SOME BASIC CONCEPTS OF CHEMISTRY

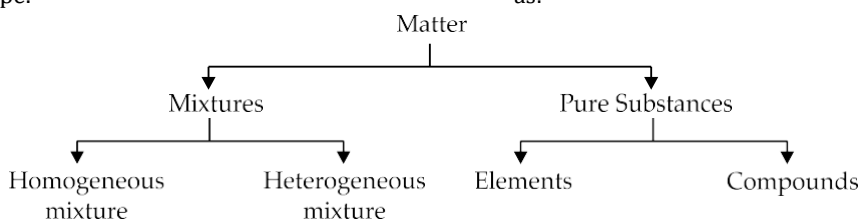| **Topic-1** | **General Introduction and Nature of Matter** |

💬 Revision Notes

☞ Chemistry is the branch of science that deals with the composition, structure and properties of matter.

☞ **Nature of matter:** Matter is anything that has mass and occupies space.

☞ Matter exist mainly in three physical states *viz*, solid, liquid and gas. The other two less common states of matter are Plasma and Bose-Einstein condensate state.

☞ Solids have definite volume and definite shape.

☞ Liquids have definite volume but do not have definite shape.

☞ Gases have neither definite volume nor definite shape.

☞ The three states of matter are inter-convertible into each other by changing the conditions of temperature and pressure.

$$\text{Solid} \underset{cool}{\overset{heat}{\rightleftharpoons}} \text{Liquid} \underset{cool}{\overset{heat}{\rightleftharpoons}} \text{Gas}$$
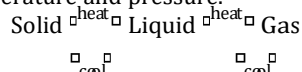
☞ **Classification of matter:** Matter can be categorised as:

Matter
- Mixtures
  - Homogeneous mixture
  - Heterogeneous mixture
- Pure Substances
  - Elements
  - Compounds

☞ The matter which contains two or more substances is called **mixture.**

☞ The mixture in which the composition is uniform throughout the mixture is called homogeneous mixture. e.g., sugar solution in water.

☞ The mixture in which the composition is not uniform throughout the mixture and sometimes different components are visible is called heterogeneous mixture. e.g., mixture of salt and sugar.

☞ Pure substances have fixed composition. These can be classified into elements and compounds.

☞ An **element** contains only one type of particles. These particles may be atoms or molecules.

☞ A **compound** is a combination of two or more atoms of different elements in a definite ratio.

☞ **Properties of Matter and their Measurement:** The general properties of matter are categorised into two types:

(i) Physical properties

(ii) Chemical properties

☞ **Some Physical Quantities:**

(a) **Mass and Weight**

  (i) **Mass:** The standard unit of mass in the International System of Units (SI) is kilogram (kg).

  (ii) **Weight:** In the International System of Units (SI), weight can be expressed in terms of the force, i.e., Newton (N).

$$\boxed{W = m \times g}$$

where, m = mass, g = gravitational force

Note: The mass of substance is constant, whereas, its weight may vary from one place to another due to change in gravity.

(b) **Volume:** SI unit of volume is m^3.

(c) **Density:**

Density = Mass/ Volume

$$d = m/V$$

● SI unit of density is $kg \, m^{-3}$.

(d) The three common scales are used to measure temperature:

[e.g., Kelvin (K), degree Celsius (°C), degree Fahrenheit (°F)].

(e) **Length:**

● Length is expressed in Angstrom (Å), nano-metre (nm) and picometre (pm). These are related to the SI unit as follows:

$$1 \text{ Å} = 10^{-10} \text{ m,}$$
$$1 \text{ nm} = 10^{-9} \text{ m,}$$
$$1 \text{ pm} = 10^{-12} \text{ m.}$$

☞ There are certain rules used for determining significant figures:

(i) All non-zero digits are significant.

(ii) Zero preceding to first non-zero digit are not significant.

(iii) Zero between two non-zero digits are significant.

(iv) Zeros at the end or right of a number are significant, provided they are on the right side of the decimal point.

➤ **Laws of Chemical Combinations:** Elements combine to form compounds in accordance with the following five basic laws, called the laws of chemical combinations.

(i) Law of Conservation of Mass: Mass can neither be created nor destroyed.

(ii) Law of Definite Proportions/Composition: A given compound always contains exactly the same proportion of elements by weight.

(iii) Law of Multiple Proportions: When two elements combine with each other to form more than one compound, the masses of one element that combine with a fixed mass of the other element, are in the ratio of small whole numbers.

(iv) Gay Lussac's Law of Gaseous Volumes: When gases combine or are produced in a chemical reaction they do so in a simple ratio by volume, provided all the gases are at same temperature and pressure.

(v) Avogadro's Law: At the same temperature and pressure, equal volume of all gases should contain equal number of molecules.

➤ **Dalton's Atomic Theory:**
- Matter consists of tiny indivisible particles.
- Atoms are indestructible and cannot be divided into smaller particles.
- All atoms of a given element have identical properties, including identical mass. Atoms of different elements differ in mass.
- When atoms of different elements react to form compounds, their atoms combine a simple fixed ratio.
- Chemical reactions involve reorganisation of atoms. These are neither created nor destroyed in a chemical reaction.

➤ **Drawbacks of Dalton's Atomic Theory:**
- Theory does not explain the occurrence of allotropes.
- Atom can be further divided into sub-parts i.e., Electron, proton, neutron.
- The theory fails to explain how atoms combine with different elements to form a group.

Key Equations

➤ **Density =** $\dfrac{\text{Mass}}{\text{Volume}}$

➤ **Temperature:** $K = °C + 273.15$;
$$°F = \frac{9}{5}(°C) + 32$$

Key Facts

➤ **The International System of Units (SI):** The SI system has seven base units.

➤ **Volume:** $V = 1 \text{ dm}^3 = 10^3 \text{ cm}^3 = 10^{-3} \text{ m}^3$.

➤ **Standard Temperature Pressure (STP):** 0 °C (273.15 K) temperature and 1 atmosphere pressure.

➤ **Normal Temperature Pressure (NTP):** 20 °C (293.15 K) temperature and 1 atmosphere pressure.

➤ **Standard Ambient Temperature Pressure (SATP):** 25 °C (298.15 K) temperature and 1 atmosphere pressure.

Mnemonics

Concept Name: Metric System
Mnemonics: The Great Morning King Henry
Mnemonics: Doesn't Usually Drink chocolate Milk
Mnemonics: Mixed with Natural Powder
Interpretation
The: Tera ($×10^{12}$)
Great: Giga ($×10^9$)
Morning: Mega ($×10^6$)
King: Kilo ($×10^3$)
Henry: Hecto ($×10^2$)
Doesn't: Deca ($×10$)
Usually: Unit ($×1$)
Drink: Deci ($×10^{-1}$)
Chocolate: Centi ($×10^{-2}$)
Milk: Milli ($×10^{-3}$)
Mixed with: Micro ($×10^{-6}$)
Natural: Nano ($×10^{-9}$)
Powder: Pico ($×10^{-12}$)

Topic-2 | Atomic and molecular mass, mole concept, Percentage, empirical and Molecular Formula

Revision Notes

➤ **Atomic Mass:** One atomic mass unit is defined as a mass exactly equal to one-twelfth of the mass of one carbon-12 atom.

Relative Atomic Mass = $\dfrac{\text{Average mass of an atom} \times 12}{\text{Mass of an atom of carbon-12}}$

- **Average Atomic Mass:** The average atomic mass of an element refers to the atomic masses of the isotopes of the element, taking into account the abundances of the element's isotopes.

  Average Atomic Mass =
  $$\dfrac{\Sigma(\text{Mass of isotopes} \times \% \text{ natural abundance})}{100}$$

- **Gram Atomic Mass:** Gram atomic mass is the mass, in grams, of one mole of atoms in a monoatomic chemical element.

  Gram Atomic Mass = Atomic mass expressed in grams

- **Molecular Mass:** Molecular mass or molecular weight refers to the mass of a molecule. It is calculated as the sum of the mass of each constituent atom multiplied by the number of atoms of that element in the molecular formula.

- **Gram Molecular Mass or Gram Molecule:** Gram molecular mass is the mass in grams of one mole of a molecular substance.

- **Formula Mass:** The formula mass of a molecule is the sum of the atomic weights of the atoms in the empirical formula of the compound.

- **Mole Concept and Molar Mass:** Mole is a fundamental unit in the system. Molar mass is the mass of one mole of any substance, i.e., element or compound.

- **Percentage Composition:** Percentage composition of a compound is the ratio of the amount of each element to the total amount of individual elements present in a compound multiplied by 100.

- **Empirical Formula:** A formula that gives the simplest whole number ratio of various atoms in a compound.

- **Molecular Formula:** It is a formula in which the exact number of different types of atoms present in a molecule of a compound.

- **Steps for writing molecular formula:**
  - **(i)** Conversion of mass percent to grams.
  - **(ii)** Convert into number moles of each element.
  - **(iii)** Divide each of the mole values obtained above by the smallest number amongst them.
  - **(iv)** Write down the empirical formula by mentioning the numbers after writing the symbols of respective elements.
  - **(v)** **Writing molecular formula:**
    - (a) Determine empirical formula mass by adding the atomic masses of various atoms present in the empirical formula.
    - (b) Divide molar mass by empirical formula mass.
    - (c) Multiply empirical formula by n obtained above to get the molecular formula.

⊙━ᴴᴾ Key Formulae

- Number of moles of atoms = $\dfrac{\text{Mass of element}}{\text{Atomic mass}}$

- Number of moles of molecules
  $$= \dfrac{\text{Mass of molecules}}{\text{Molecular mass}}$$

- Number of moles of gas
  $$= \dfrac{\text{Volume of the gas (STfl)}}{22.4 \text{ L}}$$

- Number of molecules = Number of moles × N_A
- Where, N_A = Avogadro's number = 6.022×10^{23}
- Number of atoms = Number of molecules × Atomicity

- Mass percentage = $\dfrac{\text{Total mass of element}}{\text{Molar mass}} \times 100$

- **Percentage Composition:**

  Mass % of the element =
  $$\dfrac{\text{Mass of element in a molecule of the compound}}{\text{Molecular mass of the compound}} \times 100$$

- **Relationship between Empirical and Molecular Formulae:**

  Molecular Formula = n × Empirical formula

  where $n = \dfrac{\text{Molar mass}}{\text{Empirical formula mass}}$

⊙━ᴴᴾ Key Term

- **Molar Volume (V_m):** It is the volume occupied by one mole of any substance.

📑 Key Facts

- 1 amu = 1.66056×10^{-24} g
- Mass of hydrogen atom in terms of amu
  $$= \dfrac{1.6736 \times 10^{-24}\,\text{g}}{1.66056 \times 10^{-24}\ \text{g/amu}}$$
  $$= 1.0078 \text{ amu}$$
- Now, 'amu' has been replaced by 'u' which is called unified mass.
- 1 mole of a substance = Molar mass of substance = Avogadro's number of chemical units = 22.4 L volume at STP of gaseous substance

  e.g., 1 mole of CH_4 = 16 g of CH_4 = 6.022×10^{23} molecules of CH_4 = 22.4 L at STP

  $$n = \dfrac{w_g}{M_m} = \dfrac{V_L(\text{at STfl})}{22.4 \text{ L}} = \dfrac{x \text{ particles}}{N_A} = \dfrac{MV}{1000}$$

- Molar volume of gas = 22.4 L at STP (273K, 1 atm) or 22.7 L at SATP (273 K, 1 bar)

  Calculating Molar Volume : PV = nRT

  $$\therefore V = \dfrac{nRT}{P} = \dfrac{1 \text{ mol} \times 0.0821 \text{ L atm K}^{-1} \text{ mol}^{-1} \times 273 \text{ K}}{1 \text{ atm}}$$
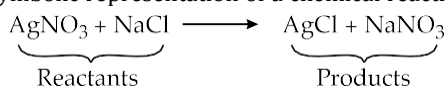 $$= 22.4 \text{ L}$$

Topic-3	Chemical reactions, stoichiometry and Calculation based on Concentration

💬 Revision Notes

☛ **Chemical Equation:** A chemical equation is the symbolic representation of a chemical reaction.

$$\underbrace{AgNO_3 + NaCl}_{Reactants} \longrightarrow \underbrace{AgCl + NaNO_3}_{Products}$$

☛ **Stoichiometry and Stoichiometric Calculations:**

● Stoichiometry is the calculation of masses (sometimes volumes also) of the reactants and products involved in a chemical reaction.

● Balancing a chemical equation:
Step 1: Write down the chemical equation using correct formulas of the reactants and products.
Step 2: Write down the number of atoms per element.
Step 3: Starting balancing with single element one by one.
Step 4: Verify that the number of atoms of each element is balanced in the final equation.

☛ **Mass-Mole Number Relationship:**

$$\text{Number of Moles} = \frac{\text{Mass of g}}{\text{Molar mass in g mol}^{-1}}$$
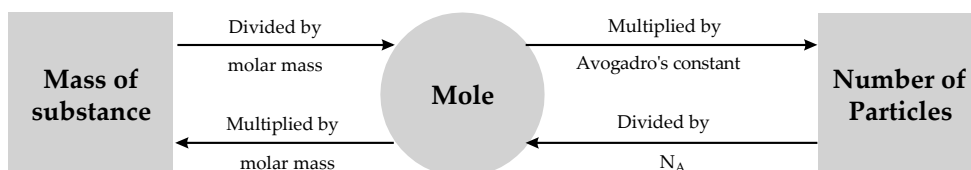
➢ **Limiting Reagent:** The reactant which gets consumed first, limits the amount of product formed and is, called the limiting reagent. It is present in smaller amount.

● **Mole Fraction of component:** The ratio of the number of moles of a given component of a mixture to the total number of moles of all the components.

Two components A and B

Mole fraction of A

$$x_A = \frac{\text{Number of moles of A}}{\text{Number of moles of solution}} = \frac{n_A}{n_A + n_B}$$

n_A and n_B are the mole of A and B respectively.

Mole fraction of B,

$$x_B = \frac{\text{Number of moles of B}}{\text{Number of moles of solution}} = \frac{n_B}{n_A + n_B}$$

Also, remember that $x_A + x_B = 1$

☛ **Molarity:** It is defined as the number of moles of solute dissolve per 1000g or 1 kg of solvent

$$m = \frac{W_B \times 1000}{M_B \times W_A}$$

➢ **Modes of expressing concentration of solution:**

● **Mass Percent:**

$$\text{Mass percent} = \frac{\text{Mass of solute}}{\text{Mass of solution}} \times 100$$

☛ **Molality:** The number of moles of solute per kilogram of solvent. Unit is mol kg^{-1} or m (molal).

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

$$m = \frac{\text{Mass of solute} \times 1000}{\text{Molar mass of solute} \times \text{mass of solvent (in g)}}$$

☛ **Strength of Solution:** It is defined as the amount of solute dissolved per litre of solution.

Strength = M × Molecular weight

M = Molarity

☛ **Normally:** It i defined as number of gram equivalents of solute dissolved per litre of solution

$$N = \frac{W_B \times 1000}{E_B \times V}$$

🔑 Key Formulae

☛ % by $\left(\frac{v}{V}\right)$ strength $= \frac{\text{Volume of solute}}{\text{Volume of solution}} \times 100$

☛ % by $\left(\frac{w}{V}\right)$ strength $= \frac{\text{Weight of solute}}{\text{Volume of solution}} \times 100$

☛ $M = \frac{\% \text{ Strength} \times \text{density} \times 10}{\text{Molecular weight of solute}}$

☛ $M = \frac{1000 \times M}{M \times \text{Molar mass of solute} - 1000\, d}$

where, d = density

M = Molarity

m = molality

☛ Specific gravity = $\frac{\text{Mass of liquid}}{\text{Vol. of liquid}}$

☛ Molecular weight = 2 × Vapour density

> For dilution, molarity equation is:
$$M_1V_1 = M_2V_2$$
Where, M_1 = initial molarity, V_1 = initial volume, M_2 = final molarity and V_2 = final volume.

🔑 Key Terms

> **Limiting Reagent:** It is the reactant which gets consumed first or limits the amount of product formed.

> **Mass Percent:** It is the mass of the solute in grams per 100 grams of the solution.

$$\text{Mass \%} = \frac{\text{Mass of solute in g} \times 100}{\text{Mass of solution in g}}$$

> **Parts per million (ppm).** If a solute is present in trace quantities, the concentration of the solution is expressed in parts per million (ppm).

$$\text{ppm} = \frac{\text{Weight of solute} \times 10^6}{\text{Weight of solution}}$$

⚙ Mnemonics

Concept: Law of conservation of mass
Mnemonics: BESABS
Interpretation: Balanced chemical equation has Same number of Atoms on Both Sides
Concept: Strength of solution in terms of molarity
Mnemonics: SSMM
Interpretation: Strength of Solution is Molarity into Molecular weight

❑❑

Chapter 2

STRUCTURE OF ATOM

Topic-1 **Fundamental Particles of an Atom, Dual Nature of Electromagnetic Radiation, Photoelectric Effect and Bohr Model**

💬 Revision Notes

> **Discovery of electron:** In mid 1850s many scientists mainly Faraday began to study electrical discharge in partially evacuated tubes, known as cathode ray discharge tubes. A cathode ray tube is made of glass containing two thin pieces of metal, called electrodes, sealed in it.
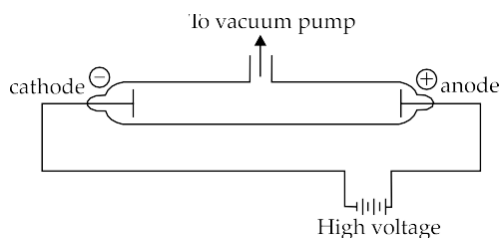

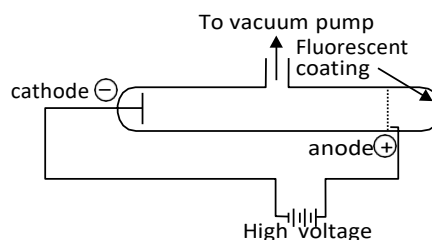**Fig. 1: A cathode ray discharge tube**

Fig. 2: A cathode ray discharge tube with perforated node and zinc sulphide coating for phosphorescence

The results of these experiments are summarised below:
(i) The cathode rays start from cathode and move towards the anode.
(ii) These rays themselves are not visible but their behaviour can be observed with the help of certain kind of materials (fluorescent or phosphorescent) which glow when hit by them.

(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 behaviour of cathode rays are similar to that expected from negatively charged particles, suggesting 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.

► **Charge to mass ratio:** In 1897, J.J. Thomson measured it by using cathode ray tube and applying electrical and magnetic field perpendicular to each other as well as to the path of electron. Thomson was able to determine the value of e/m_e as 1.758820×10^{11} C kg^{-1}.

► **Charge of electron:** It was determined by R.A. Milikan by oil drop experiment. He found that the charge on the electron to be $- 1.6 \times 10^{-19}$ C. The present accepted value of electrical charge is $- 1.6022 \times 10^{-19}$ C.

► **Discovery of proton:** Also known as canal rays. They were discovered through electrical discharge carried out in modified cathode ray tube.

► **Discovery of neutron:** These particles were discovered by Chadwick (1932) by bombarding a thin sheet of beryllium by a-particles.

Table 2.1 Properties of Fundamental Particles

Name	Symbol	Absolute charge/C	Relative charge	Mass/kg	Mass/u	Approx. mass/u
Electron	e	-1.602176×10^{19}	$- 1$	9.109382×10^{-31}	0.00054	0
Proton	p	$+1.602176 \times 10^{-19}$	$+ 1$	1.676216×10^{-27}	1.00727	1
Neutron	n	0	0	1.674927×10^{-27}	1.00867	1

► **Thomson Model of Atom:** J. J. Thomson, in 1898, proposed that an atom possesses a spherical shape in which the positive charge is uniformly distributed like plum pudding, raisin pudding or watermelon.

► **Rutherford Nuclear Model of Atom:** Rutherford and his students bombarded very thin gold foil with a–particles.

It was observed that:

(i) Most of the a–particles passed through the gold foil undeflected.

(ii) A small fraction of the a–particles were deflected by small angles.

(iii) A very few a–particles (~1 in 20,000) bounced back, that is, were deflected by nearly 180°.

Rutherford drew the following conclusions:

(i) Most of the space in the atom is empty as most of the a–particles passed through the foil undeflected.

(ii) A few positively charged a–particles were deflected. The positive charge has to be concentrated in a very small volume that repelled and deflected the positively charged a–particles.

(iii) Calculations by Rutherford showed that the volume occupied by the nucleus is negligibly small as compared to the total volume of the atom.

According to Rutherford's model of atom:

(i) The positive charge and most of the mass of the atom was densely concentrated in extremely small region called nucleus.

(ii) The nucleus is surrounded by electrons that move around the nucleus with a very high speed in circular paths called orbits.

(iii) Electrons and the nucleus are held together by electrostatic forces of attraction.

Drawbacks of Rutherford's model of atom:

(i) It cannot explain the stability of an atom.

(ii) It says nothing about the electronic structure of atoms.

► **Atomic number (Z) =** number of protons in the nucleus of an atom = number of electrons in a neutral atom

► **Mass number (A) =** number of protons (Z) + number of neutrons (n)

► **Isobars:** Isobars are the atoms with same mass number but different atomic number. For example, $_6^{14}C$ and $_7^{14}N$.

► **Isotopes:** Atoms with identical atomic number but different atomic mass number are known as isotopes. For example, protium $_1^1H$, deuterium $_1^2D$ and tritium $_1^3T$.

► **Developments Leading to the Bohr's Model of Atom**
In order to improve Rutherford's atomic model, two new concepts played a major role, these are:

(i) Dual nature of electromagnetic radiation.

(ii) Experimental results regarding atomic spectra.

► **Wave Nature of Electromagnetic Radiation:** James Maxwell (1870) suggested that when electrically charged particle moves under acceleration, alternating electrical and magnetic fields are produced and transmitted. These fields are transmitted in the form of waves called electromagnetic waves or electro magnetic radiation.

● do not require any medium for their propagation and can move in vacuum.

● The increasing order of wavelengths of these radiations is given as below :
Cosmic rays < g – rays < X – rays < Ultraviolet light < Visible light < Infrared rays < Micro waves < Radio waves.

► **Characteristics of Waves:**
  - **Wavelength (l):** The distance between two successive crests or troughs. Unit: Meter (m).
  - **Frequency (u):** It is defined as the number of waves that pass a given point in one second. Unit: Hertz (Hz) or s^{-1}.
  - **Wave number ($\bar{v}$):** The number of wavelengths per unit length. Unit: m^{-1}.

► **Relationship between Wavelength, Wave number, Frequency and Velocity**
  - These characteristics are related as :

$$c = l \times u \quad \text{or} \quad u = \frac{c}{\lambda} \quad \text{and}$$
$$\frac{1}{\lambda} = \upsilon \qquad \backslash \qquad n = c\,\bar{v}$$

► **Particle Nature of Electromagnetic Radiation:** The phenomenon like diffraction and interference can be explained by wave nature of electromagnetic radiation but it could not explain black body radiation and photoelectric effect.

► **Black Body Radiation and its Explanation:** The ideal body that emits and absorbs radiations of all frequencies, is called black body and the radiation emitted by such a body is called black body radiation.
  - According to Planck's quantum theory, atoms and molecules emit (or absorb) energy in the form of small discrete packets of energy, known as quantum. The energy of each quantum is given by the expression :
$$E = hn$$
  where, h = Planck's constant ($6·626 \times 10^{-34}$ J s)

► **Photoelectric Effect and its Explanation:**
  - The photoelectric effect is the observation that certain metals (e.g., potassium, rubidium, caesium, etc.) emit electrons when light shines upon them. Electrons emitted in this manner can be called photoelectrons.

  Total energy of photon = Work function + Kinetic energy.
$$hn = hn_0 + \frac{1}{2} mv^2$$

- Electromagnetic radiation shows wave like properties during propagation and shows particle like properties on interaction with matter.

► **Dual Nature of Electromagnetic Radiation:** Photoelectric effect shows particle nature of light. Diffraction and interference explain wave nature of light.

The branch of science that deals with the study of spectra is called **spectroscopy.**
Spectra are classified as:
  (i) Emission spectra
  (ii) Absorption spectra.

► **Emission Spectra:** The spectrum of radiation emitted by a substance that has absorbed energy is called an emission spectrum.

► **Absorption Spectra:** When the white light is first passed through the substance and the transmitted light is analyzed we get absorption spectrum. It consists of dark lines separated by bright bands.

► **Line spectra:** The emission spectra of atoms in the gas phase emit light only at specific wavelengths with dark spaces between them. Such spectra are called line spectra or atomic spectra.

► **Line Spectrum of Hydrogen:** All series of lines in the hydrogen spectrum can be described by Johannes Rydberg expression:
$$\upsilon = 109,677 \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right) cm^{-1}$$

where $n_1 = 1, 2, ...$ and $n_2 = n_1 + 1, n_1 + 2, ...$

► **The spectral Lines for Atomic Hydrogen are given as below:**

Series	n_1	n_2	Spectral region
Lyman	1	2, 3,..................	Ultraviolet
Balmer	2	3, 4,.................	Visible
Paschen	3	4, 5, ...	Infrared
Brackett	4	5, 6, ...	Infrared
Pfund	5	6, 7, ...	Infrared

► From the line spectrum of different elements, it can be concluded that:
  (i) Line spectrum of an element is unique.
  (ii) There is a regularity in the line spectrum of each element.

► **Bohr's Model for Hydrogen atom:** Neils Bohr (1913) proposed a new model of atom based upon Planck's quantum theory quantitatively explaining the general features of the hydrogen atom structure and its spectrum.

► **Postulates of Bohr's Atomic Model:**
  - In an atom, the electrons revolve around the nucleus in certain definite circular paths of fixed radius called orbits or shells.
  - Each shell or orbit corresponds to a definite energy. Therefore, these circular orbits are also known as energy levels or energy shell.
  Electron can move from one orbital to another either by absorption of energy or by loss of energy.
  - The frequency of radiation absorbed or emitted is calculated by Bohr's frequency rule :
$$v = \frac{\Delta E}{h} = \frac{E_1 - E_1}{h}$$

where, E_1 and E_2 are the energies of the lower and higher allowed energy states respectively.

- **The angular momentum of an electron is quantised:** Angular momentum of orbits in which electron revolves must be an integral multiple of $\dfrac{h}{2\pi}$, where h is Planck's constant ($h = 6.626 \times 10^{-34}$ Js).

$$\therefore \quad m_e = n.\dfrac{h}{2\pi}$$

where n = 1, 2, 3, ...

► **According to Bohr's Theory for Hydrogen Atom:**

(i) The stationary states for electron are numbered n = 1,2,3.......... These integral numbers are known as Principal quantum numbers.

(ii) The radii of stationary states are given by:

$$r_n = n^2 a_0$$

where $a_0 = 52.9$ pm. As n increases the value of r will increase.

(iii) The energy of stationary state is given by:

$$E_n = -R_H\left(\dfrac{1}{n^2}\right)$$

where n = 1, 2, 3, ... and R_H (Rydberg constant) = 2.18×10^{-18} J.

(iv) For hydrogen like ions i.e., one electron system (e.g., He^+, Li^{2+}, Be^{3+}), the radii is given by,

$$r_n = \dfrac{52.9}{Z} n^2 \text{ pm}$$

and energies of the stationary states are given by:

$$E_n = -2.18 \times 10^{-18}\left(\dfrac{Z^2}{n^2}\right)$$

(v) It is also possible to calculate the velocities of electrons moving in these orbits.

- If fails to explain zeeman effect (be splitting of spectral line in the presence of magnetic field) and Tark effect be slitting of spectral line the presence of electric field.

► **Limitations of Bohr's Model:**

- It fails to explain doublet observed in the hydrogen spectrum.
- It fails to explain the ability of atoms to form molecule by chemical bonds.
- It fails to explain Zeeman effect (i.e., splitting of spectral line in the presence of magnetic field) and stark effect (i.e., splitting of spectral line in the presence of electric field)

🔑 Key Formulae's

► $$c = \mathbf{l} \times v$$
$$\dfrac{1}{\lambda} = \bar{\upsilon}$$

► $$v = c\,\bar{\upsilon}$$

► $$E = hv$$

► $$hv = hv_0 + \dfrac{1}{2}mv^2$$

► $$\bar{v} = 109{,}677\left(\dfrac{1}{n_1^2} - \dfrac{1}{n_2^2}\right)\text{cm}^{-1}$$

► $$v = \dfrac{\Delta E}{h} = \dfrac{E_1 - E_1}{h}$$

► $$m_e vr = n.\dfrac{h}{2\pi}$$

► $$r_n = n^2 a_0$$

► $$E_n = -R_H\left(\dfrac{1}{n^2}\right)$$

🔑 Key Terms

► **Electromagnetic Radiation:** Energy emitted from any source in the form of waves in which electric and magnetic fields oscillated perpendicular to each other and travel with a velocity of light is called electromagnetic radiation.

► **Amplitude:** The height of crest or depth of a trough is called amplitude. It is denoted by the symbol 'a'.

► **Velocity:** The distance travelled by a wave in one second is called velocity.

► **Photon:** A packet or particle of light energy is called photon.

► **Photoelectric Effect:** The phenomenon of ejection of electrons from a metal surface when a light radiation of suitable frequency falls on metal surface is called photoelectric effect.

► **Threshold Frequency:** The minimum frequency (n_o) below which photoelectric effect is not observed, is called threshold frequency.

⚙ Mnemonics

1. Concept: H-atom spectral lines
Mnemonics: Myan Mer Pasta Bread Fund
Interpretation: Lyman ($n1$ = 1)
Balmer ($n1$ = 2)
Paschen ($n1$ = 3)
Brackett ($n1$ = 4)
Pfund ($n1$ = 5)

2. Concept: Bohr Model of an atom
Mnemonics: Electronic video Recording (EVR)
Interpretation: Energy (E) µ Z
Velocity (V) µ Z
Radius (R) µ n

📑 Key Facts

► Energy wise order of electromagnetic radiation: Cosmic rays < g-rays < X-rays < UV light < Visible light < IR rays < Micro waves < Radio waves

$\longrightarrow$	Wavelength ($\mathbf{l}$) increases
$\longrightarrow$	Frequency (n) decreases
$\longrightarrow$	Wave number (v) decreases
$\longrightarrow$	Energy (e) decreases

► The value 109, 677 cm^{-1} is called the Rydberg constant for hydrogen.

Topic-2 | de-Broglie Equation, Heisenberg's Uncertainty Principle and Quantum Mechanical Model

📝 Revision Notes

► **Dual Behaviour of Matter:** Einstein had suggested that light can behave as a wave as well as like a particle. i.e., it has dual character.

In 1924, de Broglie suggested that matter like radiations, should also exhibit a dual character – i.e., wave and particle like properties. This means that just as the photon has momentum as well as wavelength, electron should also have both.

According to de-Broglie, the wavelength associated with a particle of mass m, moving with velocity n is given by the relation,

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

where h = Planck's constant
n = Velocity of particle
($p = mv$) = momentum of the particle.

► **Heisenberg's Uncertainty Principle**

Heisenberg's uncertainty principle states that, "It is not possible to determine simultaneously both the exact position and momentum (or velocity) of an electron, with absolute accuracy."

Mathematically, this law may be expressed as :

$$\mathrm{D}x \times \mathrm{D}p_x \; ³ \; \frac{h}{4\mathrm{p}}$$

$$\mathrm{D}x.\mathrm{D}(mv_x) \; ³ \; \frac{h}{4\mathrm{p}}$$

Or, $$\mathrm{D}x \times \mathrm{D}v_x \; ³ \; \frac{h}{4\mathrm{p}m}$$

where,

$\mathrm{D}x$ = uncertainty in position,
$\mathrm{D}p_x$ = uncertainty in momentum,
$\mathrm{D}v_x$ = uncertainty in velocity.

► **Quantum Mechanical Model of Atom and Concept of Atomic Model:**

Quantum mechanics was developed independently by **Heisenberg** and **Schrodinger.**

Schrodinger equation is $\hat{H}y = Ey$ where $\hat{H}$ is a mathematical operator called **Hamiltonian,** E is the total energy of the system and y is the wave function.

Important Features of the Quantum Mechanical Model of Atom

1. The energy of the electrons in atoms is quantized.
2. The existence of quantized electronic energy level is a direct result of the wave like properties of electrons.
3. Both the exact position and exact velocity of an electron in an atom cannot be determined simultaneously. Therefore, only probability of finding an electron at different points is required.
4. An atomic orbital is the wave function y for an electron in an atom.
5. The probability of finding an electron at a point within an atom is proportional to the square of the orbital wave function, i.e., $|y|^2$ at that point $|y|^2$. It is also known as probability density. The value of probable density is always positive.

From the value of $|y|^2$ at different points within an atom, it is possible to predict the region around the nucleus where the electron will most likely be found.

Topic-3 | Atomic Orbital, Quantum Numbers and Electronic Configuration

Revision Notes

► **Orbitals and Quantum Numbers**

- **Orbitals:** A wave function for an electron in an atom is called an atomic orbital, which describes a region of space in which there is a high probability of finding the electrons. These can be distinguished by their size, shape and orientation.

- **Quantum Numbers:** Electron have only certain permissible values of energy and angular momentum. These permissible states of an electron in any atom are called orbitals which are identified by a set of four numbers. These numbers are called Quantum Numbers.

  The various quantum numbers are :

  (a) Principal quantum number (n)

  (b) Azimuthal or angular momentum quantum number (l).

  (c) Magnetic quantum number (m_l).

  (d) Spin quantum number (m_s).

(a) Principal quantum number (n): This quantum number determines the size energy associated with it. The principal quantum number 'n' is a positive integer with value of n = 1,2,3........ The maximum number of electrons which a shell can accommodate is $2n^2$. All the orbitals of a given value of 'n' constitute a single shell of atom and are represented by the following letters

n = 1 2 3 4 ....

Shell = K L M N ....

(b) Azimuthal or subsidiary or orbital angular quantum number (l): This quantum number defines the three dimensional shape of the orbital. It can have positive integer values from zero to (n – 1) where n is the principal quantum number, i.e., l = 0, 1, 2, 3, (n – 1).

