aqueous solution of copper sulphate, since Zn lies above Cu in the electrochemical series.

2. Reaction between cobalt and nickel ion.



Here Co is oxidised to Co^{2+} and Ni^{2+} is reduced to Ni.

Oxidation number

Oxidation number of an element in a compound is the residual charge on the element when all the other atoms are removed from it as ions.

For example oxidation number of Mn in KMnO_4 is the residual charge on Mn when one K atom and four O atoms removed from it as K^+ and O^{2-} ions respectively.

Rules used for the calculation of oxidation number

- The oxidation number of all elements in the free or the uncombined state is zero. For e.g. oxidation number of H_2 , O_2 , Cl_2 , O_3 , P_4 , S_8 , Na , Mg , Al etc. is zero.
- For simple ions, the oxidation number is equal to the charge on the ion. Thus Na^+ ion has an oxidation number of +1, Mg^{2+} ion +2, Fe^{3+} ion +3, Cl^- ion -1, O^{2-} ion -2 and so on.
- All alkali metals have oxidation number of +1 and all alkaline earth metals have an oxidation number of +2. Aluminium shows an oxidation number of +3 in all of its compounds.
- The common oxidation number of oxygen is -2. But in peroxides (like H_2O_2 , Na_2O_2 etc.), oxidation number of oxygen is -1 and in superoxides (e.g., KO_2 , RbO_2), it is $-\frac{1}{2}$. In oxygen difluoride (OF_2) and dioxygen difluoride (O_2F_2), oxygen is assigned an oxidation number of +2 and +1 respectively.
- The common oxidation number of hydrogen is +1. But it shows an oxidation number of -1 in metal hydrides (like NaH , CaH_2 etc.).
- The common oxidation number of halogens is -1. Fluorine shows only -1 oxidation number in all of its compounds. But other halogens show positive oxidation numbers also in their oxides and oxoacids.
- The algebraic sum of the oxidation numbers of all the atoms in a compound is zero.
- In polyatomic ion, the sum of the oxidation numbers of all the atoms is equal to charge on the ion.

Stock Notations

Alfred Stock proposed some notations to represent the oxidation number of a metal in a compound. According to this, the oxidation number is represented in Roman numeral in brackets after the symbol of the metal in the molecular formula. Thus aurous chloride and auric chloride are written as Au(I)Cl and Au(III)Cl_3 . Similarly, stannous chloride and stannic chloride are written as Sn(II)Cl_2 and Sn(IV)Cl_4 . Stock notation for MnO_2 is Mn(IV)O_2 .

III. Oxidation number Concept: According to this concept, *oxidation is the process of increase in the oxidation number of an element and reduction is the process of decrease in the oxidation number of an element.*

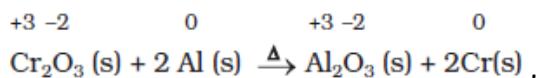
A reagent that can increase the oxidation number of an element in a given substance is called oxidising agent or oxidant and a reagent which lowers the oxidation number of an element in a given substance is called reducing agent or reductant. A redox reaction is a reaction which involves change in oxidation number of the interacting species.

E.g. In the reaction,



the oxidation number of Zn increases from 0 to +2 and that of Cu in CuSO_4 decreases from +2 to 0. So Zn is oxidised and Cu in CuSO_4 is reduced.

In the reaction:

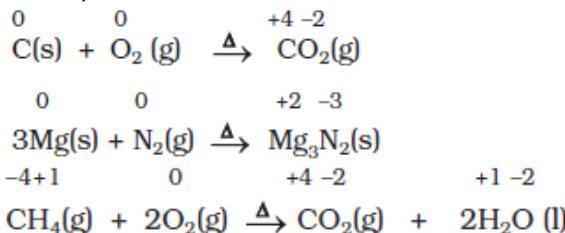


the oxidation number of Cr decreases from +3 to 0. So it is reduced and is the oxidising agent. The oxidation number of Al increases from 0 to +3. So it is oxidised and is the reducing agent.

Types of redox reactions

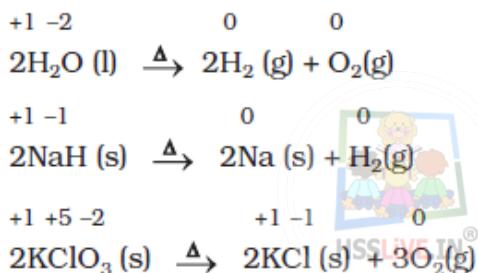
1. Combination reactions:

A combination reaction may be denoted as $\text{A} + \text{B} \rightarrow \text{C}$
Here either A or B or both A and B must be in the elemental form. All combustion reactions are combination redox reactions, since here one of the reactants is O_2 . Examples are:

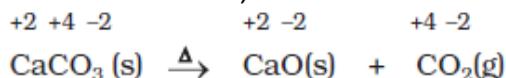


2. Decomposition reactions:

Decomposition reactions are the opposite of combination reactions. It involves the breakdown of a compound into two or more components, in which at least one must be in the elemental state. It may be denoted as: $\text{C} \rightarrow \text{A} + \text{B}$. Examples are:



All decomposition reactions are not redox reactions. For example, decomposition of calcium carbonate is not a redox reaction, since it does not involve any change in the oxidation number.

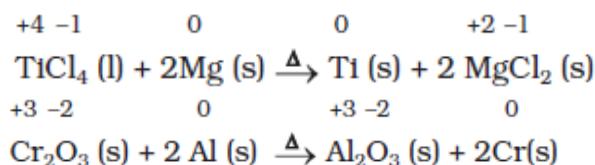
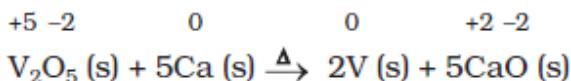
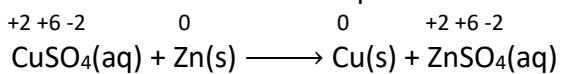


3. Displacement reactions:

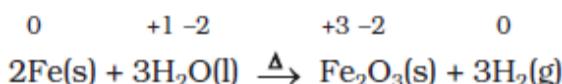
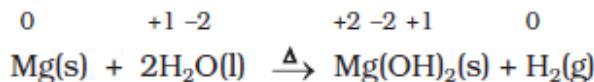
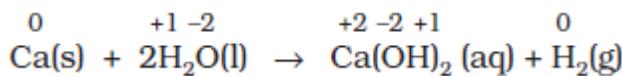
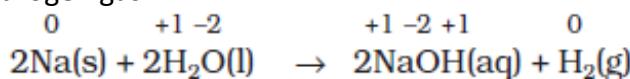
Here an ion (or an atom) in a compound is replaced by an ion (or an atom) of another element. It may be denoted as: $\text{X} + \text{YZ} \rightarrow \text{XZ} + \text{Y}$

Displacement reactions are divided into two - metal displacement and non-metal displacement.

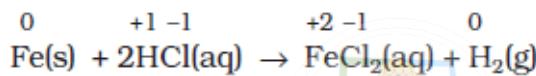
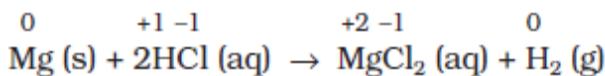
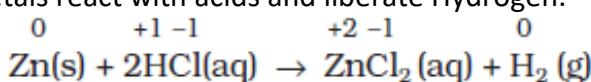
a) **Metal displacement reactions**: Here a metal in a compound is displaced by another metal in the uncombined state. These reactions find many applications in metallurgical processes in which pure metals are obtained from their compounds in ores. Some examples are:



b) **Non-metal displacement reactions:** The non-metal displacement redox reactions mainly include hydrogen displacement. All alkali metals and some alkaline earth metals (Ca, Sr, and Ba) will displace hydrogen from cold water. Less active metals such as magnesium and iron react with steam and produce hydrogen gas.

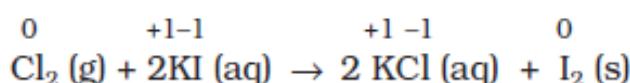
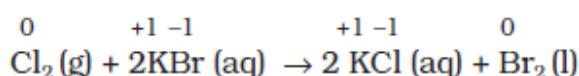
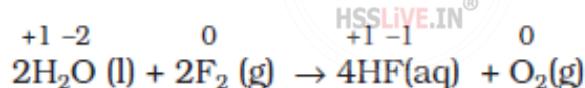


Most of the metals react with acids and liberate Hydrogen.



Other examples of non-metal displacement reactions are:

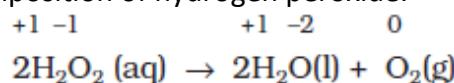
Fluorine can displace O₂ from water. Chlorine can displace bromine and iodide from their aqueous salt solutions.



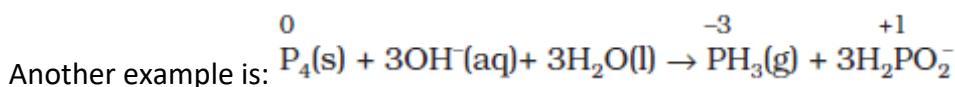
4. Disproportionation reactions:

These are a special type of redox reaction. In a disproportionation reaction, an element in one oxidation state is simultaneously oxidised and reduced. One of the reacting substances always contains an element that can exist in at least three oxidation states. The element in the reactant is in the intermediate oxidation state and both higher and lower oxidation states of that element are formed in the reaction.

E.g. The decomposition of hydrogen peroxide.



Here the oxygen of peroxide is in -1 state and it is converted to zero oxidation state in O₂ and -2 oxidation state in H₂O.



Another example is:

Balancing of Redox Reactions

There are two methods for balancing a redox reaction – Oxidation number method and half reaction method.

1. Oxidation Number Method: This method involves the following steps:

Step 1: Write the correct formula for each reactant and product.

Step 2: Assign the oxidation number of each element and identify the atoms which undergo change in oxidation number.

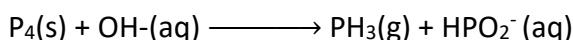
Step 3: Calculate the change in oxidation number per atom and equate them by multiplying with suitable coefficients.

Step 4: Balance all the atoms except oxygen and hydrogen.

Step 5: Now equate the ionic charges on both sides of the equation by adding H^+ or OH^- ions on the appropriate side. If the reaction is carried out in acidic solution, use H^+ ions in the equation; if in basic solution, use OH^- ions.

Step 6: Make the numbers of hydrogen atoms in the expression on the two sides equal by adding water (H_2O) molecules to the reactants or products. Now, also check the number of oxygen atoms.

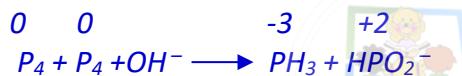
Q1) Balance the following Redox equation by oxidation number method :



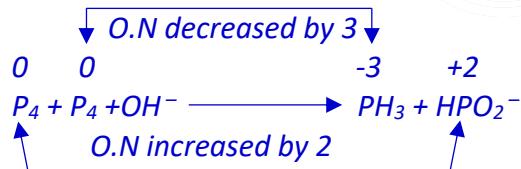
Ans:

Step 1: Write the skeletal equation. $P_4 + OH^- \longrightarrow PH_3 + HPO_2^-$

Step 2: Assign the oxidation number of each element and identify the atoms which undergo change in oxidation number.



Step 3: Calculate the change in oxidation number per atom and equate them by multiplying with suitable coefficients.



Step 4: Balance all the atoms except oxygen and hydrogen.



Step 5: Now equate the ionic charges on both sides. Since the reaction occurs in basic medium, add 11 OH^- ions on LHS.



Step 6: Now balance the hydrogen atoms by adding 12 water (H_2O) molecules on LHS.



Now the equation becomes balanced.

2. Half reaction method: In this method, the equation is divided into 2 half reactions – oxidation half reaction and reduction half reaction. They are balanced separately and then added together to get the net balanced equation. The different steps involved in this method are:

Step 1: Produce unbalanced equation for the reaction in ionic form. Assign the oxidation number of each element and find out the substance oxidised and reduced.

Step 2: Separate the equation into half reactions - oxidation half reaction and reduction half reaction.

Step 3: Balance the atoms other than O and H in each half reaction individually.

Step 4: For reactions occurring in acidic medium, add H_2O to balance O atoms and H^+ to balance H atoms. In basic medium also add equal number of OH^- ions on both sides of the equation.

Step 5: Now balance the ionic charges. For this add electrons to one side of the half reaction. Make the number of electrons equal in the two half reactions by multiplying one or both half reactions by appropriate coefficients.

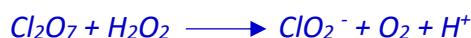
Step 6: Now add the two half reactions to get the overall reaction and cancel the electrons on each side.

Step 7: Verify that the equation contains the same type and number of atoms and the same charges on both sides.

Q2) Balance the following Redox equation by ion-electron method (Half reaction method)



Ans: Step-1: Assign the oxidation number of each element and find out the substance oxidised and reduced.



Here the oxidation number of O is increased and that of Cl is decreased. So O in H_2O_2 is oxidised and Cl in Cl_2O_7 is reduced.

Step-2: Separate the equation into 2 half reactions -oxidation half reaction and reduction half reaction.



Step-3: Balance the atoms other than O and H in each half reaction individually.



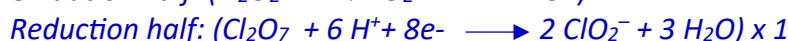
Step-4: Now balance O and H atoms. Add H_2O to balance O atoms and H^+ to balance H atoms since the reaction occurs in acidic medium.



Step -5: Now balance the ionic charges. For this add electrons to one side of the half reaction.



Step-6: Now add the two half reactions after equating the electrons.

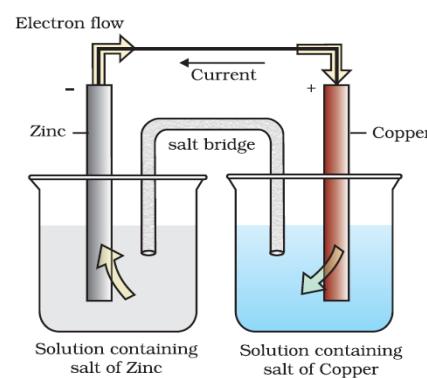


Now the equation is balanced.

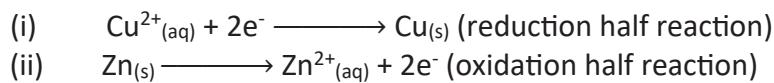
REDOX REACTIONS AND ELECTRODE PROCESSES

Redox reactions find applications in electrode processes in electrochemical cells. An **electrochemical cell (Galvanic cell)** is a device that converts chemical energy of a redox reaction to electrical energy. Any electrochemical cell contains two electrodes – anode and cathode. The electrode at which oxidation takes place is the anode and the other electrode at which reduction occurs is the cathode.

An example for electrochemical is **Daniel cell**. It contains a Zn rode dipped in $ZnSO_4$ solution and Copper rode dipped in $CuSO_4$ solution. The two solutions are connected externally by a metallic wire through a voltmeter and a switch and internally by a salt bridge. The reaction taking place in a Daniel cell is:



This reaction is a combination of two half reactions:



The reduction half reaction occurs on the copper electrode while the oxidation half reaction occurs on the zinc electrode. These two portions of the cell are also called **half-cells or redox couples**. The copper electrode may be called the reduction half-cell or cathode and the zinc electrode, the oxidation half-cell or anode.

The flow of current is possible only if there is a potential difference between the copper electrode and zinc electrode. The potential associated with each electrode is known as **electrode potential**. It is the tendency of the electrode to lose or gain electron.

When the concentration of the electrolyte is unity and if the reaction is carried out at 298K, the potential is called the Standard Electrode Potential (E^0). By convention, the standard electrode potential of hydrogen electrode (H^+/H_2 couple) is 0.00 volts. A negative E^0 means that the redox couple is a stronger reducing agent than the H^+/H_2 couple. A positive E^0 means that the redox couple is a weaker reducing agent than the H^+/H_2 couple.

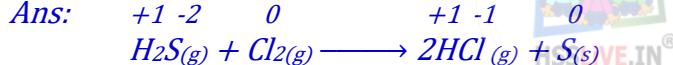
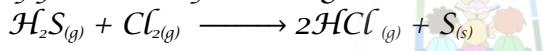
Q1) In an experiment a copper rod is dipped in AgNO_3 solution. What happens to the colour of the solution and why? Identify the oxidizing and reducing agents in this reaction.

Ans: The solution becomes pale blue in colour. This is because Cu displaces Ag from AgNO_3 solution.



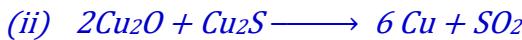
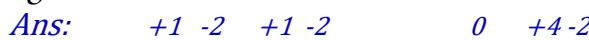
Oxidizing agent is AgNO_3 and reducing agent is Cu

Q2) Justify that the following reaction is a redox reaction:



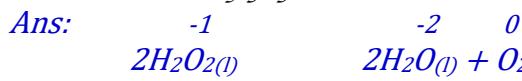
Here the oxidation number of sulphur is increased (oxidation) and that of chlorine is decreased (reduction). So, it is a redox reaction.