Value of n	Value of l	Name of sub-shell	Number of the sub-shells
1	0	1s	one
2	0,1	2s, 2p	two
3	0, 1, 2	3s, 3p, 3d	three
4	0, 1, 2, 3	4s, 4p, 4d, 4f	four

(c) Magnetic Orbital Quantum Number (m_l) : This describes the spatial orientation of the orbitals along the standard set of co-ordinate axis. Co-ordinate for a given value of l, the possible values of m_l vary from – l, 0 to + l.

(d) Spin Quantum Number (m_s): This quantum number describes the spin orientation of the electron. Since the electron can spin in only two ways- clockwise or anti-clockwise and, therefore, the spin quantum number can take only two values, +½ or – ½.

Mnemonics

1. Concept: Quantum Numbers

Mnemonics: SPAM

Interpretation:

S – Spin Quantum no. (ms)

P – Principal Quantum no. (n)

A – Azimuthal Quantum no. (l)

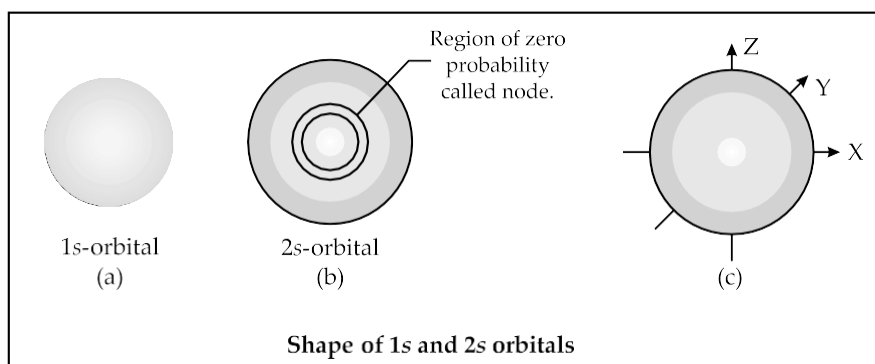**M –** Magnetic Quantum no. (m)

2. Concept: Sequence of orbitals

Mnemonics: Sober Physicists Don't Find Giraffes Hiding In Kitchen

Interpretation: s,p,d,f,g,h,i,k

► **Boundary Surface Diagrams:**
- **Shape of s-orbitals:** s-orbitals are non-directional and spherically symmetrical.

Region of zero probability called node.

1s-orbital (a)   2s-orbital (b)   (c)

Shape of 1s and 2s orbitals

- **Shape of *p*-orbitals:** For *p*-orbitals ($l = 1$), there are three possible orientations corresponding to $m_l =$ – 1, 0, + 1 values. This means that there are three *p*-orbitals in each *p*-sub-shell.
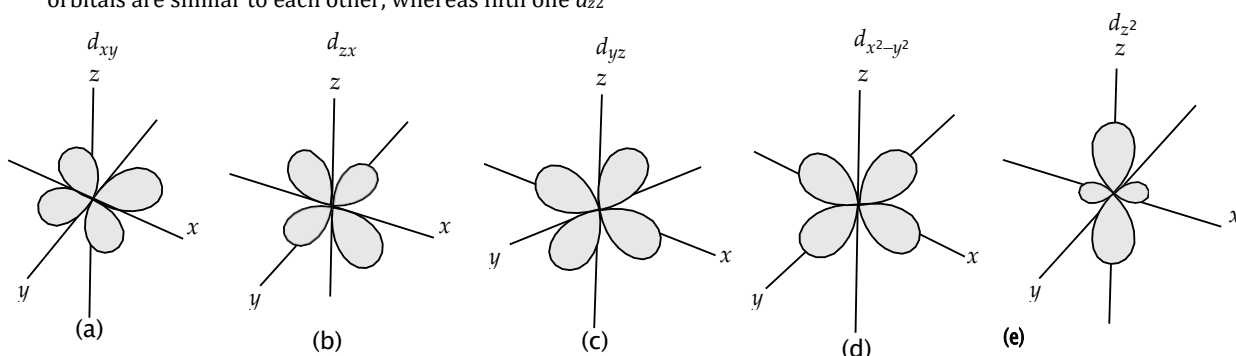
These are designated as p_x, p_y, and p_z.
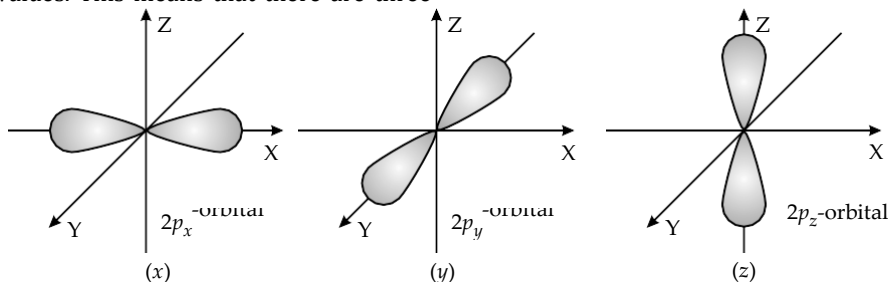
Fig. 2.2: Shape of *p*-orbitals

- **Shape of *d*-orbitals:** The five d-orbitals, designated as d_{xy}, d_{yz}, d_{zx}, d_{x2-y2}, d_{z2}. The shapes of first four *d*-orbitals are similar to each other, whereas fifth one d_{z2} is different from others but all the five *d*-orbitals are equivalent in energy, i.e., degenerate.

Fig. 2.3: Shape of five *d*-orbitals

The total number of nodes are given by (n – 1), i.e., sum of l angular nodes and (n – l – 1) radial nodes.

- **Nodes and Nodal Planes:** The place or point where probability density function reduces to zero are called nodes or nodal surface.

- **Degenerate Orbitals:** The orbitals with same energy are called degenerate orbitals, e.g., p sub-shell has three degenerate orbitals namely p_x, p_y and p_z.

- **Shielding Effect:** The term shielding effect refers to a decrease in attraction between electrons and the nucleus in an atom. Electrons are highly attracted to the nucleus, because they have a negative charge and the nucleus contains protons, which have a positive charge.

- **$n + l$ Rule:** Orbitals are filled in the order of increasing $n + l$. For equal $n + l$ values, the orbital with the lower n is most often filled first. Here, n is the principal quantum number and l is the angular momentum quantum number.

- **Filling of Electrons in Atomic Orbitals:**

The filling of electrons in different orbitals is governed by the following rules:

(i) **Aufbau Principle:** This principle states that the electrons are filled in the various orbitals in an increasing order of their energies, i.e., orbital having lowest energy will be filled first and the orbital having highest energy will be filled last.
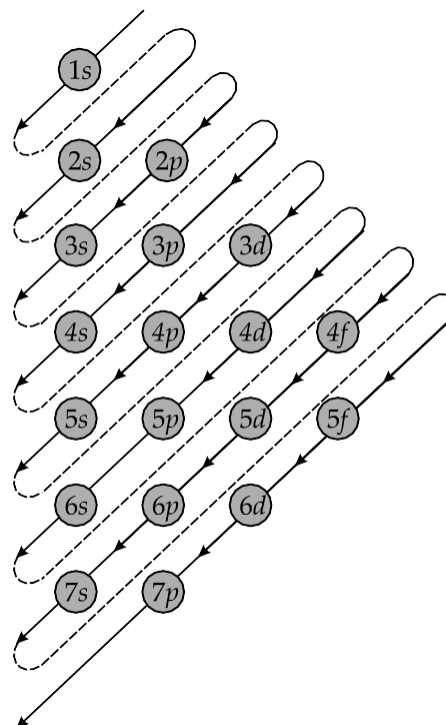

Fig. 2.4: Order of filling of electrons in orbitals

(ii) **Pauli's Exclusion Principle:** According to this principle, no two electrons in an atom can have the same set of four quantum numbers. It can also be stated as only two electrons may exist in

the same orbital and they must be of opposite spin quantum numbers'. The maximum number of electrons in the shell with principal quantum number n is equal to $2n^2$.

(iii) **Hund's Rule of Maximum Multiplicity:** No electron pairing takes place in p, d and f orbitals until each orbital in the given sub-shell contains one electron having parallel spin, e.g., N_2 (7) has electronic configuration $1s^2, 2s^2, 2px^1, 2py^1, 2pz^1$ according to Hund's rule:

$1s$	$2s$	$2p_x$	$2p_y$	$2p_z$
↑↓	↓↑	↑	↑	↑
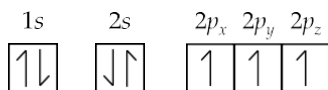
► **Electronic Configuration of Atoms:**
The distribution of electrons in different orbitals is known as electronic configuration of the atom.

► **Significance of Electronic Configuration:** The number of valence electrons in an atom determines how readily an atom will react with other atoms. If it has 7 or 1 valence electron, then it only needs to gain/loss 1 electron which is relatively easier than gaining/losing 3 or 4 electrons.

The completely filled and completely half filled sub-shells are stable due to the following reasons:

1. Symmetrical distribution of electrons
2. Exchange energy: Higher maximum energy leads to higher stability.

► **Electronic Configuration of Ions:**
Examples:
Cl (No. of electrons = 17): $1s^2, 2s^2, 2p^6, 3s^2, 3p_x^2, 3p_y^2, 3p_z^1$

Cl$^-$ (No. of electrons = 18): $1s^2, 2s^2, 2p^6, 3s^2, 3p_x^2, 3p_y^2, 3p_z^2$

Mg (No. of electrons = 12): $1s^2, 2s^2, 2p^6, 3s^2$

Mg^{2+} (No. of electrons = 10): $1s^2, 2s^2, 2p^6$
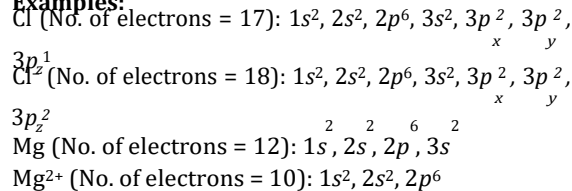
⚷ Key Terms

► **Effective nuclear charge:** It is the net positive charge an electron experiences in an atom with multiple electrons. It may be approximated by the equation

$$Z_{eff} = Z - S$$

where, Z = atomic number
  S = number of shielding electrons

❑❑

Chapter 3

CLASSIFICATION OF ELEMENTS AND PERIODICITY IN PROPERTIES

Topic-1 Classification of Elements and Periodic Table

🗨 Revision Notes

► **Classification of Elements**:
Arranging the elements in such a way that similar elements are placed together while dissimilar elements are separated from one another is known as classification of elements.
On the basis of this classification, periodic table may be defined as:
The arrangement of the known elements according to their properties in a tabular form.

► **Historical Development of Periodic Table:**

Some of the earlier important attempts to classify the elements are briefly summed up below:

(i) **Dobereiner's triads:** In 1829, a German scientist, Johann Dobereiner classified the elements in groups of three elements called **triads**.
The elements in a triad had similar properties and the atomic weight of the middle member of each triad was very close to the arithmetic mean of the other two elements.

DOBEREINER'S TRIADS

Li	Lithium	Ca	Calcium	Cl	Chlorine
Na	Sodium	Sr	Strontium	Br	Bromine
K	Potassium	Ba	Barium	I	Iodine

Elements	**Atomic weight**
Lithium	7
Sodium	23
Potassium	39

$$\text{Atomic weight of Na} = 23$$
$$\text{Mean of other two elements} = \frac{7 + 39}{2}$$
$$= 23$$

(ii) Newlands' Law of Octaves: In 1865, John Alexander Newlands gave Law of Octaves which state that "when the elements are arranged in the increasing order of atomic weights, the properties of every eighth element are similar to the first one."

Newlands' called this relation as the law of octaves due to similarity with the musical scale.

Table 3.2 : Newland's Octaves

Element	Li	Be	B	C	N	O	F
At. wt.	7	9	11	12	14	16	19
Element	Na	Mg	Al	Si	P	S	Cl
At. wt.	23	24	27	29	31	32	35.5
Element	K	Ca					
At. wt.	39	40					

(iii) Mendeleev's Periodic Law: The physical and chemical properties of elements are periodic function of their atomic weights.

Table 3.3 : Mendeleev's Prediction for the Elements *Eka-aluminium* (Gallium) and *Eka-silicon* (Germanium)

Property	*Eka-aluminium* (predicated)	Gallium (found)	*Eka-silicon* (predicted)	Germanium (found)
Atomic weight	68	70	72	72.6
Density/(g/cm^3)	5.9	5.94	5.5	5.36
Melting point /K	Low	302.93	High	1231
Formula of oxide	E_2O_3	Ga_2O_3	EO_2	GeO_2
Formula of chloride	ECl_3	$GaCl_3$	ECl_4	$GeCl_4$

► **Characteristics of Mendeleev's Periodic Table:**

(i) Eight vertical columns, called groups: Except for VIII group, each group is further sub-divided in A and B. This sub-division is made on the basis of difference in their properties.

(ii) Seven horizontal rows, called periods.

Significance of Mendeleev's Periodic Table:

(i) Instead of studying properties of elements separately, they can be studied in groups containing elements with same properties. It led to the systematic study of the elements.

(ii) Prediction of new elements: At his time, only 56 elements were known. He left blank spaces for unknown elements.

(iii) Mendeleev's periodic table corrected the doubtful atomic weights.

► **Defects in the Mendeleev's Periodic Table:**

(i) Hydrogen was placed in group IA: However, it resembles both group IA elements (alkali metals) and VII A (halogens). Therefore, the position of hydrogen in the periodic table is **anomalous or controversial.**

(ii) Anomalous pairs of elements: Some elements with higher atomic weight like Argon (39.9) precede potassium (39.1) with lower atomic weight.

(iii) Based upon atomic weights, **isotopes of an element could be assigned different groups** but as they are the atoms of same element (with only difference in their molecular mass) they must be in same group.

(iv) Some dissimilar elements are grouped together while some similar elements are placed in different groups. For example, alkali metals in group IA which are highly reactive are in the same group as coinage metals like Cu, Ag, Au of group IB. At the same time, certain chemically similar elements like Cu (group IB) and Hg (group IIB) have been placed in different groups.

(v) Position of elements of group VIII: No proper place was allotted to nine elements of group VIII which have been arranged in three triads without any justification.

► **Modern Periodic Law:** It states that "The physical and chemical properties of the elements are periodic functions of their atomic number."

According to the recommendations of IUPAC, the groups are numbered from 1 to 18 replacing the older notation of groups IA ... VIIA, VIII, IB ... VIIB and 0.

There are 7 periods. The first period contains 2 elements. The subsequent periods contain 8, 8,

18, 18, 32 elements respectively. The 7th period is incomplete and the 6th period would have a theoretical maximum of 32 elements. In this form of periodic table, the elements of both sixth and seventh periods (lanthanoids and actinoids respectively) are placed in separate panels at the bottom.

➤ **Long Form of Periodic Table:**
General characteristics of the long form of the periodic table:

First period	2 elements	Shortest period
Second and Third period	8 elements each	Short period
Fourth and Fifth period	18 elements each	Long period
Sixth period and Seventh period	32 elements each	Longest period

(i) There are in all, 18 vertical columns or 18 groups in the long form periodic table.

(ii) These groups are numbered from 1 to 18 starting from the left.

(iii) There are seven horizontal rows called **periods** in the long form of periodic table. Thus, there are seven periods in the long form of periodic table.

(iv) The elements of group 1, 2 and 13 to 17 are called the **main group elements.** These are also called **typical or representative or normal elements.**

(v) The elements of group 3 to 12 are called **transition elements.**

(vi) Elements with atomic number 58 to 71 (Ce to Lu) occurring after lanthanum (La) are called **Lanthanoids.** Elements with atomic number 90 to 103 (Th to Lr) are called **Actinoids.** These elements are called f-block elements and also as inner-transition elements.

➤ **Defects of long form of the periodic table**
- In periodic table, the position of hydrogen is not clear.
- It is placed in the separate box just above the group I.
- Lanthanoids and actinoids have not been merged with in the main body of the periodic table.

Mnemonics

Concept: Genesis of Periodic Classification
Mnemonics: **L**ondon and **T**urkey **D**onates **L**ots of **N**uts to **P**eru, **L**ibya and **M**alaysia but denied to **M**exico, **P**oland, **L**iberia and **M**aldives
Interpretation: Laws of Trieds – Dobereiner
Laws of Octaves – Newland
Periodic Law – Mendeleev
Modern Periodic Law – Moseley

Key Terms

➤ **Periods:** The horizontal rows in the periodic table are called periods.
➤ **Groups:** The vertical columns in the periodic table are called groups.

Key Facts

➤ At present, 118 elements are known.
➤ In modern periodic table, there are 18 groups.

Group 1 and 2: s-block elements in which last electron entered in s-sub shell [ns^1, ns^2].

Group 3 to 12: d-block 'or transition' elements elements in which last electron entered in d-sub shell $(n-1)d^{-10}$

Group 13 to 18: p-block elements in which last electron entered in p-sub shell [np^1 to np^6].

Group 18: Noble gases. Group 1-2, 13-17 are known as typical or normal or representative elements.

➤ In 's' and 'p' – block elements, the last electron enters in the outermost shell.
➤ In d-block elements, the last electron enters in the penultimate shell $(n-1)$.
➤ In f-block elements, the last electron enters in the sub-penultimate shell $(n-2)$.
➤ Elements with atomic number 58 to 71 (Ce to Lu) occurring after lanthanum (La) are called Lanthanoids. Elements with atomic number 90 to 103 (Th to Lr) are called Actinoids. These elements are called f-block elements and also as inner-transition elements.

Topic-2	**Nomenclature and Relation between Electronic Configuration and Periodic Table**

💬 Revision Notes

► **Nomenclature of Elements with Atomic Number Greater than 100:**

(i) The name is derived directly from the atomic number of the element using the latin numeral roots.

(ii) The symbol of the element is composed of the initial letters of the numeral roots which make up the name.

(iii) The root 'un' is pronounced with a long 'u' to rhyme with 'moon'. In the element names, each root is to be pronounced separately.

► **Electronic Configuration of Elements and the Periodic Table:**

We can classify the elements into four blocks viz, s-block, p-block, d-block and f-block depending on the type of atomic orbitals that are being filled with electrons.

► **Electronic Configuration in Periods:** The period indicates the value of n for the outermost or valence shell.

It can be readily seen that the number of elements in each period is twice the number of atomic orbitals available in the energy level that is being filled.

(i) **Elements in first period:** The first period ($n = 1$) starts with the filling of the lowest level ($1s$) and therefore has two elements – hydrogen ($1s^1$) and helium ($1s^2$) when the first shell (K) is completed.

(ii) **Elements in second period:** There are 8 elements, in the second period $n = 2$ (L shell) starting from lithium $1s^2$, $2s^1$ to neon $1s^2$, $2s^2 2p^6$.

(iii) **Elements in third period:** There are 8 elements in third period $n = 3$ (M shell) starting from Sodium $1s^2$, $2s^2$, $2p^6$, $3s^1$ to Argon, $1s^2$, $2s^2$, $2p^6$, $3s^2 \, 3p^6$

(iv) **Elements in fourth period:** There are 18 elements in $n = 4$ (N shell) starting from Potassium $1s^2$, $2s^2$, $2p^6$, $3s^2$, $3p^6$, $4s^1$ to Krypton $1s^2$, $2s^2$, $2p^6$, $3s^2 \, 3p^6$, $4s^2$, $3d^{10} \, 4p^6$.

(v) **Elements in fifth period:** It starts with Rb (37) with $5s$ orbital followed by filling of $4d$ orbitals, then $5p$ orbitals and ends at Xe (54), having total 18 elements forming $4d$ transition series.

(vi) **Elements in sixth period:** It has 32 elements forming lanthanoid series and successive electrons are filled in $6s$, $4f$, $5d$ and $6p$ orbitals, in that order.

(vii) **Elements in seventh period:** This period corresponds to $n = 7$ forming actinoid series and just like sixth period it involves the filling of $7s$, $5f$, $6d$ and $7p$. This period contains synthetic or man-made radioactive elements.

► **Group-wise Electronic Configuration:** Elements in a group have similar electronic configuration, same number of electrons in valence orbitals and similar properties, e.g., Group 1 (alkali) metals have general electronic configuration ns^1.

► **Position of Helium:** The electronic configuration of helium is $1s^2$. So it should be in s-block, but it is placed in p-block due to the presence of completely filled valence shell ($1s^2$) and similarity in properties with other noble gases.

► **Position of Hydrogen:** Electronic configuration of hydrogen is $1s^1$. Because of the presence of only one electron in s-orbital, it can be placed in group 1 with alkali metals and it also achieves the electronic configuration of inert gas so, it can also be placed in 17 group.

► **s-Block Elements:**

● The elements of group 1 **(alkali metals)** and group 2 **(alkaline earth metals)** which have ns^1 and ns^2 outermost electronic configuration belong to the s-block elements.

● They are all reactive metals with low ionization enthalpies. They lose the outermost electron(s) readily to form +1 ion (in the case of alkali metals) or +2 ion (in the case of alkaline earth metals).

● The metallic character and the reactivity increase as we go down the group. Because of high reactivity they are never found pure in nature.

● The compounds of the s-block elements, with the exception of those of lithium and beryllium are predominantly ionic.

► **p-Block Elements:**

● The p-block elements comprise those belonging to groups 13 to 18 and these together with the s-block elements are called the **Representative Elements or Main Group Elements.**

● The outermost electronic configuration varies from $ns^2 np^1$ to $ns^2 np^6$ in each period. At the end of each period is a noble gas element with a closed valence shell $ns^2 np^6$ configuration. All the orbitals in the valence shell of the noble gases are completely filled by electrons and it is very difficult to alter this stable arrangement by the addition or removal of electrons. The noble gases exhibit very low chemical reactivity due to completely filled valence shell.

● Preceding the noble gas family are chemically important groups of non-metals, i.e., chalcogens and halogens.

- The non-metallic character increases as we move from left to right across a period and metallic character increases as we go down the group.

► **d-Block Elements (Transition Elements):**
- These are the elements of Group 3 to 12 in the centre of the Periodic Table.
- These are characterised by the filling of inner $(n-1)d$ orbitals by electrons and are therefore referred to as. These elements have the outer electronic configuration $(n-1)d^{1-10}ns^{0-2}$. They are all metals.
- However, Zn, Cd and Hg which have the electronic configuration, $(n-1)d^{10}ns^2$ do not show most of the properties of transition elements.

► **f-Block Elements (Inner-Transition Elements):**
- The two rows of elements at the bottom of the Periodic Table, called **Lanthanoids**, Ce (Z = 58) – Lu (Z = 71) and Actinoids, Th (Z = 90) – Lr (Z = 103) are characterised by the outer electronic configuration $(n-2)f^{1-14}(n-1)d^{0-1}ns^2$.
- They all are metals. The chemistry of the early actinoids is more complicated than the corresponding lanthanoids due to large number of oxidation states.
- Actinoids are radioactive in nature.

$1s^1$			$1s^2$
s-block Elements ns^{1-2}	d-block Elements $(n-1)d^{1-10}ns^{0-2}$		p-block Elements ns^2np^{1-6}

f-block Elements $(n-2)f^{0-14}(n-1)d^{0-1}ns^2$

Division of Periodic Table into s, p, d, f-Blocks

► **Metals, Non-metals and Metalloids:**
  (i) Metals:
- Metals comprise more than 78% of all known elements and appear on the left side of the Periodic Table.
- Metals are usually solid at room temperature (Mercury is an exception ; gallium and caesium also have very low melting point 303 K and 302 K).
- Metals usually have high melting and boiling point except gallium and caesium.

  (ii) Non-Metals
- These are present only in p-block and appear on the right hand side of the periodic table.
- These can be either solid or gases at room temperature exceptional case is bromine (which is liquid at room temperature).
- Melting and boiling points are very low except boron and carbon.
- They are brittle and neither malleable nor ductile.

  (iii) Metalloids: The elements like silicon, germanium, arsenic, antimony and tellurium (Si, Ge, As, Sb, Te) which show properties of both metals and non–metals are called Metalloids.

🧠 Mnemonics

Concept: Classification of Elements and Periodicity in Properties.

1. Elements of Atomic No (1-18)
Mnemonics:
Happy **H**arry **L**isten **BBC** **N**etwork **O**ver **F**rench **N**etwork. **N**ative **M**agpies **A**lways **S**it **P**eacefully **S**earching **C**lear **A**reas
Interpretation:
H, He, Li, Be, B, C, N, O, F, Ne, Na, Al, Si, P, S, Cl, Ar

2. Group I Elements
Little Nasty Kids Rub Cats Fur
Lithium (Li), Sodium (Na), Potassium (K), Rubidium (Rb) Caesium (Cs), Francium (Fr)

3. Group II Elements
Mnemonics: Beer Mugs Can Snap Bar's Reputation
Interpretation: Beryllium (Be), Magnesium (Mg), Calcium (Ca),
Strontium (Sr), Barium (Ba), Radium (Ra)

4. Group III Elements
Mnemonics: BAGIT
Interpretation:
Boron (B), Aluminium (Al), Gallium (Ga), Indium (In), Thallium (Tl)

5. Group IV B Elements
Mnemonics: Can Simple Germans Surprise Public
Interpretation: Carbon (C), Silicon (Si), Germanium (Ge), Tin (Sn), Lead (Pb)

6. Group V B Elements
New Police Assign Subordinate Bikram on Duty
Nitrogen (N), Phosphorus (P), Arsenic (As), Antimony (Sb), Bismuth (Bi)

7. Group VI B Elements
Old Saharanpur Seems Terribly Polluted
Oxygen (O), Sulphur (S), Selenium (Se), Tellurium (Te), Polonium (Po)

8. Group VII B Elements
First Class Biryani In Australia
Fluorine (F), Chlorine (Cl), Bromine (Br), Iodine (I), Astatine (Al)

9. Group VIII B/18 Elements
He never Arrived; Karan exited with Rohan
Helium (He), Neon (Ne), Argon (Ar), Krypton (Kr), Xenon (Ex), Radon (Rn)

10. 3d-Series

Scary Tiny Vicious Creatures are
Mean females come to Night Club Zen
Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn,

11. 4d-Series

Yes S(z)sir Nob. Most Technicians Rub Rod's Pale Silver Cadillac
Y, Zr, Nb>Mo, Tc, Ru, Rh, Pd, Ag, Cd

12. 5d-Series

Late Harry Took Walk, Reached
Office In Pajamas After an Hour
La......., Hf, Ta, W, Re, OS, Ir, Pt, Au, Hg

13. Lanthanides

Ladies Can't Put Needles Properly in
Slot-machines. Every Girl Tries Daily
However, Every Time You'd be lose
La, Ce, Pr, Nd, Pm, Sm, Eu Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu

14. Actinides series

Three Planets: Uranus, Neptune, and Pluto. Amy
Cured Berkeley, California. Einstein and Fermi Made
NobleLaws.(Ac) Th Pa U Np Pu Am Cm Bk Cf Es Fm
Md No Lr

Topic-3 Periodic Properties and their Periodic Trends

💬 Revision Notes

➤ **Atomic Radii:** The term atomic radius means the distance from the centre of the nucleus to the outermost shell of electrons.

➤ On the basis of the nature of combining atoms, atomic radius can be of following types:

$$r_{covalent} = \frac{\text{Internuclear distance between two bonded atoms}}{2}$$

- **Metallic Radius:** Metallic radius is taken as one-half of the internuclear distance between the two neighbouring atoms of a metal in a metallic lattice.

- **van der Waals Radius:** Noble gas atoms are held together by weak van der Waals forces of attraction. The van der Waals radius is half of the distance between the centre of nuclei of atoms.

➤ **Variation of Atomic Radii in the Periodic Table:**

- **Variation in a period:** In general, the atomic radii decrease with increase in atomic number on going from left to right due to the increase of effective nuclear charge.

  For example, in the second period, the atomic radii decrease from Li to Ne through Be, B, C, N, O and F.

- **Variation in a group:** The atomic radii of elements increase from top to bottom in a group. On moving down a group, the effective nuclear charge decreases with increase in atomic number and we expect that the size of atom should increase.

➤ **Ionic Radii:** The effective distance from the centre of the nucleus of the ion to which it has an influence in the ionic bond.

The ionic radii show the same trends as atomic radius.

➤ **Covalent Radius:** Covalent radius may be defined as "one-half of the distance between the centre of nuclei of two similar atoms bonded by a single covalent bond.

For homonuclear molecules,

The study of ionic radii leads to two important generalizations:

(i) The radius of positive ion (cation) is always smaller than that of the parent atom because it has lesser electrons but same nuclear charge.

(ii) The radius of negative ion (anion) is larger than that of the parent atom because extra electrons are added due to which repulsion among electrons increases and effective nuclear charge decrease.

➤ **Isoelectronic Species:** These are the atoms or ions having the same number of electrons. e.g., O^{2-}, F^-, Na^+ and Mg^{2+} have 10 electrons.

➤ **Ionization Enthalpy:** It is defined as the amount of energy required to remove the loosely bound electron from isolated gaseous atom in its ground state.

The first ionization enthalpy (IE_1) is the energy required to remove the most loosely bound electron of the neutral atom and the second ionisation enthalpy (IE_2) is the energy required to remove the second electron from the resulting cation and so on. Thus first ionisation enthalpy of an element (X) may be defined with the reaction represented as :

$$X(g) \xrightarrow{IE_1} X^+(g) + e^-$$
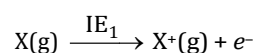
- ► **Factors Affecting Ionization Enthalpy:**
    - ● **Size of the atom:** The ionisation enthalpy depends upon the distance between the electron and the nucleus, i.e., size of the atom. It decreases with increase in atomic size.
    - ● **Charge on the nucleus:** With the increase in nuclear charge it becomes more difficult to remove an electron from valence shell and therefore ionization enthalpy increases.
    - ● **Screening effect:** The reduction in force of attraction by the electrons of shells present in between the nucleus and valence electrons is called screening effect or shielding effect. The greater the number of intervening electrons between valence electron and nucleus, the greater will be shielding or screening effect. An increase in the number of inner electrons tends to decrease the ionization enthalpy.
    - ● **Penetration effect of electrons:** s-electrons are more penetrating towards the nucleus than p-electrons and the penetration power decreases in a given shell in the order.
      $$s > p > d > f$$
      For the same shell, the ionization enthalpy would be more to remove an s-electron than the energy required to remove a p-electron, which in turn will be more than that for the removal of a d-electron and so-on.
    - ● **Electronic Arrangement:** The ionization enthalpy also depends upon the electronic configuration of the atom.

      For example, half filled and completely filled shells have extra stability associated with them.
      - (i) The noble gases have the most stable electronic configurations (ns^2np^6) in each period and therefore, have high ionization enthalpies.
      - (ii) The elements like Be ($1s^2$ $2s^2$) and Mg ($1s^2$ $2s^2$ $2p^6$ $3s^2$) have completely filled orbitals and their ionisation enthalpies are large.

- ► **Variation down a group:** Within a group, there is a gradual decrease in ionization enthalpy in moving from top to bottom.

  The decrease in ionization enthalpy down a group can be explained as:
    - ● While going from top to bottom in a group, the nuclear charge increases atomic size increases and shielding effect increase.
    - ● There is a gradual increase in atomic size due to an additional main energy shell (n).
    - ● There is increase in shielding effect on the outermost electron due to increase in the number of inner electrons that outweighs the increasing nuclear charge and removal of the outermost electron requires less energy down a group.

- ► **Variation along a period:** In general, the ionisation enthalpy increases with increasing atomic number in a period.
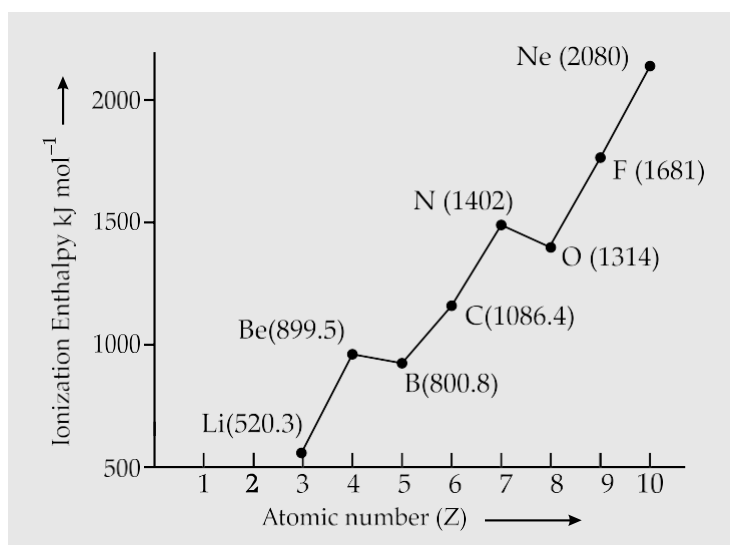
Variation of ionization enthalpy with atomic number in second period

The general Increase of ionisation enthalpy along a period car be explained on the basis of atomic & nuclear change:
  - (i) On moving across a period from left to right, the effective nuclear charge increases.
  - (ii) The atomic size decreases along a period though the main energy level remains the same.

- ► **Successive Ionization Enthalpies:** The energies required to remove subsequent electrons from the atom in the44 gaseous state are known as successive ionization enthalpies.

  It has been found that
  $$IE_1 < IE_2 < IE_3$$

- ► **Electron Gain Enthalpy ($D_{eg}H$):** It is defined as the enthalpy change, when a neutral gaseous atom takes up extra electrons to form an anion.
  $$X(g) + e^- \longrightarrow X^-(g)$$
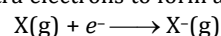
The value of electron gain enthalpy depends upon atomic size, nuclear charge, etc. With increase in size, the electron gain enthalpy decreases as the nuclear attraction decreases. Thus, electron gain enthalpy generally decreases in moving from top to bottom in a group (F < Cl > Br > I). In a period from left to right, the electron gain enthalpy generally increases due to increase in effective nuclear charge.

➤ **Factors Affecting Electron Gain Enthalpy:**
  ● **Nuclear charge:** The electron gain enthalpy becomes more negative as the nuclear charge increases. This is due to greater attraction for the incoming electron if nuclear charge is high.
  ● **Size of the atom:** With the increase in size of the atom, the distance between the nucleus and the incoming electron increases consequently, the electron gain enthalpy becomes less negative.
  ● **Electronic configuration:** The elements having stable electronic configuration of half-filled and completely filled valence sub shells show very small tendency to accept additional electron and thus electron gain enthalpies are less negative.