Q3) In a reaction $2\text{Cu}_2\text{O} + \text{Cu}_2\text{S} \longrightarrow 6\text{Cu} + \text{SO}_2$. Identify oxidizing agent and reducing agent.



Here the oxidation number of Cu in both Cu_2O and Cu_2S is decreased from +1 to 0. So, Cu is reduced and it is the oxidizing agent. While the oxidation number of S is increased from -2 to +4. So, S in Cu_2S is oxidized and hence it is the reducing agent.

Q4) Check whether the reaction $2\text{H}_2\text{O}_{2(\text{l})} \longrightarrow 2\text{H}_2\text{O}_{(\text{l})} + \text{O}_{2(\text{g})}$ is a disproportionation reaction. Justify your answer.



Here the oxidation number of oxygen is simultaneously increased and decreased. So, it is a disproportionation reaction.

Q5) Calculate the oxidation number of Cr in $\text{K}_2\text{Cr}_2\text{O}_7$.

Ans: Let the oxidation number of Cr be x

Then $2x(+1) + 2x + 7x(-2) = 0$

$+2 + 2x + (-14) = 0$

$2x - 12 = 0 \quad \text{OR}, X = 12/2 = 6$

i.e., Oxidation number of Cr = +6

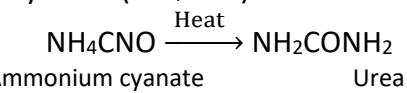
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8. ORGANIC CHEMISTRY - SOME BASIC PRINCIPLES AND TECHNIQUES

Organic chemistry is the branch of chemistry that deals with carbon compounds. But all carbon compounds are not considered as organic compounds. (E.g. CO_2 , CO, metal carbonates, bicarbonates etc.). So **organic chemistry can be defined as the branch of chemistry that deals with hydrocarbons and their derivatives.** Hydrocarbons are the major class of organic compounds and they *contain only carbon and hydrogen atoms*. All other organic compounds are formed by replacing one or more hydrogen atoms of hydrocarbons by other atoms or groups (They are called hydrocarbon derivatives).

All carbon compounds present in plants and animals are organic compounds. E.g. carbohydrates, proteins, vitamins, nucleic acids, amino acids, fats and oils, natural polymers etc. Petroleum and coal are the major source of organic compounds (hydrocarbons).

In ancient times, it was believed that a vital force (living body) is necessary for the production of an organic compound. But in 1828, Frederic Wohler prepared urea in the laboratory, by heating ammonium cyanate (NH_4CNO). It was the first organic compound prepared in the laboratory.



Another scientist Kolbe synthesized acetic acid and Berthelot synthesized methane in the laboratory. Nowadays about 95% of the organic compounds are synthesized in the laboratory.

Chemistry behind the existence of large number Carbon compounds

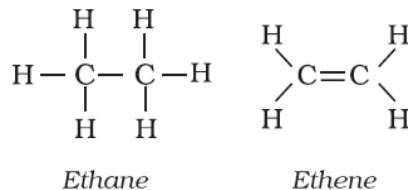
Carbon is a unique element and it can form large number of compounds due to the following reasons:

- i) Tetravalency of carbon: In all of its compounds, the valency of carbon is four. Carbon has 4 electrons in its valency shell and requires 4 more electrons to complete the octet. So it attains the octet configuration by forming 4 covalent bonds.
- ii) Ability to form single bond and multiple bonds: C can form single bond and multiple bond (double or triple bond) with itself and also with other elements like oxygen, nitrogen etc. This is possible by sp^3 , sp^2 or sp hybridisation.
- iii) Catenation: Carbon shows catenation. It is the self-linking property of an element to form long chains and rings.
- iv) Isomerism: Carbon compounds can show isomerism. It is the phenomenon in which compounds having same molecular formula but different structural formula or spatial arrangement of atoms.

Structural representation of organic compounds

An organic compound can be represented by the following ways:

1. **Complete structural formula:** Here all the bonds between atoms are denoted by dashes (---). A single dash represents a single bond, a double dash represents a double bond and a triple dash represents a triple bond. E.g.



2. **Condensed structural formula:** Here the carbon-hydrogen bonds or all the bonds are omitted except the multiple bonds. It is a simplified representation of an organic compound.

E.g. ethane - CH_3CH_3 , propane - $\text{CH}_3\text{CH}_2\text{CH}_3$, butane - $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3$, ethene - $\text{CH}_2=\text{CH}_2$ etc.

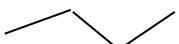
The condensed formula can again simplified as follows:

Butane – $\text{CH}_3(\text{CH}_2)_2\text{CH}_3$, Hexane- $\text{CH}_3(\text{CH}_2)_4\text{CH}_3$, Decane – $\text{CH}_3(\text{CH}_2)_8\text{CH}_3$ etc.

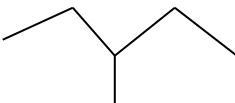
3. Bond line representation: It is the simplest form of representation of an organic compound.

Here carbon and hydrogen atoms are not shown and the lines representing carbon-carbon bonds are drawn in a zig-zag fashion. The only atoms specifically written are oxygen, chlorine, nitrogen etc. The free terminals denote methyl ($-\text{CH}_3$) groups.

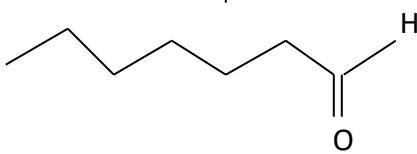
E.g. butane:



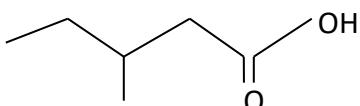
3-methyl pentane:



Heptanal:

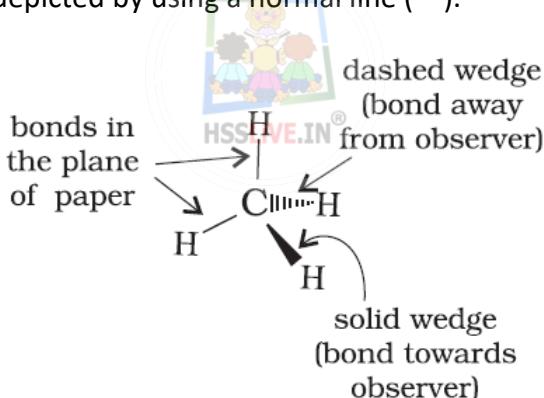


3-Methyl pentanoic acid:



4. Three-Dimensional Representation (Wedge Representation): Here the structure of an organic molecule can be represented by using solid (—) and dashed (·····) wedges. The solid-wedge is used to indicate a bond projecting out of the plane of paper, towards the observer. The dashed-wedge indicates the bond projecting out of the plane of the paper and away from the observer. The broad end of the wedge is always towards the observer. The bonds lying in plane of the paper are depicted by using a normal line (—).

E.g. methane



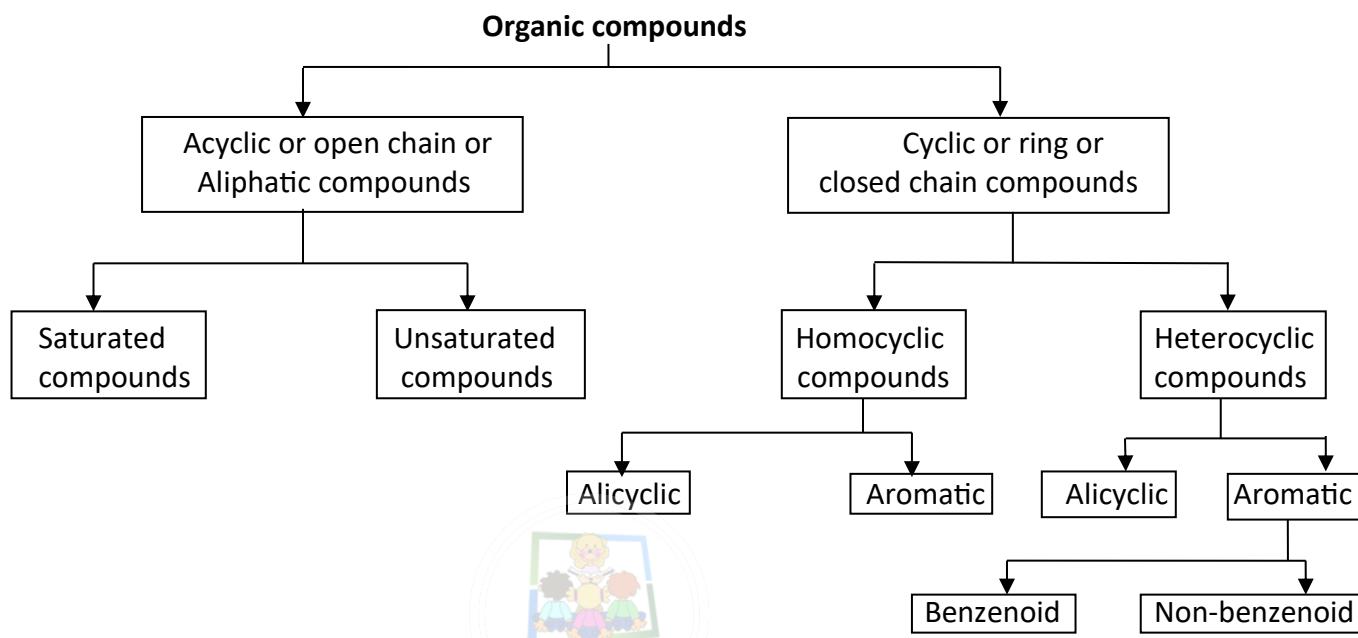
Classification of Organic compounds

Organic compounds can be broadly classified into two – Acyclic or open chain compounds and cyclic or ring compounds.

- Acyclic or open chain or aliphatic compounds:** In these compounds, the carbon atoms are joined together to form long chains which may be straight chain or branched chain. They are further classified as *saturated compounds* and *unsaturated compounds*. **Saturated compounds** contain only carbon – carbon single bonds. But **unsaturated compounds** contain atleast one carbon – carbon multiple bond (double or triple bond). Saturated hydrocarbons are called *alkanes* and unsaturated hydrocarbons are of two types – *alkenes* and *alkynes*.
- Cyclic or closed chain or ring compounds:** In these compounds, the carbon atoms are joined together to form rings. These rings may be *homocyclic* or *heterocyclic*. If the ring contains only carbon atoms, it is called homocyclic compound and if it contains atoms other than carbon (like O, N, S etc), it is called heterocyclic compound.

Homocyclic compounds are further classified into two – *Alicyclic compounds and Aromatic compounds*. **Alicyclic compounds** contain atleast one carbo-cyclic ring. **Alicyclic hydrocarbons** are of three types – *cycloalkanes, cycloalkenes and cycloalkynes*. **Aromatic compounds** are some special type of compounds. These are of two types. Aromatic compounds containing benzene ring are called *benzenoid compounds* and those which do not contain benzene ring are called *non-benzenoid compounds*. E.g. for a non-benzenoid aromatic compound is tropolone.

Heterocyclic compounds may be alicyclic heterocyclic compounds or aromatic heterocyclic compounds. The classification of organic compounds can be diagrammatically represented as follows:



Functional groups: Atoms or group of atoms (except hydrogen) which are bonded to carbon atoms are called **functional groups**. These groups are responsible for the characteristic chemical properties of the organic compounds. Some important functional groups, their names and name of the compounds are listed below:

Functional group	Name of the group	Name of compound
-OH	Hydroxyl group	Alcohol
-NH ₂	Amino group	Amine
-X	Halo group	Halo compound
-CHO	Aldehydic (formyl) group	Aldehyde
-CO- or >CO	Carbonyl (keto) group	Ketone
-COOH	Carboxyl group	Carboxylic acid
-O-	Oxy group	Ether
-CN	Cyano group	Nitrile
-NO ₂	Nitro group	Nitro compound

Homologous series: A series or group of organic compounds in which adjacent members are differed by a -CH₂ group is called a **homologous series**. The members of a homologous series are called *homologues*. They contain same functional groups. So they have similar chemical properties and show gradation in physical properties. They can be prepared by some general methods of preparation. E.g. for homologous series are alkanes, alkenes, alkynes, alcohols, ethers, carboxylic acids, aldehydes, ketones, amines, halo compounds etc.

Nomenclature of organic compounds

An organic compound has two types of names – Common name and IUPAC name. The common name is based on the source or some properties. For e.g. citric acid is named so because it is found in citrus fruits and the acid found in red ant is named formic acid since the Latin word for ant is formica.

IUPAC Nomenclature of organic compounds

A systematic name of an organic compound is generally derived by identifying the parent hydrocarbon and the functional group(s) attached to it. This name is called IUPAC name. It contains two parts – word root and suffix or prefix. The word root indicates the number of carbon atoms in the compound. The word roots for compounds containing 1 -12 carbon atoms are as follows:

No. of C atoms	Word root	No. of C atoms	Word root
C ₁	Meth-	C ₇	Hept-
C ₂	Eth-	C ₈	Oct-
C ₃	Prop-	C ₉	Non-
C ₄	But-	C ₁₀	Dec-
C ₅	Pent-	C ₁₁	Undec-
C ₆	Hex-	C ₁₂	Dodec-

There are two types of suffixes – primary suffix and secondary suffix. Primary suffix indicates saturation or unsaturation [for alkane the primary suffix is –ane, alkene –ene and for alkyne –yne]. Secondary suffix indicates the type of functional group. Some functional groups are also indicated as prefixes.



Nomenclature of branched chain alkanes:

A branch (side chain or substituent) is obtained by removing a hydrogen atom from an alkane. The resulting group is called an **alkyl group** [alkane – H = alkyl (i.e. **word root + yl**)]. The names of some common branches are as follows:

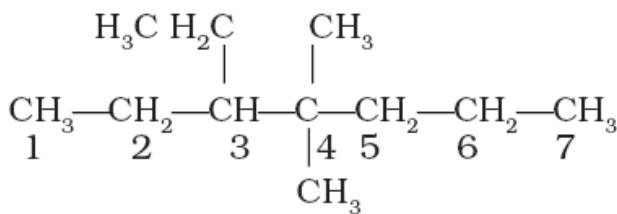
Branch	Name
-CH ₃	Methyl
-CH ₂ -CH ₃	Ethyl
-CH ₂ -CH ₂ -CH ₃	n-propyl (normal propyl)
(CH ₃) ₂ CH-	Isopropyl
-CH ₂ -CH ₂ -CH ₂ -CH ₃	n-butyl
CH ₃ -CH-CH ₂ -CH ₃	sec-butyl (secondary butyl)
(CH ₃) ₂ CH-CH ₂ -	Isobutyl
(CH ₃) ₃ C-	tert-butyl (tertiary butyl)
(CH ₃) ₃ C-CH ₂ -	Neopentyl

Rules for naming branched chain alkanes:

IUPAC recommended the following rules for naming a branched chain alkane.

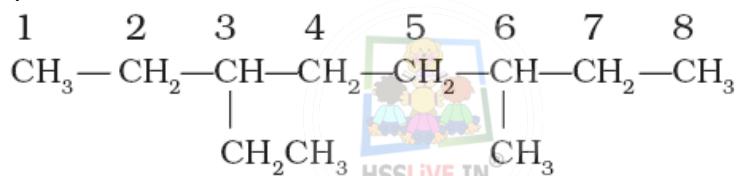
1. Select the longest continuous chain of carbon atoms. This chain is called parent chain or root chain. If there is more than one such chain, the chain that contains maximum number of branches is selected as the parent chain. Also identify all the branches or substituents.

2. Number the carbon atoms of the parent chain in such a way that the branched carbon atoms get the lowest possible numbers.
 3. The names of alkyl groups attached as branches are then prefixed to the name of the parent alkane and position of the substituents is indicated by the appropriate numbers.
 4. If different alkyl groups are present, they are listed in alphabetical order. In alphabetical order, the prefixes iso- and neo- are considered to be the part of the fundamental name of alkyl group. The prefixes sec- and tert- are not considered to be the part of the fundamental name.
 5. If two or more identical substituent groups are present then their numbers are indicated by prefixes like di (for 2), tri (for 3), tetra (for 4), penta (for 5) etc and the numbers are separated by commas. The number and word are separated by a hyphen. (The IUPAC name is written as a single word).
- For example:

*3-Ethyl-4,4-dimethylheptane*

6. If the two substituents are found in equivalent positions, the lower number is given to the one coming first in the alphabetical listing.

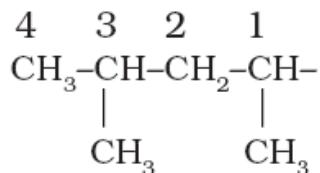
For example:



The above compound is *3-ethyl-6-methyloctane* and not *6-ethyl-3-methyloctane*.