➤ **Important Trends in Electron Gain Enthalpy:**
  ● Halogens have the highest negative electron gain enthalpies
  ● Electron gain enthalpy values of noble gases are positive while those of Be, Mg, N and P are almost zero
  ● Electron gain enthalpy of fluorine is unexpectedly less negative than of chlorine: However, it is observed that F-atom has unexpectedly less negative electron gain enthalpy than Cl-atom. This is due to the very small size of F-atom. As a consequence of small size, there are strong inter electronic repulsions in the relatively compact $2p$-subshell of fluorine and thus the incoming electron does not feel much attraction.

➤ **Electronegativity:**
  ● It is a qualitative measure of the ability of an atom in a chemical compound to attract shared pair of electrons towards itself.
  ● Pauling scale is generally used on which fluorine (most electronegative element) was assigned a value of 4.0 arbitrarily.
  ● Electronegativity generally increases on moving across a period because of increase in effective nuclear charge.
  ● It decreases on moving down a group because of decrease in effective nuclear charge.

➤ **Summary of the trends in the periodic properties of elements in the periodic table:**
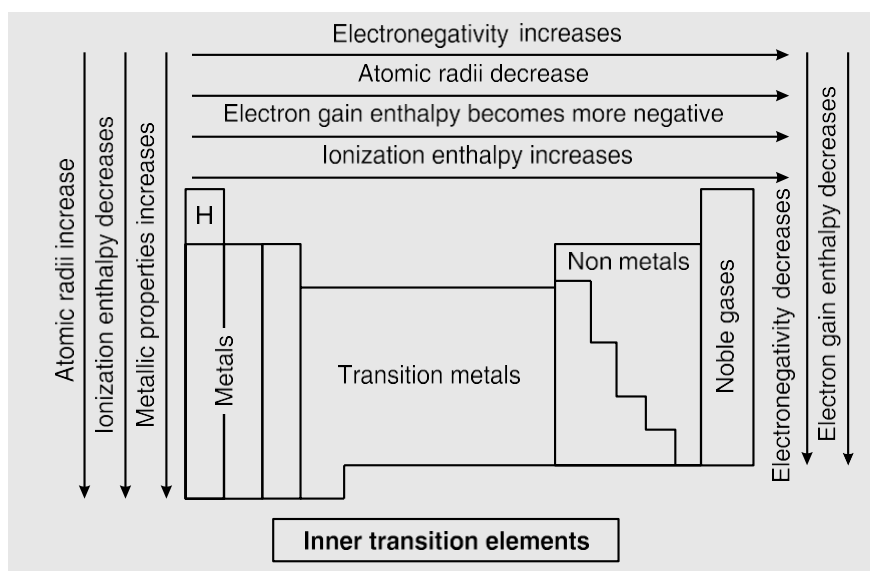
➤ **Valency:** The electrons present in the outermost shell of an atom are called valence electrons and the number of these electrons determine the valence or the valency of the atom. It is because of this reason that the outermost shell is also called the valence shell of the atom and the orbitals present in the valence shell are called **valence orbitals.**

⚙ **Mnemonics**

Concept: Electronegativity
Mnemonics: First off, cloud now. Bring in some caps, hats and pants
Interpretation: Fluorine > Oxygen > Chlorine > Nitrogen > Bromine > Iodine > Sulfur > Carbon > Hydrogen ≥ Phosphorus
Pronounce: FOClN BrIS CHP.
(F)irst (O)ff, (Cl)oud (N)ow, (Br)ing (I)n (S)ome (C)aps, (H)ats, and (P)ants

► **Diagonal Relationship:**

	Group 1	Group 2	Group 13	Group 14
	Li	Be	B	C
	Na	Mg	Al	Si
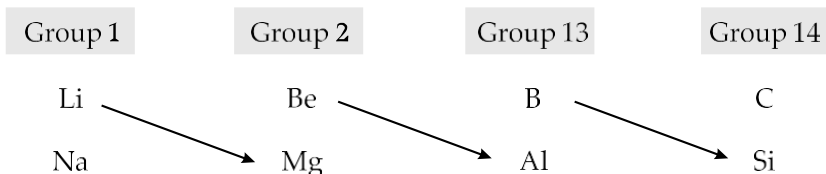
The resemblance of properties of Li with Mg (which is diagonally situated): Be with Al and B with Si is called diagonal relationship. It is due to similar polarising power.

► **Periodic Trends and Chemical Reactivity:**
- The ionization enthalpy of the extreme left element in a period is the least and the electron gain enthalpy of the element on the extreme right is the highest negative (excluding noble gases).
- Alkali metals (at extreme left) has maximum tendency to form cation (by loss of an electron) and halogens (at extreme right) has maximum tendency to form anion (by gain of an electron).
- Metallic character is maximum at the left and non-metallic character is maximum at the right within a period.
- The oxides formed by the elements at the left of the periodic table are basic (e.g., Na_2O) while oxides formed by the elements at the right of the periodic table are acidic (e.g., Cl_2O_7). However, oxides of elements in the centre are either amphoteric (e.g., Al_2O_3, Sb_2O_3) or neutral (e.g., CO, NO, N_2O).
- In transition metals, change in atomic radii is much smaller than representative elements.
  Their ionization enthalpies are between *s*- and *p*-block elements. Therefore, they are less electropositive than group 1 and 2 metals.

General Trends of Periodic Properties in Periodic Table

Trends of Atomic Radius
► Noble gases have large atomic radius than group 17 elements due to complete filling of electron in outer shell electron-electron repulsion mildly increases.

Trends of Ionization Enthalpy
First Ionization Enthalpy:
$Li < B < Be < C < O < N < F < Ar$
Second Ionization Enthalpy:
$Be < C , B < N < F < O < Ne$

► **Metallic Behaviour:** Decreases from left to right in a period due to increase in ionization enthalpy.
► **Non-metallic Behaviour:** Increases from left to right due to more number of electron in outermost shell and added electron goes towards nucleus.
► **Radius of Cation < Atomic radius**
It is due to more number of protons than the number of electrons in a cation. Coulombic force increases, size decreases.
$Mg^{2+} < Mg^+ < Mg$
► **Radius of Anion > Atomic Radius**
It is due to more number of electrons than the number of protons in an anion.

$N^{3-} > O^{2-} > F^-$
Electron – electron repulsion increases, coulombic force of attraction decreases and size increases.

► **For Isoelectronic Species:**
- Greater the charge of cation, lesser will be the size.
- Greater the charge of anion, greater will be the size.
  Eg., $O^{2-} > F^- > Na > Na^+ > Mg^{2+}$

Trends of Electron Gain Enthalpy:
Halogen > Oxygen > Nitrogen > Metal of group 1 and 13 and non-metal of group 14 > Metal of group 2.

► Chlorine has maximum electron gain enthalpy.
► Phosphorus and sulphur have negative electron gain enthalpy then nitrogen and oxygen respectively.

Trends of Electronegativity:
► Highest electronegative atoms in periodic table :
$F > O > N$

► Effective nuclear change (Z_{eff}) = Nuclear charge – shielding effect

Trend : Z_{eff} increases from left to right in a period.
Z_{eff} decreases from top to bottom in a group.

⚙ Mnemonics

1. Alkali Metals
Concept: Trends in Atomic and physical properties
Mnemonics:
H – Hydrogen-His
Li – Lithium-Last
Na – Sodium-Son
K – Potassium-Plays
Rb – Rubidium-Rugby
Cs – Caesium-Cricket
Fr – Francium-Football
2. Atomic/Ionic radii, metallic, reducing, characteristics (group)
Mnemonics: Like Nadia Kareena likes Rugby & Cricket
Interpretation: $Li < Na < K < Rb < Cs$
3. Ionisation Energy, melting/boiling
points, reactivity with Hydrogen/Halogens, Enthalpy
Mnemonics: Little Naughty Krishna Rules Close friends
Interpretation: $Li > Na > K > Rb > Cs$
Electronegativity
Mnemonics: Cat Sings Gentle Songs in Public
Interpretation: $C < Si = Ge = Sn < Pb$

Chapter 4

CHEMICAL BONDING AND MOLECULAR STRUCTURE

Topic-1	General Introduction to Bonding: Ionic, Covalent Bonds and Lewis structures

📝 Revision Notes

➤ **Chemical Bond:** The attractive force which holds various constituent particles (atoms, ions or molecules) together in a chemical species is known as chemical bond.

➤ **Octet Rule:** The octet rule or the electronic theory of chemical bonding was developed by Kossel and Lewis. According to this rule, atoms can combine either by transfer of valence electrons from one atom to another (gaining or losing) or by sharing their valence electrons. The principle of attaining maximum of eight electrons in the valence shell of atoms is called octet rule. Lewis postulated that atoms achieve the stable octet when they are linked by chemical bonds.

➤ **Limitations of the Octet Rule:** Some limitations of octet rule are:

- In periodic table in and beyond the third period (after silicon) this rule is not applied. These elements can "expand their octet" and have more than eight valence electrons around the central atom, e.g., PF_5, SF_6 etc.
- Molecules with an odd number of electrons such as NO and NO_2 cannot satisfy the octet rule.
- In some molecules, the central atom cannot possibly have eight valence electrons. For example, LiCl, $BeCl_2$ and BCl_3 do not obey the octet rule.
- It is based upon the chemical inertness of noble gases. However, some noble gases such as Xenon and Krypton combine to form a number of compounds like XeF_2, KrF_2, $XeOF_2$, etc.
- This theory does not account for the shape of molecules.

➤ **Lewis Structure of Ionic Compounds:**

(i) $(Na^+)(:\overset{..}{\underset{..}{Cl}}:^-)$
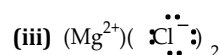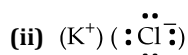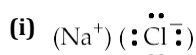
- It also does not explain the relative stability of the molecules.

➤ **Ionic or Electrovalent Bond:** "Ionic bonding is a type of chemical bond that involves the electrostatic attraction between oppositely charged ions together is known as ionic bond and electrovalent bond." Thus, the electrovalence is equal to the number of unit charge on the ion.

"Electrovalent compounds are those compounds in which constituent particles are ions or positively charged species and they are formed by transfer of electron from a metal to a non-metal.

$$Na\overset{\frown}{\cdot} + \cdot\overset{..}{\underset{..}{Cl}}: \longrightarrow Na^+ + \left[:\overset{..}{\underset{..}{Cl}}:\right]^-$$
$$(2, 8, 1) \quad (2, 8, 7) \qquad\qquad (2, 8) \quad (2, 8, 8)$$
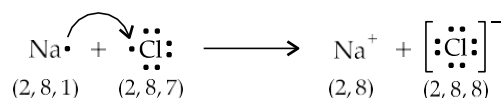
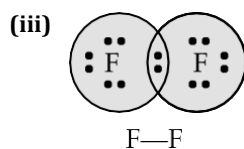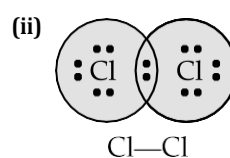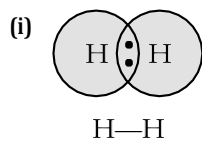➤ **Properties of Ionic Compounds:**

- Ionic compounds have high melting points and high boiling points.
- They have higher enthalpies of fusion and vaporization than molecular compounds.
- They are hard and brittle.
- These compounds conduct electricity when they are dissolved in water or in molten state.
- Ionic solids are good insulators.
- The ionic bond is non-directional. This is because each ion is surrounded by oppositely charged ions uniformly distributed all around the ion.
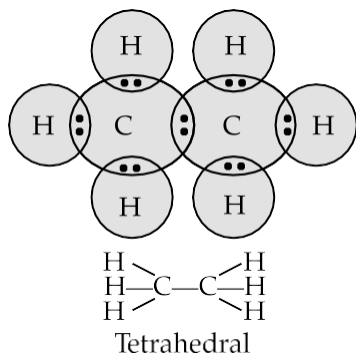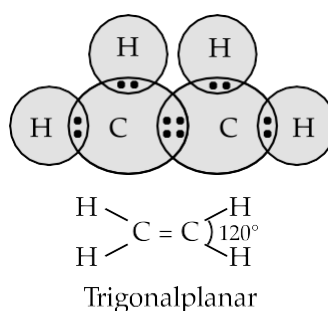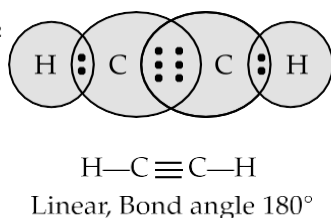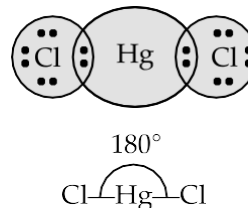
➤ **Covalent Bond:** A covalent bond is a chemical bond that involves the sharing of electron pairs between atoms. The stable balance of attractive and repulsive forces between atoms when they share electrons is known as covalent bonding.

$$\overset{\bullet}{H} + \overset{\bullet}{H} \longrightarrow H\overset{\bullet}{\underset{\bullet}{\,}}H \quad Or \quad H-H$$
Sharing of electrons

(ii) $(K^+)(:\overset{..}{\underset{..}{Cl}}:^-)$

(iii) $(Mg^{2+})(:\overset{..}{\underset{..}{Cl}}:^-)_2$

(iv) $(K^+)_2 \, (:\!\overset{..}{\underset{..}{O}}\!:)^{2-}$ **(v)** $(Mg^{2+}) \, (:\!\overset{..}{\underset{..}{O}}\!:)^{2-}$ **(vi)** $(Ca^{2+}) \, (:\!\overset{..}{\underset{..}{O}}\!:)^{2-}$

(vii) $(Na^+)_2 \, (:\!\overset{..}{\underset{..}{S}}\!:)^{2-}$ **(viii)** $(Na^+)_3 \, (:\!\overset{..}{\underset{..}{P}}\!:)^{3-}$ **(ix)** $(Li^+)_2 \, (:\!\overset{..}{\underset{..}{O}}\!:)^{2-}$

(x) $(Ca^{2+})_3 \, (:\!\overset{..}{\underset{..}{N}}\!:)^{3-}_2$
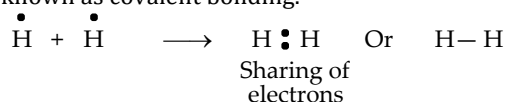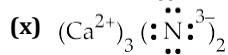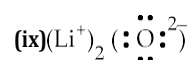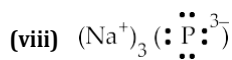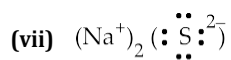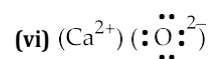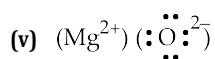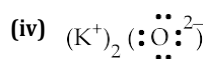
▶ **Lewis Structure of Covalent Compounds:**

(i)

H—H

(ii)

Cl—Cl

(iii)

F—F

(iv)

H—Cl

(v)

H—Br

(vi) H_2O

O
104.5°
H   H
Bent molecule

(vii) H_2S

S
92.5°
H   H
Bent molecule

(viii) NH_3

N
H 107° H
H
Pyramidal

(ix) CCl_4

Cl
C 109.5°
Cl   Cl
Cl
Tetrahedral

(x) CH_4

H
C 109.5°
H   H
H
Tetrahedral

(xi) C_2H_6

H—C—C—H (structure shown with H atoms)

Tetrahedral

(xii) C_2H_4

$$\begin{array}{c} H \\ \diagdown \\ H \diagup \end{array} C = C \begin{array}{c} H \\ \diagup \\ \diagdown H \end{array} 120°$$

Trigonalplanar

(xiii) C_2H_2

H—C≡C—H
Linear, Bond angle 180°

(xiv) $HgCl_2$

180°
Cl—Hg—Cl
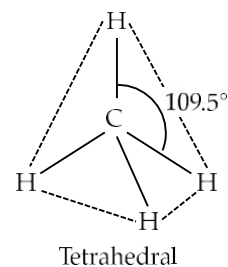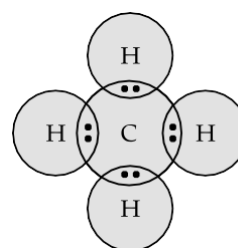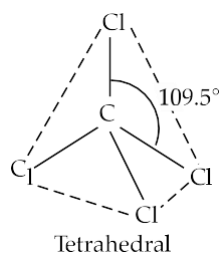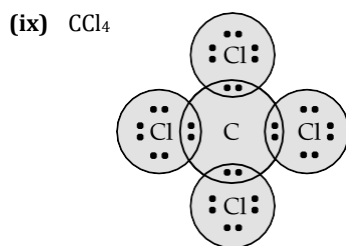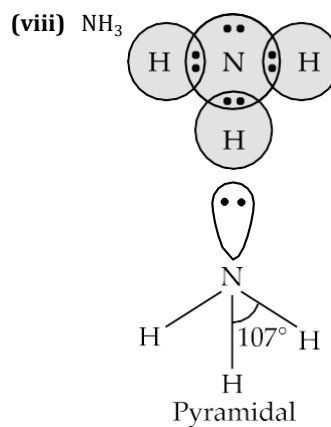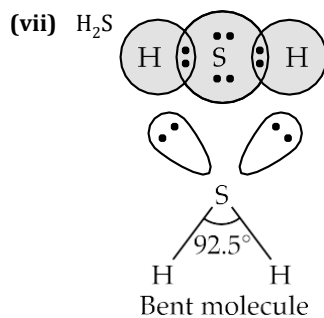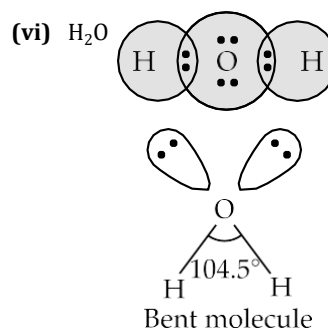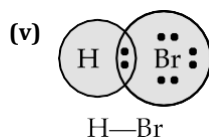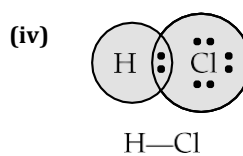
☞ **Formal Charge:** The formal charge of an atom in a polyatomic ion or molecule is defined as – "The difference between the number of valence electrons in an isolated or free state and the number of electrons assigned to that atom in a Lewis structure."

It may be expressed as:

Formal charge on an atom in a Lewis structure = (Total number of valence electrons in free atom) – (Total number of non-bonding (lone pair) electrons)

$-\dfrac{1}{2}$ (Total number of bonding (shared) electrons)

$$FC = V - L - \dfrac{1}{2} S$$

where FC = Formal charge on an atom

V = Total number of valence electrons in the free atom

L = Total number of non-bonding (lone pair) electrons

S = Total number of bonding (shared) electrons.

☞ **Properties of Covalent Compounds:**

● **Low melting and boiling points:** Covalent compounds consist of molecules held by weak forces. These can be easily overcome by heat.

● **Non-conduction nature:** Covalent compounds do not conduct electricity, i.e., electricity does not pass through the covalent compounds. This is because the covalent compounds do not contain ions or free electrons.

● **Solubility:** Covalent compounds are non-polar and do not dissolve in polar solvents like water. The covalent compounds however, dissolve in non-polar solvents like benzene, toluene, etc.

● **Slow rate of reaction:** The reaction of the covalent compounds are quite slow. The reaction is molecular, and the molecular reactions are slow.

☞ **Bond Parameters:** The various characteristic features shown by a bond are called the bond parameters.

● **Bond length:** Bond length is defined as "the equilibrium distance between the centres of the nuclei of two bonded atoms in a molecule." Bond lengths are measured by spectroscopic, X-ray diffraction and electron diffraction techniques.

$$R = r_A + r_B$$
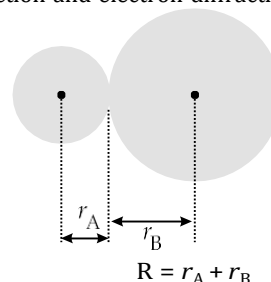
In case of covalent bond, the covalent radius is measured as the radius of an atom's core which is in contact with core of an adjacent atom in a bonded situation.

Covalent radius $= r_A + r_B = \dfrac{d}{2}$ [if $r_A = r_B$]

The van der Waals radius represents the overall size of the atom which includes its valence shell in a non-bonded situation.

Single covalent radius decreases from left to right along a period and increases down a group just like atomic radii.

● **Bond angle:** It is defined as the angle between the orbitals containing bonding electron pairs around the central atom in a molecule/complex ion. For example, the bond angle in some compounds can be represented as under:
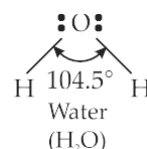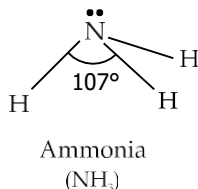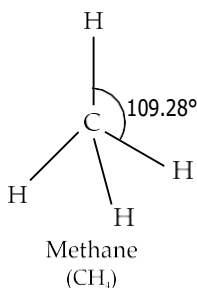
H 104.5° H

Water
(H_2O)

Methane
(CH₄)

Ammonia
(NH₃)

- **Bond enthalpy:** It is defined as the amount of energy required to break one mole of bonds of a particular type between two atoms in a gaseous state. The unit of bond enthalpy is kJ mol^{-1}. For example H – H bond enthalpy in hydrogen molecule is 435.8 kJ mol^{-1}.

  $H_2(g) \longrightarrow H(g) + H(g)$; $\Delta_a H^{\ominus}$ = 435.8 kJ mol^{-1}
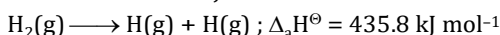
- **Bond order:** In the Lewis description of covalent bond, the bond order is given by the number of bonds between the two atoms in a molecule. Bond order in H_2 is one, in O_2, it is two and in N_2 it is three.

  Isoelectronic molecules and ions have identical bond orders. For example F_2 and O_2^{2-} have bond order

  1 and N_2, CO and NO$^+$ have bond order 3.

  Thus, the stabilities of molecules can be understood by the statement "**with increase in bond order, bond enthalpy increases and bond length decreases.**"

► **Types of Covalent Bond:** Depending upon the nature of combining atoms, the covalent bonds can be of two types:

- **Non-polar Covalent Bond:** This type of bond is formed between the two atoms of the same element. Atoms of the same element attract electron equally. This type of covalent bond is described as a non-polar covalent bond.

  For example: H_2, O_2 and Cl_2, etc.

- **Polar Covalent Bond:** When two dissimilar atoms, having different electronegativities combined together to form a covalent bond, For example, in case of a heteronuclear molecule like HF, the shared electron pair between the two atoms gets displaced more towards fluorine since the electronegativity of fluorine is far greater than that of hydrogen. The atom with higher affinity for electrons develops a slight negative charge and atom with lesser affinity for electrons develops a slight positive charge. Eg., HCl, H_2O etc.

► **Dipole Moment:** It is defined as "the product of the magnitude of the charge and the distance of separation between the charges."

Dipole moment (μ) = Charge (Q) × Distance of separation (r)

It is usually expressed in Debye units (D).

Dipole moment is also expressed in the units of C m (Coulomb meter):

$$1D = 3.33564 \times 10^{-30} \text{ C m}$$

The dipole of HF may be represented as :
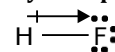
The presence of dipole moment is represented by the crossed arrow ($+\!\!\longrightarrow$.

🗝 Key Terms

► **Valence Electrons:** The outermost shell electrons which take part in the formation of chemical bond are called valence electrons.

► **Lattice Enthalpy:** The lattice enthalpy of an ionic solid is defined as the energy required to completely separate one mole of a solid ionic compound into gaseous constituent ions.

► **Bond Enthalpy:** It is defined as the amount of energy required to break one mole of bonds of a particular type between two atoms in a gaseous state.

► **Electrovalency:** The valence of an ion, equal to the number of positive or negative charges acquired by an atom through a loss or gain of electrons is known as electrovalency.

► **Covalency:** The bond formed between two atoms by mutual sharing of electrons between them so as to complete their octets is known as covalent bond and number of electrons involved is covalency.

🧠 Mnemonics

Concept: Chemical Bond Strength

I can't Handle Dirty Vans

Ionic > Covalent > H–bonds > Dipole > van Der Waal

5. Bond Polarity

SNAP

Symmetrical Ⓡ Non Polar

Asymmetrical Ⓡ Polar

Topic-2   Resonance and VSEPR Theory

💬 Revision Notes

➤ **Resonance:** When a molecule cannot canonically be represented by a single structure but its characteristic properties; position of nuclei, bonding and non-bonding pairs of electrons can be described by two or more than two canonical structures, then actual structure is said to be a resonance hybrid of these structure. Resonance is represented by a double headed arrow. Some of the examples of resonance structure are O_3 molecule, CO_3^{2-}, CO_2 molecule.

➤ **Conditions for Writing Resonating Structure:**
- The contributing structures should have same atomic positions, same number of unpaired electrons and nearly same energy.
- The structures should be written such that negative charge is present on an electronegative atom and positive charge is present on an electropositive atom.
- In these structures, the like charges should not reside on adjacent atoms.

➤ Resonance stabilizes the molecule because the energy of the resonance hybrid is less than the energy of any single canonical structures. Resonance also averages the bond characteristics as a whole.

➤ **Resonance Energy:** It is the difference between the actual bond energy of the molecule and that of the most stable resonating structures (having least energy). Thus,

> Resonance energy = Actual bond energy – Energy of the most stable resonating structure

➤ **Valence Shell Electron Pair Repulsion (VSEPR) Theory:** In 1940, Sidgwick and Powell proposed a simple theory based on the repulsive interactions of the electron pairs in the valence shell of the atoms. It was further developed and refined by Nyholm and Gillespie in 1957.

They suggested that the shapes of molecules can be determined by the number of electron pairs (bonding as well as non-bonding) in the valence shell of the central atom.

➤ **Postulates of VSEPR Theory:**
- The geometry of a molecule depends upon the total number of valence shell electron pairs (bonded or non-bonded) around the central atom in the molecule.
- Pairs of electrons in the valence shell repel one another since their electron clouds are negatively charged.
- These pairs of electrons tend to occupy such positions in space that minimise repulsion and thus maximise distance between them.
- The valence shell is taken as a sphere with the electron pairs localising on the spherical surface at maximum distance from one another.
- 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.
- Where two or more resonance structures can represent a molecule, the VSEPR model is applicable to any such structure.

📑 Key Facts

➤ The repulsive interaction of electron pairs decrease in the order –
$$lp - lp > lp - bp > bp - bp$$
(where, lp = lone pair, bp = bond pair)

The presence of lone pairs in addition to bond pairs will result in certain distortions in the regular geometry of molecules.

Topic-3   Valence Bond Theory, Hybridization, Molecular Orbital Theory and Hydrogen Bonding

💬 Revision Notes

➤ **Valence bond Theory by Heitler and London.** According to theory, a covalent bond is formed between the two atoms by the overlap of half filled valence atomic orbitals of each atom containing one unpaired electron.

- The bond is formed when two atoms approach each other in such a way that occupied orbitals with similar energies are able to overlap.
- Greater the overlap, stronger is the bond.
- **Types of overlapping and nature of covalent bonds:** Depending upon the type of overlapping, the covalent bonds may be divided into two types:

(a) Sigma (s) bond and **(b)** Pi (p) bond

(a) Sigma (s) bond: This type of covalent bond is formed by the end to end (head on) overlapping of bonding orbitals along the internuclear axis. The overlap is known as **head on overlap** or **axial overlap**.

(i) s-s overlapping: In this type, two half filled s-orbitals overlap along the internuclear axis as shown below.

s-orbital   s-orbital   s-s overlap
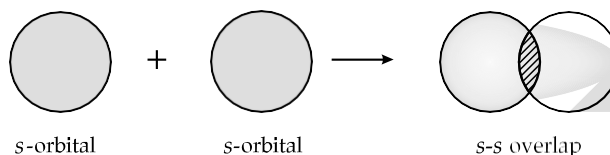
(ii) s-p overlapping: This type of overlapping between the half filled s-orbital of one atom and p-orbital of the other atom.

s-orbital   p-orbital   s-p overlap
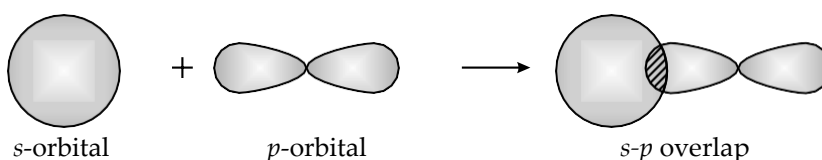
(iii) p-p overlapping: This type of overlapping occurs between half filled p-orbitals of the two approaching atoms.

p-orbital   p-orbital   p-p-overlap
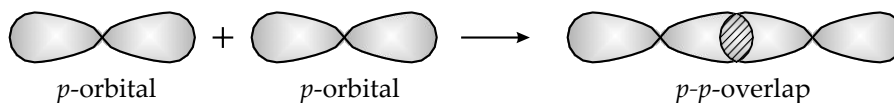
(b) Pi (p) bond: This type of covalent bond is formed by the sidewise overlapping of the half filled atomic orbitals of bonding atoms. Such an overlap is known as **sidewise** or **lateral overlap**. The atomic orbitals overlap in such a way that their axis remain parallel to each other and perpendicular to the internuclear axis. The orbital obtained as a result of sidewise overlap consists of two saucer type charged clouds above and below the plane of the participating atoms.

p-orbital   p-orbital   p-p-overlap
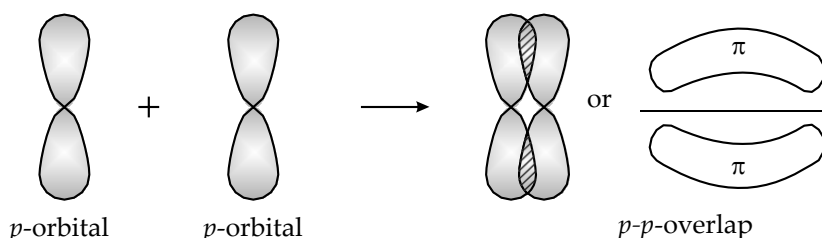
- **Strength of sigma and pi-bonds:** The strength of a covalent bond depends upon the extent of overlapping of atomic orbitals forming the bond. During the formation of a sigma bond, the overlapping of orbitals takes place to a larger extent.

  On the other hand, during the formation of a pi-bond, the overlapping occur to a smaller extent. Therefore, a sigma bond is strong than a pi-bond.

- **Hybridisation:** According to Pauling, This may be defined as—

  "The process of intermixing of the orbitals of slightly different energies so as to redistribute their energies resulting in the formation of new set of orbitals of equivalent energies and shape."

- **Characteristics of Hybridisation:**
  - The number of hybrid orbitals equals the number of orbitals that become hybridised; also, the hybridised orbitals are always equivalent in energy and shape; additionally, the hybrid orbitals are more efficient at creating stable bonds than the pure atomic orbitals.
  - The type of hybridisation indicates the geometry of the molecule.

- **Conditions for Hybridisation:**
  - Only the orbitals present in the valence shell of the atom are hybridised.
  - The orbitals undergoing hybridisation should have only a small difference in energy, i.e., should have almost equal energy. The orbitals which differ largely in energy cannot take part in hybridisation.
  - Promotion of electron is not essential condition prior to hybridisation.
  - It is not essential that only half filled orbitals participate in hybridisation. In certain cases, even filled orbitals of valence shell participate in hybridisation.

► **Types of Hybridisation:**

- **sp Hybridisation:** In *sp* hybridisation, one *s* and one *p* orbital mix and form two equivalent *sp* hybrid orbitals. The orbitals suitable for *sp* hybridisation are *s* and p_z orbitals, if the hybrid orbitals are to lie along *z*-axis. Each *sp* hybrid orbitals has 50% *s*-character and 50% *p*-character. These two *sp* hybrid orbitals are oriented in opposite direction forming an angle of 180° with linear shape.
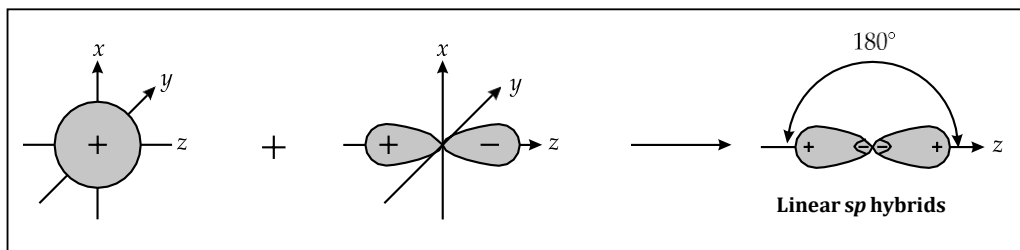
Fig. 4.1 : Formation of *sp* hybrid orbitals

Example: BeF_2, $BeCl_2$, etc.

- **sp² Hybridisation:** The combination of one *s* and two *p* orbitals gives rise to three *sp*² hybrid orbitals. These three hybrid orbitals lie in the same plane and are directed towards the three corners of an equilateral triangle in a plane have an angle of 120° and shape trigonal. Each *sp*² hybrid orbital has 33.3% *s*-character and 66.7% *p*-character.
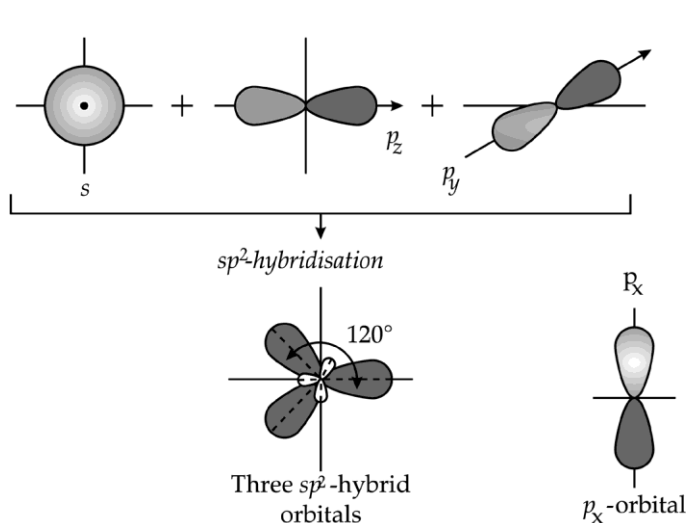
Fig. 4.2 : Formation of *sp*² hybrid orbitals

Example : BCl_3, BF_3, etc.

- **sp³ Hybridisation:** In *sp*³ hybridisation, one *s* and three *p* orbitals mix and form four *sp*³ hybrid orbitals of equivalent energies and shape. Each *sp*³ hybrid orbitals has 25% *s*-character and 75% *p*-character. The four *sp*³ hybrid orbitals are directed towards the four corners of the tetrahedron. The angle between *sp*³ hybrid orbital is 109°5'and shape tetrahedron.
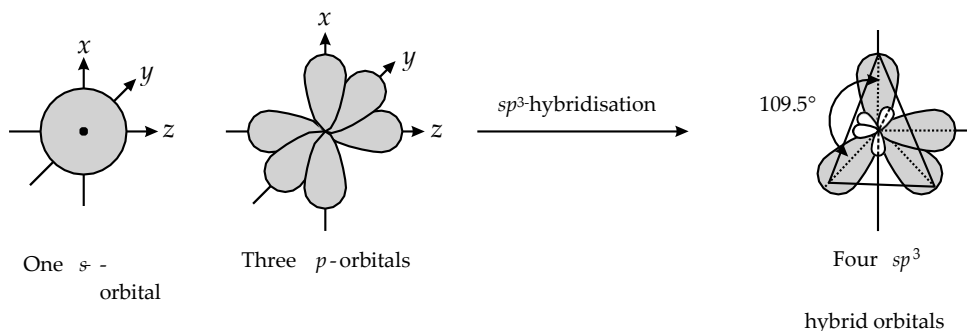
Fig. 4.3 : Formation of *sp*³ hybrid orbitals

Example: CH_4, CCl_4, etc.

- **sp³d Hybridisation:** This hybridisation involves the mixing of one *s*, three *p* and one *d*-orbitals. These five orbitals hybridise to form five *sp*³*d*-hybrid orbitals. These hybrid orbitals point towards the corners of a trigonal bipyramidal geometry.
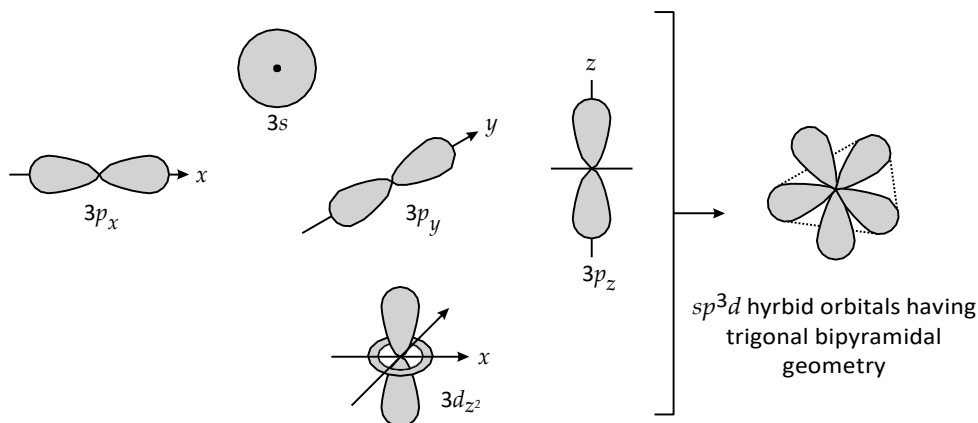
Fig. 4.4 : Formation of sp^3d hybrid orbitals

Example : Phosphorus pentachloride, PCl_5.

- **sp^3d^2 Hybridisation:** A combination of one s, three p and two d atomic orbitals ($d_{x^2-y^2}$, d_{z^2}) leads to six sp^3d^2 hybrid orbitals which are directed octahedrally with bond angle of 90°.

  Example: SF_6
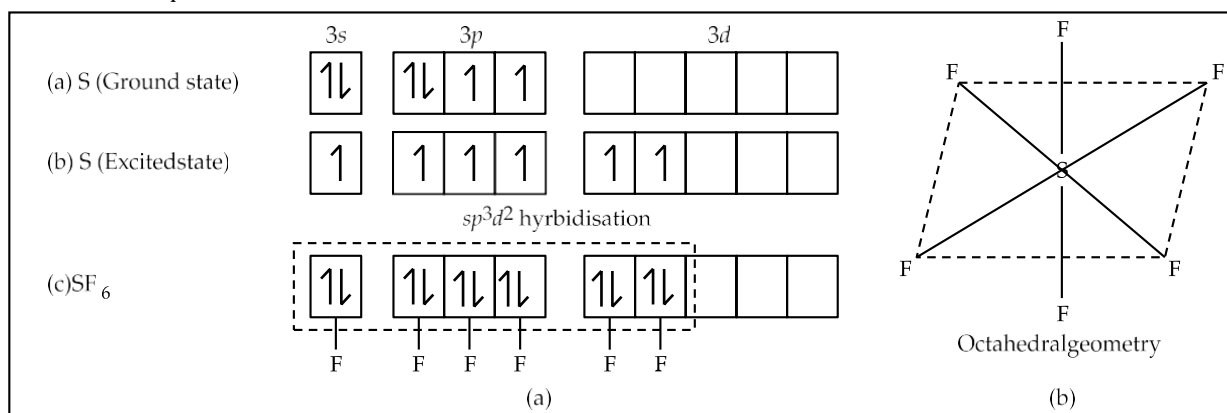
(a) Formation of SF_6 molecule involving sp^3d^2-hybridisation (b) Octahedral geometry of SF_6 molecule

- **sp^3d^3 Hybridisation:** This involves the mixing of one s, three p and three d-orbitals forming seven sp^3d^3-hybrid orbitals having pentagonal bipyramidal geometry. The geometry of IF_7 molecule can be explained on the basis of sp^3d^3 hybridisation.

  Example: IF_7
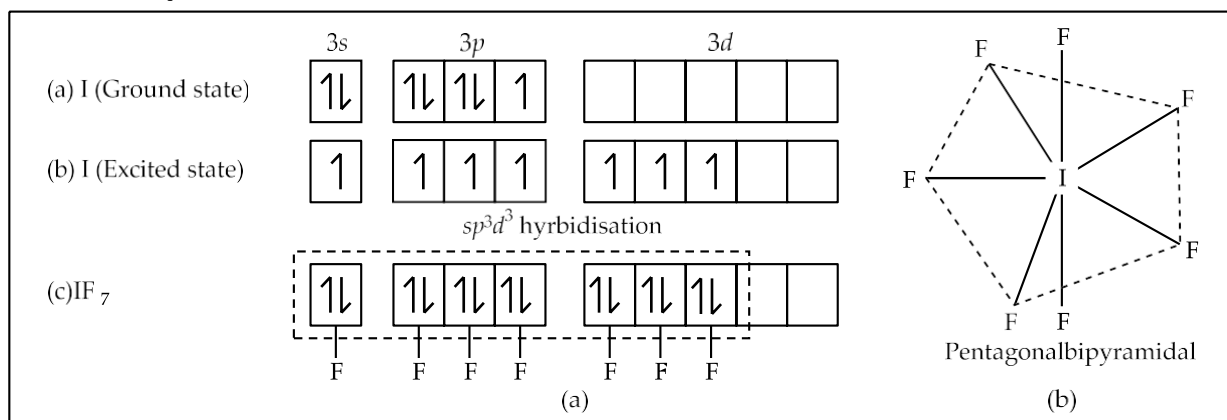
(a) Formation of IF_7 molecule involving sp^3d^3-hybridisation (b) Pentagonal bipyramidal geometry of IF_7 molecule

☛ **Molecular Orbital Theory:**

Molecular orbital theory was proposed by F. Hund and R.S. Mulliken in 1932.

Salient Features of Molecular Orbital Theory:

- Just like an atom, molecule has orbitals of definite energy levels. Like electrons of atoms are present in atomic orbitals, electrons of a molecule are present in different molecular orbitals.

- Molecular orbitals are formed by the combination of atomic orbitals of proper symmetry and comparable energies. The atomic orbitals of these atoms merge into molecular orbitals.
- An electron in an atomic orbital is under the influence of only one nucleus. However, an electron in a molecular orbital is under the influence of two or more nuclei depending upon the number of atoms present in the molecule.
- The number of molecular orbitals formed is equal to the number of combining atomic orbitals. When two atomic orbitals combine, they form two molecular orbitals. These are called bonding molecular orbital and antibonding molecular orbital.
- The bonding molecular orbital has lower energy and hence greater stability whereas corresponding antibonding molecular orbital has more energy and hence lesser stability.
- The molecular orbital formed by the addition of two atomic orbitals is called bonding molecular orbital.
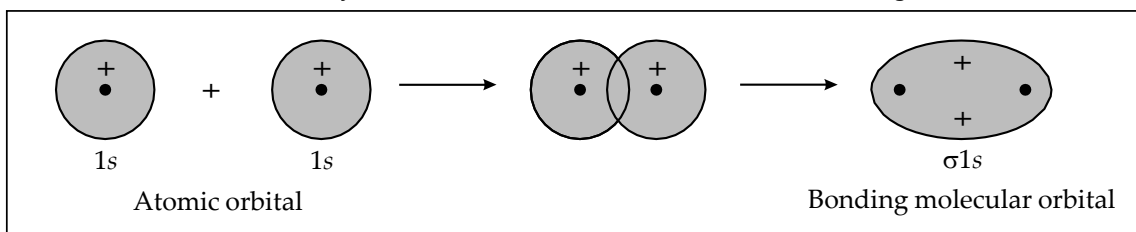
Fig. 4.5 : Formation of bonding molecular orbital

- The molecular orbital formed by the subtraction of two atomic orbitals is called antibonding molecular orbital.
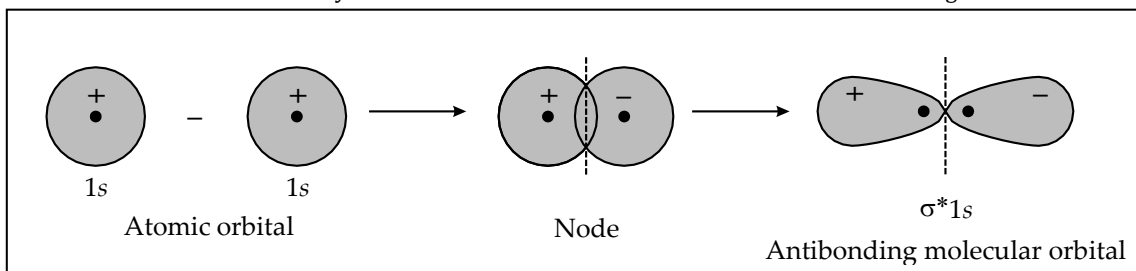
Fig. 4.6 : Formation of antibonding molecular orbital

It is clear from the figure that the electron density in between the two nuclei is practically zero and is concentrated in regions away from each nucleus. In this case, the electron probability densities of two atomic orbitals get cancelled in the centre (by subtraction) so that there is no probability of finding the electron in the region of overlap, i.e. between the nuclei. This situation does not favour the bond formation. Such an orbital is called antibonding molecular orbital. It is designated as s*1s (called sigma star 1s). The asterisk '*' is used to represent antibonding molecular orbital.

➤ **Conditions for the Combination of Atomic Orbitals:**
- The combining atomic orbitals must have same or nearly the same energies.
- The extent of overlapping between the atomic orbitals of two atoms should be maximum.
- The combining atomic orbitals must have the same symmetry about the molecular axis.

➤ **Types of Molecular Orbitals:**
- **Bonding molecular orbitals:** A molecular orbital that is obtained by the addition overlap The energy of bonding molecular orbital is less than that of the constituent overlapping atomic orbitals.

- **Non-bonding molecular orbitals:** They do not play any part in the formation of molecule. When atomic orbitals do not interact with each other, formation of non-bonding molecular orbitals takes place. The reasons for no interaction may be one of the following:
  (i) One orbital is far away from other orbital, so overlapping is not possible.
  (ii) Symmetries of atomic orbitals are not same.
  (iii) Energies of atomic orbitals are not same.
- **Antibonding molecular orbitals**: A molecular orbital that is obtained by the subtraction overlap (i.e., when the lobes of atomic orbitals overlap with the opposite sign) of two atomic orbitals is known as antibonding molecular orbital.

  For molecules O_2 onwards, the increasing order of energies for molecular orbitals in which they are filled is as follows :
 $\sigma 1s < \sigma^* 1s < \sigma 2s < \sigma^* 2s < \sigma 2p_z < (p2p_z = p2p_y) < (p^*2p_z = p^*2p_y) < \sigma^*2p_z$
➤ However, for homonuclear diatomic molecules of second row elements such as, Li_2, Be_2, B_2, C_2, N_2, the $s2p_z$ MO is higher in energy than $p2p_x$ and $p2p_y$ MOs.

The increasing order of energies order for MOs for their molecules is

$\sigma 1s < \sigma^*1s < \sigma 2s < \sigma^*2s < (p2p_x = p2p_y) < \sigma 2p_z < (p^*2p_x = p^*2p_y) < \sigma^*2p_z$

➤ Presence of unpaired electron shows that molecule is paramagnetic, however, paired electrons show that it is diamagnetic.

➤ **Hydrogen Bonding:** When hydrogen atom is bonded to atoms of highly electronegative elements such as fluorine, oxygen or nitrogen, the hydrogen atom forms a weak bond with the electronegative atom of the other molecule. This weak bond is called hydrogen bond. For example, in hydrogen fluoride, HF, hydrogen atom forms a weak bond with fluorine atom of the high bonding molecule while remaining bonded to its fluorine atom. This may be shown as :

........H^{d+} — F^{d-} .... H^{d+} — F^{d-}·········H^{d+}— F^{d-}
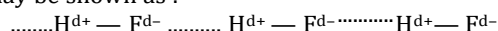
The hydrogen bond is represented by dotted line ($\_\_\_\_\_$) while the covalent bond is represented by solid line (––).

➤ **Types of Hydrogen Bond:** Hydrogen bonds can be classified into two types:

(a) Intermolecular hydrogen bond

(b) Intramolecular hydrogen bond

(a) Intermolecular hydrogen bond: Intermolecular hydrogen bond is formed between different molecules of the same or different substances.

For example,

(i) hydrogen bond between the molecules of hydrogen fluoride.

(ii) hydrogen bond in alcohol or water molecules.

(b) Intramolecular hydrogen bond: Intramolecular hydrogen bond is formed when the hydrogen atom is between the two highly electronegative atom (F, O or N) present within the same molecule.

For example,

Ortho-nitrophenol   *Ortho*-nitrobenzoic acid
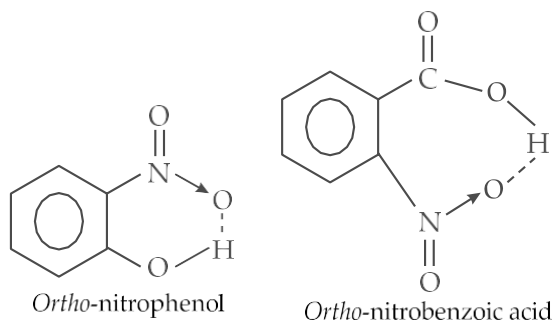
➤ **Applications of Intermolecular H-bonding:**

● **Very high Melting point and boiling point of water:** Water has the lowest molecular weight among the hydrides of group 16 elements yet it has the highest melting and boiling points. It is due to intermolecular H–bonding in H_2O.

● **Ice has less density than water:** In crystal structure of ice, every water molecule is associated with four other water molecules by H-bonding in a cage like tetrahedral structure. On melting, H-bonds in the ice are broken and space between water molecules decreases and density of water increases up to 4°C. Above 4°C, more H-bond are broken. The water molecules get apart from each other and the density again decreases. Thus, water has maximum density at 4°C.

➤ **Applications of Intramolecular H-Bonding:**

● **Volatile character of nitrophenols:** *ortho*-nitrophenol is more volatile (b.p. 214°C) as compared to *meta* (b.p. 290°C) and *para* (b.p. 279°C). It is due to chelation.
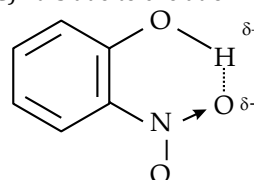
● In *meta* and *para* isomer, chelation is not possible due to the formation of desired size of ring.

Key Terms

➤ **Bond Order:** It is defined as one half the difference between the number of electrons present in the bonding and the anti bonding orbitals. [Bond order = $\frac{1}{2}$ ($N_b - N_a$)]

Key Facts

➤ A positive bond order (i.e., $N_b > N_a$) means a stable molecule while a negative (i.e., $N_b < N_a$) or zero (i.e., $N_b = N_a$) bond order means an unstable molecule.

where, N_b = No. of electrons in bonding molecular orbital.

N_a = No of electrons in anti-bonding molecular orbital.

Mnemonics

1. Concept: Formal Charge

Mnemonics: For Very Lovely Son!

Interpretation: [Formal Charge (F.C) = Valence e– in free state (V.E)

– Lone pair (l.p) –1/2 × Shared e–(S.E)]

2. Concept: Hydrogen

Mnemonics: H-bonding is FON (Fun)!

Interpretation: Fluorine, Oxygen, Nitrogen

Chapter 5

CHEMICAL THERMODYNAMICS

Topic-1	Types of System, Heat, Work, Energy and Enthalpy

📝 Revision Notes

- **Thermodynamics** is the branch of science that deals with quantitative aspects of interconversion of various forms of energy and the conversion of energy into work and vice versa.
- **System:** Part of universe selected for observations.
- **Surrounding:** Part of universe other than the system.
- **Boundary:** The wall that separates the system from the surroundings.
- **System can be classified as:**
  Open system can exchange matter and energy both with its surroundings.
  Closed system can exchange only energy with its surroundings but not the matter.
  Isolated system can neither exchange matter nor energy with surroundings.
- **State of system:** The conditions of existence of a system when its macroscopic properties have a definite value.
- Properties of a system can be classified into state and path function.
- **State Functions:** The thermodynamic quantities which depend only on initial and final state of the system. e.g., pressure, volume and temperature are the variables which are used to describe the state of the system.
  Path function: Thermodynamic properties which depends upon the path taken by the system during a change in state, e.g., heat and work.

⚙️ Mnemonics

Concept: State Function
Mnemonics: PVT HUGS
Interpretation: Pressure, Volume, Temp, Enthalpy (H), Internal Energy (U), Gibbs free energy (G) Entropy (S)

- **Isothermal process** is the one which is carried out at a constant temperature.
- **Isobaric process** is the one which is carried out at a constant pressure.
- **Isochoric process** is the one during which the volume remains constant.

- **Adiabatic process** is the one during which no heat is gained or lost by the system to the surroundings.
- A **reversible process** is a process in which the direction of process may be reversed at any stage by a small change in a variable like temperature, pressure, etc. It occurs infinitesimally slowly. All real processes are irreversible in nature.
- A cyclic process is the one that after undergoing a change in state returns back to its initial state.
- An **extensive property** is a property whose value depends on the quantity or size of matter present in the system, e.g., mass, volume, internal energy, enthalpy, heat capacity, etc.
- An **intensive property** is a property which is independent of the mass or quantity or size of matter present in the system e.g., temperature, density, pressure, etc.
- Heat and work are the two common forms of energy which are exchanged between a system and surroundings. Both are path functions and appear only during a change in state.
- **Heat (q):** It is an exchange of energy which results in a temperature difference.
- **Work (w):** It is an organised form of energy.
- Heat is positive if it is gained by the system (i.e., heat is transferred from the surroundings to the system) and heat is negative if it is lost by the system (i.e., heat is transferred from system to the surroundings.)
- Work is positive when it is done on the system and negative when done by the system.
- **Internal energy (U):** It is a type of energy associated with the system at particular condition of temperature and pressure.

  Or

  Internal energy is the quantity that represents all the form of the energy of the system, i.e., kinetic and potential energies of the system.
- **Internal energy change (DU):** It is a measure of heat change occur during the process at constant temperature and constant volume.

$$\mathrm{D}U = U_2 - U_1 = q_v$$

- **Enthalpy (H):** It is the sum of internal energy and pV energy of the system at particular conditions of temperature and pressure. It is also called heat content of the system.

$$H = U + pV.$$

- **Enthalpy change (DH):** It is the measure of heat change taking place during the process at constant temperature and constant pressure.

$$\mathrm{D}H = q_p$$

DH is negative for exothermic reactions and is positive for endothermic reactions.

- **Law of conservation of energy:** It is also called **first law of thermodynamics** and states that energy of universe always remains constant during physical or chemical changes.

Or

Energy can neither be created nor be destroyed. Mathematically, it can be written as:

$$\mathrm{D}U = q + W$$

- **Relation between DH and DU:**

$$\mathrm{D}H = \mathrm{D}U + p\mathrm{D}V$$

$$\mathrm{D}H = \mathrm{D}U + \mathrm{D}n_g RT$$

- The magnitude of temperature change during heat transfer depends upon the heat capacity of the system according to the relation.

$$q = m \times c \times \mathrm{D}t$$

- Specific heat or specific heat capacity is the quantity of heat required to raise the temperature of one unit mass of a substance by one degree celsius (or one kelvin).

- **Limitations of First Law of Thermodynamics :**
  - This law fails to explain the extent and direction of the convertibility of one form of energy into another.
  - This law fails to explain that how much energy would be transferred from one system to another.

- Work done $W = F \times dx$
  where F = force
  dx = distance

| Work done on the system = Positive |

- Work done by the system is considered as negative.

| Work done by the system = Negative |

- If a system loses energy, work is done by the system.
- If a system gains energy, work is done on the system.
- **Thermodynamic Processes:**
  - Isothermal process: $\mathrm{D}T = 0$
  - Adiabatic process: $\mathrm{D}q = 0$
  - Isobaric process: $\mathrm{D}p = 0$
  - Isochoric process: $\mathrm{D}V = 0$
  - Cyclic process : $\mathrm{D}U = 0$
- Sign Conventions for Heat (Q)
  q = +ve, if heat is absorbed by the system
  q = –ve, if heat is evolved by the system
- Work of expansion/compression: $W = -p_{ext}(V_f - V_i)$
  where, p_{ext} = External pressure
  V_i = Initial volume
  V_f = Final volume
- Work done in isothermal reversible expansion of an ideal gas:

$$W_{rev} = -2.303\, nRT \log \frac{V_f}{V_i}$$

Or,

$$W_{rev} = -2.303\, nRT \log \frac{p_i}{p_f}$$

- Significance of DH and DU: DH = q_p and DU = q_v
- **Relation between DH and DU:**
  For gaseous reaction, DH = DU + $(n_p - n_r)$RT
  - If $(n_p - n_r) = 0$, then DH = DU
    e.g., $H_2(g) + I_2(g) \longrightarrow 2HI(g)$

- If $(n_p - n_r)$ = positive, then DH > DU
  e.g., $PCl_5(g)$ —® $PCl_3(g) + Cl_2(g)$
- If $(n_p - n_r)$ = negative, then DH < DU
  e.g., $N_2(g) + 3H_2(g)$ —® $2NH_3(g)$

▶ $q = C.\Delta T$

where   C = Heat capacity

     ΔT = Change in temperature

     q = Amount of heat

Or

     $q = C_s \times m \times \Delta T$

where C_s = Specific heat capacity

     m = Mass of substance

Or

     $q = C_m \times n \times \Delta T$

where C_m = Molar heat capacity

     n = No. of moles of a substance

▶ According to first law of thermodynamics,

     $\Delta U = q + W$

where $\Delta U = (U_2 - U_1)$ = DE (change in internal energy)

     q = Heat

     W = Work done on the system

▶ When a system undergoes isothermal change,

$\Delta U = 0$

i.e., there is no increase or decrease in the internal energy of the system ($\Delta U = 0$) then first law reduces to

     $0 = q + W$

Or, $q = -W$

▶ When a system undergoes adiabatic change $q = 0$, i.e., there is no exchange of heat between system and surrounding, the first law reduces to :

     $\Delta U = W_{ad}$

$\backslash$ The work is done at the expense of internal energy.

▶ 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.

▶ $C_p - C_n = R$

Topic-2   Enthalpy Change

▤ Revision Notes

- **Enthalpy of Reaction (D$_r$H)—**The enthalpy change accompanying the chemical reaction in which number of moles of reactants consumed and those of products formed are the same as the stoichiometric coefficients.

- **Enthalpy of Neutralisation (D$_n$H):** It is the enthalpy change taking place during neutralisation of 1 g equivalent of acid with 1 g equivalent of a base in dilute aqueous solution.

- **Standard Enthalpy of Fusion (D$_{fusion}$H^Q):** It is the enthalpy change taking place during the fusion of one mole solid at its melting point.

- **Standard Enthalpy of Vaporisation (D$_{vap}$H^Q):** It is the enthalpy change taking place during the vaporisation of 1 mole of liquid at its boiling point and under standard pressure (1 bar).

- **Standard Enthalpy of Sublimation, (D$_{sub}$H^Q):** It is the change in the enthalpy when one mole of a solid substance sublimes at a constant temperature and under standard pressure (1 bar).

- **Standard Enthalpy of Formation (D$_f$H^Q):** It is enthalpy change accompanying the formation of 1 mole of the substance from its constituent elements in their standard state.

D$_f$H° can be > 0 or < 0.

- **Factors affecting Enthalpy of Phase Transformation:** The enthalpy change depends upon the strength of intermolecular forces working on the substances that undergo phase transformation.

- **Hess's law of constant heat summation:** The enthalpy change in a chemical or physical process is same whether the process is carried out in one step or in several steps or if a reaction takes place in several steps then its standard reaction enthalpy is the sum of the standard enthalpies of the intermediate reactions into which the overall reaction may be divided at the same temperature.

- **Applications of Hess's Law:**

  - to determine enthalpies of formation of compounds.
  - to determine enthalpies of extremely slow reactions.
  - to determine enthalpies of transformation of one allotropic form into another.
  - to determine bond energies (D H$_{reaction}$ = S bond energies of reactants – S bond energies of products)
  - to determine resonance energy.

- **Standard Enthalpy of Combustion ($D_cH°$):** It is the enthalpy change occurring during the combustion of one mole of the substances in excess of oxygen. $D_cH°$ is always less than zero.
- **Enthalpy of Atomisation ($D_aH°$):** It is the enthalpy change accompanying the dissociation of 1 mole of substance into gaseous atoms.
- **Bond Enthalpy ($D_{bond}H°$):** The average amount of energy required to break one mole of the bond of a particular type in gaseous molecules.
- **Enthalpy of Solution ($D_{sol}H°$):** It is the enthalpy change taking place when 1 mole of the solute is dissolved in specified amount of solvent. The enthalpy of solution at infinite dilution is the enthalpy change observed on dissolving the substance in an infinite amount of solvent when the interactions between the ions (or solute molecules) are negligible.
- **Enthalpy of Hydration ($D_{hyd}H°$):** It is the enthalpy change occurring during the hydration of 1 mole of anhydrous salt by combining with specific number of moles of water.
- **Lattice Enthalpy ($D_{lattice}H°$):** Lattice Enthalpy of an ionic compound is the enthalpy change which occurs when one mole of an ionic compound dissociates into its ions in gaseous state.
- Enthalpy of reaction $D_rH = \sum_i a_i H_{products} - \sum_i b_i H_{reactants}$

  where $\sum_i a_i H_{products}$ = sum of enthalpies of products,

  $\sum_i b_i H_{reactants}$ = sum of enthalpies of reactants
- **Standard enthalpy of reaction ($D_rH°$):** It is the enthalpy change for a reaction when all the participating substances are in their standard states.

Topic-3 Spontaneity

💬 Revision Notes

- **Spontaneous process:** A process which has an urge or a natural tendency to occur in a particular direction either of its own or after proper initiation under a given set of conditions.
- **Entropy** is a thermodynamic property which is a measure of disorder or randomness in an isolated system. It is related to heat absorbed at a constant temperature by the system in a reversible process as:

  $$DS = \frac{q_{rev}}{T}$$

  For a spontaneous change, total entropy change is positive.
- **Second law of Thermodynamics:** The entropy of universe always tends to increase during any spontaneous process.
- A system at higher temperature has greater randomness in it than one at lower temperature.
- $DS_{total} = DS_{system} + DS_{surr} > 0$
- When a system is in equilibrium, the entropy is maximum and the change in entropy, $DS = 0$
- The entropy for a spontaneous process increases till it reaches maximum and at equilibrium the change in entropy is zero. Since, entropy is a state property, we can calculate the change in entropy of a reversible process by :

  $$DS_{sys} = \frac{q_{sys.rev}}{T}$$
- For reversible and irreversible expansion for an ideal gas, under isothermal conditions, $DU = 0$, but DS_{total}, i.e., $DS_{sys} + \Delta S_{surr}$ is not zero for irreversible process. Hence, DU does not discriminate between reversible and irreversible process, whereas DS does.
- **Third law of Thermodynamics:** At absolute zero, the entropy of any perfectly crystalline substance approaches zero.
- **Gibbs Energy (Extensive property)**: It is the maximum amount of energy available to a system, during a process, that can be converted into useful work. It is also called free energy or Gibbs free energy. It is related to changes in enthalpy and entropy of the system during a process as:

  $$DG = DH - TDS$$

  (Gibbs Helmholtz equation)

For a spontaneous change, $DG_{sys} < 0$, for a non-spontaneous change, $DG_{sys} > 0$, and $DG_{sys} = 0$ shows equilibrium.

► If the system is in thermal equilibrium with the surrounding, then the temperature of the surrounding is same as that of the system. Increase in enthalpy of the surrounding is equal to decrease in the enthalpy of the system.

► For spontaneous process $DS_{total} > U$.

► DG (Change in free energy) gives a criteria for spontaneity at constant pressure and temperature.

  (i) If DG is negative (< 0), the process is spontaneous.

  (ii) If DG is positive (> 0), the process is non-spontaneous.

► $D_rG^Q = -RT \ln K = -2.303\, RT \log K$

  where R = Gas constant

          T = Temperature (in Kelvin)

          K = Equilibrium constant

⊙━ᴴᴾ Key Formulae

- $DU = q + W$
- $DH = DU + pDV$
- $DH° = SD_fH°$ (Products) $- SD_fH°$ (Reactants)
- $DH° =$ [Sum of bond energies of reactants] $-$ [Sum of bond energies of products]
- $DS = \dfrac{q_{(rev)}}{T}$
- For process to be spontaneous

  $DS_{system} + DS_{surr} > 0$

- $DG = DH - TDS$
- $DG_{sys} = -TDS_{Total}$

⊙━ᴴᴾ Key Formulae

- $D_rG° = SD_fG°$ (Products) $- S_fG°$ (Reactants)
- $DG_{T,\,P} < 0$ refers to spontaneous process.

⊙━ᴴᴾ Key Terms

► **Phase Transition:** The change of matter from one state to another is known as phase transition.

► **Standard Free Energy Change:** It is defined as the free energy change for a process at 298K and 1 atm pressure in which the reactants in their standard state are converted into products in their standard state. It is denoted by DG°.

⊛ Mnemonics

Concept: Enthalpy of Atomisation

Mnemonics: Be mMy Guest Please

Interpretation: B(a bond) M(1) GP>

Concept: Criteria of Spontaneity

Mnemonics: Good Physicists Have Studied Under Very Ambitious Teachers

Interpretation:

(dH)S,P<0

(dU)S,V<0

(dG)P,T<0

(dA)V,T<0

(dS)H,P>0

(dS)U,V>0

6. Concept: Gibb's Free Energy

Mnemonics: Get High Test Scores

DG = DH – TDS

❑❑❑

Chapter 6

EQUILIBRIUM

Topic-1	Physical and Chemical Equilibrium

🗨 Revision Notes

► **Equilibrium State:** A state of the system when its observable properties do not change at a given set of conditions. At equilibrium, the forward and backward reactions proceed at same rate.

- The state of equilibrium in which the rate of a forward reaction and rate of backward reaction are equal and there is no net change in composition is known as dynamic equilibrium.
- Equilibrium reached in physical processes is termed as **physical equilibrium**. It may involve an equilibrium between different phases like solid-liquid, liquid-vapour and solid-vapour phases or a dissolution equilibrium of a solid or gaseous solute in a liquid solvent.
- Equilibrium reached in chemical processes is termed as **chemical equilibrium.**
- **Henry's Law:** It states that the mass of a gas dissolved in a given mass of a solvent at any temperature is proportional to the pressure of the gas above the solvent.

$$m \propto P$$

- **Law of Mass Action:** A theoretical concept which states that at constant temperature rate of reaction is directly proportional to the product of molar concentrations of reactants raised to the power equal to stoichiometric coefficient of that species in the balanced chemical equation.
- **Rate constant:** It is the rate of reaction, when concentration of each reacting species is unity.
- The state of chemical equilibrium is characterised by its equilibrium constant K_c or K_p.
- K_c, concentration equilibrium constant is calculated by using equilibrium concentrations of all the reactants and products.
- K_p, pressure equilibrium constant is calculated by using the equilibrium partial pressures of gaseous reactants and products.
- **Equilibrium constant:** It is the ratio of product of
- Some Features of Physical Equilibria:

the equilibrium concentrations of the products to that of the reactants with each concentration term raised to the power equal to the stoichiometric coefficient of the substance in the balanced chemical equation.
- **Law of Chemical Equilibrium:** At a given temperature, the product of concentrations of the reaction products raised to the respective stoichiometric coefficient in the balanced chemical equation divided by the product of concentrations of the reactants raised to their individual stoichiometric coefficients has a constant value.

For an equilibrium,

$$aA + bB \rightleftharpoons cC + dD$$
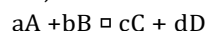
Equilibrium constant (K_c) is expressed as:

$$K_c = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

where   [A] and [B] = Equilibrium concentrations of the reactants

[C] and [D] = Equilibrium concentrations of the products

- For solid $\rightleftharpoons$ liquid equilibrium, there is only one temperature (melting point) at 1 atm (1.013 bar) at which the two phases can coexist. If there is no exchange of heat with the surroundings, the mass of the two phases remains constant.
- For liquid $\rightleftharpoons$ vapour equilibrium, the vapour pressure is constant at a given temperature.
- For dissolution of solids in liquids, the solubility is constant at a given temperature.
- For dissolution of gases in liquids, the concentration of a gas in liquid is proportional to the pressure (concentration) of the gas over the liquid.