7. While naming the branched alkyl groups, the carbon atom of the branch that attaches to the root alkane is numbered 1.

For example:

*1,3-dimethyl butyl-*

IUPAC nomenclature of compounds containing functional groups

For naming organic compounds containing functional group, the following rules are used:

1. Select the longest continuous chain containing the functional group.
2. Number the carbon atoms in such a way that the carbon to which the functional group is attached should get the lowest possible number. In the case of functional groups containing carbon atom like $-\text{CHO}$, $-\text{CN}$, $-\text{COOH}$, $-\text{CONH}_2$, $-\text{COX}$, $-\text{COOR}$ etc. the numbering should start from the carbon atom of the functional group. (i.e. carbon atom of these groups should be numbered as 1). (But for ketones, the functional group $-\text{CO-}$ should get the lowest possible number).
3. The name of the functional group is indicated by the following suffix or prefix.

Functional group	Name of compound	Suffix/Prefix	IUPAC name
-OH	Alcohol	-ol	Alkanol
-NH ₂	Amine	-amine	Alkanamine
-X	Halo compound	Halo-	Haloalkane
-CHO	Aldehyde	-al	Alkanal
>CO	Ketone	-one	Alkanone
-COOH	Carboxylic acid	-oic acid	Alkanoic acid
-O-	Ether	Alkoxy-	Alkoxyalkane
-CN	Nitrile	-nitrile	Alkanenitrile
-NO ₂	Nitro compound	Nitro-	Nitroalkane
-C=C-	Alkene	-ene	Alkene
-C≡C-	Alkyne	-yne	Alkyne
-COOR	Ester	-oate	Alkyl alkanoate
-CONH ₂	Acid amide	-amide	Alkanamide
-COX	Acid halide	-oyl halide	Alkanoyl halide
-SO ₃ H	Sulphonic acid	-sulphonic acid	Alkanesulphonic acid

In the case of suffixes, the ending -e of the corresponding alkane is replaced. E.g. IUPAC name of the alcohol CH₃-OH is methanol (methane + ol). But for nitriles, the -e of the corresponding alkane is retained. E.g. IUPAC name of CH₃-CH₂-CN is propanenitrile.

In the case of alkenes and alkynes, the suffix -ane of the alkane is replaced by -ene and -yne respectively. (i.e. word root + ene or yne). For naming alkenes or alkynes, the numbering is done in such a way that the double or triple bond should get the lowest possible number.

Some examples are:

Compound	IUPAC Name
CH ₃ -CH ₂ -CH=CH ₂	But-1-ene OR 1-Butene
CH ₃ -CH=CH-CH ₃	But-2-ene OR 2-Butene
CH ₃ -CH ₂ -C≡C-CH ₃	Pent-2-yne OR 2-Pentyne
CH ₃ -CH ₂ -CH ₂ -CH ₂ -CH ₂ -C≡CH	Hept-1-yne OR 1-Heptyne
CH ₃ -CH ₂ -OH	Ethanol
CH ₃ -CH ₂ -CHOH-CH ₂ -CH ₂ -CH ₃	Hexan-3-ol OR 3-Hexanol
CH ₃ -CH ₂ -CH ₂ -CHO	Butan-1-al or Butanal
HCHO	Methanal
CH ₃ -CO-CH ₃	Propanone
CH ₃ -CO-CH ₂ -CH ₂ -CH ₃	Pentan-2-one OR 2-Pantanone
CH ₃ -CH ₂ -CH ₂ -CO-CH ₂ -CH ₂ -CH ₂ -CH ₃	Octan-4-one OR 4-Octanone
HCOOH	Methanoic acid
CH ₃ -COOH	Ethanoic acid
CH ₃ -CH ₂ -CH ₂ -COOH	Butan-1-oic acid OR Butanoic acid

CH ₃ -CH ₂ -Cl	Chloroethane
CH ₃ -CH ₂ -CHBr-CH ₃	2-Bromobutane
CH ₂ Cl-CH ₂ -CH ₂ -CH ₂ -CH ₃	1-Chloropentane
CH ₃ -CH ₂ -CH ₂ -NO ₂	1-Nitropropane
CH ₃ -CH ₂ -CH ₂ -CN	Butanenitrile
CH ₃ -CH ₂ -CH ₂ -CH ₂ -CN	Hexanenitrile
CH ₃ -O-CH ₃	Methoxymethane
CH ₃ -CH ₂ -O-CH ₃	Methoxyethane
CH ₃ -CH ₂ -CH ₂ -O-CH ₂ -CH ₃	1-Ethoxypropane
CH ₃ -CH ₂ -NH ₂	Ethanamine
CH ₃ -CH ₂ -CH(NH ₂)-CH ₃	Butan-2-amine OR 2-Butanamine
CH ₃ -CH ₂ -COOCH ₃	Methylpropanoate
CH ₃ -CH ₂ -COOCH ₂ -CH ₃	Ethylpropanoate
CH ₃ -CH ₂ -COCl	Propanoylchloride
CH ₃ -CH ₂ -CH ₂ -CH ₂ -COBr	Pantanoylbromide
CH ₃ -CH ₂ -CH ₂ -CONH ₂	Butanamide
CH ₃ -CONH ₂	Ethanamide

Nomenclature of organic compounds containing more than one functional groups (Poly functional compounds)

Here one of the functional groups is chosen as the **principal functional group** and the compound is named on that basis. The remaining functional groups (called **subordinate functional groups**) are named as substituents using the appropriate prefixes. The choice of principal functional group is made on the basis of **order of preference**. The decreasing order of priority for some functional groups is -COOH, -SO₃H, -COOR, -COCl, -CONH₂, -CN, -CHO, >CO, -OH, -NH₂, >C=C<, -C≡C-. The groups like alkyl (-R), phenyl (C₆H₅-), halogens (F, Cl, Br, I), nitro (-NO₂), alkoxy (-OR) etc. are always prefix substituents.

For example if a compound contains both alcoholic and aldehydic groups, it is named as hydroxyalkanal, since here aldehydic group is the principal functional group and -OH group is the subordinate functional group.

The prefix names of some functional groups are as follows:

Functional group	Prefix name
-OH	Hydroxyl-
-NH ₂	Amino-
-X	Halo-
-CHO	Formyl-
>CO	Oxo-
-COOH	Carboxy-
-O-	Alkoxy-
-CN	Cyano-
-NO ₂	Nitro-
-COOR	Alkoxy carbonyl-
-CONH ₂	Carbamoyl-
-COX	Halocarbonyl-

While numbering the carbon chain, the principal functional group should get the lowest possible number.

Some examples are:

Compound	IUPAC Name
CH ₃ -CHOH-CH ₂ -CO-CH ₃	4-Hydroxy-2-pentanone
CH ₂ Cl-CH ₂ -CHBr-CH ₂ -CH ₂ OH	3-Bromo-5-chloropentan-1-ol or, 3-Bromo-5-chloro-1-pentanol
CH ₃ -CH ₂ -CO-CH ₂ -CH ₂ -CHO	4-Oxohexanal
CH ₃ -CHNH ₂ -CH ₂ -COOH	3-Aminobutanoic acid
CH ₃ -CH ₂ -CHCl-CH ₂ -CO-CH ₂ -COOH	5-Chloro-3-oxo-heptanoic acid

If a compound contains more than one same functional group, their number is indicated by adding the numeral prefixes di, tri, etc. before the suffix. In such cases the full name of the parent alkane is written before the suffix. However, the ending –ne of the parent alkane is dropped in the case of compounds having more than one double or triple bonds.

When both double and triple bonds are present, the double bonds are given the lowest numbers. Here first give the suffix of the double bond (-ene) and then that of the triple bond (-yne) [the ending –e of the suffix –ene is avoided].

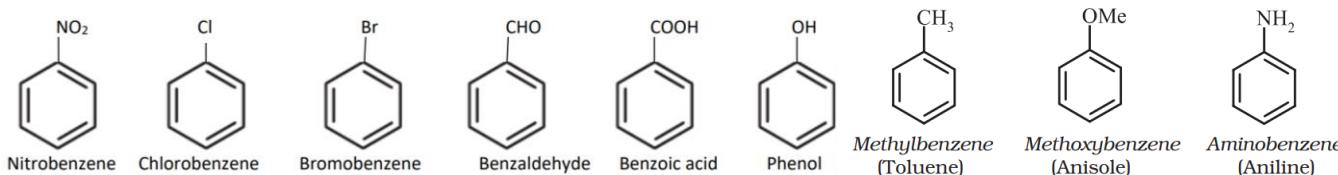
Examples:

Compound	IUPAC Name
CH ₂ OH-CH ₂ OH	Ethane-1,2-diol (Ethylene glycol)
CH ₂ OH-CHOH-CH ₂ OH	Propane-1,2,3-triol (Glycerol)
CHO-CHO	Ethane-1,2-dial (Glyoxal)
COOH-COOH	Ethane-1,2-dioic acid (Oxalic acid)
CH ₃ -CO-CH ₂ -CO-CH ₃	Pentane-2,4-dione
CH ₂ =CH-CH=CH ₂	1,3-Butadiene or Buta-1,3-diene
CH≡C-CH ₂ -C≡CH	1,4-Pentadiene or Penta-1,4-diene
CH ₂ =CH-CH ₂ -C≡CH	Pent-1-en-4-yne
CH≡C-CH=CH-C≡CH	Hexa-1,3-dien-5-yne

(The names given in the bracket are the common names)

Nomenclature of Substituted Benzene Compounds

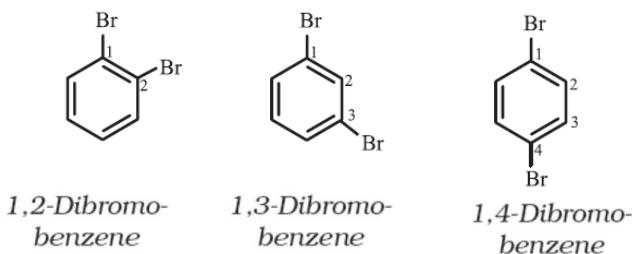
For IUPAC nomenclature of substituted benzene compounds, the substituent is placed as prefix to the word benzene. But common names of some compounds are accepted by IUPAC



Nomenclature of di or polysubstituted benzene

If benzene ring is disubstituted, the position of substituents is indicated by numbering the carbon atoms of the ring such that the substituents get the lowest possible numbers.

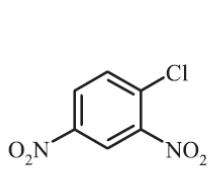
Example – Dibromobenzene



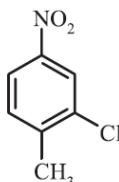
In the common system of nomenclature the terms ortho (o), meta (m) and para (p) are used as prefixes to indicate the relative positions 1,2- 1,3- and 1,4- respectively. So 1,2-dibromobenzene is named as ortho-dibromobenzene (o-dibromobenzene), 1,3-dibromobenzene as meta-dibromobenzene (m-dibromobenzene) and 1,4-dibromobenzene as para-dibromobenzene (p-dibromobenzene).

For tri - or higher substituted benzene derivatives, these prefixes cannot be used and the compounds are named by identifying substituent positions on the ring by following the lowest locant rule. In some cases, common name of benzene derivatives is taken as the base compound. Substituent of the base compound is assigned number 1 and then the direction of numbering is chosen such that the next substituent gets the lowest number. The substituents are named in alphabetical order.

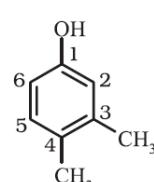
Some examples are:



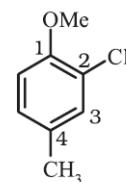
1-Chloro-2,4-dinitrobenzene



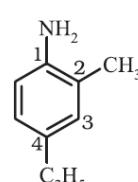
2-Chloro-1-methyl-4-nitrobenzene



3,4-Dimethylphenol



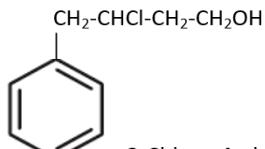
2-Chloro-4-methylanisole



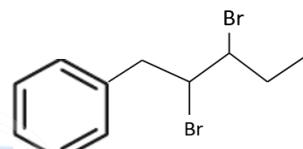
4-Ethyl-2-methylaniline

When a benzene ring is attached to an alkane with a functional group, it is considered as substituent, instead of a parent. The name for benzene as substituent is phenyl (C_6H_5- , also abbreviated as Ph).

Example:



3-Chloro-4-phenylbutan-1-ol



2,3-Dibromo-1-phenylpentane

Isomerism

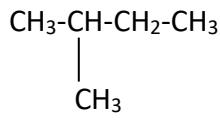
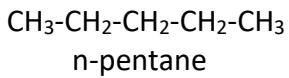
The phenomenon of existence of two or more compounds having the same molecular formula but different structural formula or spatial arrangement of atoms is known as isomerism. Such compounds are called as isomers. Isomers have different physical and chemical properties. Isomerism can be broadly classified into two –structural isomerism and stereo isomerism.

1. Structural isomerism

Compounds having same molecular formula but different structural formula (arrangement of atoms) are called structural isomers and the phenomenon is called structural isomerism. There are mainly four types of structural isomerism:

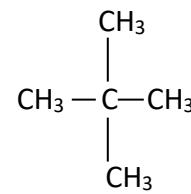
- a) **Chain Isomerism:** Isomers differ in carbon chain or skeleton are called chain isomers and the phenomenon is called chain isomerism.

E.g.: Pentane (C_5H_{12})



isopentane

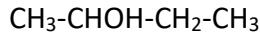
(2-Methylbutane)



neopentane (2,2-Dimethylpropane)

- b) **Position isomerism:** Isomers which differ in the position of the substituent or side chain are called position isomers and the phenomenon is called position isomerism.

E.g. : Alcohol with molecular formula $C_4H_{10}O$ may be 1-butanol or 2-butanol

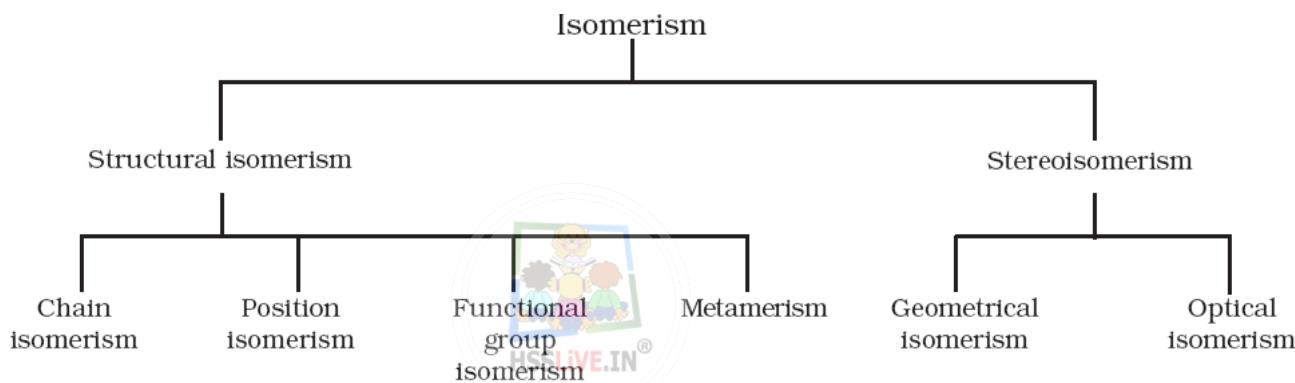


- c) **Functional group isomerism:** Isomers which differ in the functional group are called functional group isomers and the phenomenon is called functional group isomerism. This isomerism is shown by alcohols and ethers and aldehydes and ketones.
E.g. compound with the molecular formula C₂H₆O may be an alcohol ethanol (CH₃-CH₂OH) or an ether methoxy methane (CH₃-O-CH₃).
- d) **Metamerism:** Isomers which differ in the carbon chain (alkyl groups) around the functional group are called metamers and the phenomenon is called metamerism. It is commonly shown by ethers.
E.g.: Ether with molecular formula C₅H₁₂O may be methoxybutane (CH₃-O-CH₂-CH₂-CH₂-CH₃) or ethoxypropane (CH₃-CH₂-O-CH₂-CH₂-CH₃).

2. Stereo isomerism

Compounds having same molecular formula but different spatial arrangement of atoms are called stereoisomers and the phenomenon is called stereoisomerism. They have same atom to atom bond. There are two types of stereo isomerism – *Geometrical isomerism and Optical isomerism*.

The diagrammatic representation of different types of isomerism is:



ORGANIC REACTION MECHANISM - Fundamental Concepts

In an organic reaction, the organic molecule (called substrate) reacts with an attacking reagent to form one or more intermediates and finally the products.

Substrate + attacking reagent → Intermediate → Products

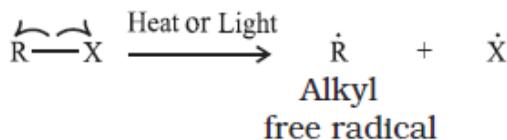
A sequential account of different steps in which the reactants are converted to products is called *reaction mechanism*.

Fission of a covalent bond

A covalent bond can be broken either by homolysis or by heterolysis.

1. Homolysis:

It is a type of bond fission in which each of the bonded atoms gets one of the electrons of the shared pair. Here the movement of a single electron takes place. The single electron movement is shown by half-headed arrow or fish hook arrow (↗).



The species formed as a result of homolysis is called **free radical**. These are *species which contain an odd electron or an unpaired electron*.