Process	Conclusion
● Liquid $\rightleftharpoons$ Vapour $H_2O(l) \rightleftharpoons H_2O(g)$	p_{H_2O} constant at given temperature.
● Solid $\rightleftharpoons$ Liquid $H_2O(s) \rightleftharpoons H_2O(l)$	Melting point is fixed at constant pressure
● Solute(s) $\rightleftharpoons$ Solute (solution) Sugar(s) $\rightleftharpoons$ Sugar (solution)	Concentration of solute in solution is constant at a given temperature
● Gas(g) $\rightleftharpoons$ Gas(aq) $CO_2(g) \rightleftharpoons CO_2(aq)$	[gas(aq)]/[gas(g)] is constant at a given temperature

- **Equilibrium Constant in Gaseous Systems:**

Consider a general reaction,

$$aA + bB \rightleftharpoons cC + dD$$

$$K_p = \frac{[P_C]^c [P_D]^d}{[P_A]^a [P_B]^b}$$

$$= \frac{[C]^c [D]^d (RT)^{(c+d)}}{[A]^a [B]^b (RT)^{(a+b)}}$$

$$= \frac{[C]^c [D]^d}{[A]^a [B]^b} (RT)^{(c+d)-(a+b)}$$

$$= \frac{[C]^c [D]^d}{[A]^a [B]^b} (RT)^{\Delta n_g}$$

where $\quad K_p = K_c (RT)^{\Delta n}$

R = Gas constant

T = Absolute temperature

Δn_g = (Number of moles of gaseous products – Number of moles of gaseous reactants) in balanced chemical equation.

$= (c + d) - (a + b)$

➤ **Homogeneous Equilibria:** In a homogeneous system, all the reactants and products are in the same phase.

For example, in the gaseous reaction below, reactants and products are in homogeneous phase.

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$
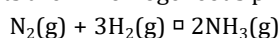
➤ **Heterogeneous Equilibria:** Equilibrium in a system having more than one phase is called heterogeneous equilibrium. For example, equilibrium between water vapour and liquid water in a closed container.

$$H_2O(l) \rightleftharpoons H_2O(g)$$
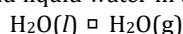
Mnemonics

Concept: Homogeneous Equilibria
Mnemonics: RPSP
Interpretation: Reactant and Product in Same Phase
Concept: Hetrogeneous Equilibria
Mnemonics: RPDP
Interpretation: Reactant and Product in Different Phase

➤ **Applications of Equilibrium Constant:**
- To predict the extent of a reaction on the basis of its magnitude.
- To predict the direction of the reaction.
- To calculate equilibrium concentrations.

➤ **Predicting the Extent of a Reaction:** The magnitude of K_c or K_p is directly proportional to the concentrations of products (as these appear in the numerator of equilibrium constant expression) and inversely proportional to the concentrations of the reactants (these appear in the denominator).

➤ **Reaction Quotient (Q):** The ratio of the product of molar concentrations of the products to the product of molar concentrations of reactants with each concentration terms raised to the power equal to the stoichiometric coefficient of that species is called reaction quotient.
- At equilibrium, Q = K.
- At concentration other than equilibrium $Q \neq K$.
- If $Q_c > K_c$, the reaction, will proceed in the direction of reactants (backward reaction).
- If $Q_c < K_c$, the reaction will proceed in the direction of the products (forward reaction).
- If $Q_c = K_c$, the reaction mixture is already at equilibrium.

➤ $K = e^{-\Delta G°/RT}$

From this equation, we can predict the spontaneity of the reaction.

- If $\Delta G° < 0$, then $-\Delta G°/RT$ is positive and $e^{-\Delta G°/RT} > 1$,

  $\therefore$ K > 1, the reaction is spontaneous.
- If $\Delta G° > 0$, then $-\Delta G°/RT$ is negative and $e^{-\Delta G°/RT} < 1$,

  $\therefore$ K < 1, the reaction is non-spontaneous.

➤ $\Delta G = \Delta G° + RT \ln Q$

At equilibrium, $\Delta G° = - RT \ln K = - 2.303 RT \log K$.

➤ **Le Chatelier's Principle:** It states that a change in any of the factors that determine the equilibrium conditions of a system will cause the system to change in such a manner so as to reduce or to counteract the effect of the change.

➤ Factors Affecting Equilibria:

(i) Effect of Concentration Change: When the concentration of any of the reactants or products in a reaction at equilibrium is changed, the composition of the equilibrium mixture changes so as to minimize the effect of concentration changes.

(ii) Effect of Pressure Change: On increasing the pressure, the reaction occurs in that direction in which number of moles of the gas or pressure decreases or the direction in which Δn_g is negative and vice-versa. If the reaction involves solids and/or liquids, i.e., $\Delta n_g = 0$, then there is no effect of pressure change on the system.

(iii) Effect of Temperature Change: The equilibrium constant for an exothermic reaction decreases as the temperature increases. The equilibrium constant for an endothermic reaction increases as the temperature increases.

(iv) Effect of Inert Gas Addition: Addition of inert gas at constant volume does not affect the equilibrium.

(v) Effect of Catalyst: Addition of catalyst does not alter the equilibrium, it just help in attaining the equilibrium faster.

Mnemonics

Concept: Effect of Concentration Change
Mnemonics: Class Rooms gives Ideal Final Result
Interpretation: Concentration of Reactant Increases Forward Reactiona (CRIFR)
Concept: Effect of Pressure Change
Mnemonics: Nuclear Power Plant is Issue For Review
Interpretation: if, Δn_g Pressure Increases Forward Reaction (NPPIFR)
Concept: Effect of Temperature Change
Mnemonics: TIP for Final Exam
Interpretation: Temperature Increases Product Formation for
Exothermic TIPFE

► **Relation between Equilibrium Constants for a General Reaction and its Multiples:**

Chemical Equation	Equilibrium Constant
● $aA + bB \rightleftharpoons cC + dD$	K
● $cC + dD \rightleftharpoons aA + bB$	$K_c' = (1/K_c)$
● $naA + nbB \rightleftharpoons ncC + ndD$	$K_c'' = (K_c^n)$
● $1/n\, aA + 1/n\, bB \rightleftharpoons 1/n\, cC + 1/n\, dD$	$K_c''', = (K_c^{1/n})$

► 1 pascal (Pa) = 1 Nm^{-2}
1 bar = 10^5 Pa

► The free energy change at equilibrium state is zero, i.e., DG = 0

► The value of the equilibrium constant changes with change to temperature.

$$\log \frac{K_2}{K_1} = \frac{\Delta H}{2.303\,R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$$

Topic-2 Ionic Equilibrium: Acids, Bases and their Ionization

💬 Revision Notes

► Substances that conduct electricity in aqueous solutions are called electrolytes, e.g., acids, bases and salts are electrolytes and their solution conduct electricity due to the process of ions formed by dissociation of electrolytes in aqueous solution.

► Strong electrolytes completely dissociate in their solutions.

► Weak electrolytes dissociate partially and an equilibrium exists between the ions and the undissociated electrolyte.

► **Acid:** A substance which furnishes H^+ ions in aqueous solution (Arrehenius concept); proton donor (Bronsted concept) and acceptor of electron pair (Lewis concept). Acids turn blue litmus paper into red. Acids liberate dihydrogen on reacting with some metals.

► **Base:** A substance which gives OH^- ions in aqueous solution (Arrehenius concept); acceptor of proton (Bronsted concept) and donor of electron pair (Lewis concept). Bases turn red litmus paper into blue. Bases taste bitter and feel soapy. A common example of a base is washing soda used for washing purposes.

► **Neutralisation:** A combination of $\overset{+}{H}$ and $\overset{-}{OH}$ ions in solution (Arrhenius concept); transference to proton (Bronsted concept); formation of dative bond (Lewis concept).

► The acid-base pair that differs only by one proton is called a conjugate acid-base pair. If Bronsted acid is a strong acid then its conjugate base is a weak base and vice-versa.

⚙ Mnemonics

1. Concept: Lewis concept
Mnemonics: LeeLAA
Interpretation: Lone pair Accepter is Acid
2. Concept: Lewis concept
Mnemonics: BaDaL
Interpretation: Base is Donor of Lone pair
3. Concept: Acids and Bases
Mnemonics: BAAD
Interpretation: Bases accept H^+, acids donate H^+
4. Concept: Bronsted Acid-Base Concept
Mnemonics: Strong Army, Lost to Carelessly Weak Bandits
Interpretation: Strong Acid gives Weak Conjugate Base

► Ionic product of water, K_w, is the product of the concentration of hydronium ions and hydroxyl ions in pure water at a particular temperature.

$$K_w = [H_3O^+][OH]^-$$
$$= 1 \times 10^{-14} \text{ mol}^2 \text{ L}^{-2} \text{ at } 298 \text{ K}$$

➤ Dissociation refers to the process of separation of ions in water already existing as such in the solid state of the solute, as in sodium chloride. While ionization corresponds to a process in which a neutral molecule splits into charged ions in the solution.

➤ A bare proton (H^+) is very reactive and can not exist freely in aqueous solutions. So, it bonds to the oxygen atom of a solvent water molecule to give hydronium ion (H_3O^+). It's geometry is trigonal bipyramidal.

➤ If Bronsted acid is a strong acid then its conjugate base in a weak base and vice-versa.

➤ **pH range:**

$1 \longleftarrow \qquad \longrightarrow 7 \longleftarrow \qquad \longrightarrow 14$

(Acidic solution) (pH<7) (Neutral solution) (pH = 7) (Basic solution) (pH>7)

➤ $pH = -\log_{10}[H^+]$

➤ $[H^+] = 10^{-pH}$

➤ $K_w = [H_3O^+][OH^-] = 10^{-14}$

where K_w = Ionic product of water

➤ $pK_w = pH + pOH = 14$

➤ Relative order of acidic strength among halogen acids:

$\xrightarrow{\text{Size increases}}$

$$HF << HCl << HBr << HI$$

$\xrightarrow{\hspace{4cm}}$
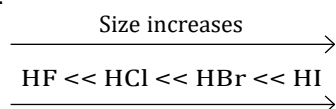
Acid strength increases

As the size of halogen (X) increases down the group, H – X bond strength decreases and therefore the acid strength increases.

➤ Relative order of acidic strength among CH_4, NH_3, H_2O and HF (HA) is:

electronegativity of 'A' increases

$\xrightarrow{\hspace{4cm}}$

$$CH_4 < NH_3 < H_2O < HF$$

$\xrightarrow{\hspace{4cm}}$
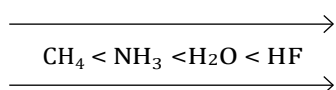
Acid strength increases

➤ **pH of solution:** Potency of H^+ in solution. It is negative logarithm of H_3O^+ ion concentration in solution. $pH = -\log[H_3O^+]$

➤ **pOH of solution:** It is negative logarithm of OH^- ion concentration of the solution.

➤ For any solution at 25°C.

$$pK_w = pH + pOH = 14$$
$$pH = -\log[H_3O^+]$$

$$pOH = -\log[OH^-]; pK_w = -\log K_w$$

➤ K_w ionic product of water $(H^+)(OH^-) = 1 \times 10^{-14}$ at 0°C.

➤ Strength of acids or bases is measured in terms of their respective dissociation constants K_a (or pK_a) and K_b or (pK_b).

➤ Larger the value of K_a or lower value of pK_a

➤ The density of pure water is 1000 g/L and its molar mass is 18.0 g/mol.

$$\text{Molarity of pure water} = \frac{\text{Density}}{\text{Molar Mass}}$$

$$= \frac{1000 \text{ g/L}}{18.0 \text{ g/mol}}$$

$$= 55.55 \text{ M}$$

➤ We can distinguish acidic, neutral and basic aqueous solutions by the relative values of the H_3O^+ and OH^- concentrations :

Acidic : $[H_3O^+] > [OH^-]$

Neutral : $[H_3O^+] = [OH^-]$

Basic : $[H_3O^+] < [OH^-]$

corresponds to greater acidic strength of acids. Similarly larger the value of K_b or lower value of pK_b corresponds to more stronger base.

➤ Dissociation constants of conjugate acid-base pair to each other as:

$$K_a \cdot K_b = K_w$$
$$pK_a + pK_b = pK_w = 14 \text{ (at 298 K)}$$

➤ For monobasic acid H_A, if C is the molar concentration of H_A and a is the degree of dissociation then

$$(H_3O^+) = Ca = \sqrt{K_a \times C}$$

➤ Similarly for monoacid base$[OH^-$

$$] = Ca = \sqrt{K_b \times C}$$

➤ Strength of an acid depends upon (i) strength of H—A bond: weaker the bond, stronger is the acid and (ii) polarity of H—A bond: greater the polarity, stronger is the acid.

➤ **Ostwald's dilution law:** Relationship between the dissociation constant and the degree of dissociation of a weak electrolyte (acid or base).

$K = a_2 C$

or $K = a_2/V$

where K = Dissociation constant

a = Degree of dissociation

C = Concentration of the solution

V = Volume of the solution

➤ Dissociation of weak acids and bases is suppressed in the presence of common ion furnished by their salts. This phenomenon is known as **common ion effect.**

➤ **Hydrolysis:** It is reverse of neutralization. It involves the interactions of ions of electrolyte with H_2O molecules in solution to give acidic or basic solution.

➤ Salts of strong acids and strong bases do not undergo hydrolysis and their aqueous solutions are neutral.

➤ Salts of strong acids with weak bases undergo cationic hydrolysis and give acidic solutions.

- Salts of strong bases with weak acids undergo anionic hydrolysis and give basic aqueous solutions.

Key Facts

- Hydrochloric acid present in the gastric juice is secreted by the lining of our stomach in a significant amount of 1.2 – 1.5 L/day and is essential for digestive process.
- Acetic acid is known to be the main constituent of vinegar.
- Lemon and orange juices contain citric acid and ascorbic acid.
- Tartaric acid is found in tamarind paste.
- As most of the acids taste sour, the term `acid' has been derived from a Latin word "*acidus*" meaning sour.

- When acids and bases are mixed in the right proportion, they react with each other to form salts.
- The electrostatic forces between two charges are inversely proportional to dielectric constant of the medium.
- Water acts as a **universal solvent**. It possesses a **very high dielectric constant** of 80.
- When sodium chloride is dissolved in water, the electrostatic interactions are reduced by a factor of 80 and this facilitates the ions to move freely in the solution.
- The extent to which ionization occurs, depends upon the strength of the bond and the extent of solvation of ions produced.
- Salt of weak acid and strong base: CH_3COONa
- Salt of strong acid and weak base: NH_4Cl
- Salt of weak acid and weak base: CH_3COONH_4

Topic-3 Buffer Solution and Solubility Product

Revision Notes

- Buffer solution is the solution which resists change in pH on dilution or with the addition of small amounts of acid or alkali.
- pH of buffer solution is given by Henderson-Hasselbalch equation:

$$pH = pK_a + \log \frac{[Salt]}{[Acid]} \quad \text{(for acidic buffers)}$$

$$pOH = pK_b + \log \frac{[Salt]}{[Base]} \quad \text{(for basic buffers)}$$

- $pH = pK_a$ when $[Salt] = [Acid]$
- $pOH = pK_b$ when $[Salt] = [Base]$
- During dissolving of the sparingly soluble salt in water to form a saturated solution, equilibrium is established between undissolved solid and the ions in a saturated solution.

$$AB \, (s) \rightleftharpoons A^{n+} \, (aq) + B^{n-} \, (aq)$$
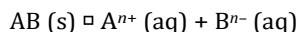
$$K_{sp} = [A^{n+}] [B^{n-}] = (S) (S) = S^2$$

- **Solubility Product (K_{sp})—**It is a product of the concentration of ions of electrolyte at the saturation point with each concentration term raised to the power equal to numerical coefficient of that species in the balanced equation. It is the highest value of ionic product for a sparingly soluble salt.
- The solubility of a sparingly soluble salt further decreases due to **Common Ion Effect**.
- Solubility of a salt of a weak acid increases as the pH of the solution decreases as the concentration of H_3O^+ ions increases.

- From the value of K_{sp} (solubility product) and Q (ionic product), we can predict whether the precipitation of salt or dissolution of salt will take place.
  - If $Q > K_{sp}$, then precipitation will take place.
  - If $Q < K_{sp}$, then dissolution will take place.
  - If $Q = K_{sp}$, then reaction is at equilibrium.

Key Terms

- **Polarity:** Polarity is a separation of electric charge leading to a molecule or its chemical groups having an electric dipole moment, with a negatively charged end and a positively charged end.

Key Facts

- Many body fluids, e.g., blood or urine have definite pH and any deviation in their pH indicates malfunctioning of the body.
- Buffer solutions of known pH can be prepared from the knowledge of pK_a of the acid or pK_b of the base and by controlling the ratio of the salt and acid or salt and base.
- For a salt to dissolve in a solvent, the strong forces of attraction between its ions (lattice enthalpy) must be overcome by the ion-solvent interactions.
- The amount of solvation enthalpy depends on the nature of solvent. If solvent is non-polar, the solvation enthalpy is small and therefore, not sufficient to overcome lattice enthalpy of the salt.

Chapter 7

REDOX REACTIONS

Topic-1	**Concept of Oxidation-Reduction, Redox Reactions and Oxidation Number**

Revision Notes

➤ **Oxidation:** It is defined as the addition of oxygen/electronegative element to a substance or removal of hydrogen/electropositive element from a substance.
eg., $CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(l)$
(Addition of oxygen)
$Mg(s) + F_2(g) \longrightarrow MgF_2(s)$
(Addition of electronegative element)
$2H_2S(g) + O_2(g) \longrightarrow 2S(s) + 2H_2O(l)$
(Removal of hydrogen)
$2K_4[Fe(CN)_6](aq) + H_2O_2(aq) \longrightarrow$
$2K_3[Fe(CN)_6](aq) + 2KOH(aq)$
(Removal of electropositive element)

➤ **Reduction:** It is defined as the removal of oxygen/electronegative element from a substance or addition of hydrogen/electropositive element to a substance.
e.g.,

$2HgO(s) \xrightarrow{\Delta} 2Hg(l) + O_2(g)$
(Removal of oxygen)

$2FeCl_3(aq) + H_2(g) \longrightarrow 2FeCl_2(aq) + 2HCl(aq)$
(Removal of electronegative element)

$CH_2 = CH_2(g) + H_2(g) \longrightarrow CH_3 - CH_3(g)$
(Addition of hydrogen)

$2HgCl_2(aq) + SnCl_2(aq) \longrightarrow Hg_2Cl_2(s) + SnCl_4(aq)$
(Addition of electropositive element)

➤ **Redox Reaction:** The reaction which involves oxidation and reduction reactions simultaneously is called redox reaction.
e.g., $2\,Na(s) + Cl_2(g) \longrightarrow 2NaCl(s)$

➤ **Redox Reaction in Terms of Electron Transfer Reaction:** Consider a redox reaction,

(Oxidation half reaction)

$2Na(s) \longrightarrow 2Na^+ + 2e^-$

$Cl_2(g) + 2e^- \longrightarrow 2Cl^-(g)$
(Reduction half reaction)

According to electronic concept, the half reaction that involves loss of electron is called oxidation half reaction and the half reaction that involves gain of electron is called reduction half reaction.

➤ **Oxidising Agent:** The species which can oxidise other substance and itself reduces is called oxidising agent. It is an acceptor of electrons.

➤ **Reducing Agent:** The species which can reduce other substance and itself oxidises is called reducing agent. It is a donor of electrons.

➤ **Oxidation Number:** Oxidation number denotes the oxidation state of an element in a compound ascertained according to a set of rules formulated on the basis that electron pair in a covalent bond belongs entirely to a more electronegative element.

➤ According to oxidation number concept,
  ● Oxidation is defined as an increase in the oxidation number of the element in the given substance.
  ● Reduction is defined as a decrease in the oxidation number of the element in the given substance.
  ● Oxidising agent is a reagent which can increase the oxidation number of an element in a given substance.
  ● Reducing agent is a reagent which can decrease the oxidation number of an element in a given substance.
  ● Redox reactions are those reactions which involve change in oxidation number of the interacting species.

➤ An element, in the free or the uncombined state, bears an oxidation number of zero.
e.g., Each atom in H_2, O_2, O_3, P_4, Na, Mg, etc., has the oxidation number zero.

➤ For ions composed of only one atom, the oxidation number is equal to the charge on the ion.

e.g.,

Ion	Oxidation Number
Na^+	+1
Mg^{2+}	+2
Fe^{3+}	+3
Cl^-	1
O^{2-}	2

- The oxidation number of oxygen in most compounds is –2.
- **Exception:**
  (i) In case of peroxides and superoxides, the oxidation numbers of oxygen are –1 and –1/2 respectively.

    e.g., Peroxides = H_2O_2, Na_2O_2

    (Oxidation number of O = –1)

    Superoxides = KO_2, RbO_2

    (Oxidation number of O = –1/2)

  (ii) When oxygen is bonded to fluorine, then in such compounds, e.g., oxygen difluoride (OF_2) and dioxygen difluoride (O_2F_2), the oxidation numbers of oxygen are +2 and +1 respectively.
- The oxidation number of hydrogen in most compounds is +1.
- **Exception:** When hydrogen is bonded to metals in binary compounds. e.g., LiH, NaH and CaH_2 , in such cases, the oxidation number of hydrogen is –1.
- The oxidation number of fluorine in all of its compounds is –1.

  Other halogens like Cl, Br and I also possess an oxidation number of –1, when they occur as halide ions in their compounds.

  However, when Cl, Br or I is combined with oxygen like oxoacids and oxoanions, then these halogens possess positive oxidation numbers.

  e.g., Cl_2O_7, in this compound, oxidation number of Cl is +7.
- The algebraic sum of the oxidation number of all the atoms in a compound must be zero.
- In polyatomic ion, the algebraic sum of all the oxidation numbers of atoms of the ion must equal the charge on the ion.

| Topic-2 | Types of Redox Reactions, Balancing of Redox Reactions and Electrode Processes |

💬 Revision Notes

- **Redox reactions are of various types:**

  1. Combination Reactions: The reactions which involve combination of two or more atoms or molecules to give only a single compound are called combination reactions.

    e.g.,

    $$\overset{0}{C}(s) + \overset{0}{O_2}(g) \xrightarrow{\Delta} \overset{+4\ -2}{CO_2}(g)$$
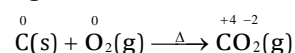
  2. Decomposition Reactions: The reactions which lead to the breakdown of a compound into two or more components at least one of which must be in the elemental state are called decomposition reactions.

    e.g.,

    $$2\overset{+1\ -1}{Na\,H}(s) \xrightarrow{\Delta} 2\overset{0}{Na}(s) + \overset{0}{H_2}(g)$$
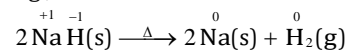
  3. Displacement Reactions: The reactions which involve replacement of an atom (or ion) by an atom (or ion) of another element from a compound are called displacement reactions. These reactions can be represented as:

    e.g.,
    X + YZ $\longrightarrow$ XZ + Y

    These reactions can further be classified into following categories:

(i) Metal Displacement Reactions: In these reactions, a metal in a compound can be displaced by another metal in the uncombined state.

e.g.,

$$\overset{+2\,+6\,+-2}{CuSO_4}(aq) + \overset{0}{Zn}(s) \longrightarrow \overset{0}{Cu}(s) + \overset{+2\,+6\,-2}{ZnSO_4}(aq)$$
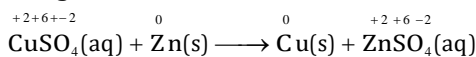
(ii) Non-metal Displacement Reactions: These reactions include hydrogen displacement and a rarely occurring reaction involving oxygen displacement.

e.g.,

$$2\overset{0}{Na}(s) + 2\overset{+1\,-2}{H_2O}(l) \longrightarrow 2\overset{+1\,-1}{NaOH}(aq) + \overset{0}{H_2}(g)$$

$$\overset{0}{Mg}(s) + 2\overset{+1\,-2}{H_2O}(l) \xrightarrow{\Delta} \overset{+2\,-1}{Mg(OH)_2}(s) + \overset{0}{H_2}(g)$$
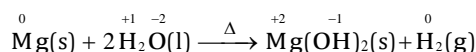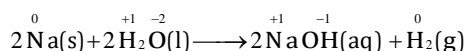
4. Disproportionation Reactions : These reactions are a special type of redox reactions. In these reactions, an element in one oxidation state is simultaneously oxidized and reduced.

e.g.,

$$2\overset{+1\,-1}{H_2O_2}(aq) \longrightarrow 2\overset{+1\,-2}{H_2O}(l) + \overset{0}{O_2}(g)$$

$$\overset{0}{fl_4}(s) + 3OH^-(aq) + 3H_2O(l) \longrightarrow \overset{-3}{flH_3}(g) + 3\overset{+1}{H_2flO_2^-}(g)$$
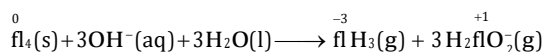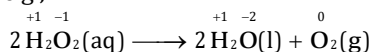
➤ **Balancing of Redox Reactions:** Following methods are used to balance chemical equations for redox processes:

1. Oxidation Number Method: It involves following steps:

- Write the correct chemical formula for each reactant and product.
- Identify atoms which undergo change in oxidation number in the reaction by assigning oxidation number to all elements in the reaction.
- Calculate the increase or decrease in the oxidation number per atom and for the entire molecule/ion in which it occurs. If these are not equal, then multiply by suitable number so that these become equal.
- Ascertain the involvement of ions if the reaction is occurring in water, add H^+ or OH^- to the expression on the appropriate side so that the total ionic charges of reactants and products are equal.

  If the reaction is carried out in acidic solution, use H^+ ions in the equation; if in basic solution, use OH^- ions.

- Make the numbers of H–atoms in the expression on the two sides equal by adding H_2O molecules to the reactants or products.

  Now, check the number of O–atoms. If there are the same number of oxygen atoms in the reactants and products, then the equation represents the balanced redox reaction.

2. Half Reaction Method: It involves following steps:

- Produce unbalanced equation for the reaction in ionic form.
- Separate the equation into half reactions, i.e., oxidation and reduction half reactions.
- Balance the atoms other than O and H in each half reaction individually.
- For reactions occurring in acidic medium, add H_2O to balance O atoms and H^+ to balance H atoms.
- Add electrons to one side of the half reaction to balance the charges. If required, make the number of electrons equal in the two half reactions by multiplying one or both half reactions by appropriate number.
- Now, add two half reactions to achieve overall reaction and cancel the electrons on each side. This gives the net ionic equation.
- Verify that the equation contains the same type and number of atoms and the same charges on both sides of the equation.

Note: For the reaction in a basic medium, first balance the atoms as is done in acidic medium. Then for each H^+ ions, add an equal number of OH^- ions to both sides of the equation. Where H^+ and OH^- appear on the same side of the equation, combine these to give H_2O.

➤ **Electrode Processes:**

- The redox reactions in which the oxidation and reduction half reactions take place in the same container, are called the **direct redox reactions**.

  e.g.,When Zn strip is placed in $CuSO_4$ solution, Zn is oxidized to Zn^{2+} and $CuSO_4$ is reduced to metallic copper. Such type of cell is called electrolytic cell and the phenomenon is known as electrolysis.

- The redox reactions in which the oxidation and reduction half reactions take place in the separate containers, are called **indirect redox reactions**. Such type of cell is called **electrochemical cell**.

  For e.g., $CuSO_4$ solution is placed in a beaker with a copper strip or rod and $ZnSO_4$ solution is placed in separate beaker with a zinc strip or rod. In this experiment, two redox couples are represented as:

  $$Zn/Zn^{2+} \text{ and } Cu^{2+}/Cu$$
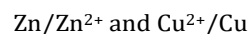
  The solutions of two beakers are connected by a salt bridge (a U-tube containing a solution of KCl or NH_4NO_3). The Zn and Cu rods are connected by a metallic wire with a provision for an ammeter and switch. This set-up is known as Daniel cell. The two half reactions taking place are :

  $$Zn \longrightarrow Zn^{2+} + 2e^- \text{ (Oxidation) at anode}$$

  $$Cu^{2+} + 2e^- \longrightarrow Cu \text{ (Reduction) at cathode}$$

  Overall reaction, $Zn + Cu^{2+} \longrightarrow Zn^{2+} + Cu$
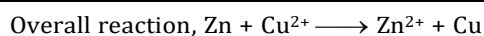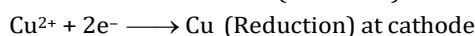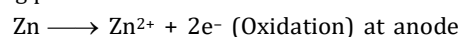
- **Redox Couple:** It is defined as having together the oxidized and reduced forms of a substance taking part in an oxidation or reduction half reaction.
- **Electrode:** It is an electrical conductor used to make contact with a non-metallic part of a circuit.
- **Electrode Potential:** The potential associated with each electrode is called electrode potential.
- **Salt Bridge:** It is an inverted U-tube that contains an electrolyte and connects the two half cells in a galvanic cell.
- **Functions of Salt bridge in an Electrochemical cell :**
  - It completes the cell circuit by connecting the solutions of two half cells, without allowing them to mix with each other.
  - It maintains the electrical neutrality of the solutions in the two half cells due to the flow of ions.
- **Representation of an Electrochemical Cell**

Flow of electrons →

← Flow of current

$$Zn(s) \mid Zn^{2+}(aq) \parallel Cu^{2+}(aq) \mid Cu(s)$$

Left electrode (Anode) Oxidation (Negative)	Salt bridge	Right electrode (Cathode) Reduction (Positive)
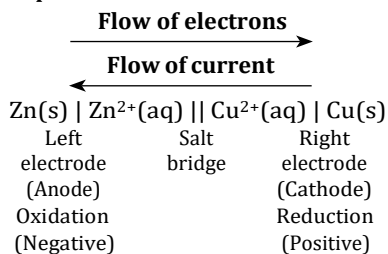
- A metal having more negative value of E^Q (Standard electrode potential) can displace the metal having less negative value of E^Q from their salt solution.

  e.g., Zn can displace Cu from $CuSO_4$ solution

  ($Zn^{2+}/Zn = -0.76V$, $Cu^{2+}/Cu = 0.34V$)

  So,   Zn is more reactive than Cu.
- The feasibility of a reaction is decided by its electromotive force (emf) or cell potential.

  i.e., $E°_{cell} = E°_{cathode} - E°_{anode}$
  - A positive value of $E°_{cell}$ suggests that the cell reaction is feasible.
  - A negative or zero value of $E°_{cell}$ suggests that the cell reaction does not feasible.
- **Standard Electrode Potential:** The potential of an electrode in which the concentration of each species taking part in the electrode reaction is unity (if any gas is involved in the electrode reaction, its pressure is taken as 1 atmosphere) and the temperature is maintained at 298 K is called the standard electrode potential.
- The standard electrode potential (E^Q) value for each electrode process is a measure of the relative tendency of the active species in the process to remain in the oxidized/reduced form.
- A negative E^Q means that the redox couple is a **stronger** reducing agent than the H^+/H_2 couple.
- A positive E^Q means that the redox couple is a **weaker** reducing agent than the H^+/H_2 couple.
- **Electrochemical Series:** The series in which different electrodes are arranged in decreasing order of their standard reduction potentials (E^Q) is called electrochemical series.

🧠 Mnemonics

Concept: An Oil Rig Cat
Mnemonics: At the ANode, Oxidation Involves Loss of electrons.
Interpretation: Reduction Involves Gaining electrons at the Cathode
Concept: Electrons flow From Anode To Cathode
Mnemonics: Fat Cat
Interpretation: LOAN: Left side, Oxidation, Anode, Negative
Concept: soak a jerk
Mnemonics: SOAC a GERC
Interpretation: Strongest Oxidizing Agent at the Cathode Gains Electrons and is Reduced at the Cathode.
Concept: Activity Series of Metals
Mnemonics: Please Stop Calling Me A Cute Zebra I Like Her Call Smart Goat. Kangaroos Naturally Muck About in Zoos For Purple Hippos Chasing Aardvarks.
Interpretation: Calcium > Magnesium >Aluminium> (Carbon)* > Zinc > Iron > Lead > Hydrogen > Copper > Silver
> Gold), OR (K > Na > Mg > Al > Zn > Cr > Fe > Pd > H > Cu > Au)
Concept: For Galvanic Cell
Mnemonics: LOAN
Interpretation: Loss of e–Oxidation Anode Negative
Concept: Electrolytic Cell
Mnemonics: LOAP
Interpretation: Loss of e–Oxidation Anode Positive

🔑 Key Terms

- **Electrochemical Cell:** It is a device which is used to convert chemical energy into electrical energy.

📋 Key Facts

- All combustion reactions, which make use of elemental dioxygen, as well as other reactions involving elements other than dioxygen, are redox reaction.
- All decomposition reactions are not redox reactions. For example, decomposition of calcium carbonate is not a redox reaction.

$$\overset{+2\ +4\ -2}{Ca\,CO_3}(s) \xrightarrow{\Delta} \overset{+2\ -2}{CaO}(s) + \overset{+4\ -2}{CO_2}(g)$$
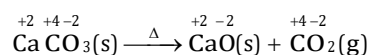
- All alkali metals and some alkaline earth metals (Ca, Sr and Ba) which are very good reducing agents, will displace hydrogen from cold water.

  e.g., $Ca(s) + 2H_2O(l) \longrightarrow Ca(OH)_2(aq) + H_2(g)$
- Less active metals such as magnesium and iron react with steam to produce dihydrogen gas.

$$2Fe(s) + 3H_2O(g) \xrightarrow{\Delta} Fe_2O_3(s) + 2H_2(g)$$
$$\text{steam}$$
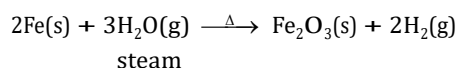
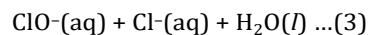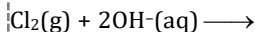- Many metals, including those which do not react with cold water, are capable of displacing hydrogen from acids.
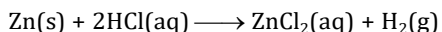
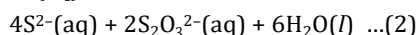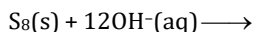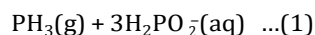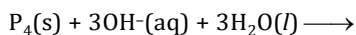 $Zn(s) + 2HCl(aq) \longrightarrow ZnCl_2(aq) + H_2(g)$
  This reaction is used to prepare dihydrogen gas in the laboratory.

- Very less active metals, which may occur in the native state such as silver (Ag) and gold (Au) do not react even with hydrochloric acid.

- Fluorine is so reactive that it can replace chloride, bromide and iodide ions in solution. Infact, fluorine is so reactive that it attacks water and displaces the oxygen of water.

  $2H_2O(l) + 2F_2(g) \longrightarrow 4HF(aq) + O_2(g)$

- Phosphorus, sulphur and chlorine undergo disproportionation in the alkaline medium as shown below :

  $P_4(s) + 3OH^-(aq) + 3H_2O(l) \longrightarrow$
  $$PH_3(g) + 3H_2PO_2^-(aq) \quad ...(1)$$
  $S_8(s) + 12OH^-(aq) \longrightarrow$
  $$4S^{2-}(aq) + 2S_2O_3^{2-}(aq) + 6H_2O(l) \quad ...(2)$$

$Cl_2(g) + 2OH^-(aq) \longrightarrow$
$$ClO^-(aq) + Cl^-(aq) + H_2O(l) \quad ...(3)$$

The third reaction describes the formation of household bleaching agents. The hypochlorite ion (ClO^-) formed in the reaction oxidises the colour bearing stains of the substances to colourless compounds.

- The reaction that takes place in the case of fluorine is as follows:

  $2F_2(g) + 2OH^-(aq) \longrightarrow 2F^-(aq) + OF_2(g) +$
  $$H_2O(l)$$
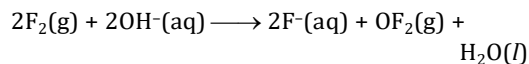
- In acid-base systems, titration is used to find the strength of one solution against the other using a pH sensitive indicator.

- Highly reactive metals (i.e. having negative value of $E^{\ominus}$) displace hydrogen from acids. For e.g., Metals like Mg, Al, Zn, Fe etc. can replace hydrogen from HCl or H_2SO_4.
  However, metals with positive values of $E^{\ominus}$ are not capable to replace hydrogen from mineral acids.

❑❑

Chapter 8

ORGANIC CHEMISTRY-SOME BASIC PRINCIPLES AND TECHNIQUES

| **Topic-1** | **General Introduction, Classification, Nomenclature and Isomerism in Organic Compounds** |

💬 Revision Notes

- **General Introduction:** The hydrides of carbon (hydrocarbons) and their derivatives are called organic compounds. The branch of chemistry which deals with these compounds is called organic chemistry.

- Berzilius (1808) defined organic chemistry as the chemistry of substances found in living matter and gave the vital force theory. Urea is the first organic compound synthesised in laboratory by F. Wohler in 1828.

- **Properties:** Organic compounds may be gases, liquids or solids. Being covalent in nature, these have low boiling point and melting point and soluble in organic solvents. These are generally volatile and inflammable. They do not conduct electricity because of the absence of free ions. They possess distinct colour and odour.

- Reasons for large number of organic compounds:

  (i) Catenation: It is the tendency of self-combination or self linkage of atoms of an

element to form a ring or chain, and carbon shows maximum catenation property. A carbon atom can combine with other carbon atoms by single, double or triple bonds. Thus, it forms more compounds than the others.

(ii) **Tetravalency**: Carbon being tetravalent is capable of bonding with four other C atoms or some other monovalent atoms.

Bond angles in sp^3 hybridised C is 109°28′, in sp^2 hybridised C is 120° and in sp hybridised C is 180°.

The C–C, C = C and C ≡ C bond lengths are 1.54 Å, 1.34 Å and 1.20 Å respectively (the shorter the bond, greater is its strength). Also, greater the bond strength, greater is the bond energy.

(iii) **Small size**: Furthermore, these compounds are exceptionally stable because of the small size of carbon. Carbon forms straight, branched and ring structured compounds.

➤ The three dimensional structure of organic molecule can be represented on paper by using wedge-and-dash representation. In these formulas, the solid wedge (◤) is used to show a bond coming out of the paper towards the observer and dashed wedge (␣␣ıııııllIlll) is used to show a bond going away from the observer.

➤ **Classification of organic compound:** Organic compounds are broadly classified as follows:

Organic compounds
- Acyclic or open chain compounds
- Cyclic or closed chain or ring compounds
  - Alicylic
    - Homocyclic or carbocyclic
    - Heterocyclic or non-aromatic
  - Aromatic
    - Benzenoid
    - Heterocyclic aromatic
    - Non-benzenoid
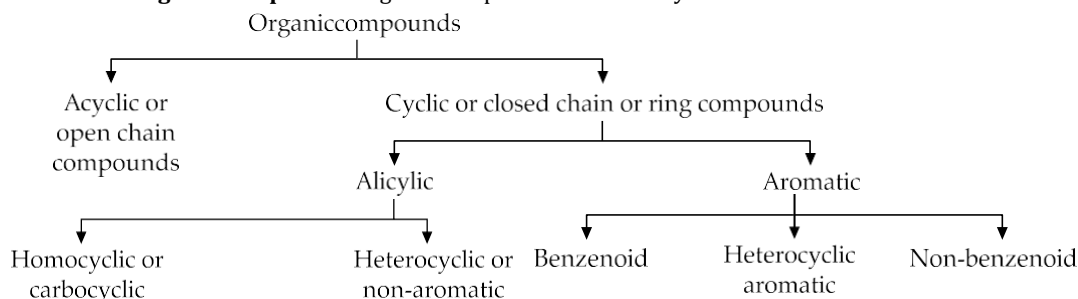
➤ **Functional Group:** The atom or group of atoms e.g., –COOH, – CHO, which is responsible for the chemical properties of the molecule, is called functional group. Double and triple bonds are also functional groups.

R – ← functional group

➤ **Homologous series**: Homologous series is defined as a family or group of structurally similar organic compounds all members of which contain the same functional group, show a gradation in physical and similarity in chemical properties and any two adjacent members of which differ by –CH₂ group. The individual members of this group are called homologous and the phenomenon is called homology.

➤ **Nomenclature of Organic Compounds : Common name (Common system)**: Before the IUPAC system of nomenclature, organic compounds were named after the sources of origin, for example, urea was so named because it was obtained from the urine of mammals.

IUPAC (International Union of Pure and Applied Chemistry) System:

According to IUPAC system, the name of an organic compound contains three parts: (i) word root, (ii) suffix, (iii) prefix.

 (i) **Word root:** Word root represents the number of carbon atoms present in the principal chain, which is the longest possible chain of carbon atoms.

(ii) **Suffix:** Suffix is of two types, primary suffix and secondary suffix.

 (a) **Primary Suffix**: It indicates the type of bond in the carbon chain.

 (b) **Secondary Suffix:** Secondary suffix is used to represent the functional group.

(iii) **Prefix:** Prefix is a part of IUPAC name which appears before the word root. Prefix is of two types:

(a) **Primary prefix:** For example, primary prefix cyclo is used to differentiate cyclic compounds.

(b) **Secondary prefix:** Some functional groups are considered as substituent and denoted by secondary prefixes. For example :

Substituted Group	Secondary prefix
— F	Fluoro
— Cl	Chloro
— Br	Bromo
— NO₂	Nitro
— NO	Nitroso
— CH₃	Methyl
— OCH₃	Methoxy

Naming of Compounds Containing Functional Groups : (i) The longest chain of carbon atoms containing the functional group is numbered in such a manner that the functional group is attached at the carbon atoms possessing lowest possible number in the chain. In case of polyfunctional compounds, one of the functional group is selected as principal functional group and the compound is named on that basis. The choice of principal functional group is made on the basis of order of preference.
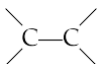
The order of decreasing priority for the functional group is :

–COOH, –SO₃H, –COOR (R=alkyl group), COCl, –CONH₂, –CN, –HC=O, >C=O, –OH, -NH₂, >C=C<, –C≡C–.

(ii) The number of carbon atoms in parent chain is denoted by proper root word.

(iii) Name the groups attached to the parent chain and prefix with the number of carbon atoms to which they are attached in the parent chain.

(iv) If the compound contains two or more functional groups, numerical prefixes like di, tri, tetra are used and the terminal e from the primary suffix is retained while writing the IUPAC name.

Some functional Groups and Classes of Organic Compounds

Class of compounds	Functional group structure	IUPAC group prefix	IUPAC group suffix	Example
Alkanes	$\diagdown C - C \diagup$		-ane	Butane, $CH_3(CH_2)_2CH_3$
Alkenes	$>C=C<$		-ene	But-1-ene, $CH_2=CHCH_2CH_3$
Alkynes	$-C\equiv C-$		-yne	But-1-yne, $CH\equiv CCH_2CH_3$
Arenes	—			Benzene
Halides	-X (X=F, Cl, Br, I)	halo-		1-Bromobutane, $CH_3(CH_2)_2CH_2Br$
Alcohols	-OH	hydroxy-	-ol	Butan-2-ol, $CH_3CH_2CHOHCH_3$
Aldehydes	-CHO	Formyl, or oxo	-al	Butanal, $CH_3(CH_2)_2CHO$
Ketones	$>C=O$	oxo-	-one	Butan-2-one, $CH_3CH_2COCH_3$
Nitriles	$-C\equiv N$	cyano	nitrile	Pentanenitrile, $CH_3CH_2CH_2CH_2CN$
Ethers	-R-O-R-	alkoxy-		Ethoxyethane, $CH_3CH_2OCH_2CH_3$
Carboxylic acids	-COOH	carboxy	-oic acid	Butanoic acid, $CH_3(CH_2)_2CH_2H$
Carboxylate ions	$-COO^-$		-oate	Sodium butanoate, $CH_3(CH_2)2CO_2^-Na^+$
Esters	-COOR	alkoxycarbonyl	-oate	Methyl propanoate, $CH_3CH_2COOCH_3$
Acyl halides	-COX (X=F, Cl, Br, I)	halocarbonyl	-oyl halide	Butanoyl chloride, $CH_3(CH_2)_2COCl$
Amines	$-NH_2$, $>NH, >N-$	amino-	-amine	Butan-2-amine, $CH_3CHNH_2CH_3CH_3$
Amides	$-CONH_2$, -CONHR, $-CONR_2$	-carbamoly	-amide	Butanamide, $CH_3(CH_2)2CONH_2$
Nitro compounds	$-NO_2$	nitro		1-Nitrobutane, $CH_3(CH_2)_3NO_2$
Sulphonic acids	$-SO_3H$	sulpho	sulphonic acid	Methylsulphonic acid CH_3SO_3H

🔄 **Mnemonics**

1. Concept: Functional group preference order
Mnemonics: ASEHA NAKAA Delhi Training Camp
Interpretation: Carboxylic Acid > Sulphonic Acid > Ester > Acid
Halides > Acid Amides >Nitrile > Aldehyde > Ketone > Alcohol > Amines = > =

2. Concept: No Preference Functional Group
Mnemonics: NAHE
Interpretation: Nitro, Alkyl / Aryl, Halo, Ethers

3. Concept: Carbon Chain
Mnemonics: Monkey Eat Peeled Bananas
Interpretation: Meth, Eth, Prop, But

4. Concept: To Learn Order of Bond Enthalpy
Mnemonics: To Do Sum
Interpretation: C-C Triple bond > Double bond > Single bond To Learn Bond Length
See Duet Trial -C-C Single bond>Double bond > Triple bond

► **Isomerism:** Two or more compounds having the same molecular formula but different physical and chemical properties are called isomers and this

phenomenon is called isomerism**.** It is of two types-

(1) Structural Isomerism: Structural isomerism is shown by compounds having the same molecular formula but different structural formulae differing in the arrangement of atoms. Structural Isomerism is of four types:

(i) Chain isomerism: When two or more compounds have similar molecular formula but different carbon skeletons, these are referred to as chain isomers and the phenomenon is termed as chain isomerism. For example, C_5H_{12} represents three compounds-

$$CH_3CH_2CH_2CH_2CH_3 \qquad CH_3-\overset{\overset{\displaystyle CH_3}{|}}{C}H CH_2CH_3 \qquad CH_3-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}-CH_3$$

Pentane   Isopentane   Neopentane
            (2-Methylbutane)   (2, 2-Dimethyl propane)
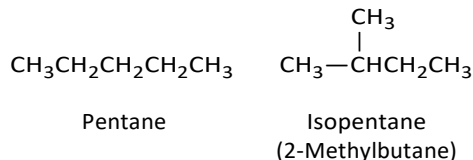
(ii) Position Isomerism: When two or more compounds differ in the position of substituent atom or functional group on the carbon skeleton, they are called position isomers and this phenomenon is termed as position isomerism. For example, the molecular formula C_3H_8O represents two alcohols:

$$CH_3CH_2CH_2OH \qquad CH_3-\overset{\overset{\displaystyle OH}{|}}{C}H-CH_3$$

Propan-1-ol   Propan-2-ol
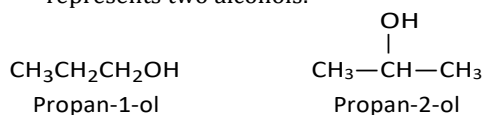
(iii) Functional Isomerism: Two or more compounds having the same molecular formula but different functional groups are called functional isomers and this phenomenon is termed as functional group isomerism. For example, the molecular formula C_3H_6O represents an aldehyde and a ketone :

$$CH_3-\overset{\overset{\displaystyle O}{|}}{C}-CH_3 \qquad CH_3-CH_2-CH=O$$

Propanone   Propanal
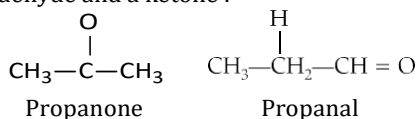
(iv) Metamerism: It arises due to different alkyl chains on either side of the functional group in the molecule. For example, $C_4H_{10}O$ represents methoxypropane $(CH_3OC_3H_7)$ and ethoxyethane $(C_2H_5OC_2H_5)$.

(2) Stereoisomerism: The compounds that have the same constitution and sequence of covalent bonds but differ in relative positions of their atoms or groups in space are called stereoisomers. This phenomenon is called as stereoisomerism.

(i) Geometrical or *Cis-trans* Isomerism: Isomerism in which the compounds possessing same molecular formula differ in their properties due to the difference in their geometry, due to difference in the direction of attachment of same atoms or groups in their molecule. For example,

$$\underset{a}{\overset{b}{>}}C-C\underset{a}{\overset{b}{<}} \qquad \underset{b}{\overset{a}{>}}C-C\underset{a}{\overset{b}{<}}$$

cis   *trans*
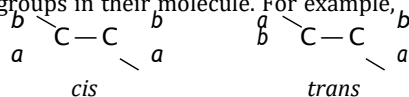
(ii) Optical Isomerism: Optical isomers are two compounds which contain the same number and kinds of atoms, and bonds (i.e., the connectivity between atoms is the same), and different spatial arrangements of the atoms, but which have non-super imposable mirror images. Each non-super imposable mirror image structure is called an enantiomer. Molecules or ions that exist as optical isomers are called chiral.

🔑 Key Terms

➤ **Aliphatic Compounds:** The compounds which have straight or branched chain are called aliphatic compounds.

➤ **Alicyclic Compounds:** The compounds which have carbon atoms joined in the form of a ring are called alicyclic compounds.

➤ **Functional Group:** It may be defined as an atom or group of atoms joined in a specific manner which is responsible for the characteristic chemical properties of the organic compounds.

📋 Key Facts

➤ Buckminsterfullerene is a common name given to the newly discovered C_{60} cluster (a form of carbon) noting its structural similarity to the geodesic domes popularised by the famous architect R. Buckminster Fuller.

➤ Acetic acid is the first organic compound synthesised in the laboratory from its elements.

🧠 Mnemonics

1. Concept: 3-D Representation
Mnemonics: So towards Do away
Interpretation: Solid ® Towards observer ( )
Dashed ® Away from observer (IIIII)

2. Concept: Structural Isomerism
Mnemonics: Poor Farmer Managing Crops (PFMC)
Interpretation:
(a) Position
(b) Functional Group
(c) Metamerism
(d) Chair

7. Concept: Optical Isomerism
Mnemonics: GO
Interpretation:
(a) Geometrical
(b) Optical

Revision Notes

▶ The general reaction is depicted as follows:

$$\text{Organic molecule (Substrate)} \xrightarrow{\text{Attacking Reagent}} \text{[Intermediate]} \longrightarrow \text{Products(s)}$$

$$\text{[Intermediate]} \longrightarrow \text{By products}$$
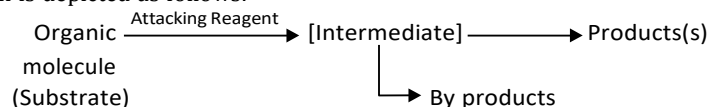
▶ The sequential account of each step, describing details of electron movement, energetics during bond cleavage and bond formation, and the rates of transformation of reactants into products (kinetics) is referred to as **reaction mechanism.**

▶ Organic reactions involve breaking and making of covalent bonds. A covalent bond can undergo fission in two ways:

 (i) By Homolytic Cleavage or Homolysis

 (ii) By Heterolytic Cleavage or Heterolysis

▶ **Homolytic Cleavage**: In this process, each of the atoms acquires one of the bonding electrons.

A-B or $A : B \longrightarrow \dot{A} + \dot{B}$
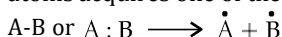
The products are called free radicals. They are electrically neutral and have one unpaired electron associated with them. Homolytic fission is the most common mode of fission in vapour phase. Alkyl radicals are classified as primary, secondary, or tertiary. Alkyl radical stability increases as we proceed from primary to tertiary:

$$CH_3 < CH_2CH_3 < CH(CH_3)_2 < C(CH_3)_3$$

Methyl	Ethyl	Isopropyl	Tert-butyl
free	free	free	free
radical	radical	radical	radical
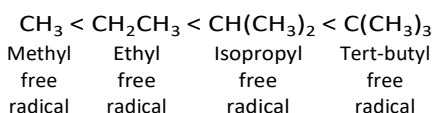
▶ **Heterolytic Cleavage**: In this process, one of atoms acquires both of the bonding (shared pair of electrons) electrons when the bond is broken. If one is more electronegative than other which thereby acquires both the bonding electrons and become negatively charged. The products of heterolytic fission are carbonium ions and carbanions.

▶ **Carbonium Ions (carbocations):** A species having a carbon atom possessing sextet of electrons and a positive charge is called a carbocation.

$$-\overset{|}{\underset{|}{C}} : Z \longrightarrow -\overset{|}{\underset{|}{C}}^+ + : Z$$
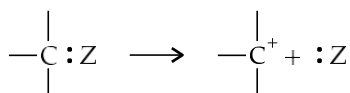
where Z is more electronegative than carbon. The carbocation is sp^2-hybridised having trigonal planar geometry. Tertiary carbonium ion is more stable than a secondary, which in turn is more stable than a primary because of inductive effect (+I) associated with alkyl group.

3° TERTIARY   2° SECONDARY   1° PRIMARY
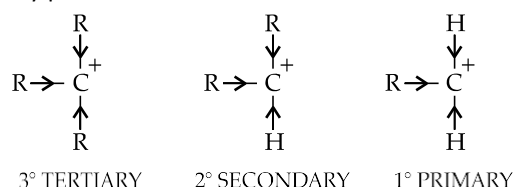
▶ **Carbanion**: Organic ion which contains a negatively charged carbon atom is called carbanion.

$$-\overset{|}{\underset{|}{C}} : Z \longrightarrow -\overset{|}{\underset{|}{C}} \overset{..}{:} + Z^+$$
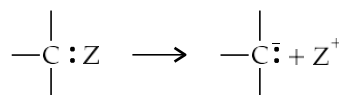
where Z is less electronegative than carbon. The carbanions are sp^3-hybridised species carrying negative charge and have pyramidal shape. Primary carbanion is more stable than a secondary, which in turn is more stable than a tertiary because of inductive effect (+I) associated with alkyl group.
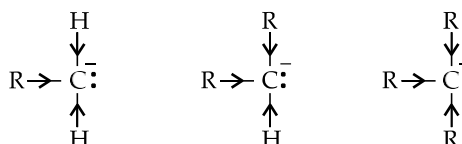
Primary > Secondary > Tertiary

▶ **Electrophile:** A reagent that takes away an electron pair from reactive site, i.e., electron seeking, e.g., H^+, CH_3^+ NH_4^+ $AlCl_3$, SO_3 , BF_3 , etc.

Nucleophile: A reagent that brings an electron pair to the reactive site, i.e., nucleus seeking, e.g., OH^-, CN^-, H_2O, R_3N, R_2NH, etc.

▶ **Electron Displacement Effects in Covalent Bonds:** Electronic displacements in covalent bonds occur due to the presence of an atom or group of different electronegativity or under the influence of some outside attacking group. These lead to a number of effects which are as follows:

 (i) Inductive effect

 (ii) Electromeric effect

 (iii) Resonance or Mesomeric effect

 (iv) Hyperconjugation.

▶ **Inductive effect**: Electron displacement along the carbon chain in an organic molecule due to the presence of a polar covalent bond at one end of the

chain. Due to different electronegativity, electrons are displaced towards the more electronegative atom. The more electronegative atom acquires a small negative charge (δ^-). The less electronegative atom acquires a small positive charge (δ^+).

► Atoms or groups which lose electrons towards a carbon atom are said to have a +I effect. Those atoms or groups which draw electrons away from a carbon atom are said to have a -I effect. Some common atoms or groups which cause +I or -I effects are shown below:

(i) The – I effect (electron attracting) shows the trend: $NO_2 > F > COOH > Cl > Br > I > OH > C_6H_5$.

(ii) The +I effect (electron releasing) shows the trend: $(CH_3)_3C— > (CH_3)_2CH— > CH_3CH_2— > CH_3$.

► **Electromeric Effect (E effect)**: It is a temporary 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 on the demand of an attacking reagent. The shifting of the electrons is shown by a curved arrow. There are two distinct types of electromeric effect:

(i) **Positive Electromeric Effect (+E effect):** In this effect, the π-electrons of the multiple bond are transferred to that atom to which the reagent gets attached. For example,

$$\underset{\text{(attacking reagent)}}{\text{C}=\text{C} + H^+} \longrightarrow \overset{+}{\text{C}}-\underset{\underset{H}{|}}{\text{C}}$$
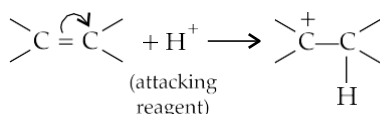
(ii) **Negative Electromeric Effect (–E effect)**: In this effect, the π - electrons of the multiple bond are transferred to that atom to which the attacking reagent does not get attached. For example,

$$\underset{\text{(attacking reagent)}}{\text{C}=\text{C} + \bar{\text{C}}\text{N}} \longrightarrow \text{C}-\underset{\underset{CN}{|}}{\bar{\text{C}}}$$
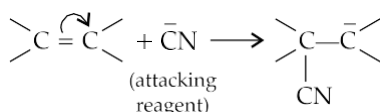
► **Resonance or Mesomeric Effect**: It is defined as the polarity produced in the molecule by the interaction of two π-bonds or between a π-bond and a lone pair of electrons present on an adjacent atom. There are two types of resonance or mesomeric effects designated as R or M effect.

Positive Resonance Effect (+R effect): Those atoms which lose electrons towards a carbon atom are said to have a +M effect or +R effect. For example: —Cl, —Br, —I, —NH₂, —NR₂, —OH, —OCH₃.
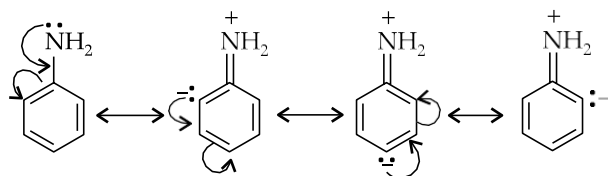
+R effect in aniline

Negative Resonance Effect (-R effect): Those atoms or groups which draw electrons away from a carbon atom are said to have a -M effect or -R effect. For example: –COOH , -CHO , -CN.
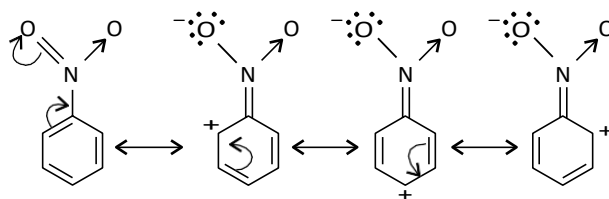
−R effect in nitrobenzene

► **Hyperconjugation:** Orbital interactions between the π systems and the adjacent sigma bonds of the substituent group (s) in organic compounds.

It involves delocalisation of σ electrons of C—H bond of an alkyl group directly attached to an atom of unsaturated system or to an atom with an unshared p orbital. The σ electrons of C—H bond of the alkyl group enter into partial conjugation with the attached unsaturated system or with the unshared p orbital. Hyperconjugation is a permanent effect which is also called "No bond resonance".
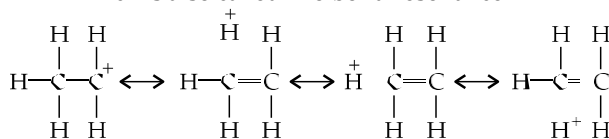
In general, greater the number of alkyl groups attached to a positively charged carbon atom, the greater is the hyperconjugation.

$$\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{CH_3—\overset{+}{C}}} > (CH_3)_2\overset{+}{CH} > CH_3\overset{+}{CH_2} > \overset{+}{CH_3}$$

►
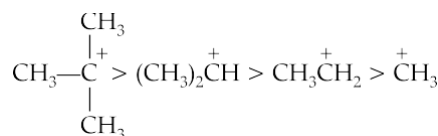
Types of Organic Reactions and Mechanisms:

(i) **Substitution reactions:** Reactions involving replacement of an atom or group in a molecule by different atoms or groups, e.g., chlorination of methane.

(ii) **Addition reactions:** Reactions when two molecules form a single product, e.g., reaction of but-1-ene with HBr to give 2-bromobutane.

(iii) **Elimination reactions:** Reactions in which two atoms or groups in a molecule are eliminated to give the product, e.g., formation of alkene from alkyl bromide.

(iv) **Rearrangement reaction:** Reactions involving migration of atoms to other position within the molecule.

Topic-3 Methods of Purification of Organic Compound

Revision Notes

► Purification of organic compounds can be done by sublimation, crystallisation, distillation, differential extraction and chromatography.

(i) Sublimation: This technique is used only for those solids which changes from solid to vapour state directly without passing through liquid state.

(ii) Crystallisation: This is used for purification of solid organic compounds. This is based on the difference in the solubilities of compound and the impurities in a suitable solvent.

(iii) Distillation: It can be used (i) to separate volatile liquids from non-volatile impurities (ii) to separate the liquids having sufficient difference in their boiling points (>25 K). Liquids having different boiling points vaporise at different temperatures. The vapours are cooled and the liquids so formed are collected separately.

There are various distillation techniques. These are:

(a) Fractional distillation: It is used for separating liquids if the difference in boiling points is not much. In this technique, vapours of a liquid mixture are passed through a fractionating column before condensation. A fractionating column provides many surfaces for heat exchange between the ascending vapours and the descending condensed liquid. This technique is used to separate different fractions of crude oil in petroleum industry.

(b) Distillation under reduced pressure: It is carried out to purify those liquids that have high boiling points and those which decompose at or below their boiling points.

(c) Steam distillation: It is used to purify those substances which are steam volatile and immiscible with water. In steam distillation, the liquids boils when the sum of vapour pressures due to the organic compound (P_1) and that due to water (P_2) becomes equal to the atmospheric pressure (P), i.e., $P = P_1 + P_2$.

(iv) Differential extraction: Here, extraction of compound takes place based on difference in solubility. An organic compound present in aqueous medium is separated by shaking it with an organic solvent in which it is more soluble than in water. Organic solvent and water being immiscible are separated by using separating funnel. Removal of organic compound by distillation or evaporation yields pure compound.

(v) Chromatography: It is based on the general principle of distributing the components of a mixture of organic compounds between two

phases-a stationary phase and mobile phase. The stationary phase can be solid or liquid supported on a solid, while the mobile phase is a liquid or a gas. When the stationary phase is a solid, the basis of separation is adsorption; when it is a liquid, the basis of separation is partition.

Based on the principle involved, chromatography is classified into two categories:

(i) **Adsorption Chromatography** is based on the fact that different compounds are adsorbed on an adsorbent to different degrees. Commonly used adsorbents are silica gel and alumina. When a mobile phase is allowed to move over a stationary phase (adsorbent), the components of the mixture move by varying distances over the stationary phase. It is of two types:

    (a) **Column chromatography** involves 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 adsorbed on adsorbent is placed on the top of the adsorbent column packed in a glass tube. An appropriate eluant which is a liquid or a mixture of liquids is allowed to flow down the column slowly. Depending upon the degree to which the compounds are adsorbed, complete separation takes place. The most readily adsorbed substances are retained near the top and others come down to various distances in the column.

    (b) **Thin layer chromatography (TLC)** is a type of adsorption chromatography, which involves separation of substances of a mixture over a thin layer of an adsorbent coated on glass plate. The plate is known as thin layer chromatography plate or chromaplate. The relative adsorption of each component of the mixture is expressed in terms of its retardation factor i.e.,

$$R_f \text{ value} = \frac{\text{Distance moved by the substance from base line } (x)}{\text{Distance moved by the solvent from base line } (y)}$$

(ii) **Partition chromatography** is based on continuous differential partitioning of components of a mixture between stationary and mobile phases. e.g., Paper chromatography. Chromatography paper contains water trapped in it, which acts as the stationary phase.

➤ **Qualitative Analysis of Organic Compounds:** Almost all the organic compounds contain carbon and hydrogen (CCl_4 is exception as it does not contain hydrogen). They may contain oxygen, nitrogen, sulphur, halogens and phosphorus.

Detection of Carbon and Hydrogen: Carbon and hydrogen are detected as carbon dioxide and water respectively by heating with cupric oxide. Carbon dioxide is detected as it turns lime water milky,

however, water is detected as it turns anhydrous copper sulphate to blue.
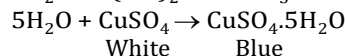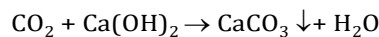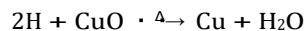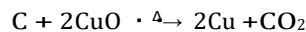
$$C + 2CuO \cdot \overset{\Delta}{\rightarrow} 2Cu + CO_2$$
$$2H + CuO \cdot \overset{\Delta}{\rightarrow} Cu + H_2O$$
$$CO_2 + Ca(OH)_2 \rightarrow CaCO_3 \downarrow + H_2O$$
$$5H_2O + CuSO_4 \rightarrow CuSO_4.5H_2O$$
$$\text{White} \qquad \text{Blue}$$

Lassaigne's test: Nitrogen, sulphur, halogens and phosphorus present in organic compound are detected by 'Lassaigne's test. In this test, organic compound is fused with sodium metal so that elements present in organic compound are converted from covalent form into the ionic form.

$$Na + C + N \cdot \overset{\Delta}{\rightarrow} NaCN$$

$$2Na + S \cdot \overset{\Delta}{\rightarrow} Na_2S$$

$$Na + X \cdot \overset{\Delta}{\rightarrow} NaX \ (X = Cl, Br \text{ or } I)$$
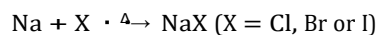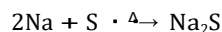
These fused mass are extracted by boiling with water to form sodium fusion extract.

Test for Nitrogen—The sodium fusion extract is boiled with iron (II) sulphate and then acidified with concentrated sulphuric acid. The formation of Prussian blue colour confirms the presence of nitrogen.
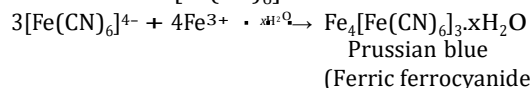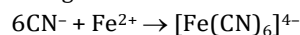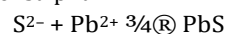
$$6CN^- + Fe^{2+} \rightarrow [Fe(CN)_6]^{4-}$$
$$3[Fe(CN)_6]^{4-} + 4Fe^{3+} \cdot \overset{xH_2O}{\rightarrow} Fe_4[Fe(CN)_6]_3.xH_2O$$
$$\text{Prussian blue}$$
$$\text{(Ferric ferrocyanide)}$$

Test for Sulphur:

(a) The sodium fusion extract is acidified with acetic acid and lead acetate is added to it. A black precipitate of lead sulphide indicates the presence of sulphur.

$$S^{2-} + Pb^{2+} \longrightarrow PbS$$
$$\text{Black}$$

(b) Add 2-3 drops of freshly prepared sodium nitroprusside solution to sodium metal extract. Appearance of violet colour confirms the presence of sulphur.
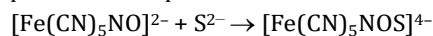
$$[Fe(CN)_5NO]^{2-} + S^{2-} \rightarrow [Fe(CN)_5NOS]^{4-}$$
$$\text{Sulpho nitroprusside ion}$$
$$\text{(violet colour)}$$

If both sulphur and nitrogen are present, sodium thiocyanate is produced in sodium metal extract which gives red colour with Fe^{3+} ions while testing for nitrogen.

$$Na + C + N + S \longrightarrow NaSCN$$
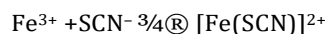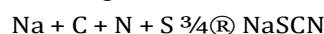
$$Fe^{3+} + SCN^- \longrightarrow [Fe(SCN)]^{2+}$$
$$\text{Blood red}$$

Test for Halogens—For this, sodium fusion extract is acidified with nitric acid and then treated with silver nitrate:
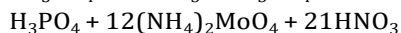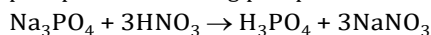
(i) A white precipitate, soluble in ammonium hydroxide shows the presence of chlorine.

(ii) A yellowish precipitate, sparingly soluble in ammonium hydroxide shows the presence of bromine.

(iii) A yellow precipitate, insoluble in ammonium hydroxide shows the presence of iodine.