There are three types of free radicals - primary (1^0), secondary (2^0) and tertiary (3^0). Their stability increases in the order $1^0 < 2^0 < 3^0$.



Methyl Ethyl Isopropyl Tert-butyl
free free free free
radical radical radical radical

Organic reactions, which take place by homolytic fission are called ***free radical or homopolar or nonpolar reactions.***

2. Heterolysis:

It is a type of bond fission in which the shared pair of electrons remains with one of the fragments.

After heterolysis, one atom has a sextet of electron and a positive charge and the other atom has an octet of electron with atleast one lone pair and a negative charge.

For example the bond cleavage in methyl bromide takes place in the following manner.



A species having a carbon atom possessing sextet of electrons and a positive charge is called a ***carbocation (carbonium ion).*** They are of three types – primary, secondary and tertiary.

Carbocations are highly unstable and reactive species. Their stability increases in the order $1^0 < 2^0 < 3^0$. The high stability of tertiary carbocations is due to inductive effect and hyper conjugation. In carbocations, carbon atom is in sp^2 hybridisation and hence they have trigonal planar (planar triangular) shape.

If the group attached to the carbon atom is less electronegative than C, due to heterolytic cleavage, a species with C atom containing a shared pair of electrons and negative charge is formed.



Such a species carrying a negative charge on carbon atom is called ***carbanion.*** They are also unstable and reactive. Their stability increases in the order : $3^0 < 2^0 < 1^0$.

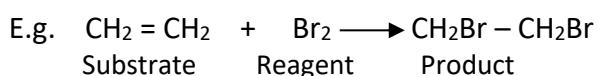
The organic reactions which proceed through heterolytic bond cleavage are called ***ionic or heteropolar or polar reactions.***

Differences between Homolysis and Heterolysis

Homolytic bond cleavage (Homolysis)	Heterolytic bond cleavage (Heterolysis)
It is a type of bond fission in which each of the bonded atoms gets one of the electrons of the shared pair.	Here, the bond breaks in such a manner that the shared pair of electrons remains with one of the fragments.
Movement of a single electron occurs.	Movement of a pair of electrons occurs.
The species formed as a result of homolysis is called <i>free radical.</i>	The species formed as a result of heterolysis, may be carbocations or carbanions.

Substrate and Reagent

A molecule whose carbon is involved in new bond formation is called substrate and the other molecule or species is called reagent. When both of the reactants contain carbon atoms, the molecule under observation is the substrate.



Nucleophiles and Electrophiles

A reagent that brings an electron pair is called a nucleophile ($:Nu^-$) and the reaction is called nucleophilic reaction. Or, nucleophiles are electron rich species attack at electron deficient centre. (The word nucleophile means nucleus seeking).

Examples for nucleophiles are OH^- , CN^- , NO_2^- , Cl^- , Br^- , I^- , H_2O , NH_3 , $R-NH_2$ etc.

A reagent that takes away an electron pair is called an electrophile (E^+) and the reaction is called electrophilic reaction. Or, electrophiles are electron deficient species attack at electron rich centre. (The word electrophile means electron seeking).

Examples for electrophiles are carbocations (R^+), $-CHO$, $>CO$, X^+ (halonium ion), NO_2^+ (nitronium ion), SO_2 etc.

Electron displacement effects in covalent bonds

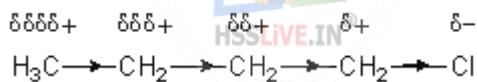
In an organic molecule, the electron displacement may take place either under the influence of an atom or in the presence of an attacking reagent. The important types of electron displacement effects are inductive effect, electromeric effect, resonance effect and hyper conjugation.

1. Inductive effect (I effect):

It is a permanent effect arising due to the shifting of sigma electrons through a carbon chain in presence of an atom or group of atom (having different electronegativity) attached to a carbon chain. This effect propagates only through C – C σ bonds. This effect decreases rapidly as the number of C atoms increases.

E.g. 1-chlorobutane $CH_3 - CH_2 - CH_2 - CH_2 - Cl$

Here Cl is more electronegative than C. So the electron pair in the C – Cl bond is shifted towards Cl and it gets a slight –ve charge (δ^-) and C gets a slight +ve charge (δ^+). This carbon attracts the electron density from the second carbon and so the 2nd carbon gets a relatively smaller positive charge ($\delta\delta^+$).



The inductive effect is related to the ability of substituents to either withdraw or donate electron density to the attached carbon atom. Based on this ability, the substituents can be classified as electron-withdrawing group (-I effect group) or electron donating groups (+I effect group) relative to hydrogen.

Groups that withdraw (attract) electrons from the carbon chain are said to have -I effect.

Example for such groups are $-X$ (F, Cl, Br, I), nitro ($-NO_2$), cyano (CN^-), carboxy ($-COOH$), ester ($-COOR$), aryloxy ($-OAr$) etc.

Groups which donate (release) electron pairs towards the carbon chain are said to have +I effect.

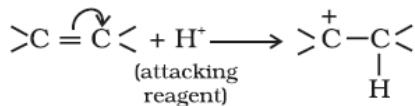
Example for such groups are alkyl groups like methyl ($-CH_3$), ethyl ($-CH_2-CH_3$) etc.

2. Electromeric effect (E effect):

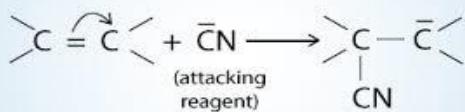
It is defined as the complete transfer of a shared pair of π -electrons to one of the atoms joined by a multiple bond in presence of an attacking reagent. It is a temporary effect. It is possible only in compounds containing multiple bonds(alkene or alkyne). This effect cancels when the attacking reagent is removed from the reaction site. The shifting of the electrons is shown by a curved arrow (\curvearrowright).

There are two types of E effects:

a) **Positive Electromeric effect (+E effect):** Here the pi electrons are transferred to that atom to which the attacking reagent gets attached.



- b) **Negative Electromeric effect (-E effect):** Here the pi electrons of the multiple bonds are transferred to that atom to which the attacking reagent does not get attached.



When inductive and electromeric effects operate in opposite directions, the electromeric effect predominates.

Differentiate between Inductive effect and Electromeric effect

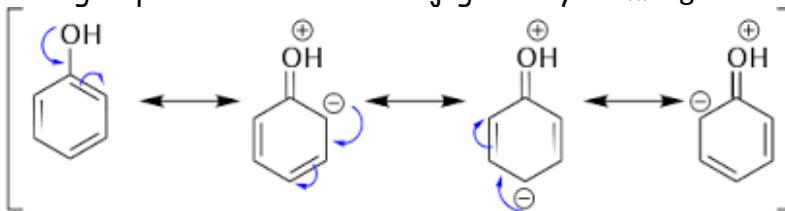
Inductive Effect	Electromeric Effect
It is the shifting of sigma electrons through a carbon chain in presence of an atom or group of atom attached to a carbon chain.	It is the complete transfer of the shared pair of π -electrons to one of the atoms joined by a multiple bond in presence of an attacking reagent.
It is a permanent effect.	It is a temporary effect.
It propagates only through C – C sigma bonds.	It is possible only in compounds containing multiple bonds.
Partial polarity is developed.	Complete polarity is developed.
No attacking reagent is required	Takes place only in presence of attacking reagent.

3. Resonance Effect (R effect) or Mesomeric effect (M effect):

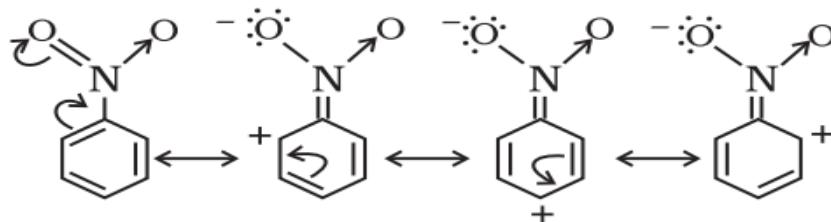
It is defined as 'the polarity (charge) produced in the molecule by the interaction of two π -bonds or between a π -bond and lone pair of electrons present on an adjacent atom'. The effect is transmitted through the chain.

There are two types of resonance effect (R effect):[®]

- a) **Positive Resonance effect (+R effect):** Here the transfer of electrons is away from an atom or substituent group attached to the conjugated system. E.g. + R effect in phenol:



- b) **Negative Resonance Effect (- R effect):** Here the transfer of electrons is towards the atom or substituent group attached to the conjugated system. E.g. - R effect in nitrobenzene:



The presence of alternate single and double bonds in an open chain or cyclic system is termed as a conjugated system.

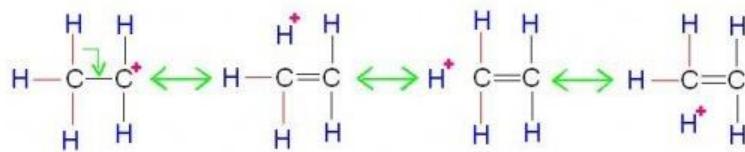
E.g. for +R effect groups: -X (halogen), -OH, -OR, -OCOR, -NH₂, -NHR, -NR₂, -NHCOR etc.

E.g. for - R effect groups: - COOH, -CHO, >C=O, - CN, -NO₂ etc.

4. Hyper conjugation:

It is a permanent effect. In this effect the σ electrons of C–H bond of the alkyl group enter into partial conjugation with the unsaturated system or with the unshared p orbital. i.e. the σ electrons of C–H bonds get delocalised.

E.g. Ethyl cation ($\text{CH}_3\text{-CH}_2^+$)



Hyper conjugation stabilizes the carbocation because electron density from the adjacent σ bond helps in dispersing the positive charge. In general, the greater the number of alkyl groups attached to a positively charged carbon atom, the greater is the hyper conjugation interaction and stabilization of the cation.

Thus the relative stability of carbocations is in the order: $(\text{CH}_3)_3\text{C}^+ > (\text{CH}_3)_2\text{CH}^+ > \text{CH}_3\text{-CH}_2^+ > \text{CH}_3^+$.

Here tertiary carbocation has 9, isopropyl has 6, ethyl carbocation has 3 and methyl carbocation has zero hyper conjugative structures.

Hyper conjugation is also called no-bond resonance and it is also possible in alkenes and alkyl arenes.

Types of Organic reactions

Organic reactions can be classified into the following categories:

- Substitution reactions
- Addition reactions
- Elimination reactions
- Rearrangement reactions

PURIFICATION OF ORGANIC COMPOUNDS

An organic compound may contain impurities and is essential to purify it. Various methods used for the purification of organic compounds are based on the nature of the compound and the impurity present in it.

The common techniques used for purification are as follows:

- Sublimation
- Crystallisation
- Distillation
- Differential extraction and
- Chromatography

1. Sublimation

It is the process of conversion of a solid substance directly to vapour by heating. It is used to separate sublimable compounds from non-sublimable impurities.

In this method, the substance is placed in a sublimation apparatus and heated under vacuum. Under this reduced pressure, the solid sublimes and condenses as a purified compound on a cooled surface. The impurities left behind on the apparatus.

This method is used for the purification of naphthalene, iodine, camphor etc.

2. Crystallisation

This is one of the most commonly used techniques for the purification of solid organic compounds. It is based on the difference in the solubilities of the compound and the impurities in a suitable solvent. The impure compound is dissolved in a solvent in which it is sparingly soluble at room temperature but appreciably soluble at higher temperature. The solution is concentrated to get a nearly saturated solution. On cooling the solution, pure compound crystallises out and is removed by

filtration. If the compound is highly soluble in one solvent and very little soluble in another solvent, crystallisation can be satisfactorily carried out in a mixture of these solvents.

3. Distillation

This method is used to separate (i) volatile liquids from non-volatile impurities and (ii) the liquids having sufficient difference in their boiling points. The principle of this method is that liquids having different boiling points vapourise at different temperatures. The vapours are cooled and the liquids so formed are collected separately.

In this method, the liquid mixture is taken in a round bottom flask and heated carefully. On boiling, the vapours of lower boiling liquid are formed first. The vapours are condensed by using a condenser and the liquid is collected in a receiver. The vapours of higher boiling liquid form later and it can be collected separately. Chloroform (b.p 334 K) and aniline (b.p. 457 K) are separated by this technique. There are different types of distillation methods. They are:

a) *Fractional distillation:*

Fractional distillation is used to separate two or more liquids that are miscible. It is a special type of distillation designed to separate a mixture of two or more liquids that have different boiling points. The process involves heating the mixture and partial condensation of the vapours along a fractionating column. The column is set up such that components with lower boiling points pass through the column and are collected earlier than components with higher boiling points. Repeated vaporization and condensation result in the separation of the components of the mixture. The efficiency of fractional distillation depends on the use of the fractionating column. The fractionating column is packed with glass beads. It provides a large surface area for vaporization and condensation of the liquid mixture.

Ethanol and water mixture, crude oil, toluene and cyclohexane etc. are separated by this method.

b) *Distillation under reduced pressure:*

This method is used to purify liquids having very high boiling points and those, which decompose at or below their boiling points. Such liquids are made to boil at a temperature lower than their normal boiling points by reducing the pressure on their surface. The pressure is reduced with the help of a water pump or vacuum pump. Glycerol can be separated from spent-lye in soap industry by using this technique.

c) *Steam Distillation:*

This technique is applied to separate substances which are steam volatile and are immiscible with water. In steam distillation, steam from a steam generator is passed through a heated flask containing the liquid to be distilled. The mixture of steam and the volatile organic compound is condensed and collected. The compound is later separated from water using a separating funnel. Aniline – water mixture is separated by this method.

4. Differential Extraction

When an organic compound is present in an aqueous medium, it is separated by shaking it with an organic solvent in which it is more soluble than in water. The organic solvent and the aqueous solution should be immiscible with each other. So they form two distinct layers which can be separated by separating funnel. The organic solvent is later removed by distillation or by evaporation to get back the compound.

5. Chromatography

This method is used to separate mixtures into their components, to purify compounds and to test the purity of compounds. Here the mixture to be separated is passed through a stationary phase, which may be a solid or a liquid. A pure solvent (sometimes a mixture of solvents or a gas) is allowed to move slowly over the stationary phase. The moving phase is called the mobile phase. The

components of the mixture get gradually separated from one another.

Based on the principle involved, there are mainly two types of chromatography:

- (a) Adsorption chromatography, and
- (b) Partition chromatography

a) Adsorption Chromatography: Adsorption chromatography is based on the fact that different compounds are adsorbed on an adsorbent in different degrees. Commonly used adsorbents are silica gel and alumina. Here a mobile phase is allowed to move over a stationary phase (adsorbent). Based on the adsorbing power, the components of the mixture are adsorbed at different places over the stationary phase. Following are two main types of chromatographic techniques based on the principle of differential adsorption.

- i) Column chromatography, and
- ii) Thin layer chromatography.

i) Column Chromatography:

It involves the separation of a mixture over a column of adsorbent (stationary phase) packed in a glass tube. The column is fitted with a stopcock at its lower end. The mixture to be separated is passed through the column. Based on the adsorbing power, the components are adsorbed at different places over the column. The most readily adsorbed substances are retained near the top and others come down to various distances in the column. Then an appropriate eluant (mobile phase) is allowed to flow down the column slowly. [Eluant is a solvent or a mixture of solvents used to move the compounds through the column]. Thus the different components can be collected separately.

ii) Thin Layer Chromatography (TLC):

It is another type of adsorption chromatography. It involves the separation of substances of a mixture over a thin layer of an adsorbent coated on a glass plate. A thin layer of an adsorbent like silica gel or alumina is coated over a glass plate of suitable size. The plate is known as *thin layer chromatography plate or chromaplate*.

The solution of the mixture to be separated is applied as a small spot, 2 cm above one end of the TLC plate. The glass plate is then placed in a closed jar containing the eluant. As the eluant rises up the plate, the components of the mixture move up along with the eluant to different distances depending on their degree of adsorption and separation takes place. The relative adsorption of each component of the mixture is expressed in terms of its **retardation factor (R_f value)**.

$$R_f = \frac{\text{Distance moved by the substance from base line (x)}}{\text{Distance moved by the solvent from base line (y)}}$$

The spots of coloured compounds are visible on TLC plate due to their original colour. The spots of colourless compounds can be detected by putting the plate under ultraviolet light.

b) Partition Chromatography:

It is based on continuous differential partitioning of components of a mixture between stationary and mobile phases. Paper chromatography is a type of partition chromatography.

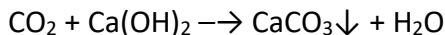
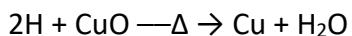
In **paper chromatography**, a special quality paper known as chromatography paper is used. Chromatography paper contains water trapped in it, which acts as the stationary phase. A strip of chromatography paper, spotted at the base with the solution of the mixture, is suspended in a suitable solvent or a mixture of solvents. This solvent acts as the mobile phase. The solvent rises up the paper by capillary action and flows over the spot. The paper selectively retains different components according to their differing partition in the two phases. The paper strip is known as a chromatogram. The spots of the separated coloured compounds are visible at different heights from the position of initial spot on the chromatogram. These spots can be visible by u.v. light or by spraying suitable reagents.

QUALITATIVE ANALYSIS OF ORGANIC COMPOUNDS

An organic compound mainly contains carbon and hydrogen. Some compounds may also contain oxygen, nitrogen, sulphur, halogens and phosphorus.

Detection of Carbon and Hydrogen

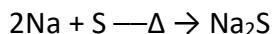
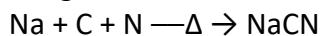
Organic compound is heated with copper (II) oxide [CuO]. Carbon present in the compound is oxidised to carbon dioxide and hydrogen to water. CO₂ can be tested by passing through lime-water, which turns milky and water can be tested with anhydrous copper sulphate, which turns blue.



Detection of Nitrogen, Sulphur and Halogens – Lassaigne's Test

Nitrogen, sulphur and halogens present in an organic compound are detected by "**Lassaigne's test**". Here the organic compound is fused with metallic sodium in a fusion tube. It is then plunged into distilled water taken in a china dish. The solution is boiled and filtered. The filtrate is known as sodium fusion extract.

Principle: In an organic compound, nitrogen, sulphur and halogen atoms are present in covalent form. By heating with metallic sodium, these elements are converted to ionic form as follows:



For the detection of the elements, the following tests are done:

No.	Experiment	Observation	Inference
1.	To one part of sodium fusion extract add freshly prepared ferrous sulphate (FeSO ₄) solution. Heated to boiling, cooled and acidified with dil. H ₂ SO ₄ .	Blue or green colouration or precipitate (ppt)	Presence of nitrogen
2.	A little of the sodium fusion extract is acidified with dil. HNO ₃ and then silver nitrate (AgNO ₃) is added.	White ppt soluble in ammonium hydroxide (NH ₄ OH)	Presence of Chlorine
		Pale yellow ppt slightly soluble in NH ₄ OH	Presence of Bromine
		Yellow ppt insoluble in NH ₄ OH	Presence of Iodine
3.	To a little of the sodium fusion extract, add sodium nitroprusside solution	Violet colouration	Presence of sulphur

Test for Phosphorus

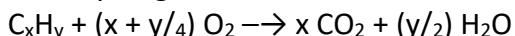
The organic compound is heated with an oxidising agent like sodium peroxide. The phosphorus present in the compound is oxidised to phosphate. The solution is boiled with nitric acid and then treated with ammonium molybdate. A yellow colouration or precipitate indicates the presence of phosphorus.

QUANTITATIVE ANALYSIS OF ORGANIC COMPOUNDS

The percentage composition of elements present in an organic compound is determined by the following methods:

1. Estimation of Carbon and Hydrogen

Carbon and hydrogen are estimated by **Liebig's combustion method**. In this method, a known mass of an organic compound is burnt in the presence of excess of oxygen and copper(II) oxide. Then carbon is oxidised to CO₂ and hydrogen is oxidised to H₂O.



The water so produced is absorbed in a weighed U-tube containing anhydrous calcium chloride and carbon dioxide is absorbed in another U-tube containing concentrated solution of potassium hydroxide. These tubes are connected in series. The increase in masses of calcium chloride and potassium hydroxide gives the amounts of water and carbon dioxide from which the percentages of carbon and hydrogen are calculated.

Calculations:

Let the mass of organic compound be w g, mass of water and carbon dioxide produced be m₁ and m₂ g respectively.

$$\text{Percentage of hydrogen} = \frac{2 \times m_1 \times 100}{18 \times w} \%$$

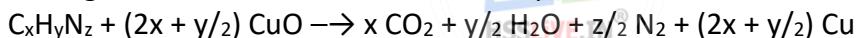
$$\text{Percentage of carbon} = \frac{12 \times m_2 \times 100}{44 \times w} \%$$

2. Estimation of Nitrogen

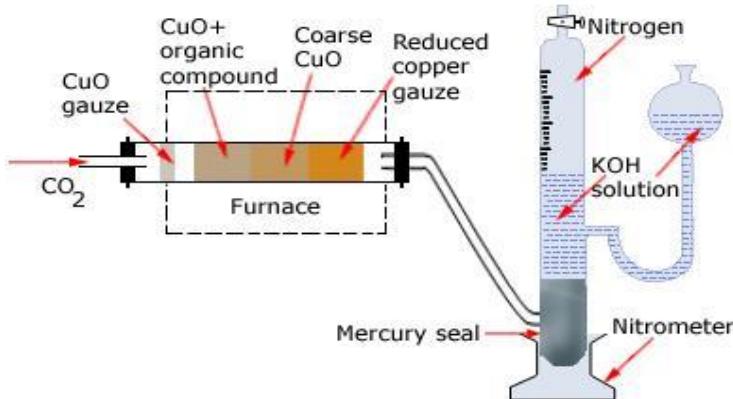
There are two methods for estimation of nitrogen: (i) Dumas method and (ii) Kjeldahl's method.

i) Dumas method:

Here the organic compound is heated with copper oxide in an atmosphere of carbon dioxide so that free nitrogen, carbon dioxide and water are produced.



This mixture of gases is collected over an aqueous solution of potassium hydroxide which absorbs carbon dioxide. Nitrogen is collected in the upper part of the graduated tube.



Calculations:

Let the mass of organic compound = w g

Volume of nitrogen collected = V₁ mL

Room temperature = T₁ K

$$\text{Volume of nitrogen at STP} = \frac{P_1V_1 \times 273}{760 \times T_1} = V \text{ mL}$$

Where P₁ and V₁ are the pressure and volume of nitrogen gas.

P₁ = Atmospheric pressure – Aqueous tension

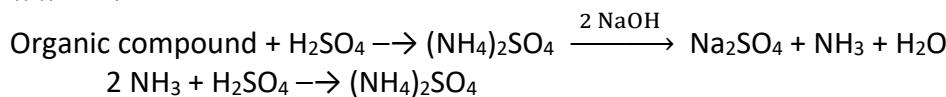
We know that 22400 mL N₂ at STP weighs 28 g.

Therefore, V mL N₂ at STP weighs = $\frac{28 \times V}{22400}$ g

Percentage of nitrogen = $\frac{28 \times V \times 100}{22400 \times w} \%$

ii) Kjeldahl's method:

Here the organic compound containing nitrogen is heated with concentrated sulphuric acid. Nitrogen in the compound gets converted to ammonium sulphate. The resulting acidic mixture is then heated with excess of sodium hydroxide. The liberated ammonia gas is absorbed in an excess of standard solution of sulphuric acid. The amount of ammonia produced is determined by estimating the amount of sulphuric acid consumed in the reaction. It is done by estimating unreacted sulphuric acid left after the absorption of ammonia by titrating it with standard alkali solution. The difference between the initial amount of acid taken and that left after the reaction gives the amount of acid reacted with ammonia.



Calculations:

Let the mass of organic compound taken = w g

Volume of H₂SO₄ of molarity M, taken = V mL

Volume of NaOH of molarity M, used for titration of excess of H₂SO₄ = V₁ mL

V₁ mL of NaOH of molarity M = $\frac{V_1}{2}$ mL of H₂SO₄ of molarity M

Volume of H₂SO₄ of molarity M used to neutralize the ammonia formed = $(V - \frac{V_1}{2})$ mL = y mL

y mL of H₂SO₄ of molarity M = 2y mL of NH₃ solution of molarity M.

1000 mL of 1 M NH₃ solution contains 17g NH₃ or 14 g of N

2y mL of NH₃ solution of molarity M contains $\frac{14 \times M \times 2y}{1000}$ g N

Percentage of N = $\frac{14 \times M \times 2y \times 100}{1000 \times w} \%$

Note: Kjeldahl's method is not applicable to compounds containing nitrogen in nitro and azo groups and nitrogen present in the ring (e.g. pyridine) as nitrogen of these compounds does not change to ammonium sulphate under these conditions.

3. Estimation of halogens (Carius method):

Here a known mass of an organic compound is heated with fuming nitric acid in the presence of silver nitrate contained in a hard glass tube known as Carius tube, in a furnace. Carbon and hydrogen present in the compound are oxidised to carbon dioxide and water. The halogen present forms the corresponding silver halide (AgX). It is filtered, washed, dried and weighed.

Calculations:

Let the mass of organic compound taken = w g

Mass of AgX formed = m₁ g

1 mol of AgX contains 1 mol of halogen

Mass of halogen in m₁g of AgX = $\frac{\text{Atomic mass of halogen} \times m_1}{\text{Molar mass of AgX}}$ g

Percentage of halogen = $\frac{\text{Atomic mass of halogen} \times m_1 \times 100}{\text{Molar mass of AgX} \times w} \%$

4. Estimation of Sulphur (Carius method):

A known mass of an organic compound is heated in a Carius tube with sodium peroxide or fuming nitric acid. Sulphur present in the compound is oxidised to sulphuric acid. It is precipitated as barium sulphate by adding excess of barium chloride solution. The precipitate is filtered, washed, dried and weighed. The percentage of sulphur can be calculated from the mass of barium sulphate (BaSO_4).

Calculations:

Let the mass of organic compound taken = w g and the mass of barium sulphate formed = m_1 g

1 mol of BaSO_4 = 233 g BaSO_4 = 32 g sulphur

m_1 g BaSO_4 contains $\frac{32 \times m_1}{233}$ g sulphur

$$\text{Percentage of sulphur} = \frac{32 \times m_1 \times 100}{233 \times w} \%$$

5. Estimation of Phosphorus

A known mass of an organic compound is heated with fuming nitric acid. Phosphorus present in the compound is oxidised to phosphoric acid. It is precipitated as ammonium phosphomolybdate $[(\text{NH}_4)_3\text{PO}_4 \cdot 12\text{MoO}_3]$ by adding ammonia and ammonium molybdate.

Calculations:

Let the mass of organic compound taken = w g and mass of ammonium phosphomolybdate = m_1 g

Molar mass of $(\text{NH}_4)_3\text{PO}_4 \cdot 12\text{MoO}_3$ = 1877 g

$$\text{Percentage of phosphorus} = \frac{31 \times m_1 \times 100}{1877 \times w} \%$$

6. Estimation of Oxygen

The percentage of oxygen in an organic compound is usually found by difference between the total percentage composition (100) and the sum of the percentages of all other elements.

i.e. percentage of oxygen = 100 – sum of the percentage of all the other elements.

Q1) On complete combustion, 0.246g of an organic compound gave 0.198g of CO_2 and 0.1014g of H_2O . Determine the percentage composition of carbon and hydrogen in the compound.

Ans: Mass of organic compound (m) = 0.246 g

Mass of CO_2 formed (m_1) = 0.198 g

$$\text{Percentage of carbon} = \frac{12 \times m_1 \times 100}{44 \times w} \% = \frac{12 \times 0.198 \times 100}{44 \times 0.246} \% = 21.95\%$$

Mass of water formed (m_2) = 0.1014 g

$$\text{Percentage of hydrogen} = \frac{2 \times m_2 \times 100}{18 \times w} \% = \frac{2 \times 0.1014 \times 100}{18 \times 0.246} \% = 4.58\%$$

Q2) In the Carius method of estimation of halogen, 0.15g of an organic compound gave 0.12g of AgBr . Find the percentage of Br in the compound.

Ans: Mass of organic compound (m) = 0.15 g

Mass of AgBr formed (m_1) = 0.12 g

Atomic mass of Br = 80

Molar mass of AgBr = 108 + 80 = 188 g/mol

$$\text{Percentage of Br} = \frac{\text{Atomic mass of Br} \times m_1 \times 100}{\text{Molar mass of AgBr} \times w} \% = \frac{80 \times 0.12 \times 100}{188 \times 0.15} \% = 34.04\%$$

9. HYDROCARBONS

Organic compounds containing carbon and hydrogen atoms only are called hydrocarbons. Depending on the types of C-C bond, they can be classified into three – saturated, unsaturated and aromatic hydrocarbons. Saturated hydrocarbons are also called alkanes. They contain only C-C single bonds. Unsaturated hydrocarbons contain atleast one carbon-carbon double bond (alkene) or carbon-carbon triple bond (alkyne). Aromatic hydrocarbons are a special type of cyclic compounds. They are also called arenes.

ALKANES

Alkanes are saturated open chain hydrocarbons containing carbon-carbon single bonds. They form a homologous series. Their general molecular formula is C_nH_{2n+2} . In alkanes, all the C atoms are sp^3 hybridised. So each C atom has a regular tetrahedral shape.

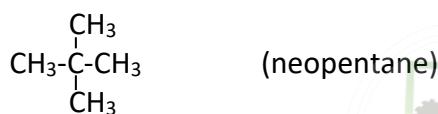
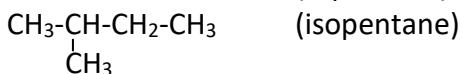
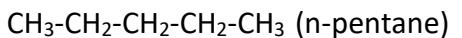
Alkanes do not react with acids, bases and other reagents under normal conditions. So they are also called paraffins. (In Latin paraffin means little affinity).

Isomerism in Alkanes

Alkanes show two types of structural isomerism – **chain isomerism** and **position isomerism**.

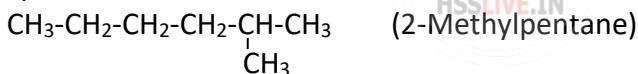
Chain isomers differ in the carbon skeleton. i.e arrangement of carbon atoms in the chain.

E.g.: The chain isomers of alkane with molecular formula C_5H_{12} are:



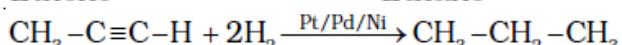
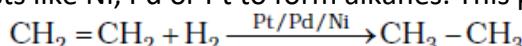
Position isomers differ in the position of the side chain or branch.

E.g. The position isomers of alkane with molecular formula C_6H_{14} are:



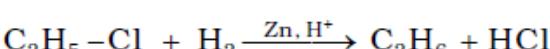
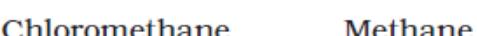
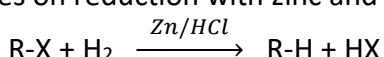
Preparation of alkanes

- From unsaturated hydrocarbons: Alkenes and alkynes add Hydrogen in presence of finely divided catalysts like Ni, Pd or Pt to form alkanes. This process is called **hydrogenation**.



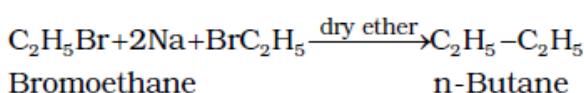
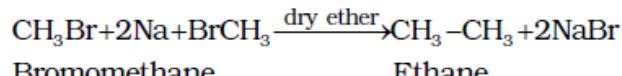
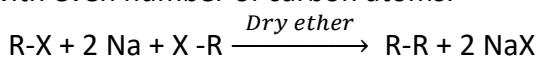
- From alkyl halides:

- Alkyl halides on reduction with zinc and dil. HCl, we get alkanes.



b) ***Wurtz reaction:***

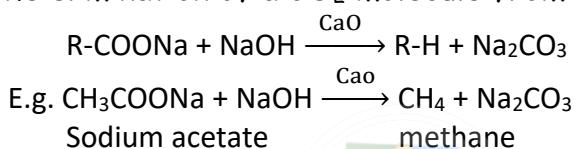
Alkyl halides react with metallic sodium in dry ether to form alkanes. This reaction is known as Wurtz reaction. The alkane so formed contains double the number of C atoms than that present in the alkyl halide. Hence this method is used for the preparation of alkanes with even number of carbon atoms.



When two different alkyl halides are used, we get a mixture of alkanes.

3. **From carboxylic acids:**

a) ***Decarboxylation:*** Sodium salt of carboxylic acids (R-COONa) on heating with soda lime (a mixture of NaOH and CaO), we get an alkane containing one carbon atom less than that of the carboxylic acid. This process is known as decarboxylation, since it involves the elimination of a CO_2 molecule from the carboxylic acid (R-COOH).



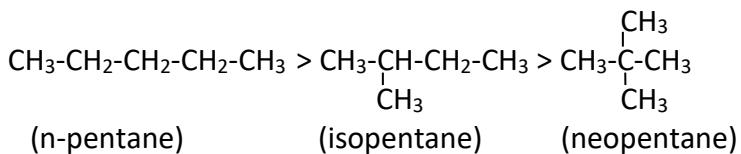
b) ***Kolbe's Electrolytic method:*** An aqueous solution of sodium or potassium salt of a carboxylic acid on electrolysis gives alkane containing even number of carbon atoms.



Physical Properties

Boiling point of alkanes increase with increase of molecular mass (or with number of C atoms). This is because in alkanes there is only weak van der Waal's force of attraction between different molecules. As the molecular size increases, the surface area increases and hence van der Waal's force increases. So the boiling point increases.

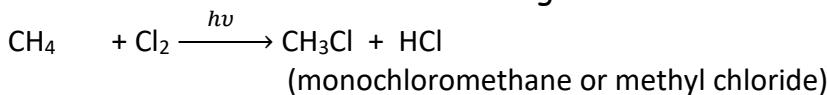
The boiling point of isomeric alkanes decreases with branching. As the branching increases, the molecule attains the shape of a sphere. So the surface area decreases and hence the b.p. So among three isomeric pentane boiling point decreases in the order: n-pentane > isopentane > neopentane.