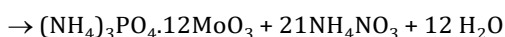$$X^- + Ag^+ \rightarrow AgX \ (X = -Cl, -Br, -I)$$
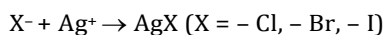
Test for Phosphorus—The compound is heated with an oxidising agent (e.g., sodium peroxide), that oxidises phosphorus to phosphate. This solution on boiling with nitric acid followed by treatment with ammonium molybdate produces canary yellow precipitate confirming phosphorus:

$$Na_3PO_4 + 3HNO_3 \rightarrow H_3PO_4 + 3NaNO_3$$

$$H_3PO_4 + 12(NH_4)_2MoO_4 + 21HNO_3$$

<div align="center">Ammonium</div>
<div align="center">molybdate</div>

$$\rightarrow (NH_4)_3PO_4.12MoO_3 + 21NH_4NO_3 + 12 \ H_2O$$

<div align="center">Ammonium</div>
<div align="center">phosphomolybdate</div>
<div align="center">(Canary yellow precipitate)</div>
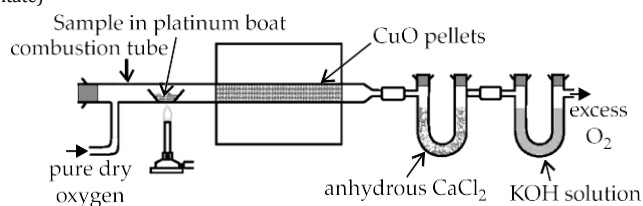
Fig. 8.1

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. Let the mass of organic compound be m g, mass of water and carbon dioxide produced be m_1 and m_2 g respectively.

Percentage of carbon $= \dfrac{12 \times m_2 \times 100}{44 \times m}$

Percentage of hydrogen $= \dfrac{2 \times m_1 \times 100}{18 \times m}$

➤ **Estimation of Nitrogen:**

(i) Dumas method: The nitrogen containing organic compound, when heated with copper oxide in an atmosphere of carbon dioxide, yields free nitrogen in addition to carbon dioxide and water.

$$C_xH_yN_z + (2x + y/2)CuO \ \frac{3}{4}Ⓡ \ xCO_2 + y/2H_2O + z/2N_2 + (2x+y/2)Cu$$
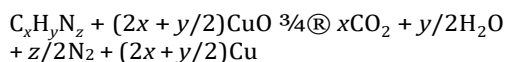
Traces of nitrogen oxides formed, if any, are reduced to nitrogen by passing the gaseous mixture over a heated copper gauze. The mixture of gases so produced is collected over an aqueous solution of potassium hydroxide which absorbs carbon dioxide.

Nitrogen is collected in the upper part of the graduated tube.

➤ **Quantitative analysis**: Quantitative analysis of organic compound gives the percentage composition of elements in an organic compound.

➤ **Estimation of Carbon and Hydrogen** : A known mass of an organic compound is burnt in the presence of excess of oxygen and copper(II) oxide. Carbon and hydrogen in the compound are oxidised to carbon dioxide and water respectively.

$$C_xH_y + (x + y/4) \ O_2 \ \frac{3}{4}Ⓡ \ xCO_2 + (y/2)H_2O$$
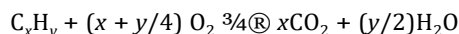
The mass of water produced is determined by passing the mixture through a weighed U-tube containing anhydrous calcium chloride. Carbon dioxide is absorbed in another U-tube containing concentrated solution of potassium hydroxide. These tubes are connected in series.
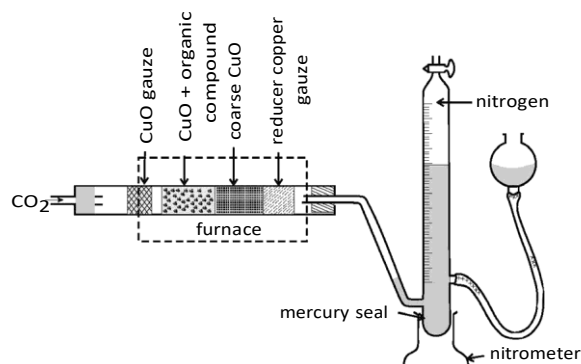
Fig. 8.2

Let the mass of organic compound = m g

Volume of nitrogen collected = V_1 mL

Room temperature = T_1K

Volume of nitrogen at STP $= \dfrac{p_1 \times V_1 \times 273}{760 \times T_1}$

Percentage of nitrogen

$= \dfrac{28 \times \text{volume of } N_2 \text{ at STP} \times 100}{22400 \times \text{Mass of organic compound}}$

(ii) Kjeldahl's method: The compound containing nitrogen is heated with concentrated sulphuric acid. Nitrogen in the compound gets converted to ammonium sulphate.
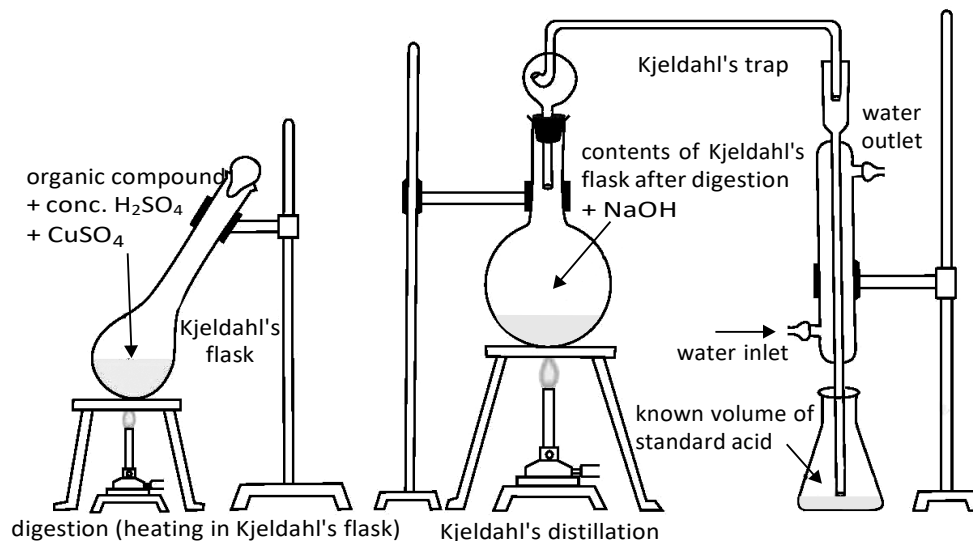
digestion (heating in Kjeldahl's flask)   Kjeldahl's distillation

Fig. 8.3

The resulting acid 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.

Organic compound $+ H_2SO_4 ¾® (NH_4)_2SO_4 \xrightarrow{2NaOH}$

$$Na_2SO_4 + 2NH_3 + 2H_2O$$

$$2NH_3 + H_2SO_4 ¾® (NH_4)_2SO_4$$
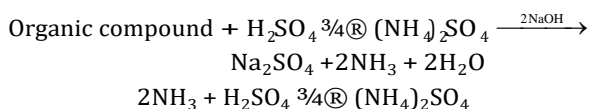
Let the mass of organic compound taken = m g

Volume of H_2SO_4 of molarity, M, taken = V mL

Volume of NaOH of molarity, M, used for titration of excess of H_2SO_4 = V_1 mL

V_1 mL of NaOH of molarity M = $V_1/2$ mL of H_2SO_4 of molarity M

Volume of H_2SO_4 of molarity M unused

= $(V - V_1/2)$ mL

$(V - V_1/2)$ mL of H_2SO_4 of molarity M

= $2(V - V_1/2)$ mL of NH_3 solution of molarity M.

1000 mL of 1 M NH_3 solution contains 17g NH_3 or 14 g of N

2 $(V - V_1/2)$ mL of NH_3 solution of molarity M contains :

$$\frac{14 \times M \times 2(V - V_1/2g_N)}{1000}$$

Percentage of N = $\dfrac{1.4 \times M \times 2(V - V_1/2)}{m}$

► **Estimation of Halogens**:

Carius method: 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.
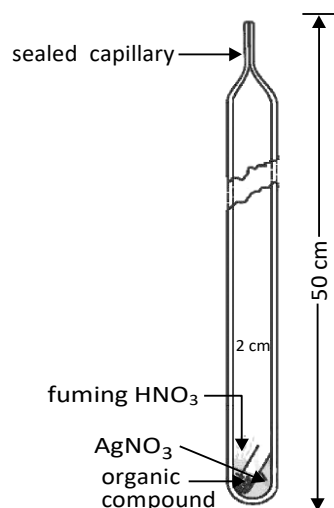
Fig. 8.4

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.

Let the mass of organic compound taken = m g

Mass of AgX formed = m_1 g

1 mol of AgX contains 1 mol of X

Mass of halogen in m_1g of AgX

$$= \frac{\text{Atomic mass of X} \times m_1 g}{\text{Molecular mass of AgX}}$$

Percentage of halogen = $\dfrac{\text{Atomic mass of X} \times m_1 \times 100}{\text{molecular mass of AgX} \times m}$

► **Estimation of Sulphur:** 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 in water. The precipitate is filtered, washed, dried and weighed.

Let the mass of organic compound taken = m 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 $\dfrac{32 \times m_1}{233}$ g of sulphur

Percentage of sulphur = $\dfrac{32 \times m_1 \times 100}{233 \times m}$

➤ **Estimation of Phosphorus:** A known mass of an organic compound is heated with fuming nitric acid whereupon phosphorus present in the compound is oxidised to phosphoric acid. It is precipitated as ammonium phosphomoly date, $(NH_4)_3PO_4$. $12MoO_3$, by adding ammonia and ammonium molybdate. Alternatively, phosphoric acid may be precipitated as $MgNH_4PO_4$ by adding magnesia mixture which on ignition yields $Mg_2P_2O_7$.

Let the mass of organic compound taken = m g
and mass of ammonium phosphomolydate = m_1g
Molar mass of $(NH_4)_3PO_4.12MoO_3$ = 1877 g

Percentage of phosphorus = $\dfrac{31 \times m_1 \times 100}{1877 \times m}$ %

If phosphorus is estimated as $Mg_2P_2O_7$,

Percentage of phosphorus = $\dfrac{62 \times m_1 \times 100}{222 \times m}$ %

➤ **Estimation of Oxygen:** A definite mass of an organic compound is decomposed by heating in a stream of nitrogen gas. The mixture of gaseous products containing oxygen is passed over red-hot coke when all the oxygen is converted to carbon monoxide. This mixture is passed through warm iodine pentoxide (I_2O_5) when carbon monoxide is oxidised to carbon dioxide producing iodine.

Compound $\xrightarrow{\text{Heat}}$ O_2 + other gaseous products

$2C + O_2 \xrightarrow{1373\,K} 2CO]\times 5$ (A)

$I_2O_5 + 5CO ¾® I_2 + 5CO_2]\times 2$ (B)

On making the amount of CO produced in equation (A) equal to the amount of CO used inequation (B) by multiplying the equations (A) and (B) by 5 and 2 respectively; we find that each mole of oxygen liberated from the compound will produce two moles of carbondioxide.

Thus, 88 g carbon dioxide is obtained if 32 g oxygen is liberated.

Let the mass of organic compound taken be m g

Mass of carbon dioxide produced be m_1 g

$\backslash$ m_1 g carbon dioxide is obtained from $\dfrac{32 m_1}{88} g O_2$

$\backslash$ Percentage of oxygen = $\dfrac{32 \times m_1 \times 100}{88 \times m}$ %

❏❏

Chapter 9

HYDROCARBONS

| **Topic-1** | **Saturated Hydrocarbons (Alkanes)** |

💬 Revision Notes

➤ **Classification of Hydrocarbons:** Hydrocarbons are carbon and hydrogen compounds derived mainly from coal and petroleum. Classified into three categories:

1. **Saturated hydrocarbon** – C – C single bonds; eg. $CH_3 – CH_3$ ethane
2. **Unsaturated hydrocarbon** – C = C, and C ⁰ C or both e.g $CH_2 = CH_2$, ethene, or CH ⁰ CH, ethyne.
3. **Aromatic hydrocarbon**-One aromatic ring atleast; e.g., C_6H_6, benzene.

➤ **Alkanes:** Alkanes are the simplest organic compounds made of carbon and hydrogen only. They have the general formula C_nH_{2n+2} (where n = 1, 2, 3, etc.) Alkanes contain strong C —C and C —H bonds. Therefore, this class of hydrocarbons is relatively chemically inert. Hence, they are sometimes referred to as paraffins (Latin: parum affinis = little affinity).

➤ Methane (CH_4) is the first member of this family. In methane, carbon forms single bonds with four hydrogen atoms. All H—C—H bond angles are of 109.5°. Methane has a tetrahedral structure. C—C and C—H bonds are formed by head-on overlapping of sp^3 hybrid orbitals of carbon and $1s$ orbitals of hydrogen atoms.

➤ Alkanes exhibit chain isomerism, position isomerism and conformational isomerism.

➤ Based upon the number of carbon atoms attached to a carbon atom, the carbon atom is termed as primary (1°), secondary (2°), tertiary (3°) or quaternary (4°).

➤ Groups or substituents derived from alkanes by removal of one hydrogen atom is known as alkyl groups. Their general formula is C_nH_{2n+1}.

➤ **Steps to write correct structure from the given IUPAC name:**

(i) Write the longest chain of carbon atoms corresponding to the parent alkane.

(ii) Give number to carbon atoms.

(iii) The substituents are attached to the correct carbon atoms after their numbering.

(iv) Satisfy the valency of each carbon atom by putting the correct number of hydrogen atoms.

➤ **Preparation of Alkanes:**

(i) Alkanes can be prepared by hydrogenation of unsaturated hydrocarbons in the presence of catalyst (Ni, Pd or Pt).

$$CH_2 = CH_2 + H_2 \xrightarrow{Ni/fld/flt} CH_3—CH_3$$
Ethene   Ethane

$$HC \equiv CH + 2H_2 \xrightarrow{Ni/fld/flt} H_3C—CH_3$$
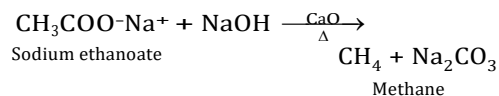Ethyne   Ethane
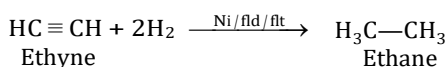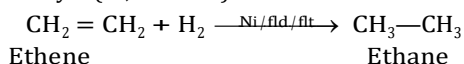
(ii) **By reduction of alkyl halides:** Alkanes can be prepared by the reduction of alkyl halides (except fluorides) with zinc and dilute hydrochloric acid.
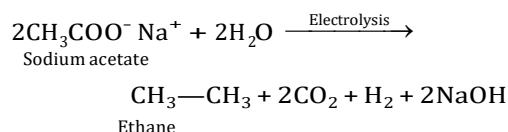
$$CH_3—Cl + H_2 \xrightarrow{Zn, H^+} CH_4 + HCl$$
Chloromethane   Methane
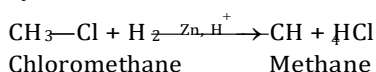
(iii) **Wurtz Reaction:** This reaction is used to increase the length of the carbon chain.

$$CH_3Br + 2Na + BrCH_3$$

$$\xrightarrow{dry\ ether} CH_3—CH_3 + 2NaBr$$
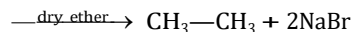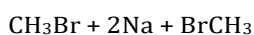
(iv) **Decarboxylation:** Sodium salts of carboxylic acids on heating with soda lime (mixture of sodium hydroxide and calcium oxide) give alkanes containing one carbon atom less than the carboxylic acid.
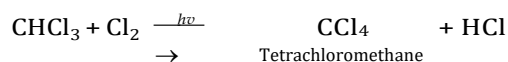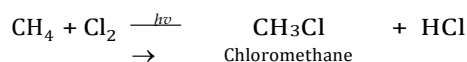
$$CH_3COO^-Na^+ + NaOH \xrightarrow[\Delta]{CaO}$$
Sodium ethanoate
$$CH_4 + Na_2CO_3$$
Methane

(v) **Kolbe's Electrolytic Method:**

$$2CH_3COO^- Na^+ + 2H_2O \xrightarrow{Electrolysis}$$
Sodium acetate
$$CH_3—CH_3 + 2CO_2 + H_2 + 2NaOH$$
Ethane

➤ **Physical properties:** Alkanes are almost non-polar molecule. They possess weak van der Waals forces. Due to the weak forces, the first four members, C_1 to C_4 are gases, C_5 to C_{17} are liquids and those containing 18 carbon atoms or more are solids at 298 K. They are colourless and odourless. With the increase of branching, the boiling points of alkanes decrease as on increasing the branching, the molecule attains the shapes of a sphere, decreasing surface area, thereby decreasing van der Waals forces. Alkanes with even number of carbon atoms have higher melting points as compared to next higher or lower alkanes with odd number of carbon atoms.

➤ **Chemical Properties:**

(i) **Substitution Reactions:** One or more atom of alkanes is replaced by halogens, nitro group and sulphonic acid group, e.g., halogenation.

$$CH_4 + Cl_2 \xrightarrow{hv} CH_3Cl + HCl$$
Chloromethane

$$CH_3Cl + Cl_2 \xrightarrow{hv} CH_2Cl_2 + HCl$$
Dichloromethane

$$CH_2Cl_2 + Cl_2 \xrightarrow{hv} CHCl_3 + HCl$$
Trichloromethane (chloroform)

$$CHCl_3 + Cl_2 \xrightarrow{hv} CCl_4 + HCl$$
Tetrachloromethane

Mechanism:

(i) **Initiation:** Homolysis of chlorine molecule in the presence of light or heat.
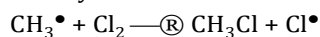
$$Cl_2 \xrightarrow{hv} 2Cl^\bullet$$
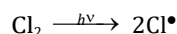
(ii) **Propagation:** Chlorine free radical attacks the methane molecule and takes the reaction in the forward direction by breaking the C–H bond to generate methyl free radical with the formation of H–Cl.
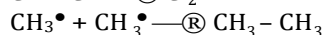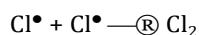
$$Cl^\bullet + CH_4 \longrightarrow HCl + CH_3^\bullet$$
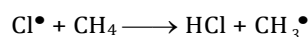
The methyl radical obtained attacks the second molecule of chlorine to form CH_3–Cl with the

liberation of another chlorine free radical by homolysis of chlorine molecule.
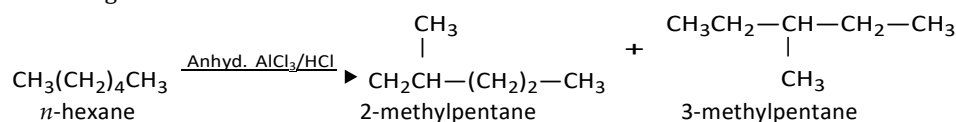
$CH_3^\bullet + Cl_2 \longrightarrow CH_3Cl + Cl^\bullet$

(iii) Termination:

$Cl^\bullet + Cl^\bullet \longrightarrow Cl_2$

$CH_3^\bullet + CH_3^\bullet \longrightarrow CH_3 - CH_3$

$Cl^\bullet + CH_3^\bullet \longrightarrow CH_3Cl$

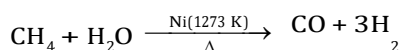**(ii) Combustion:** Due to the evolution of a large amount of heat during combustion, alkanes are used as fuels.

$$C_nH_{2n+2} + \left(\frac{3n+1}{2}\right)O_2 \longrightarrow nCO_2 + (n+1)H_2O$$

e.g., $C_4H_{10}(g) + \frac{13}{2}O_2(g) \longrightarrow 4CO_2(g) + 5H_2O(l)$;

$\Delta H° = -2875.84$ kJ mol^{-1}

(iii) Controlled Oxidation:

(i) $2CH_4 + O_2 \xrightarrow{Cu/523K/100\ atm} 2CH_3OH$
Methanol

(ii) $CH_4 + O_2 \xrightarrow[\Delta]{Mo_2O_3} HCHO + H_2O$
Methanal

(iii) $2CH_3CH_3 + 3O_2 \xrightarrow{(CH_3COO)_2\ Mn}$
$2CH_3COOH + 2H_2O$
Ethanoic acid

(iv) $(CH_3)_3CH \xrightarrow[[O]]{KMnO_4} (CH_3)_3COH$
2-Methylpropane   2-Methylpropan-2-ol
(3°-alkane)
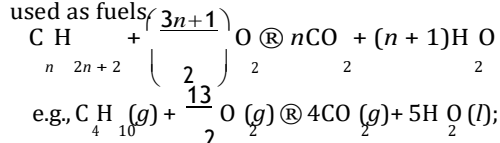
(iv) Isomerisation: *n*-Alkanes on heating in the presence of anhydrous aluminium chloride and hydrogen chloride gas isomerise to branched chain alkanes.

$CH_3(CH_2)_4CH_3 \xrightarrow{Anhyd.\ AlCl_3/HCl}$
n-hexane

CH_3
|
$CH_2CH-(CH_2)_2-CH_3$
2-methylpentane

+

$CH_3CH_2-CH-CH_2-CH_3$
|
CH_3
3-methylpentane

(v) Aromatization or Reforming: Dehydrogenation and cyclization to benzene and its homologues.

$\xrightarrow[10-20atm]{\substack{Cr_2O_3\ or\ V_2O_5 \\ or\ Mo_2O_3,\ 773K}}$

Benzene

n–Hexane
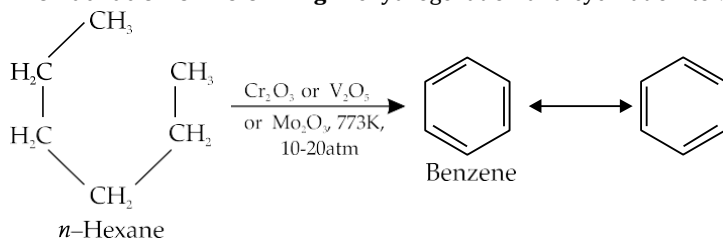
(vi) Reaction with steam: (Industrial preparation of dihydrogen gas)

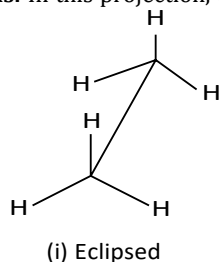$CH_4 + H_2O \xrightarrow[\Delta]{Ni(1273\ K)} CO + 3H_2$

(vii) Pyrolysis: Decomposition of higher alkanes to lower alkanes by the application of heat is called pyrolysis or cracking.

$C_6H_{14} \xrightarrow{773\ K}$

$\longrightarrow C_6H_{12} + H_2$

$\longrightarrow C_4H_8 + C_2H_6$
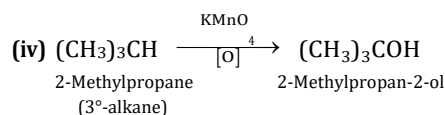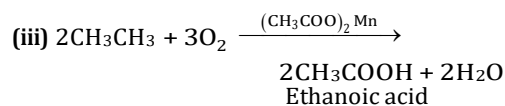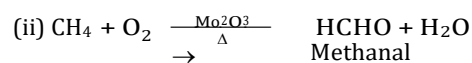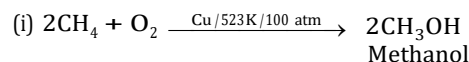
$\longrightarrow C_3H_6 + C_2H_4 + CH_4$
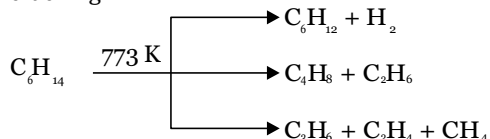
➤ **Conformations of Alkanes:** Alkanes have C—C sigma (s) bonds and rotation about C—C single bond is allowed. This rotation results in different spatial arrangements of atoms in space which can change into one another, such spatial arrangements are called conformations or conformers or rotamers. Alkanes can have infinite number of conformations. Ethane shows eclipsed, staggered and skew conformations. Eclipsed form is least stable but staggered form is most stable due to greater distance between the bond pairs or lesser torsional strain. The energy difference between the two extreme forms is of the order of 12.5 kJ mol^{-1}.

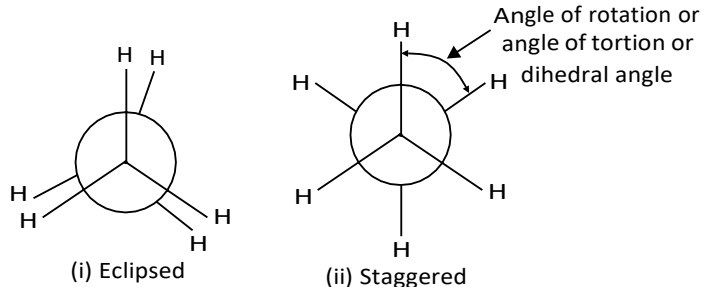**(i) Sawhorse projections:** In this projection, the molecule is viewed along the molecular axis.

(i) Eclipsed   (ii) Staggered

(ii) Newman projections: In this projection, the molecule is viewed at the C–C bond head on.

(i) Eclipsed   (ii) Staggered

🧠 Mnemonics

Concept: Newmann Projection for Staggered and Eclipsed Conformations of *n*-Butane After Every 60 Degree Rotation.
Mnemonics: Fish-Giraffe-Elephant-Ant-EagleGoat
Interpretation: Fully eclipsed-Gauche-Eclipsed-Anti-EclipsedGauche
Concept: Conformations of Cyclohexane As Per Stability And Energy
Mnemonics: Cat Twigs But Horse-Clubs
Interpretation: Chair>Twist-boat>Boat>Half- Chair

🔑 Key Terms

► **Cycloalkanes:** Cyclic hydrocarbons having molecular formula C_nH_{2n}. These are isomeric with alkenes.
► **Cracking:** The process of breaking down less volatile higher molecular mass hydrocarbons from petroleum into different types of more volatile lower molecular mass hydrocarbons by heating in the presence of catalyst.
► **Reforming:** Cyclization followed by aromatization (or dehydrogenation of 6-8 C alkanes on heating to 773 K in the presence of Pt catalyst (e.g., *n*-heptane ® methyl cyclohexane ® toluene).
► **Knocking:** A sharp metallic rattling sound produced in an internal combustion engine.
► **Octane Number:** A scale for determining knocking quality in petrol. *n*-Heptane with very high knocking has octane number 0 while iso-octane has maximum value 100.

► **Cetane Number:** A scale for determining knocking quality of a diesel fuel. Cetane number of *n*-hexadecane (cetane) is 100 and that of a-methylnapthalene is zero.
► **Conformation isomerism:** the different arrangements of atoms in space that results from free rotation of groups about the carbon-carbon bond axes is known as conformation for rotational isomers and the phenomena is known as conformational or rotational isomerism

🔑 Key Facts

► Iodination is a reversible reaction. So it is carried out by heating alkane in the presence of oxidising agent like iodic acid (HIO_3) or nitric acid (HNO_3) or mercuric oxide (HgO) which oxidises HI formed during the reaction.

$$CH_4 + I_2 \rightleftharpoons CH_3I + HI \quad HIO_3$$
$$+ 5HI \longrightarrow ® 3I_2 + 3H_2O$$
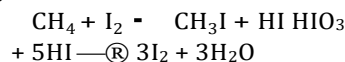
► Fluorination of alkane takes place explosively resulting even in the rupture of C—C bond in higher alkanes.
► Petroleum is an important source of aliphatic hydrocarbons. It is refined in to several useful fractions and is a source of several petrochemicals. Coal tar is a rich source of aromatic hydrocarbons.
► LPG and CNG are petroleum products used as energy source in automobile industry and domestic fuel. Natural gas contains about 90% CH_4.

Topic-2 Unsaturated Hydrocarbons (Alkenes and Alkynes)

💬 Revision Notes

► **Alkenes:** These are unsaturated non-cyclic hydrocarbons containing at least one double bond and have sp^2-hybridisation with 120° bond angle. Alkenes are also called olefins [oil forming] which indicates their high reactive nature. Alkenes have general formula C_nH_{2n}, where *n* = 2,3,4 ...
Example- C_2H_4 (ethene), C_3H_6 (propene), etc.
► **Structure of Double Bond:** Carbon-carbon double bond in alkenes consists of one strong sigma (s) bond (bond enthalpy about 397 kJ mol^{-1}) due to head-on overlapping of sp^2 hybridised orbitals and one weak pi (p) bond
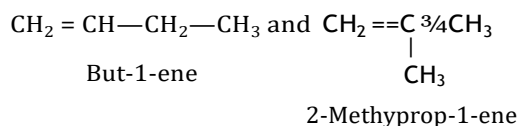
(bond enthalpy about 284 kJ mol⁻¹) obtained by lateral or sideways overlapping of the two 2p orbitals of the two carbon atoms. The double bond is shorter in bond length (134 pm) than the C–C single bond (154 pm).
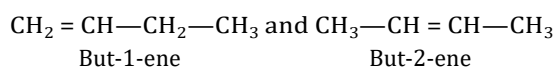
► **Nomenclature:**

    (i)   The longest chain of carbon atoms containing the double bond is selected.

    (ii)   Numbering of the chain is done from the end which is nearer to the double bond.

    (iii) The suffix 'ene' replaces 'ane' of alkanes.

► **Isomerism:** Alkenes show chain, position and geometrical isomerism.

Chain isomers have different chains of carbon atoms, e.g.,

$$CH_2 = CH—CH_2—CH_3 \text{ and } CH_2 ==C ¾CH_3$$
$$| $$

             But-1-ene CH_3

                                    2-Methyprop-1-ene

Position isomers differ in the position of double bonds.

$$CH_2 = CH—CH_2—CH_3 \text{ and } CH_3—CH = CH—CH_3$$

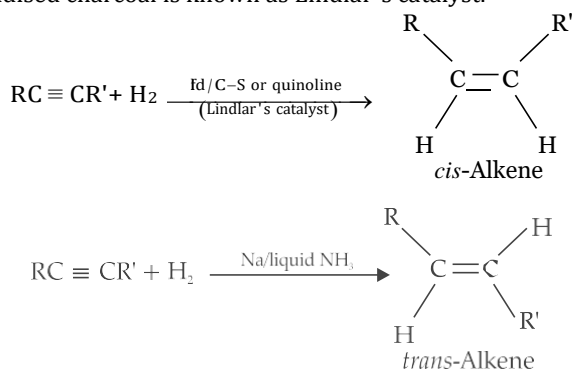   But-1-ene   But-2-ene

The stereoisomerism is exhibited by alkenes due to difference in the spatial arrangement of groups around double bonded carbon atoms. The simplest alkene that can exhibit geometrical isomerism is but-2-ene. Cis form of alkene is more polar than the trans form.


             cis-But-2-ene   *trans*-But-2-ene
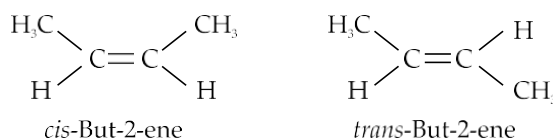
The boiling point of *cis*-form is more than the *trans*-form due to high polarity of *cis*-form. However, melting point of trans-form is more than that the *cis*-form.

► **Preparation of Alkenes:**

  (i) **From alkynes:** Alkynes on partial reduction with calculated amount of dihydrogen in the presence of palladised charcoal partially deactivated with poisons like sulphur compounds or quinoline give alkenes. Partially deactivated palladised charcoal is known as Lindlar's catalyst.

$$RC \equiv CR' + H_2 \xrightarrow[\text{(Lindlar's catalyst)}]{\text{Pd/C–S or quinoline}}$$

                                                             cis-Alkene

$$RC \equiv CR' + H_2 \xrightarrow{\text{Na/liquid NH}_3}$$

                                                            trans-Alkene

  (ii) **From alkyl halides:** Alkyl halides (R-X) on heating with alcoholic potash (potassium hydroxide dissolved in alcohol) eliminate one molecule of halogen acid to form alkenes. This reaction is known as dehydrohalogenation, i.e., removal of halogen acid. This is example of b-elimination reaction, since hydrogen atom is eliminated from the b carbon atom.



                  (X = Cl, Br, I)
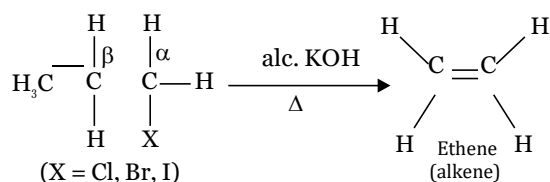
       The rate of the reaction:

   **For halogens:** Iodine > Bromine > Chlorine

       For alkyl group: Tertiary > Secondary > Primary

(iii) From vicinal dihalides: Dihalides in which two halogen atoms are attached to two adjacent carbon atoms are known as vicinal dihalides. Vicinal dihalides on treatment with zinc metal lose a molecule of ZnX_2 to form an alkene. The reaction is known as dehalogenation.

$$CH_3CHBr—CH_2Br + Zn ® CH_3CH = CH_2 + ZnBr_2$$
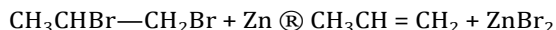
(iv) From Alcohols: Alcohols on heating with concentrated sulphuric acid form alkenes with the elimination of one water molecule. This reaction is known as acidic dehydration of alcohols.
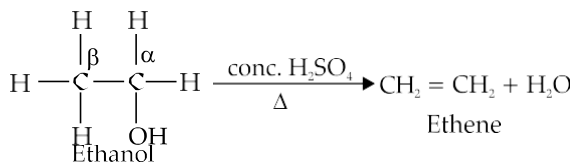

- ► **Physical Properties:** Alkenes as a class resembles alkanes in physical properties, except in types of isomerism and difference in polar nature. Ethene is a colourless gas with a faint sweet smell. All other alkenes are colourless and odourless, insoluble in water but fairly soluble in nonpolar solvents like benzene, petroleum, ether. Alkenes show a regular increase in boiling point with increase in size.
- ► **Chemical Properties:** Alkenes undergo electrophilic addition reaction because of loosely held p-electrons.

(i) Addition of dihydrogen:

$$H_2C = CH_2 \xrightarrow[Ni/flt/fld]{H_2} H_3C—CH_3$$
$$\text{Ethene} \qquad\qquad \text{Ethane}$$
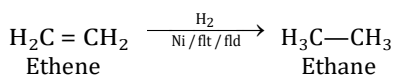
(ii) Addition of halogen: This reaction is used for the test of unsaturation.
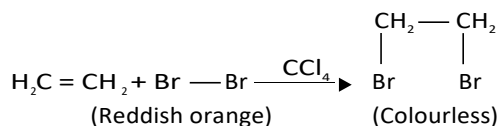
(iii) Addition of hydrogen halides: The order of reactivity of the hydrogen halide is HI > HBr > HCl.