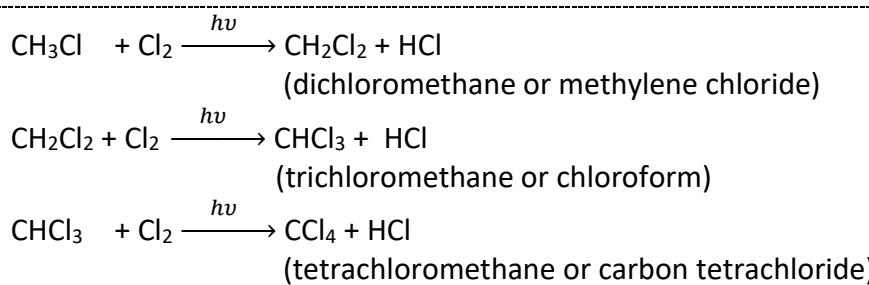


Chemical Properties

1. **Substitution reactions**

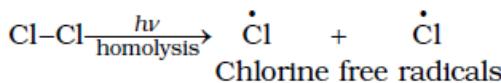
These are reactions in which hydrogen atom of an alkane is replaced by other atoms or atom groups. E.g. when an alkane is treated with halogen in the presence of diffused sunlight or uv light, we get haloalkane. This reaction is known as halogenation reaction.



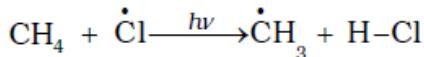
**Mechanism**

Halogenations takes place by free radical chain mechanism and it involves three steps – initiation, propagation and termination.

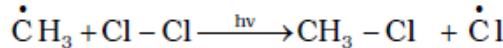
- i) *Initiation step:* The reaction is initiated by the homolysis of chlorine molecule in presence of sunlight.



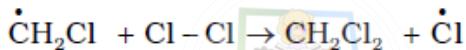
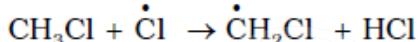
- ii) *Propagation step:* The chlorine free radical attacks the methane molecule and form methyl free radical and HCl.



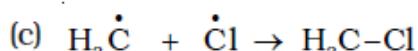
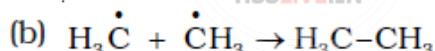
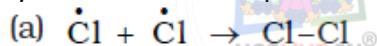
The methyl radical then attacks the second Cl₂ molecule to form CH₃Cl and Chlorine free radical.



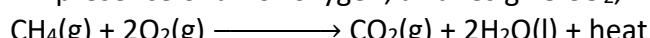
The above two steps repeat and thus the reaction propagates.



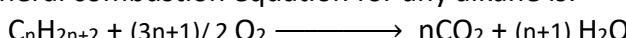
- iii) *Termination step:* The reaction stops after some time due to any one of the following reactions:

**2. Combustion (Oxidation):**

On combustion in presence of air or oxygen, alkanes give CO₂, H₂O and large amount of heat.



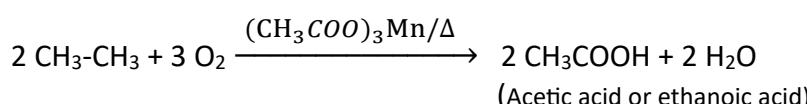
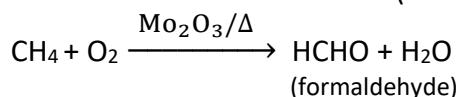
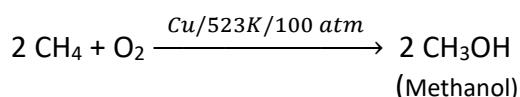
The general combustion equation for any alkane is:



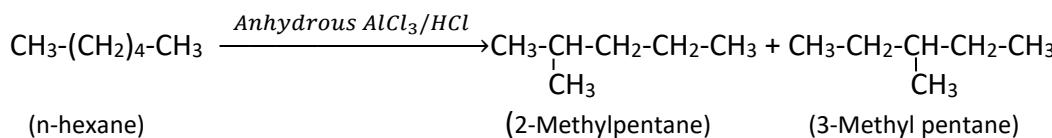
Incomplete combustion of alkanes with insufficient amount of air or O₂ gives carbon black.

3. Controlled Oxidation:

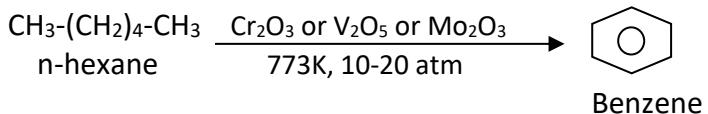
Alkanes on heating with O₂ at high pressure and in presence of suitable catalysts to form different products like alcohol, aldehyde or carboxylic acid.



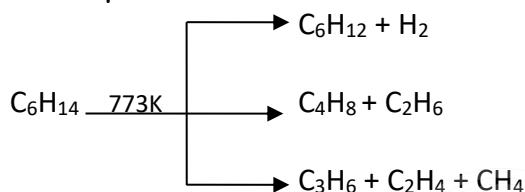
4. Isomerisation: n-Alkanes on heating in the presence of anhydrous aluminium chloride and hydrogen chloride gas isomerise to branched chain alkanes.



5. Aromatization: n-Alkanes having six or more carbon atoms on heating to 773K at 10 to 20 atmospheric pressure in the presence of oxides of vanadium, molybdenum or chromium supported over alumina, we get aromatic compounds. This reaction is known as aromatization or reforming.



6. Pyrolysis: Alkanes having six or more carbon atoms on heating at higher temperature decompose to form lower alkanes, alkenes etc. This reaction is known as pyrolysis.



Conformations of Alkanes

Alkanes contain carbon-carbon sigma (σ) bonds. Since, electron distribution of the sigma bonds is symmetrical around the bond axis, rotation around C–C bond is allowed. This rotation changes the spatial arrangements of atoms attached to C atoms. These different spatial arrangements of atoms arising due to free rotation around a C-C single bond are called conformations or conformers or rotamers.

Conformations of Ethane

Ethane contains a C–C σ bond and each carbon atom contains three hydrogen atoms. Due to free rotation of C atoms around the single bond, the spatial arrangement of hydrogen atoms attached to the C atoms change. Thus ethane can show an infinite number of conformational isomers.

If we fix one carbon atom and rotate the other, there arise two extreme cases called eclipsed and staggered conformations.

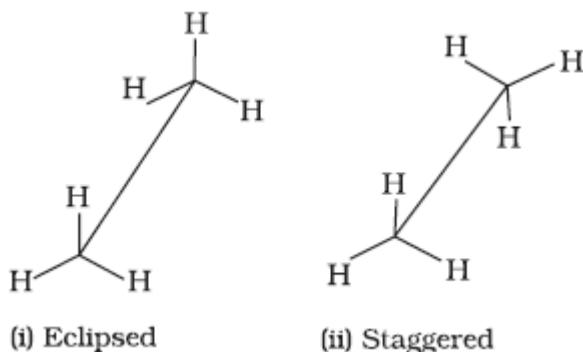
In eclipsed conformation, the hydrogen atoms attached to each carbon atoms are closed together as possible. Or, here the hydrogen atoms of the 2nd carbon atoms are exactly behind that of the first.

In staggered conformation, the hydrogen atoms are far apart as possible. Any conformations between eclipsed and staggered conformations are called skew conformations.

Staggered conformation is stabler than eclipsed form. This is because in staggered form, the electron clouds of carbon-hydrogen bonds are very far apart. So there is minimum repulsive forces, minimum energy and maximum stability. But in eclipsed form, the electron clouds are close to each other. So the repulsion is maximum and the stability is minimum. Eclipsed and staggered conformations can be represented by **Sawhorse and Newman projection formulae**.

1. Sawhorse projections:

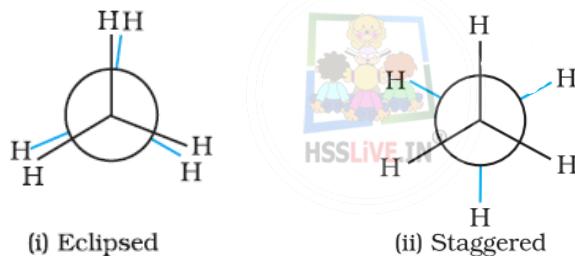
Here the molecule is viewed along the molecular axis. C–C bond is denoted by a longer straight line. The front carbon is shown at the lower end of the line and the back carbon is shown at the upper end. Each carbon has three lines at an angle of 120° corresponding to three hydrogen atoms. Sawhorse projections of eclipsed and staggered conformations of ethane are as follows:



2. Newman projections:

Here the molecule is viewed at the C–C bond head on (i.e. from the front side). The front carbon atom is represented by a point. Three hydrogen atoms attached to this carbon atom are shown by three lines drawn at an angle of 120° to each other. The back carbon atom is represented by a circle and the three hydrogen atoms are shown attached to it are denoted by shorter lines drawn at an angle of 120° to each other.

The Newman's projections for eclipsed and staggered conformations of ethane are as follows:



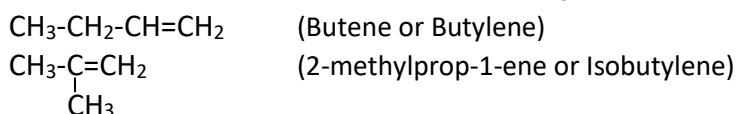
ALKENES

Alkenes are unsaturated hydrocarbons containing at least one C=C (carbon-carbon double bond). They are also known as *olefins* (oil forming) since the first member, ethylene or ethene (C_2H_4) forms an oily liquid on reaction with chlorine. The general formula for alkenes is C_nH_{2n} .

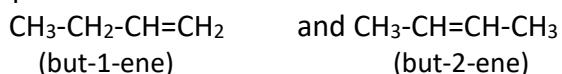
Isomerism in alkenes

Alkenes show *structural and stereo isomerism*. The important **structural isomerism** shown by alkenes are *chain isomerism and position isomerism*.

E.g. for chain isomers with molecular formula C_4H_8 are:



E.g. for position isomers with molecular formula C_4H_8 are:



The stereoisomers have same atom to atom bond but they differ only in the spatial arrangement of atoms or groups. The **stereoisomerism** shown by alkenes is geometrical isomerism.

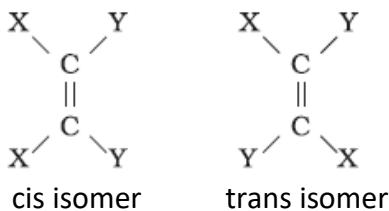
Geometrical Isomerism

The isomerism arising due to the difference in the spatial arrangement of atoms around carbon-carbon double bond is called geometrical isomerism. Such isomers are called geometrical isomers. It is a type of stereo isomerism.

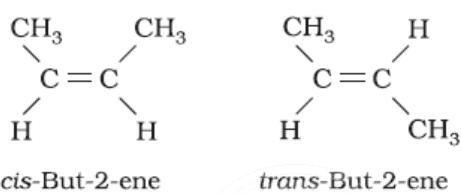
Geometrical isomerism arising due to the restricted rotation about carbon-carbon double bond. There are two types of geometrical isomers - *cis isomer* and *trans isomer*.

Isomer in which *identical atoms or groups are on the same side of the double bond is called cis isomer*. If the identical groups or atoms are on the opposite side of the double bond, it is called *trans isomer*.

Compounds with general formula $\text{YX C}=\text{C XY}$ can show geometrical isomerism as follows:

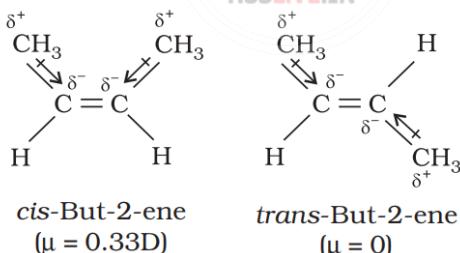


E.g. But-2-ene



Due to different arrangement of atoms or groups in space, these isomers differ in their physical properties like melting point, boiling point, dipole moment, solubility etc.

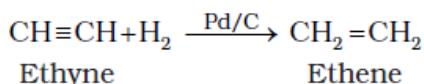
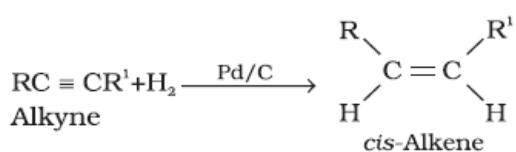
Cis form of alkene is found to be more polar than the trans form. In trans form, the bond dipoles are in opposite directions and so they get cancelled each other.



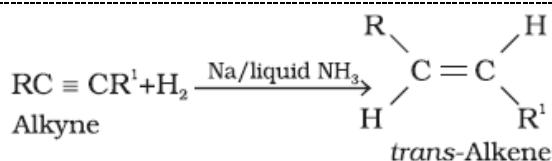
In the case of solids, the trans isomer has higher melting point than the cis form.

PREPARATION OF ALKENES

1. From Alkynes: Alkynes on partial reduction with dihydrogen in the presence of *palladised charcoal partially deactivated with sulphur compounds or quinoline* give alkenes. Partially deactivated palladised charcoal is known as Lindlar's catalyst. Alkenes thus obtained are having *cis geometry*.

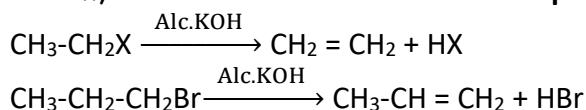


If we use sodium in liquid ammonia as the reducing agent, we get *trans* alkene.



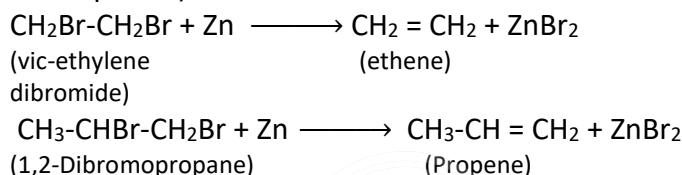
2. From Alkyl halides:

Alkyl halides (R-X) on heating with alcoholic potash, eliminate one molecule of hydrogen halide to form alkenes. This reaction is known as dehydrohalogenation (i.e., removal of hydrogen halide from a compound). Since hydrogen atom is eliminated from the β carbon atom, the reaction is also known as **β -elimination reaction**.



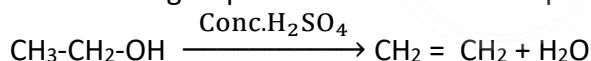
3. From vicinal dihalides:

Dihalides in which halogen atoms are attached to two *adjacent carbon atoms* are known as *vicinal* (vic) dihalides. Vicinal dihalides on treatment with zinc metal lose a molecule of ZnX_2 to form an alkene. This reaction is known as dehalogenation (i.e. elimination of halogen molecule from a compound).



4. From alcohols:

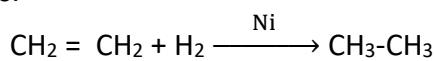
Alcohols when heated with concentrated sulphuric acid undergo dehydration (elimination of water molecule) to form alkenes. This reaction is also the example of β -elimination reaction since $-\text{OH}$ group is eliminated from the β -carbon atom.



Chemical Properties

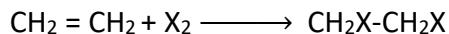
1. Addition of hydrogen:

Alkenes add hydrogen in presence of finely divided Ni, Pd or Pt to form alkanes.



2. Addition of halogen:

Alkenes add halogen (Cl_2 or Br_2) to form vicinal dihalides.

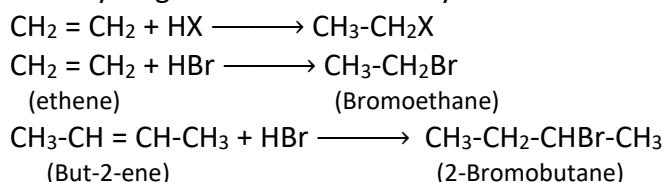


When Br_2 dissolved in CCl_4 (carbon tetrachloride) is added to unsaturated compounds (alkenes or alkynes), the reddish orange colour of bromine solution is discharged. This reaction is used as a test for unsaturation.



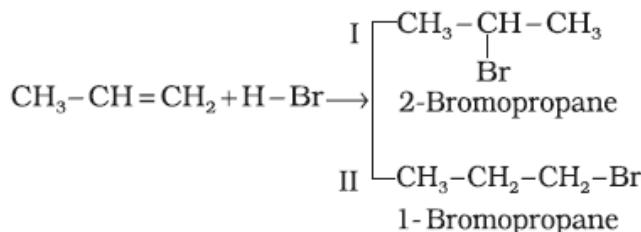
3. Addition of hydrogen halide:

Alkenes add hydrogen halide to form alkyl halides.



Addition of HBr to unsymmetrical alkenes (Markovnikov's Rule)

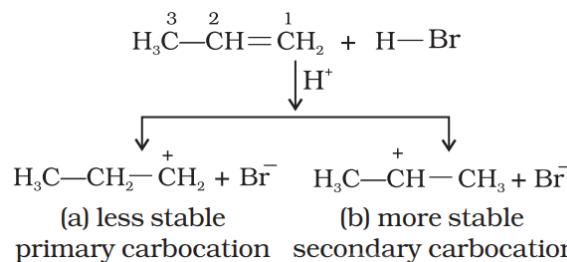
When HBr is added to propene, we get 2 products – 1-bromopropane and 2-bromopropane.



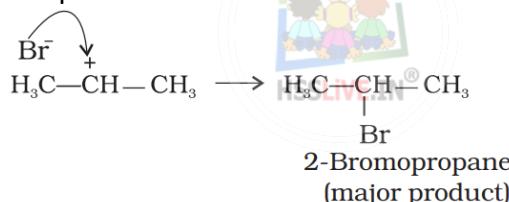
Here the major product is determined by a rule called **Markovnikov rule**. The rule states that "when an unsymmetrical reagent is added to an unsymmetrical alkene, the negative part of the addendum (adding molecule) gets attached to the double bonded carbon with lesser number of hydrogen atoms". Thus in the above reaction 2-bromopropane is the major product.

Mechanism:

- (i) Hydrogen bromide provides an electrophile H^+ , which attacks the double bond to form carbocation.

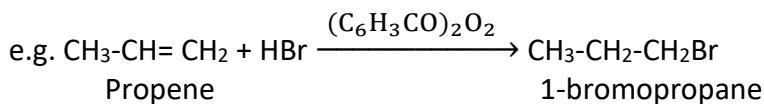


- (ii) Since secondary carbocation (b) is more stable than the primary carbocation (a), it is attacked by Br^- ion to form the product as follows :



Anti Markovnikov addition or peroxide effect or Kharash effect

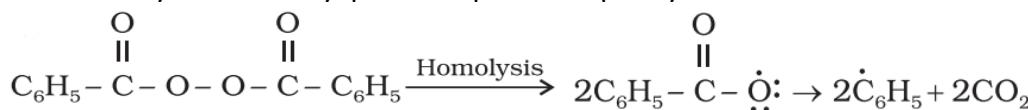
In presence of organic peroxide (e.g. acetyl peroxide $[(\text{CH}_3\text{-CO})_2\text{O}_2]$, benzoyl peroxide $[(\text{C}_6\text{H}_5\text{CO})_2\text{O}_2]$ etc.), addition of HBr to unsymmetrical alkenes takes place against Markovnikov rule. i.e. in such cases, the negative part of the reagent gets attached to the double bonded carbon atom with greater number of hydrogen atom. This is known as **peroxide effect or Kharash effect or anti-Markovnikov addition reaction**.



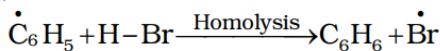
Mechanism:

Peroxide effect proceeds via *free radical chain mechanism* as follows:

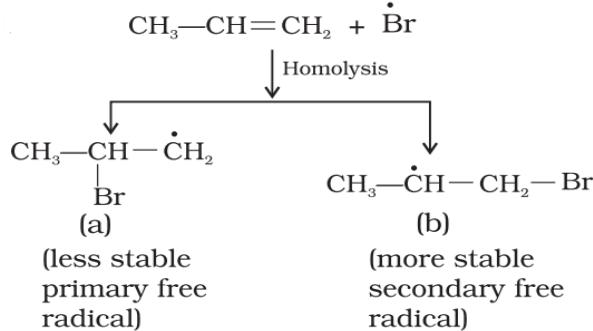
- (i) Homolysis of benzoyl peroxide produces phenyl free radical.



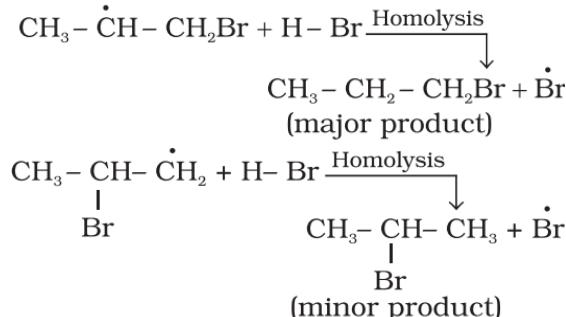
- (ii) Phenyl free radical reacts with HBr to form Bromine free radical.



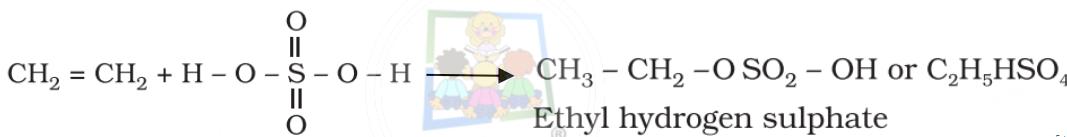
(iii) Bromine free radical attacks propene to form a primary and secondary free radicals. Since secondary free radical is stabler, it will be the major one.



(iv) These free radicals react with H-Br to form the products and Bromine free radical.

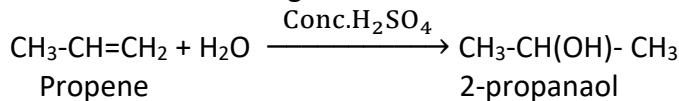


4. **Addition of sulphuric acid:** Cold concentrated sulphuric acid adds to alkenes and form alkyl hydrogen sulphate. The reaction takes place in accordance with Markovnikov rule.



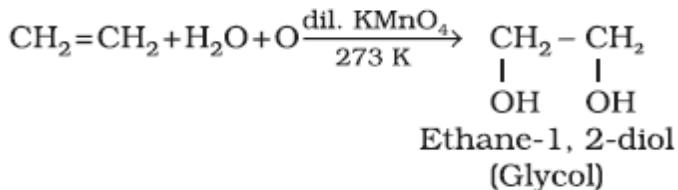
5. **Addition of water:**

Alkenes add water in presence of a few drops of concentrated sulphuric acid to form alcohols. The reaction occurs according to the Markovnikov rule.



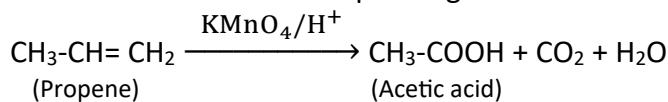
6. **Oxidation:**

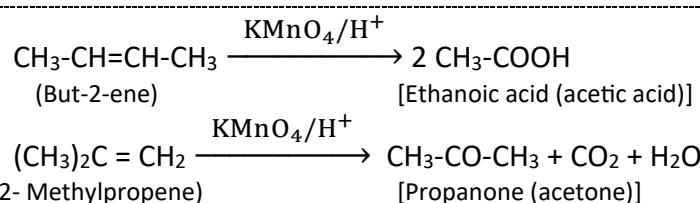
i) When oxidised using cold and dilute aqueous solution of potassium permanganate (KMnO_4) [commonly called Baeyer's reagent], alkenes give vicinal glycols.



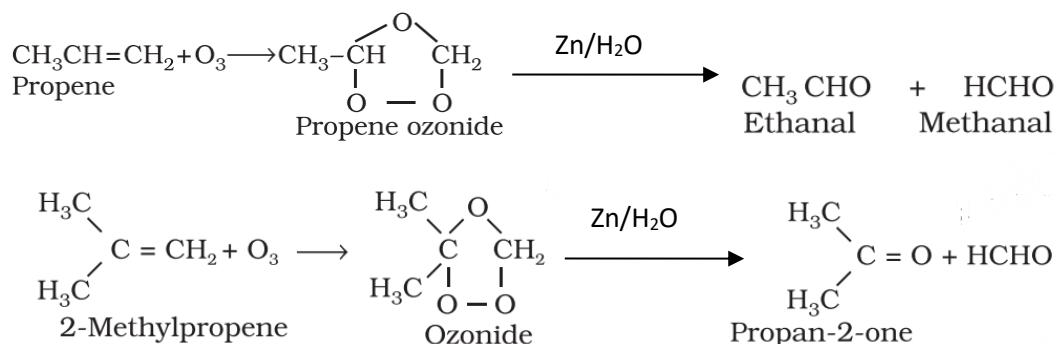
When KMnO_4 is added to alkene, its pink colour gets discharged. So this reaction is also used as a test for unsaturation.

ii) Acidified potassium permanganate (KMnO_4) or acidified potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$) oxidises alkenes to ketone or acids depending on the nature of the alkene.

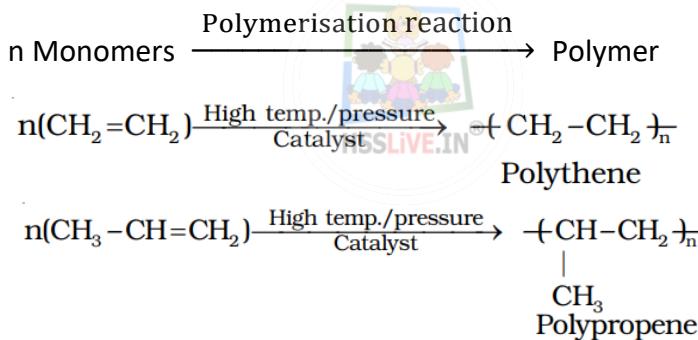




7. Ozonolysis: Alkenes add ozone to form an ozonide which on hydrolysis in presence of Zn to form carbonyl compounds (Aldehydes or ketones).



8. Polymerisation: The complex organic molecules formed by the combination of simple molecules are called polymers (macromolecules) and the reaction is called polymerisation reaction. The simple molecule from which a polymer is formed is called monomer.



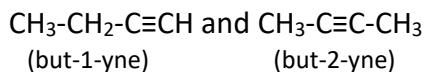
ALKYNES

They are unsaturated hydrocarbons containing at least one $\text{C}\equiv\text{C}$ bond [carbon-carbon triple bond]. Their general formula is $\text{C}_n\text{H}_{2n-2}$. The first member of alkyne series is ethyne commonly called acetylene (C_2H_2). Other members are considered as the derivatives of acetylene and so alkynes are also called Acetylenes. In alkynes, the triple bonded carbon atoms are sp hybridized and hence are linear.

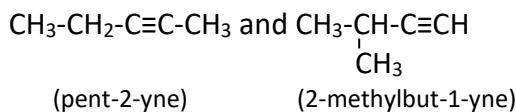
Isomerism in Alkynes

Alkynes show two types structural isomerism – Position isomerism and chain isomerism.

Position isomers of C_4H_6 are:

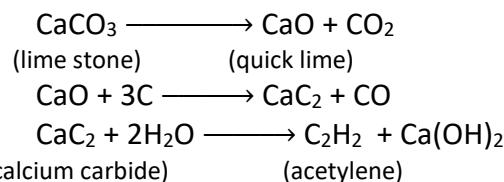


Chain isomers of C_5H_8 are:

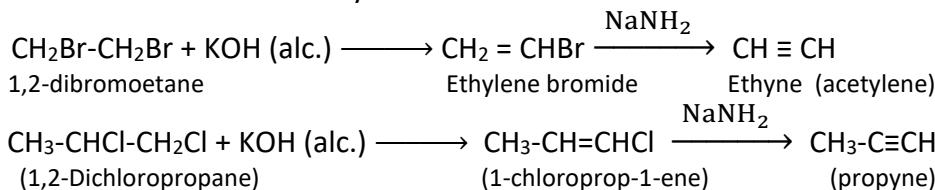


Preparation of alkynes

- 1. From calcium carbide (CaC_2):** On large scale, ethyne is prepared by treating calcium carbide with water. Calcium carbide is prepared by heating quick lime (CaO) with coke.



- 2. From vicinal dihalides:** Vicinal dihalides undergo dehydrohalogenation on treatment with alcoholic KOH to form alkenyl halide which on treatment with sodamide (NaNH_2) to form alkyne.

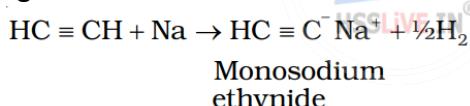


Chemical Properties

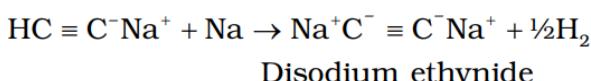
- 1. Acidic character:** 1-alkynes are acidic in nature. This is because in alkynes, the triple bonded carbon atoms are sp hybridized. Due to the greater s-character (50%), the sp hybridised orbitals of carbon atoms in ethyne molecules have highest electronegativity. So they attract the shared electron pair of the C-H bond to a greater extent and hence the hydrogen atom is removed as H^+ . So 1-alkynes are acidic in nature.



E.g. Acetylene on reaction with Na metal, we get sodium acetylide (monosodium ethynide) and hydrogen gas.



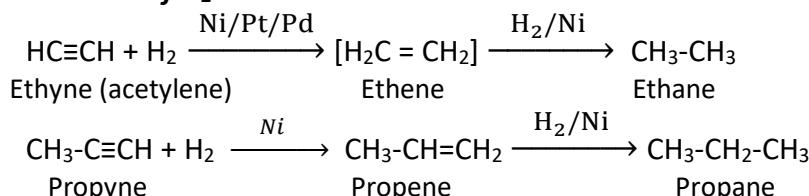
This on further reacts with Na metal to form disodium acetylide (disodium ethynide) and H_2 .



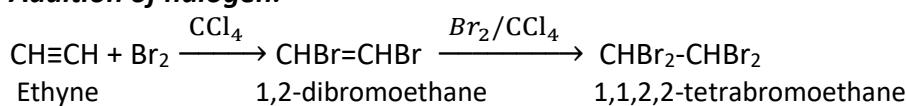
This reaction is not shown by alkenes and alkanes. Hence it is used for distinction between alkynes and alkenes or alkanes. Also this reaction is used to distinguish 1-alkynes from other isomeric alkynes. E.g. 1-butyne and 2-butyne can be distinguished by using this reaction.

2. Addition reactions:

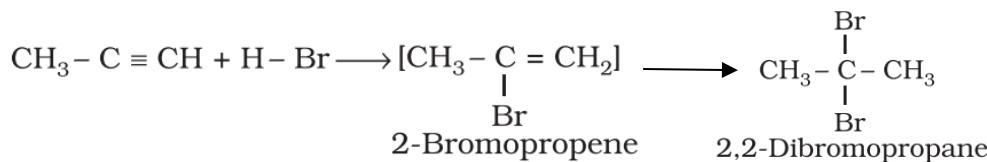
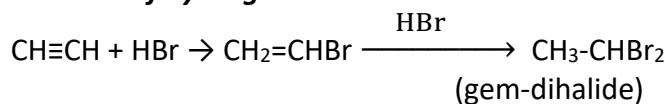
i. Addition of H_2 :



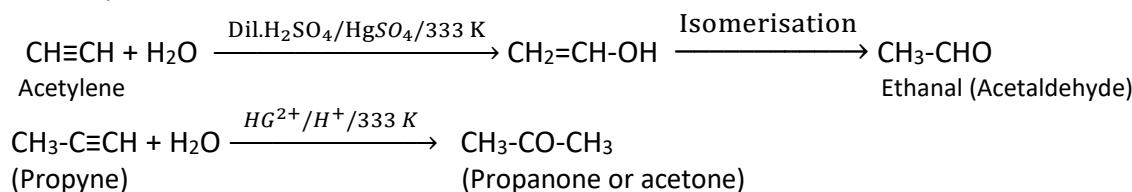
ii. Addition of halogen:



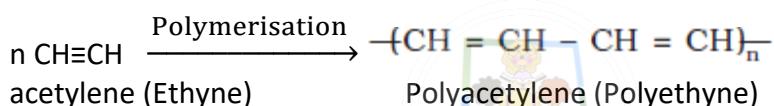
Reddish orange colour of the solution of bromine in carbon tetrachloride is decolourised. This is used as a test for unsaturation.

iii. Addition of hydrogen halide:**iv. Addition of water:**

On warming with water, alkynes add one molecule of water in presence of dil. H_2SO_4 and mercuric sulphate at 333K to form carbonyl compounds (aldehydes or ketones). Acetylene gives acetaldehyde, while all other alkynes give ketones during this reaction.

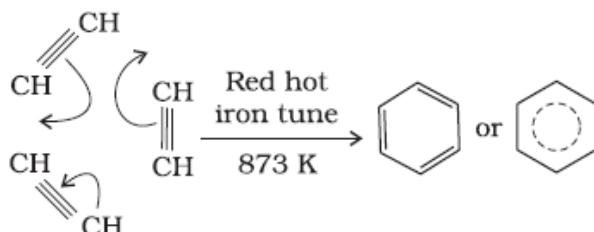
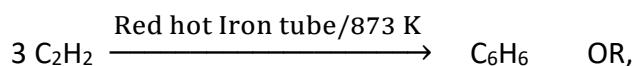
**3. Polymerisation**

- a) **Linear polymerisation:** Ethyne undergoes linear polymerisation under suitable conditions to form polyethyne or polyacetylene.



Under special conditions, this polymer conducts electricity. Thin film of polyacetylene can be used as electrodes in batteries. These films are good conductors, lighter and cheaper than the metal conductors.