**(a)** $CH_2 = CH_2 + HBr ® CH_3—CH_2—Br$
(symmetrical alkene)
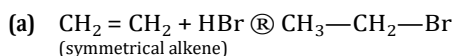
(b) However, addition of hydrogen halide to an unsymmetrical alkene takes place according to Markovnikov's rule. This rule states that, "the negative part of the addendum (adding molecule) gets attached to that carbon atom which possesses lesser number of hydrogen atoms". e.g.,
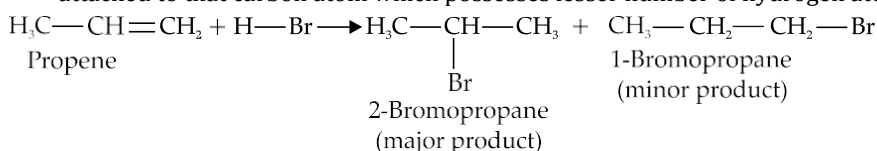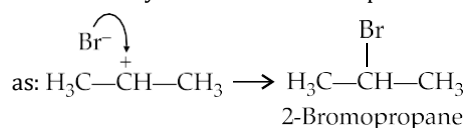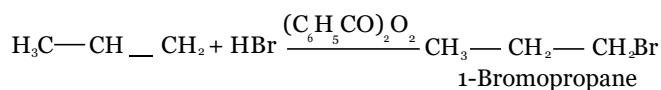

Mechanism:
Hydrogen bromide provides an electrophile, H$^+$, which attacks the double bond to form carbocation as:
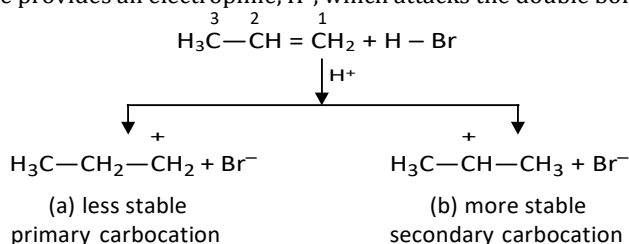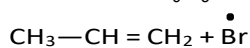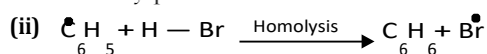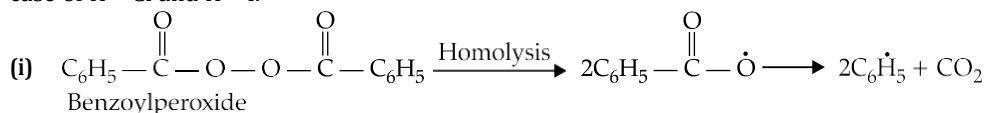

- **(i)** The secondary carbocation is more stable than the primary carbocation, therefore, the former predominates because it is formed at a faster rate.
- **(ii)** The secondary carbocation is attacked by Br⁻ ion to form the product.
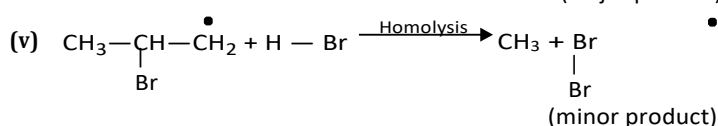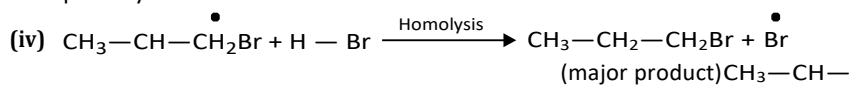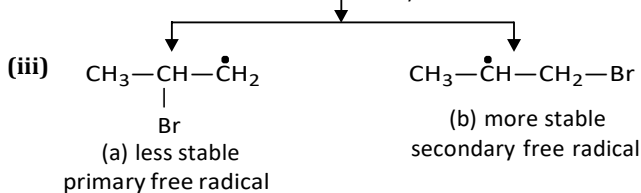

Peroxide effect or Kharash effect or Anti-Markovnikov addition: In the presence of peroxide, addition of HBr to unsymmetrical alkene takes place contrary to Markovnikov rule. This reaction is known as peroxide or Kharash effect or anti-Markovnikov addition. e.g.,
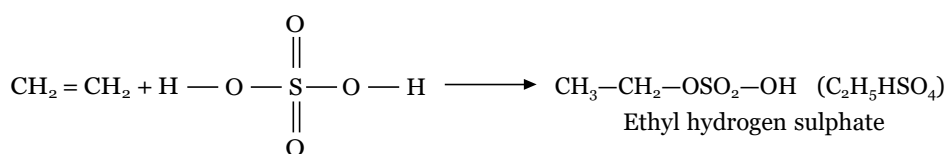
$$H_3C-CH \underline{\quad} CH_2 + HBr \xrightarrow{(C_6H_5CO)_2O_2} CH_3-CH_2-CH_2Br$$
$$\text{1-Bromopropane}$$

This reaction proceeds by free radical mechanism. Peroxide effect is observed only in case of HBr and not in case of H—Cl and H—I.

(i)
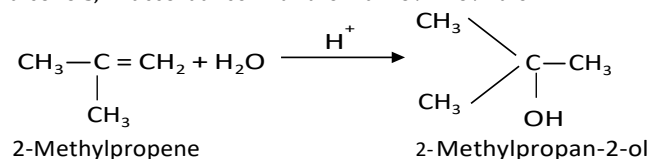$$C_6H_5-\overset{O}{\overset{\|}{C}}-O-O-\overset{O}{\overset{\|}{C}}-C_6H_5 \xrightarrow{\text{Homolysis}} 2C_6H_5-\overset{O}{\overset{\|}{C}}-\overset{\bullet}{O} \longrightarrow 2C_6\overset{\bullet}{H}_5 + CO_2$$
Benzoylperoxide

(ii)
$$\overset{\bullet}{C}H_{6\,5} + H-Br \xrightarrow{\text{Homolysis}} C_{6}H_{6} + \overset{\bullet}{Br}$$

$$CH_3-CH=CH_2 + \overset{\bullet}{Br}$$
$$\downarrow \text{Homolysis}$$

(iii)
$$\underset{\substack{| \\ Br}}{CH_3-CH-\overset{\bullet}{C}H_2} \qquad\qquad CH_3-\overset{\bullet}{C}H-CH_2-Br$$
(a) less stable   (b) more stable
primary free radical   secondary free radical

(iv)
$$CH_3-\overset{\bullet}{CH}-CH_2Br + H-Br \xrightarrow{\text{Homolysis}} CH_3-CH_2-CH_2Br + \overset{\bullet}{Br}$$
$$\text{(major product)} CH_3-\overset{\bullet}{CH}-$$

(v)
$$\underset{\substack{| \\ Br}}{CH_3-CH-\overset{\bullet}{C}H_2} + H-Br \xrightarrow{\text{Homolysis}} CH_3 + \underset{\substack{| \\ Br}}{Br}$$
(minor product)

(iv) Addition of sulphuric acid:

$$CH_2=CH_2 + H-O-\overset{O}{\underset{O}{\overset{\|}{\underset{\|}{S}}}}-O-H \longrightarrow CH_3-CH_2-OSO_2-OH \quad (C_2H_5HSO_4)$$
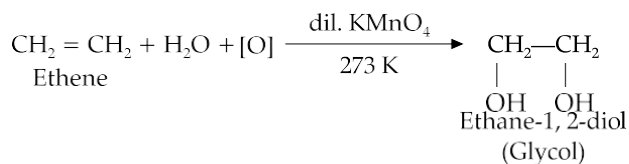$$\text{Ethyl hydrogen sulphate}$$

(v) Addition of water: In presence of few drops of concentrated sulphuric acid alkenes react with water to form alcohols, in accordance with the Markovnikov rule.

$$\underset{\substack{| \\ CH_3}}{CH_3-C=CH_2} + H_2O \xrightarrow{H^+} \underset{CH_3}{\overset{CH_3}{>}}\underset{\substack{| \\ OH}}{C-CH_3}$$
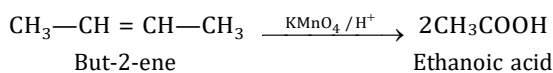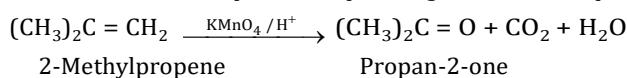2-Methylpropene   2-Methylpropan-2-ol
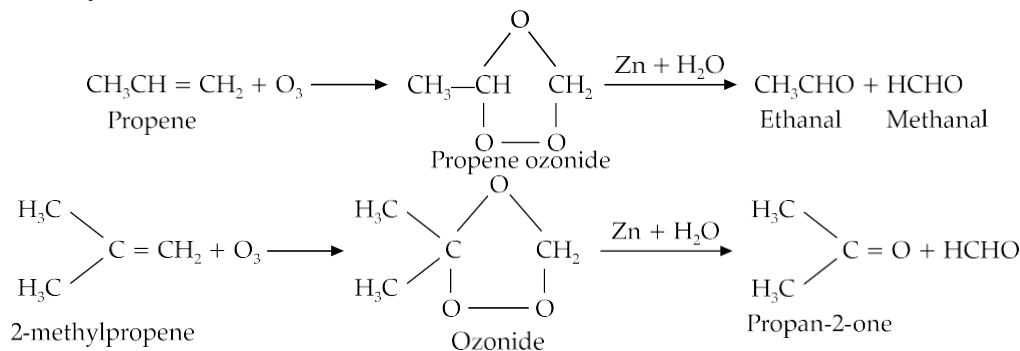
(vi) Oxidation:

(a) Oxidation with cold dilute, aqueous solution of potassium permanganate (Baeyer's reagent). This reaction is used as a test for unsaturation as it decolourises KMnO₄ solution.

$$CH_2=CH_2 + H_2O + [O] \xrightarrow[273\ K]{\text{dil. KMnO}_4} \underset{\substack{| \quad | \\ OH \quad OH}}{CH_2-CH_2}$$
Ethene   Ethane-1, 2-diol
(Glycol)

(b) Oxidation with acidic potassium permanganate or acidic potassium dichromate to ketones and/or acids.

$$(CH_3)_2C=CH_2 \xrightarrow{KMnO_4/H^+} (CH_3)_2C=O + CO_2 + H_2O$$
2-Methylpropene   Propan-2-one

$$CH_3-CH=CH-CH_3 \xrightarrow{KMnO_4/H^+} 2CH_3COOH$$
But-2-ene   Ethanoic acid

(vii) Ozonolysis:

$$CH_3CH = CH_2 + O_3 \longrightarrow \underset{\text{Propene ozonide}}{CH_3-\overset{\displaystyle O}{\underset{\displaystyle O-O}{\overset{/ \backslash}{CH}}} \quad CH_2} \xrightarrow{Zn + H_2O} \underset{\text{Ethanal} \quad \text{Methanal}}{CH_3CHO + HCHO}$$

$$\underset{\text{2-methylpropene}}{\overset{H_3C}{\underset{H_3C}{>}}C = CH_2 + O_3} \longrightarrow \underset{\text{Ozonide}}{\overset{H_3C}{\underset{H_3C}{>}}\overset{\displaystyle O}{\underset{\displaystyle O-O}{\overset{/ \backslash}{C}}} \quad CH_2} \xrightarrow{Zn + H_2O} \underset{\text{Propan-2-one}}{\overset{H_3C}{\underset{H_3C}{>}}C = O + HCHO}$$

(viii) Polymerisation: Polythene is obtained by the combination of large number of ethene molecules at high temperature, high pressure and in the presence of a catalyst. The large molecules thus obtained are called polymers. This reaction is known as polymerisation. The simple compounds from which polymers are made are called monomers.
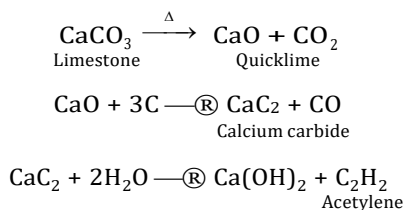
$$n(CH_2CH = CH_2) \xrightarrow[\text{Catalyst}]{\text{High Temp. (Pressure)}} \underset{\text{Polythene}}{-(-CH_2-CH_2-)_n-}$$
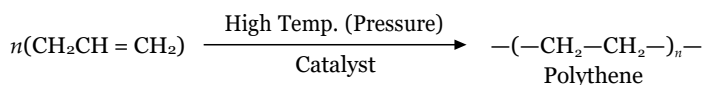
► **Alkynes:** Alkynes are unsaturated hydrocarbons that contain at least one carbon-carbon triple bond. General formula of alkyne is C_nH_{2n-2} e.g., C_2H_2 (ethyne), C_2H_4 (propyne). The first and the most important member of this series of hydrocarbons is ethyne, C_2H_2 and hence they are also called the acetylene.
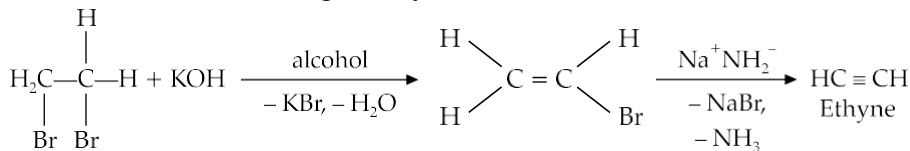
► **Structure:** In ethyne, the carbon atoms are *sp* hybridised. Carbon-carbon sigma (s) bond is obtained by the head on overlapping of the two *sp* hybridised orbitals of the two carbon atoms. The remaining *sp* hybridised orbital of each carbon atom undergoes overlapping along the internuclear axis with 1*s* orbital of each of the two hydrogen atoms forming two C–H sigma bonds. H–C–C bond angle is of 180°. Ethyne H—C º C—H is a linear molecule.

► **Preparation of alkynes:**

   (i) From calcium carbide: Ethyne is prepared by treating calcium carbide with water. Calcium carbide is prepared as follows:

$$\underset{\text{Limestone}}{CaCO_3} \xrightarrow{\Delta} \underset{\text{Quicklime}}{CaO + CO_2}$$

$$CaO + 3C \longrightarrow \underset{\text{Calcium carbide}}{CaC_2 + CO}$$

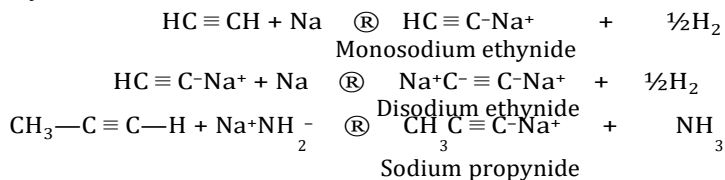$$CaC_2 + 2H_2O \longrightarrow \underset{\text{Acetylene}}{Ca(OH)_2 + C_2H_2}$$

   (ii) From vicinal dihalides: When vicinal dihalides react with alcoholic potassium hydroxide then they undergo dehydrohalogenation. One molecule of hydrogen halide is eliminated to form alkenyl halide which on treatment with sodamide gives alkyne.

$$\underset{\underset{Br \;\; Br}{|\;\;\;|}}{H_2C-\overset{\overset{H}{|}}{C}-H} + KOH \xrightarrow[-KBr, -H_2O]{\text{alcohol}} \underset{H}{\overset{H}{>}}C = C\underset{Br}{\overset{H}{<}} \xrightarrow[\substack{-NaBr, \\ -NH_3}]{Na^+NH_2^-} \underset{\text{Ethyne}}{HC \equiv CH}$$

► **Physical Properties:** Physical properties of alkynes follow the same trend of alkenes and alkanes. First three members are gases, the next eight are liquids and higher ones are solids. All alkynes are colourless. Ethyene has characteristic odour. Other members are odourless. They are weakly polar in nature. Alkynes are insoluble in water but soluble in organic solvents like ethers, carbon tetrachloride and benzene. Melting point, boiling point and density increase with increase in molar mass.
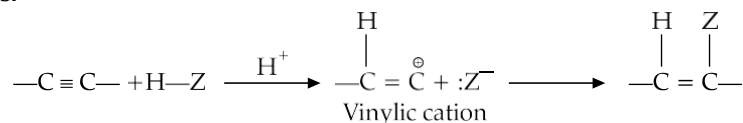
► **Chemical Properties:** Alkynes show electrophilic as well as nucleophilic addition reactions.

   (i) Acidic character of alkyne:

$$HC \equiv CH + Na \quad ® \quad \underset{\text{Monosodium ethynide}}{HC \equiv C^-Na^+} \quad + \quad \tfrac{1}{2}H_2$$

$$HC \equiv C^-Na^+ + Na \quad ® \quad \underset{\text{Disodium ethynide}}{Na^+C^- \equiv C^-Na^+} \quad + \quad \tfrac{1}{2}H_2$$

$$CH_3-C \equiv C-H + Na^+NH_2^- \quad ® \quad \underset{\text{Sodium propynide}}{CH_3C \equiv C^-Na^+} \quad + \quad NH_3$$
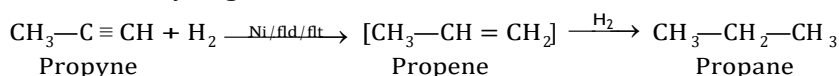
This reaction can be used for the distinction among alkynes, alkenes and alkanes and even for distinguishing terminal alkynes from non-terminal alkynes as only terminal alkynes undergo this reaction.
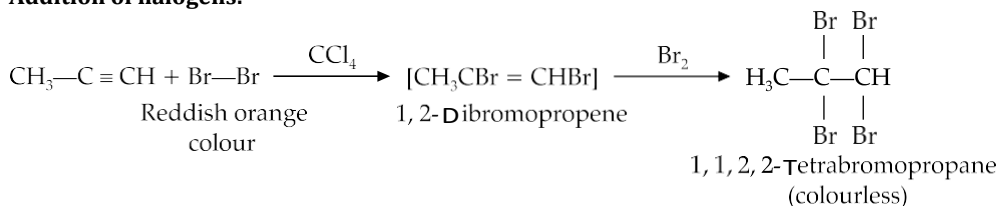
(ii) Addition reactions:

$$-C \equiv C- + H-Z \xrightarrow{H^+} \underset{\text{Vinylic cation}}{-\overset{\overset{H}{|}}{C} = \overset{\oplus}{C} + :Z^-} \longrightarrow -\overset{\overset{H}{|}}{C} = \overset{\overset{Z}{|}}{C}-$$

Alkynes undergo electrophilic addition reaction and addition to unsymmetrical alkynes takes place according to Markovnikov's rule. The addition product formed depends upon the stability of vinylic cation.

(a) Addition of dihydrogen:

$$\underset{\text{Propyne}}{CH_3-C \equiv CH} + H_2 \xrightarrow{Ni/fld/flt} \underset{\text{Propene}}{[CH_3-CH = CH_2]} \xrightarrow{H_2} \underset{\text{Propane}}{CH_3-CH_2-CH_3}$$

(b) Addition of halogens:

$$\underset{\substack{\text{Reddish orange} \\ \text{colour}}}{CH_3-C \equiv CH + Br-Br} \xrightarrow{CCl_4} \underset{\text{1, 2-Dibromopropene}}{[CH_3CBr = CHBr]} \xrightarrow{Br_2} \underset{\substack{\text{1, 1, 2, 2-Tetrabromopropane} \\ \text{(colourless)}}}{H_3C-\overset{\overset{Br}{|}}{\underset{\underset{Br}{|}}{C}}-\overset{\overset{Br}{|}}{\underset{\underset{Br}{|}}{CH}}}$$

This reaction is used as a test of unsaturation as reddish orange colour of solution of bromine in CCl₄ is decolourised.

(c) Addition of hydrogen halides:

$$H-C \equiv C-H + H-Br \longrightarrow \underset{\text{Bromoethene}}{[CH_2 = CH-Br]} \longrightarrow \underset{\text{1, 1-Dibromoethane}}{\overset{CHBr_2}{\underset{CH_3}{|}}}$$

(d) Addition of water:

$$\underset{\text{Ethyne}}{HC \equiv CH} + H-OH \xrightarrow[333\,K]{Hg^{2+}/H^+} \overset{CH_2 = C-H}{\underset{OH}{|}} \xrightarrow{\text{isomerisation}} \underset{\text{Ethanal}}{\overset{CH_3 - C-H}{\underset{O}{\|}}}$$

$$\underset{\text{Propyne}}{CH_3-C \equiv CH} + H-OH \xrightarrow[333\,K]{Hg^{2+}/H^+} \overset{CH_3-C = CH_2}{\underset{O-H}{|}} \xrightarrow{\text{isomerisation}} \underset{\text{Propanone}}{CH_3 - \overset{\|}{\underset{O}{C}}-CH_3}$$
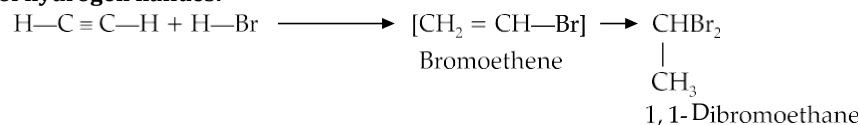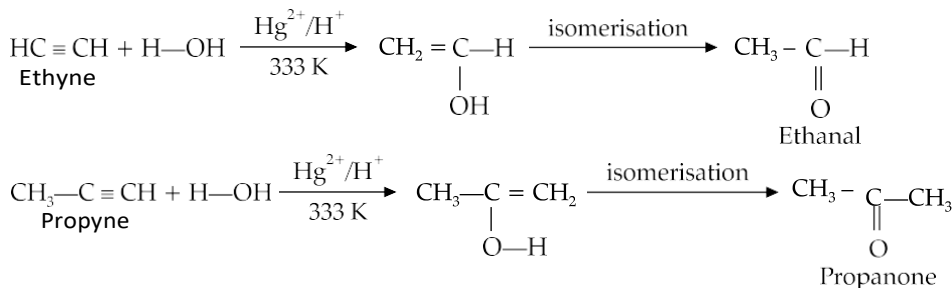
(e) Polymerization:

(1) Linear polymerization: Under suitable conditions, linear polymerisation of ethyne takes place to produce polyacetylene or polyethyne which is a high molecular weight polyene containing repeating units of (CH = CH – CH = CH) and can be represented as —(CH = CH – CH = CH)$_n$—
Acetylene ⓡ Polyacetylene

(2) Cyclic polymerization: Ethyne on passing through red hot iron tube at 873K undergoes cyclic polymerization.

Acetylene → Benzene (Red hot iron tube / 873 K)

## Topic-3 Aromatic Hydrocarbons: Benzene

Revision Notes

► These hydrocarbons are also known as 'arenes'. Most of the aromatic hydrocarbons were found to contain benzene ring. Aromatic compounds containing benzene ring are known as benzenoids and those not containing a benzene ring are known as non-benzenoids.

► Benzene molecule is a planar or flat molecule in which all the carbon atoms are sp^2 hybridised. It has hexagonal ring of six carbon atoms with three double bonds at alternate positions. It is resonance stabilised and the structure may be represented as given below.

(A) (B) (C)
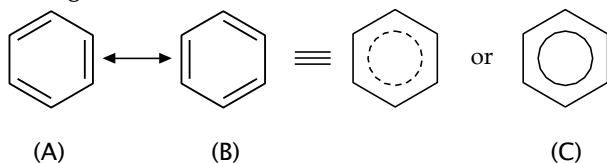
► **Isomerism:** When two hydrogen atoms in benzene are replaced by two similar or different monovalent atoms or groups, three different position isomers are possible. The 1, 2 or 1, 6 is known as the *ortho* (*o*–), the 1, 3 or 1, 5 as *meta* (*m*–) and the 1, 4 as *para* (*p*–) disubstituted compounds.

► **Structure of Benzene:** August Kekule in 1865 proposed benzene having cyclic arrangement of six carbon atoms with alternate single and double bonds and one hydrogen atom attached to each carbon atom.
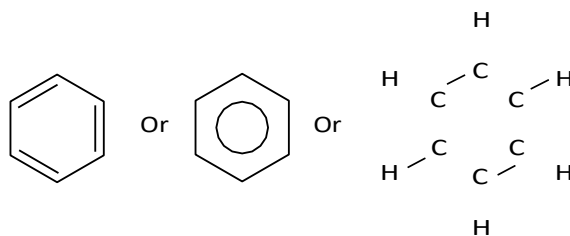
► **Aromaticity:** It is a property of the sp^2 hybridised planar rings in which the *p* orbitals allow cyclic delocalization of p electrons. Aromatic compounds have specific electronic structure in accordance with Huckel rule. The rule states that all planar cyclic conjugated polyenes containing (4n + 2)p electrons where *n* = 0, 1, 2, ... are aromatic in nature.

(i) **Aromatic:** They are cyclic, planar molecule where complete delocalisation of p electron takes place.

Huckle's rule (4*n* + 2) p electrons

(ii) **Anti aromatic:** They are cyclic planar molecule which follows 4*n*p electrons.

(iii) **Non aromatic:** These are cyclic, non planar where no delocalisation of p electron takes place.
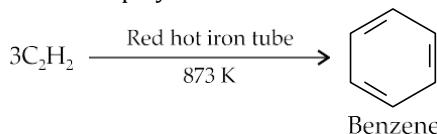
They may or may not follow Huckel's rule.

► **Preparation of benzene:**

(i) Cyclic polymerisation of ethyne: Ethyne on passing through red hot iron tube at 873 K undergoes cyclic polymerisation. Three molecules polymerise to form benzene.

$$3C_2H_2 \xrightarrow[873\ K]{\text{Red hot iron tube}} \text{Benzene}$$

(ii) Decarboxylation of Aromatic acids: Sodium salt of benzoic acid on heating with sodalime gives benzene.

COONa + NaOH $\xrightarrow[\Delta]{CaO}$ ⬡ + Na_2CO_3
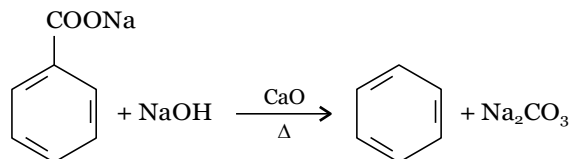
(iii) Reduction of Phenol: Phenol is reduced to benzene by passing its vapours over heated zinc dust.

OH + Zn $\xrightarrow{\Delta}$ ⬡ + ZnO
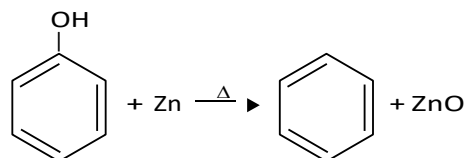
► **Physical Properties:** Aromatic hydrocarbons are non-polar molecules and are usually colourless liquids or solids with a characteristic aroma.

Benzene itself is a good solvent for many organic and inorganic substances, e.g., fat, resins, sulphur and iodine. It burns with a luminous, sooty flame in contrast to alkanes and alkenes which usually burn with a bluish flame.

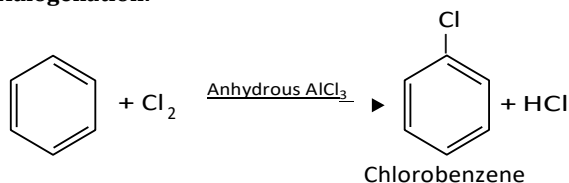► **Chemical Properties:** Benzene undergoes following types of chemical reactions:

(a) Electrophilic Substitution Reaction
(b) Addition Reaction

Electrophilic Substitution Reactions: Aromatic hydrocarbons undergo electrophilic substitution reactions, e.g., nitration, halogenation, sulphonation and Friedel-Craft alkylation/acylation.
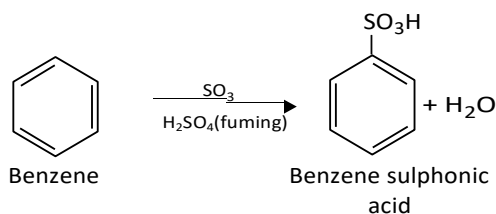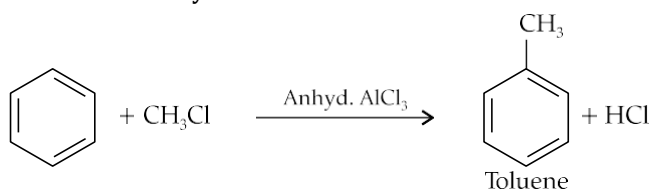
(i) Nitration:

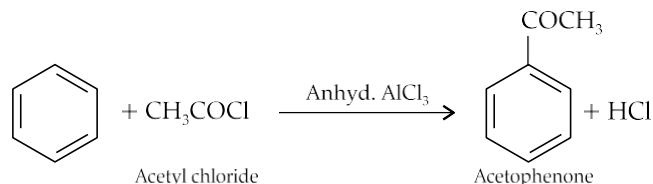⬡ + Conc. HNO_3 + conc. H_2SO_4 (nitrating mixture) $\xrightarrow{\text{323-333 K}}$ NO_2 Nitrobenzene + H_2O

(ii) Halogenation:

⬡ + Cl_2 $\xrightarrow{\text{Anhydrous AlCl}_3}$ Cl Chlorobenzene + HCl

(iii) Sulphonation:

Benzene $\xrightarrow[\text{H}_2\text{SO}_4\text{(fuming)}]{SO_3}$ SO_3H Benzene sulphonic acid + H_2O
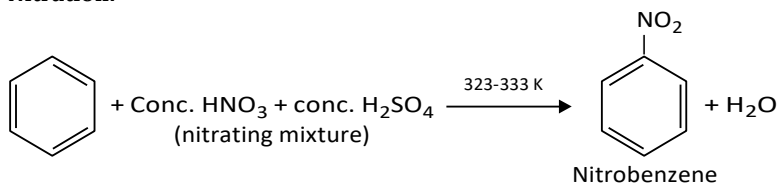
(iv) Friedel-Crafts alkylation reaction:

⬡ + CH_3Cl $\xrightarrow{\text{Anhyd. AlCl}_3}$ CH_3 Toluene + HCl

(v) Friedel-Craft's acylation reaction:
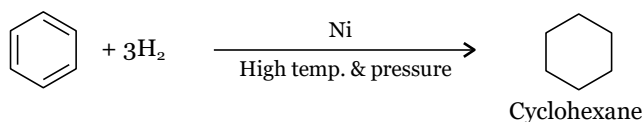

Benzene on treatment with excess of chlorine in the presence of anhydrous $AlCl_3$ can be chlorinated to hexachlorobenzene (C_6Cl_6)
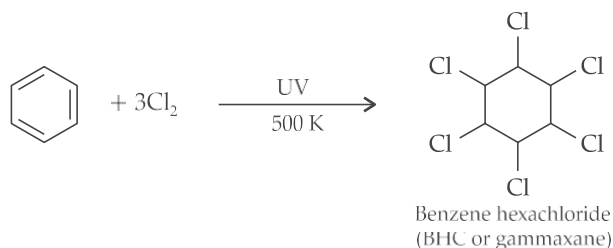

Hexachlorobenzene
(C_6Cl_6)
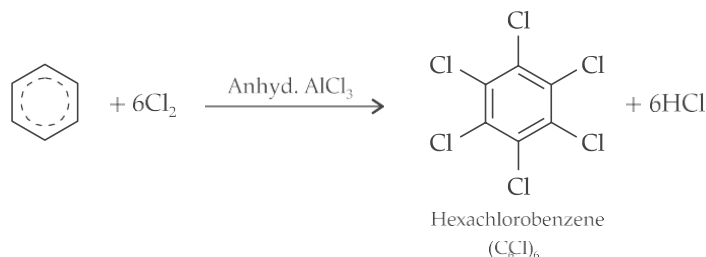
Addition reactions:

(a) Under vigorous conditions i.e. at high temperature and/or pressure in presence of nickel catalyst, hydrogenation of benzene gives cyclohexane.

Cyclohexane

(b) Under UV light, three chlorine molecules add to benzene to produce benzene hexachloride, $C_6H_6Cl_6$.

Benzene hexachloride
(BHC or gammaxane)

Combustion—When heated in air, benzene burns with sooty flame:

$$C_6H_6 + \frac{15}{2}\ O_2 \circledR 6CO_2 + 3H_2O$$
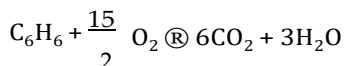
➤ The presence of substituent groups in aromatic ring activates/deactivates electrophilic substitution and also directs the orientation of incoming groups. Electron donating substituents facilitate further substitution with incoming groups at *o*- and *p*-positions while electron attracting groups deactivate the ring with substitution at *m*-position.

– CH₃, – OH, – OR, – NH₂, – NHR, – NR₂ are electron donating (or activating groups) while – NO₂, – CN, – CHO, – COOH, – SO₃H are electron withdrawing (or deactivating groups). Halogens (– Cl, – Br, – I) are *o*-, *p*-directing but moderately deactivating (due to strong – I effect).

Mnemonics

Concept: PHMTOM
Mnemonics: Please Help Me,TOM
Interpretation: Para have High M.p. Than Ortho and Meta

Mnemonics

1. Concept: m-directing Group
Mnemonics: Queen Elizabeth Second's Navy Commands, Controls
Interpretation: Quarternary amino ($-NR^{3+}$) Ester (–COOR)
Sulphonic acid ($-SO_3H$)
Nitro ($-NO_2$)
Carbonyl (–CHO)
Carboxyl (–COOH)
Cyano (–CN)
2. Concept: o, p–directing
Mnemonics: AHA AHA P
Interpretation:
Alkyl   (–R)
Halogen (–X)

Halogen (–X)

Alkoxyl (–OR)

Amino ($-NH_2$, NHR, NR_2)

Hydroxyl (–OH)

Amide ($-CONH_2$)

Phenyl (C_6H_5)

► Polynuclear aromatic hydrocarbons (PAHs) have a number of condensed benzene rings and are suspected carcinogens (toxic and they are having cancer producing property). They are actually formed due to incomplete combustion of some organic materials like tobacco, coal, petroleum, etc. For example : 1, 2-Benzanthracene, 1, 2-Benzpyrene, etc.

Key Term

► **Aromaticity:** It is a property of conjugated cycloalkenes in which the stabilization of the molecule is enhanced due to the ability of the electrons in the p orbitals to delocalize. This acts as a framework to create a planar molecule.

Key Facts

► Originally fragrant substances were called aromatic compounds.

► In the laboratory, benzene was first prepared by heating benzoic acid or phthalic acid with calcium oxide.

► Most of the benzene is produced from petroleum.

► Compounds having atoms other than carbon in a ring system, which satisfies the conditions of aromaticity are called heteroaromatics.

► Those who follow neither Huckle's rule, i.e., ($4n + 2$) p nor $4n$p electrons are non aromatic.

❑❑