- b) **Cyclic polymerisation:** Ethyne (acetylene) on passing through red hot iron tube at 873K, undergoes cyclic polymerisation to form benzene (C_6H_6).

**AROMATIC HYDROCARBONS (ARENES)**

Most of the aromatic compounds have pleasant smell (In Greek aroma means pleasant smelling) and most of them contain benzene ring. *Aromatic compounds containing benzene ring are called benzenoid compounds and those which do not contain benzene ring are called non-benzenoid compounds.*

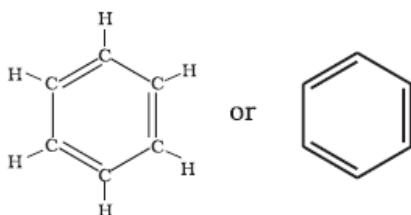
Structure of Benzene

Benzene was first isolated by Michael Faraday and its structure was first deduced by August Kekulé.

The molecular formula of benzene is C_6H_6 , which indicates a high degree of unsaturation. But benzene was found to be a stable molecule and form a triozonide which indicates the presence of three

double bonds. Also it produces only one monosubstituted derivative which indicates that all the six carbon and six hydrogen atoms of benzene are identical.

On the basis of these observations, August Kekulé proposed the following structure for benzene having cyclic arrangement of six carbon atoms with alternate single and double bonds.



The *Kekulé structure* indicates the possibility of two isomeric 1,2-disubstituted derivatives.



But actually these two structures are identical or, benzene forms only one 1,2-disubstituted derivative.

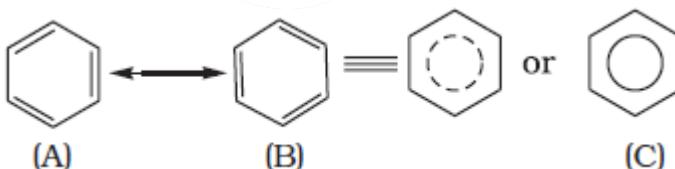
In order to overcome this problem, Kekulé suggested the concept of oscillating nature of double bonds in benzene.



Kekulé structure could not explain the stability of benzene and the preference of benzene to substitution reaction rather than addition reaction.

Resonance concept of Benzene

According to this concept, benzene is a hybrid of the following two resonance structures.

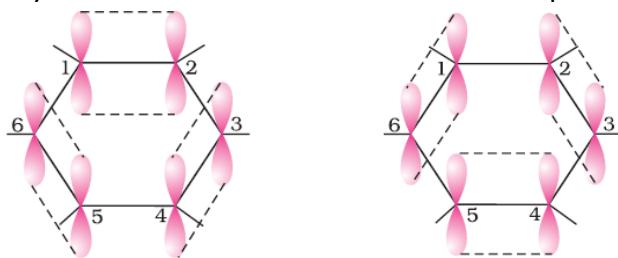


The actual structure of benzene is not A or B. It is in between these two resonating structures. So benzene is denoted by a hexagon with a dotted circle, which represents the delocalised π -electrons.

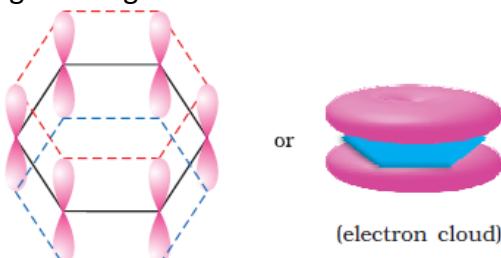
Orbital Overlap Concept of Benzene

In Benzene all the six carbon atoms are sp^2 hybridized. Two sp^2 hybrid orbitals of each carbon atom overlap with sp^2 hybrid orbitals of adjacent carbon atoms to form six C—C sigma bonds which are in the hexagonal plane. The remaining one sp^2 hybrid orbital of each carbon atom overlaps with 1s orbital of hydrogen atom to form six C—H sigma bonds.

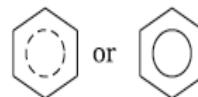
Now each carbon atom contains one unhybridised p orbital perpendicular to the plane of the ring. They overlap laterally to form three π -bonds. There are two possible overlapping.



These give two Kekulé structures with localized π electrons. But in benzene all the C-C bonds are identical and the bond length is 139 pm. To explain this, it is suggested that the p-orbitals of all the C atoms overlap each other. Thus in benzene, there is an electron cloud in the form two rings one above and one below the hexagonal ring as follows:



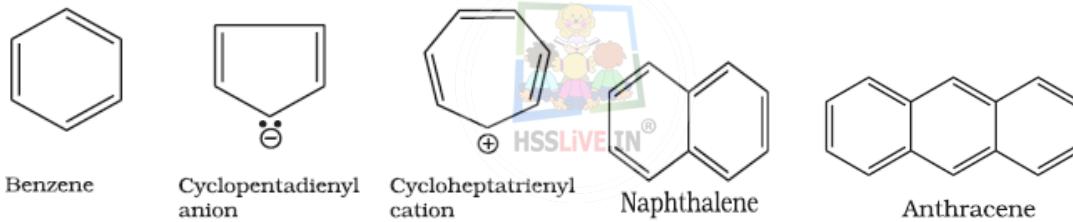
So the six π electrons are delocalised and can move freely about the six carbon nuclei. Presence of delocalised π electrons in benzene makes it more stable. The delocalised π electrons can be denoted by a circle inside a hexagonal ring. So benzene is best represented as:



Aromaticity – Huckel Rule

Aromaticity is defined by a rule called 'Huckel rule'. According to this rule, "cyclic, planar systems containing $(4n+2)$ delocalised π electrons are aromatic". Where n is an integer. n may be $0, 1, 2, 3, \dots$

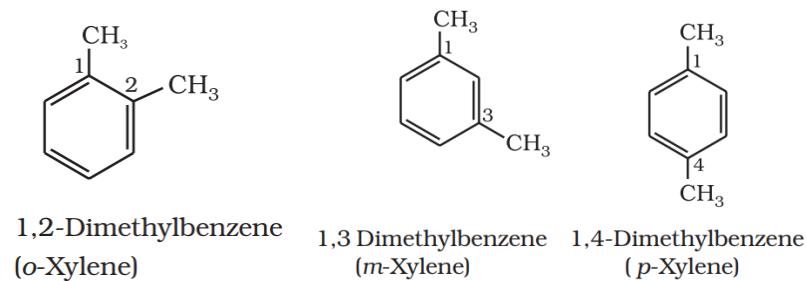
For benzene $n = 1$, so it should contain 6 delocalised π electrons. If $n = 2$, the number of delocalised π electrons = 10 and so on. Example for some aromatic compounds are:



Isomerism in Disubstituted benzene

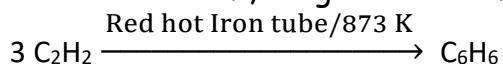
There are three position isomers for disubstituted benzene. It can be 1,2 or 1,3 or 1,4 isomers. 1,2 disubstituted isomer is called ortho isomer, 1,3 isomer is called meta isomer and 1,4 isomer is called para isomer.

E.g. xylene (Dimethyl benzene)

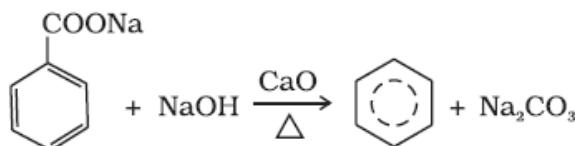


Preparation of Benzene

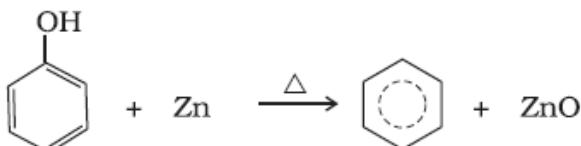
1. **Cyclic polymerisation of ethyne (acetylene):** When acetylene gas is passed through red hot iron tube at 873 K, we get benzene.



2. Decarboxylation of aromatic acids: Sodium salt of benzoic acid on heating with sodalime gives benzene.



3. Reduction of phenol: Phenol vapours are passed over heated zinc dust, it is reduced to benzene.



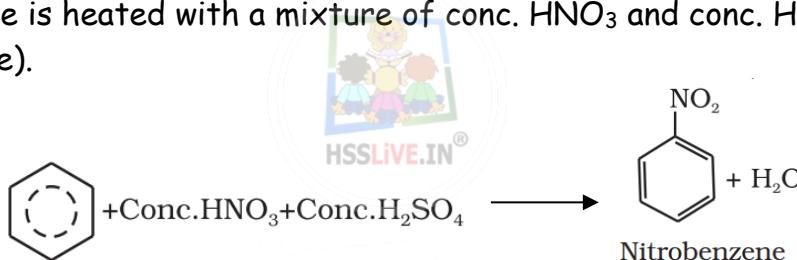
Chemical Properties

Aromatic compounds generally undergo electrophilic substitution reactions. Under special conditions, they can also undergo addition and oxidation reactions.

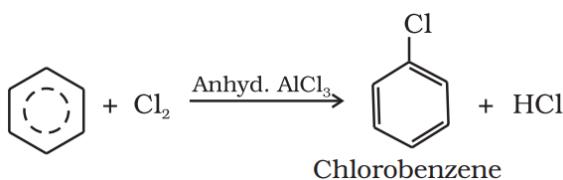
I) Electrophilic Substitution Reactions

These are reactions in which a weak electrophile is replaced by a strong electrophile. The important electrophilic substitution reactions are Nitration, Sulphonation, Halogenation and Friedel-Crafts alkylation and acylation.

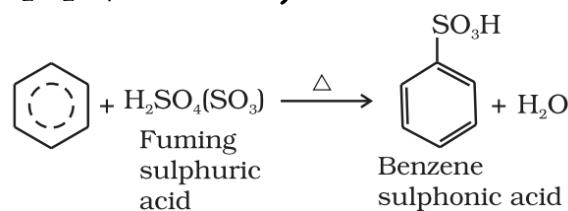
1. Nitration: It is the introduction of nitro ($-\text{NO}_2$) group to a benzene ring. For this benzene is heated with a mixture of conc. HNO_3 and conc. H_2SO_4 (nitrating mixture).



2. Halogenation: It is the introduction of halo ($-\text{X}$) group to a benzene ring. For this benzene is treated with a halogen (Cl_2 or Br_2) in presence of Lewis acids like anhydrous FeCl_3 , FeBr_3 or AlCl_3 .

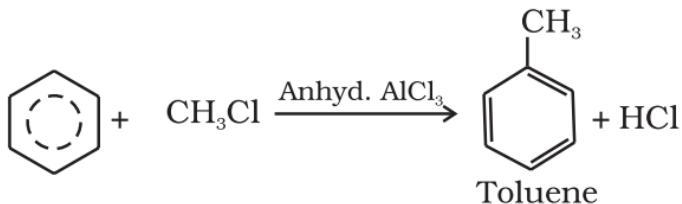


3. Sulphonation: It is the introduction of sulphonic acid ($-\text{SO}_3\text{H}$) group to a benzene ring. It is carried out by heating benzene with fuming sulphuric acid ($\text{H}_2\text{S}_2\text{O}_7$ or oleum).

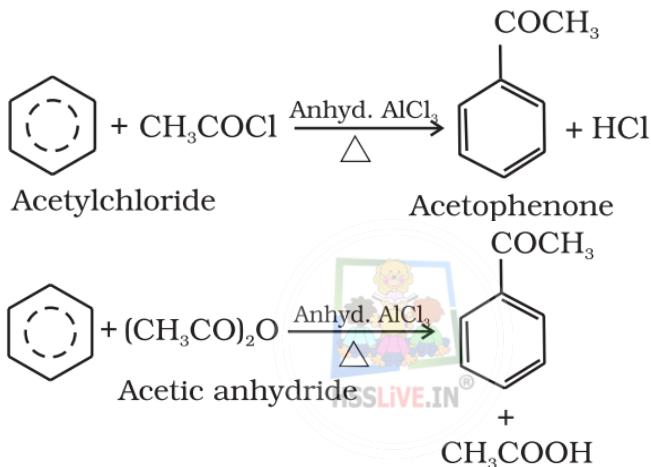


4. Friedel-Craft's reaction: It is the introduction of alkyl (-R) group or acyl (-CO-R) group to a benzene ring. It is of two types:

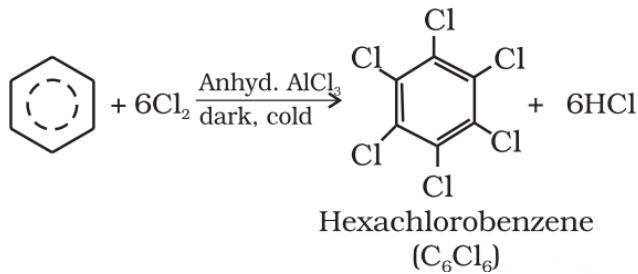
a) **Friedel-Craft's Alkylation reaction:** It is the introduction of alkyl (-R) group to a benzene ring. Here the reagents used are alkyl halide in presence of anhydrous AlCl_3 .



b) **Friedel-Craft's Acylation reaction:** It is the introduction of acyl (-CO-R) group to a benzene ring. Here the reagents used are acyl halide in presence of anhydrous AlCl_3 .

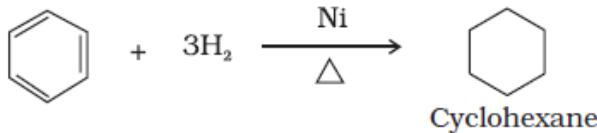


5. Benzene on treatment with excess of chlorine in the presence of anhydrous AlCl_3 in dark to form hexachlorobenzene (C_6Cl_6).

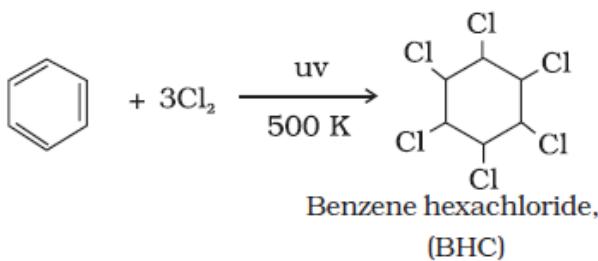


II) Addition Reactions

1. **Addition of H_2 :** Benzene add hydrogen in presence of nickel catalyst at high temperature and pressure to form cyclohexane.



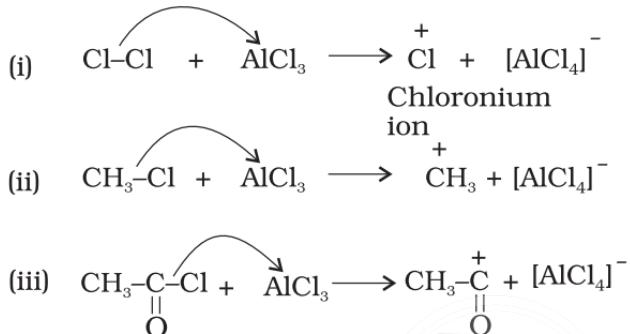
2. **Addition of halogen:** Benzene adds chlorine in presence of uv light or at 500K to form benzene hexachloride (BHC). It is also known as Gammaxane or Lindane or 666.



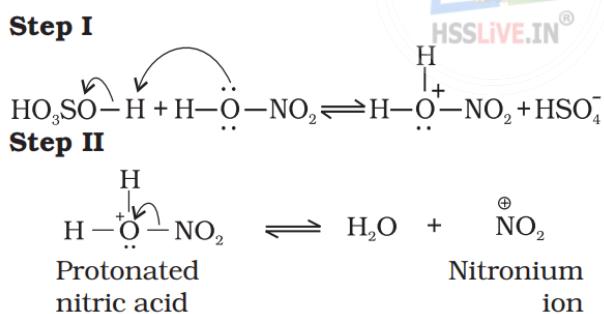
Mechanism of Electrophilic substitution reactions

Electrophilic substitution reactions proceed through three steps: (a) Generation of the electrophile (b) Formation of carbocation intermediate (c) Removal of proton from the carbocation intermediate.

(a) Generation of the Electrophile: In chlorination, alkylation and acylation of benzene, anhydrous AlCl₃ helps in the generation of the electrophile Cl⁺ (chloronium ion), R⁺ (carbocation), RCO⁺ (acylium ion) respectively by combining with the attacking reagent.

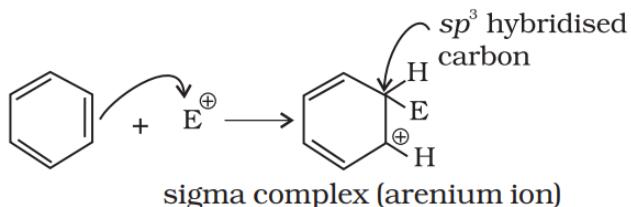


In the case of nitration, the electrophile, nitronium ion (NO₂⁺) is produced by the transfer of a proton (from sulphuric acid) to nitric acid in the following manner:



(b) Formation of Carbocation (arenium ion):

Attack of electrophile results in the formation of σ-complex or arenium ion.



The arenium ion gets stabilised by resonance:

