Chapter 1

Some Basic Concepts of Chemistry

Topic 1

General Introduction, Laws of Chemical Combination, Dalton's Atomic Theory, Atomic and Molecular Masses

» Revision Notes

- Chemistry is defined as the branch of science which deals with the study of composition, structure and properties of matter.
- Chemistry is related with all the fields of our life, *e.g.,* food, fuels, textiles, dyes, drugs, disinfectants, perfumes, building materials, paints, inks, fertilizers, insecticide, pesticide, soap, detergents, etc.
- **Matter :** Matter is anything that has mass and occupies space. For example, book, pen, pencil, water, air, all living beings etc. are composed of matter.
- **Accuracy – Freedom from mistake or error :** The quality or state of being accurate or the ability to work or perform without making mistakes.

  Accuracy = Mean value – True Value
- **Precision :** The quality, condition, or fact of being exact and accurate or the closeness of the set of values obtained from identical measurements of quantity.

  Precision = Individual Value – Arithmetic Mean Value
- **Significant Figures :** The digits in a properly recorded measurement or the total number of figures in a number including the last digit whose value is uncertain are called significant figures, *e.g.,* 180.00 has five significant figures, .018 has significant figures.
- **Laws of Chemical Combination :** 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 Compositions :** A given compound always contains exactly the same proportion of elements by weight.
  - **(iii) Law of Multiple Proportions :** If two elements can combine 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 gases are at same temperature and pressure.
  - **(v) Avogadro's Law :** At the same temperature and pressure, equal volumes of gases should contain the equal number of molecules.
- **Dalton Atomic Theory :**
  - All matter consists of tiny indivisible particles called atoms.
  - Atoms are indestructible and unchangeable.
  - All the atoms of a given element have identical properties including identical mass. Atoms of different elements differ in mass.
  - When different elements react to form compounds their atoms combine in simple fixed, whole number ratio.
  - In chemical reactions, atoms are neither created nor destroyed. They are reorganized in a chemical reaction.
- One atomic mass of an element is defined as a mass exactly equal to one-twelfth the mass of C-12 atom.
- **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.

$$\text{Average atomic mass} = f_1M_1 + f_2M_2 + f_3M_3 + \ldots + f_nM_n$$

where, f is the fraction representing the natural abundance of the isotope
and M is the mass number (weight) of the isotope.

- **Molecular mass** of a compound is the sum of atomic masses of all the constituent atoms. It is obtained by multiplying the atomic mass of each element by the number of its atoms and adding them together.

Topic 2

Mole Concept and Percentage Composition

» Revision Notes

- Mole is the amount of a substance that contains as many particles or entities as there are atoms in exactly 12 g (or 0.012 kg) of the ^{12}C isotope.
- One mole of any element has same mass as the atomic weight of the element.
- Avogadro constant is the number of entities present in 1 mole. It is denoted by "N_A" and is equal to 6.0221367×10^{23} atoms/mol.
- Number of moles of a substance $= \dfrac{\text{Mass of substance } (g)}{\text{Mass of 1 mole of substance } (g)}$

$$= \frac{\text{Number of particles}}{6.02 \times 10^{23}}$$

- Number of molecules of a substance $= 6.02 \times 10^{23} \times \dfrac{\text{Volume of gas at NTP (in litres)}}{22.4}$
- The mass of one mole of a substance in grams is called its molar mass.
- Mass percentage $= \dfrac{\text{Mass of that element in} \times 100 \text{ the compound}}{\text{Molar mass of the compound}}$

Topic 3

Empirical and Molecular Formulae, Chemical Equations, Stoichiometry

» Revision Notes

- **Empirical Formula :** A formula that gives the simplest whole number ratio of various atoms present in a compound.
- **Molecular formula :** It is a formula that shows the exact number of atoms of different elements present in a molecule of a compound.
- Steps for calculation of empirical and molecular formula :
  (i) Conversion of mass percent to grams.
  (ii) Convert into number of moles of each element.
  (iii) Divide the mole value obtained above by the smallest number.
  (iv) Write 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.
- Normality, (N) $= \dfrac{\text{Number of gram equivalent of solute}}{\text{Volume of solution } (l)}$

  (Gram equivalent of solute = w_2/equivalent weight)
- Molality and mole fraction do not change with temperature.

- Parts per million $= \dfrac{\text{Number of parts of the component} \times 10^6}{\text{Total no. of parts of all the components of the solution}}$
- Volume percent $= \dfrac{\text{Volume of the component} \times 100}{\text{Total volume of the solution}}$
- **Relation between molarity and molality :**

  Molality (m) $= \dfrac{\text{M} \times 1000}{1000 \times (\text{d} - \text{M}) \times \text{M}_2}$

  where, M- molarity of the solution, M_2 - molar mass of solute, *d*- density of the solution.
- **Chemical equation :** A chemical equation is the symbolic representation of a chemical reaction, *e.g.*,

$$\underbrace{AgNO_3 + NaCl}_{\text{Reactants}} \longrightarrow \underbrace{AgCl + NaNO_2}_{\text{Products}}$$

- **Stoichiometry and Stoichiometric Calculations :**
  - Stoichiometry is the calculation of relative masses of reactants and products involved in chemical reactions.
  - Stoichiometric problems can be solved in just four simple steps :
    - (i) Balance the equation.
    - (ii) Convert units of a given substances to moles.
    - (iii) Using the mole ratio, calculate the moles of substance yielded in the reaction.
    - (iv) Convert moles of wanted substance to desired units.
- **Limiting Reagent :** In a chemical reaction, the reagent which is completely consumed and limits the amount of product formed is called as limiting reagent.
- Ways to express concentration in a solution :

  (1) Mass percent $= \dfrac{\text{Mass of solute}}{\text{Mass of solution}} \times 100$

  (2) Mole fraction : In a binary solution, if a substance 'A' dissolves in substance 'B' and their number of moles are n_A and n_B, respectively, then

$$\text{Mole fraction of A} = \frac{n_A}{n_A + n_B}$$

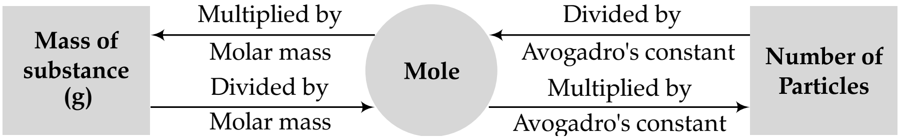
$$\text{Mole fraction of B} = \frac{n_B}{n_A + n_B}$$

  (Mole fraction of A + Mole fraction of B =1)

  (3) Molarity (M) $= \dfrac{\text{Number of moles of solute}}{\text{Volume of solution (litres)}}$

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

- **Mass-Number of moles Relationship :**
  - Number of Moles $= \dfrac{\text{Mass of g}}{\text{Molar mass in g mol}^{-1}}$



- For dilution

$$M_1V_1 = M_2V_2$$

  where, M_1 is initial molarity, V_1 is initial volume, M_2 is final molarity and V_2 is final volume.

❑❑❑

Chapter 2

Structure of Atom

Topic 1

Sub-atomic Particles, Isotopes and Isobars, Bohr's Model, Photoelectric Effect and Atomic Spectra

» Revision Notes

- Atom is the smallest particle that can take part in chemical reaction.
- Dalton's atomic theory states that element is composed of small indivisible particles called atom and atom of different elements combine to form molecules of compound.
- The individual nature of atom was discarded when discovery of sub-atomic particles took place.
- **Sub-Atomic Particles :** An atom consists of three – sub-atomic particles called electron, proton and neutron.
- **Discovery of Electron : Study of Cathode Rays :** During the latter half of the nineteenth century, it was found that the passage of electricity through gases as studied by a number of physicists, particularly by Faraday, Davy, Crookes and J.J. Thomson.

  When a current of high voltage is passed through a gas of air kept at a very low pressure blue rays are seen emerging from the case. These rays are called "Cathode Rays".
- **Characteristics of Cathode Rays :**

  (i) They are produced by the negative electrode, or cathode, in an evacuated tube and travel towards the anode.

  (ii) They travel in straight line, in the absence of electrical or magnetic field.

  (iii) These rays themselves are not visible but their behaviour can be observed with the help of certain materials (fluorescent).

  (iv) They are deflected by electric and magnetic field and behave like negatively charged particles suggesting that they consists of electronic.

  (v) The characteristics of cathode rays do not depend upon the material of electrodes and the nature of gas present in the cathode ray tube.
- Sir J.J. Thomson (1897) who discovered electron) extended the cathode ray experiment for the determination of velocity of electrons and their charge/mass ratio by applying electrical and magnetic field perpendicular to each other as well as to the path of electrons.
- **Charge to Mass Ratio of Electron :** J.J. Thomson measured the charge to mass ratio of electron :

$$\frac{e}{m_e} = 1.758820 \times 10^{11}\ \text{C kg}^{-1}$$

- **Charge on the Electrons :** R.A. Millikan (1868-1958) with the help of his oil drop experiment determined the charge on electrons and it is found to be 1.6×10^{-19} C.
- **Mass of the Electrons :** Mass of electron was determined from the value of charge on electron and charge to mass ratio of electron as follows.

$$m_e = \frac{e}{e/m_e} = \frac{1.6022 \times 10^{-19}\,\text{C}}{1.758820 \times 10^{11}\,\text{C kg}^{-1}} = 9.1094 \times 10^{-31}\ \text{kg}$$

- The mass of electron, 9.11×10^{-28} g. It is nearly 1/1837th of that of hydrogen atom.

- **Discovery of Proton : Study of Anode Rays :** Proton was discovered by Goldstein and is positively charged particle. These rays are termed as positive or canal rays.
- **Characteristics of the Anode Rays :**
  - (i) Travel in straight lines.
  - (ii) They consist of positively charged particles. Their mass is virtually the same as that of the atoms from which they are derived and is found to be equal to the atomic mass of the gas in the discharge tube.
  - (iii) The charge to mass ratio of the particles carry a multiple of the fundamental unit of electrical charge.
  - (iv) They can penetrate thin metal foils and also can produce ionization in gases.
  - (v) They are deflected by electrical and magnetic fields just as the cathode rays but in opposite directions showing that they are oppositely charged, *i.e.*, they carry positive charge.
  - (vi) They are capable of producing physical and chemical changes and also produces mechanical effect.
- The smallest and lightest positive ion was obtained by using hydrogen gas and is called proton.

  The mass of each of this particle,

$$m = \frac{e}{e/m} = \frac{1.6 \times 10^{-19}}{9.58 \times 10^{4}} = 1.67 \times 10^{-27}\ \text{g}$$

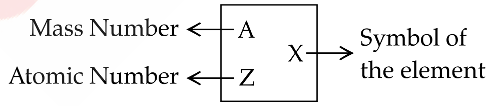
  This mass is nearly the same as that of the hydrogen atom.
- **Discovery of Neutron :** Chadwick proved the neutron theory by studying the beryllium radiation with an ionisation counter and a cloud chamber. It is a neutral particle with mass equal to 1.67493 × 10^{-27} kg. They are present in nucleus.

$${}_4\text{Be}^9 + \underset{\alpha\text{-particle}}{{}_2\text{He}^4} \longrightarrow {}_6\text{C}^{12} + \underset{\text{Neutron}}{{}_0n^1}$$

- **Nuclear model of atom :**
  - **(i) Thomson model :** J.J. Thomson proposed that atom is spherical in shape, in which positive charge is uniformly distributed and electrons are embedded in it.

    Limitations of Thomson Model : It could not explain the result of the scattering experiment performed by Rutherford. It did not have any experimental evidence in its support.
  - **(ii) Rutherford's experiment and model :** In his gold foil experiment, Rutherford bombarded a beam of alpha particles on an ultra-thin gold foil and then detected the scattered alpha particles in zinc sulfide (ZnS) screen. On the basis of his observations, Rutherford proposed that :
    - **(a)** The positive charge and most of the mass of the atom was densely concentrated in extremely small region. This centre of atom is called nucleus which is dense and hard.
    - **(b)** The nucleus is surrounded by electrons that move around the nucleus with a very high speed in circular paths called orbits.
    - **(c)** Electrons and nucleus are held together by electrostatic forces of attraction.

  Drawbacks of Rutherford's Model of an atom : Revolving electrons would lose their energy and finally should fall into nucleus. So, it could not explain the stability of atom. It could not explain the atomic spectra.
- **Atomic Number :** It is equal to number of protons present in the nucleus or number of electrons in a neutral atom and is denoted by Z.
- **Mass Number :** It is equal to total number of nucleons, *i.e.*, protons and neutrons in the nucleus. It is denoted by A.

  i.e., Mass Number of an element = Number of Protons+ Number of Neutrons.
- 

- **Isotopes :** They have same atomic numbers but different atomic mass number.
- Isotopes of an element possess identical chemical properties but differ slightly in physical properties.
- Number of neutrons present in the nuclei of various isotopes of an element is always different.
- **Isobars :** They have same atomic masses but different atomic number, *i.e.*, number of electrons or protons (atomic number) is different but the sum of number of neutrons and protons (mass number) is same.
- Isobars chemical properties are different but as their atomic masses are same so they possess almost identical physical properties.
- **Dual nature of Electromagnetic Radiation :** The light possesses both particle and wave like properties, *i.e.*, light has dual behaviour. Whenever radiation interacts with matter, it displays particle like properties. (Black body radiation and photoelectric effect) Wave like properties are exhibited when it propagates (interference and diffraction).
- **Postulates of Bohr's Atomic Model :** In an atom, the electrons revolve around the nucleus in certain definite

circular paths of definite energy called orbits, or shells. The orbits or energy levels are characterized by an integer 'n', where, n can have values 1, 2, 3 or K, L, M, ...

- **Bohr's atomic model :**

  (a) Energy of electron in n^{th} orbit (E_n)

  $$E_n = \frac{-2\pi^2 m z^2 e^4}{n^2 h^2} = -2.18 \times 10^{-18}\left(\frac{z^2}{n^2}\right) \text{J}$$

  (b) Radius : $r = \frac{n^2h^2}{4\pi^2 mze^2} = \frac{n^2}{z}$ 52.9 pm

  (c) Velocity $= \frac{2\pi ze^2 cm/sec}{nh}$

  (d) Angular momentum of n^{th} orbit, $mvr = \frac{nh}{2\pi}$

  (e) Frequency, $\nu = \frac{u}{2\pi r}$

- **Atomic spectra :** The splitting of light into series of colour bands is known as dispersion and the series of colour bands is called a spectrum.
- **Line spectrum of Hydrogen :** All series of lines in the hydrogen spectrum can be described by Johannes Rydberg Expression :

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

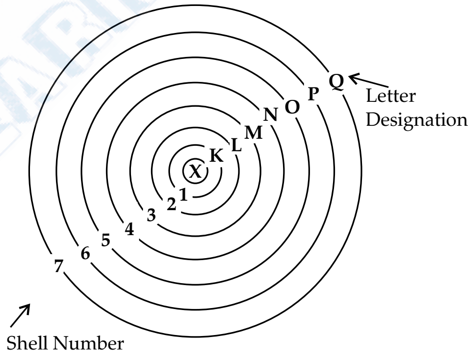
where, $n_1 = 1, 2, ...$ and $n_2 = n_1 + 1, n_2 + 2, ...$

- The spectral lines for Atomic Hydrogen

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

Concept of Shells :

- An electron shell may be thought of as an orbit followed by electrons around an atom's nucleus.



Shell Designation in an atom

- Each shell can contain only a fixed number of electrons, the n shell can hold upto $2n^2$ electrons.
- Each shell consists of one or more subshells, which are denoted by letters s, p, d and f.
- **Electromagnetic radiation :** Light of radiant energy propagates without any medium in the form of waves.
- **Relationship between wavelength, wave number, frequency and velocity :**

  These characteristics are related as,

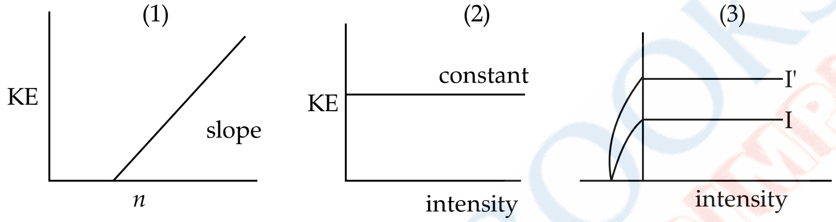
$$c = \lambda \times v \text{ or } v = \frac{c}{\lambda} \text{ and } \frac{1}{\lambda} = \bar{\nu}$$

$$\therefore \quad v = c\,\bar{\nu}$$

- **Particle nature of Electromagnetic Radiation :** Wave nature could not explain black body radiation and photoelectric effect.
- **Black body radiation :** 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. To explain the black body radiation, Planck gave his quantum theory.
- **Concept of quantization :** According to this a body emit radiations in the form of small packets of energy called quantum. Quantum of energy is often called photon.

  $E \propto \nu$; $E = h\nu$ (ν= frequency; h = Planck's constant = 6.63×10^{-34} J sec)
- Photoelectric effect is the ejection of electrons from the metal surface. If frequency of incident radiation is below a certain minimum value (threshold frequency) , no emission takes place.
- From the conservation fo energy principle, the kinetic energy of the ejected electron is given by :
  Total energy of photon = work function + kinetic energy

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



Topic 2

Dual Nature of Matter, de Broglie's Wavelength and Heisenberg’s Uncertainty Principle

» Revision Notes

- **Dual Behaviour of Matter :** French physicist, de Broglie proposed that radiations should also exhibit dual behaviour *i.e.*, both particle and waves like properties.
- **Dual nature of electron :** de-Broglie suggested that electrons should also have momentum as well as wavelength and gave the relation :

  de-Broglie's wavelength : $\lambda = \frac{h}{mv} = \frac{h}{p}$

  where, m is mass of particle, v is velocity, p is momentum

  According to de-Broglie

  “All material particles in motion possess wave characteristics.”
- Heisenberg's Uncertainly Principle states that it is impossible to determine simultaneously the exact position and exact momentum (velocity) of an electron. It is significant only for motion of microscopic objects and is negligible for macroscopic objects.

  Mathematically,

$$\Delta x \times \Delta p_x \geq \frac{h}{4\pi}$$

or

$$\Delta x \times \Delta (mv_x) \geq \frac{h}{4\pi}$$

or

$$\Delta x \times \Delta v_x \geq \frac{h}{4\pi m}$$

- Quantum mechanical model of atom : (Schrodinger concept)

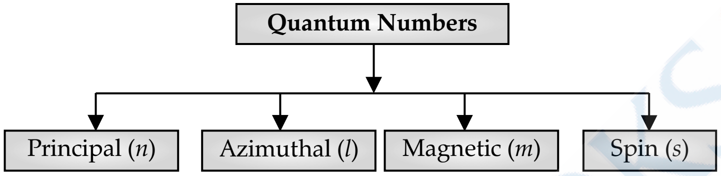
$$\frac{d^2\Psi}{dx^2} + \frac{d^2\Psi}{dy^2} + \frac{d^2\Psi}{dz^2} + \frac{8\pi^2 m}{h^2}(E-V)\psi = 0$$

Topic 3

Concept of Orbital and Rules for Filling Electrons in Orbitals

» Revision Notes

- **Quantum numbers :** There are a set of four quantum numbers which specify the energy, size, shape and orientation of an orbital. To specify an orbital only three quantum numbers are required while to specify an electron all four quantum numbers are required.

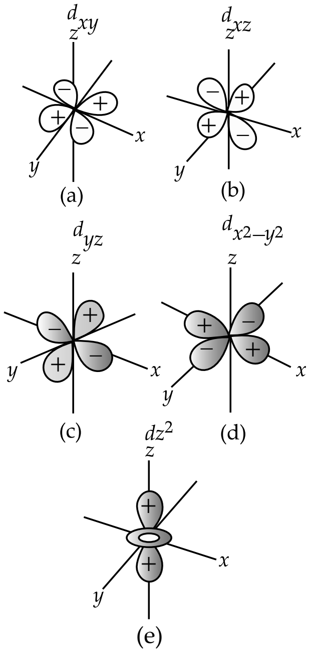


- **Orbitals :** A wave function for an electron in an atom is called an atomic orbital, this atomic orbital describes a region of space in which there is a high probability of finding the electrons.
- **Principal quantum number (*n*) :** It determines the main energy associated with it. It also determines the average distance of the electron from the nucleus in a particular shell. Maximum number of electrons which a shell can accommodate is n^2.
- **Azimuthal or subsidiary or orbital angular quantum number (*l*) :** It determines the angular momentum of the electron. It identifies the subshell and determines the shape of the orbital. For a given value of *n*, *l* can have *n* values ranging from 0 to (*n*–1) where *n* is the principal quantum number. $l = 0, 1, 2, 3, ... (n - 1)$.
- **Magnetic orbital quantum number (m_l) :** This describes the spatial orientation of the orbitals along the three axis co-ordinate for a given value of *l*, the possible values of *m* varies from – *l* to 0 and 0 to +*l*.

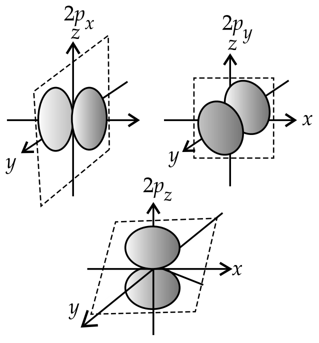
$l = 0$, m = 0		$l = 0(s)$ m = 0	$l = 2(d)$				
$l = 1$ m = –1, 0, + 1		$l = 1(p)$ m= –1, 0, +1	–2	–1	0	+ 1	+2
p_x or p_z	p_y or		d_{x2y2}		d_{z°		d_{xy}
p_y	p_x		d_{xy}	d_{xz}		d_{yz}	$d_{x^2-y^2}$
				d_{yz}		d_{xz}	

- **Electron Spin quantum numbers (m_s) :** This describes the spin orientation of the electron. It is designated by '*s*'. Since the electron can spin in only two ways – clockwise or anticlockwise, therefore, the electron spin quantum number can take only two values, +1/2 or –1/2.
- Boundary surface diagrams of constant probability density for different orbitals give a fairly good representation of the shapes of the orbitals.
- **Shape of orbitals :**

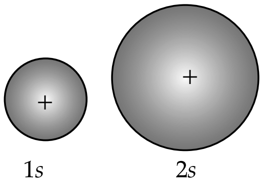
d-orbital



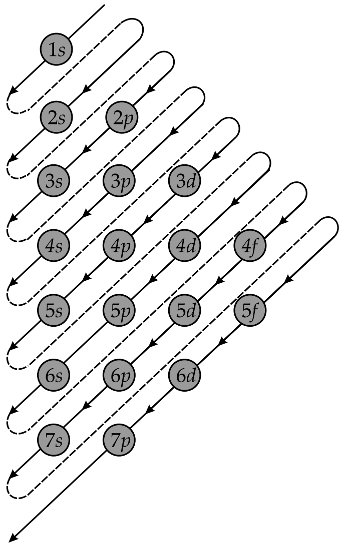
p-orbital



s-orbital



- **Electronic Configuration :** The distribution of electrons into orbitals of an atom is called its electronic configuration.
  - **(a) Aufbau's principle :** In the ground state of the atom, the orbitals are filled in order of their increasing energies.
  - **(b) Pauli's Exclusion principle :** No two electrons can have the same set of four quantum numbers or only two electrons may exist in the same orbital and these electrons must have opposite spin.
  - **(c) Hund's rule of maximum multiplicity :** Electron filling will not take place in orbitals of same energy until all the available orbitals of a subshell contain one electron each with parallel spin.



Orbital	Value of n	Value of l	Value of $(n + l)$	
1*s*	1	0	1 + 0 = 1	2*p* (n = 2)
2*s*	2	0	2 + 0 = 2	has lower
2*p*	2	1	2 + 1 = 3	energy than
3*s*	3	0	3 + 0 = 3	3*s* (n = 3)
3*p*	3	1	3 + 1 = 4	3*p* (n = 3)
				has lower
				energy than
4*s*	4	0	4 + 0 = 4	4*s* (n = 4)
3*d*	3	2	3 + 2 = 5	3*d* (n = 3)
				has lower
				energy than
4*p*	4	1	4 + 1 = 5	4*p* (n = 4)

- **Stability of completely filled and half filled subshells :** Stability of half filled and completely filled orbitals. The half-filled and fully filled orbitals have greater stability than other configurations which is due to :
  - (a) **Symmetry :** The half-filled and fully-filled orbitals are more symmetrical than any other configuration and symmetry leads to greater stability.
  - (b) **Exchange Energy :** The electrons present in the different orbitals of the same sub-shell can exchange their positions. Each such exchange leads to the decrease in energy known as Exchange Energy. Greater the number of exchanges, greater the exchange energy and hence greater the stability.

KNOW THE TERMS

- **Wavelength :** The distance between two successive troughs.
- **Frequency :** It is the number of waves that pass a given point in one second.
- **Wave number :** It is the number per unit wavelengths.
- **Emission Spectrum :** The spectrum of radiation emitted by a substance that has absorbed energy.
- **Absorption Spectrum :** When the white light is first passed through the substance and transmitted light is analysed, we get absorption spectrum. It consists of dark lines separated by bright bands.

❑❑❑

Chapter 3

Classification of Elements and Periodicity in Properties

Topic 1

Modern Periodic Law, Long Form of Periodic Table, Modern Periodic Law, Periodic trends in Atomic Radii and Ionic Radii of Elements

» Revision Notes

- **Need of Classification :** Upto the end of seventeenth century, only 31 elements were known. However, at present 118 elements are known. Therefore, it is not easy to study and remember the properties of these elements. To ease out this problem the scientists arranged the elements in a systematic way on the basis of their similarities in properties in a group. This is known as classification of elements. This arrangement not only rationalize the study of known elements but also help in predicting the new ones for furhter study.

  Such a classification of the elements has resulted in the formulation of the periodic table.

  Periodic table may be defined as :

  The arrangement of the known elements according to their properties in a tabular form.

- **Modern Periodic Law :** The physical and chemical properties of the elements are periodic functions of their atomic numbers. The modern periodic table consists of 18 groups and 7 periods. According to the recommendations of IUPAC, the groups are numbered from 1 to 18 replacing the older notation of groups 0, IA, IIA, ...
  - Elements present in any one group have the same number of valence electrons. Also, the atomic size of the elements increases as we go down the group due to increase in the number of shells.
  - Elements present in any one period, contain the same number of shells. Also, with increase in atomic number by one unit on moving from left to right, the valence shell electron increases by one unit.
  - Each period marks a new electronic shell getting filled.
  - 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 14 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 :

  (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.

First periods contain	2 elements	Shortest period
Second & Third periods contain	8 elements each	Short period
Fourth & Fifth periods contain	18 elements each	Long period
Sixth period contain	32 elements	Longest period
Seventh period	It is incomplete	Incomplete period

(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 d-block elements or transition elements.

(vi) Elements with atomic numbers 58 to 71 (Ce to Lu) occurring after lanthanum (La) are called Lanthanides (or lanthanoids). Elements with atomic numbers 90 to 103 (Th to Lr) are called Actinides (or actinoid). These elements are called *f*-block elements and also as inner-transition elements.

➢ **Defects of long form of the periodic table :**

- **Position of hydrogen :** Hydrogen shows similarities with both metals and non-metals but it is placed with alkali metals in group I.
- **Position of helium :** It is kept along with p-block elements.
- **Position of lanthanides and actinides :** Lanthanides and actinides have not been merged within the main body of the periodic table.

➢ **Electronic Configuration of Elements and the Periodic Table :** For the sake of simplicity the electronic configuration of the noble gas elements are written as $[He]^2$, $[Ne]^{10}$, $[Ar]^{18}$, $[Kr]^{36}$, $[Xe]^{54}$ and $[Rn]^{86}$.

The *Aufbau* (build up) principle and the electronic configuration of atoms provide a theoretical foundation for the periodic classification. The elements in a vertical column of the Periodic Table constitute a group or family and exhibit similar chemical behaviour. This similarity arises because these elements have the same number and same distribution of electrons in their outermost orbitals.

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. In other words, successive period in the Periodic Table is associated with the filling of the next higher principal energy level ($n = 1$, $n = 2$, etc.). 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 ($n = 1$) start with the filling of the lowest level ($1s$) and two elements - hydrogen ($1s^1$) and helium ($1s^2$) when the first shell (K) is completed.

(ii) Elements in second period : The second period ($n = 2$) starts with Lithium and has the electronic configuration $1s^22s^1$. Starting from the next elements, the $2p$ orbitals are filled with electrons, when the L shell is complete at neon ($2s^22p^6$). Thus, there are eight elements in the second period.

(iii) Elements in third period : The third period ($n = 3$) begins at sodium, and the added electrons enter $3s$ orbital. Successive filling of $3s$ and $3p$ orbitals give rise to the third period having eight elements from sodium to argon.

(iv) Elements in fourth period : The fourth period ($n = 4$) starts at potassium, and the added electrons fill up the $4s$ orbital. Also, $3d$ orbitals are filled before $4p$ orbitals because $3d$ has lower energy. Fourth period ending at Krypton has 18 elements.

(v) Elements in fifth period : It starts with Rb (37) with 55 orbital followed by filling of $4d$ orbitals, then $5p$ orbitals and ends at Xe (54), having total 18 elements.

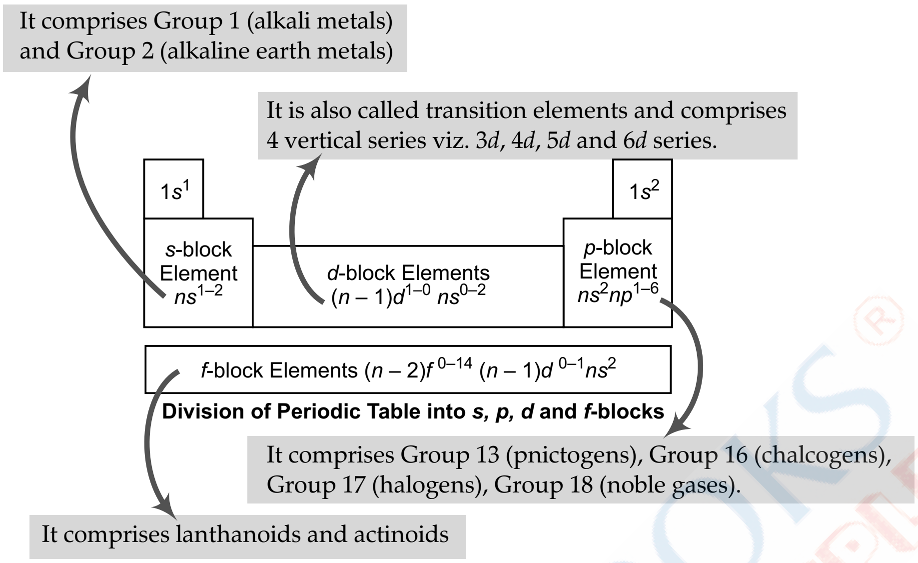
(vi) Elements in sixth period : It has 32 elements and successive electrons are filled in $6s$, $4f$, $5d$ and $6p$ orbitals, in that order.

(vii) Elements in seventh period : This period corresponds to $n = 7$ just like sixth period it involves the filling of 75, $5f$, $6d$ and $7p$. This period contains synthetic or man made radioactive elements.

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

➢ **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 I with alkali metals and it also achieves the electronic configuration of inert gas so, it can also be placed in 17th group.

➢ **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 hence, similarity in properties with other noble gases.



Division of Periodic Table into *s*, *p*, *d* and *f*-blocks

- **Metals and non-metals :** The elements can be divided into metals and non-metals.

Properties of Metals and Non-Metals

Properties of Metals	Properties of Non-metals
(i) They are malleable.	(i) They exist in solid, liquid or gaseous state.
(ii) They are ductile.	(ii) Non-metals are generally brittle.
(iii) They are good conductors of heat and electricity.	(iii) They are non-conductors.
(iv) They have generally 1 to 3 valence electrons.	(iv) They have 4 to 8 valence electrons.
(v) They have the same or less number of electrons in their outermost shell than the number of shells.	
(vi) They are mostly solids.	

- **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.

Periodic Trends in Properties of Elements

- **Atomic Radii :** The term atomic radius means the distance from the centre of the nucleus to the outermost shell of electrons.
- Depending upon the nature of combining atoms, atomic radius can be of following types :
  - **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,

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

  - **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 :** Nobel gases do not have molecules, so it is not possible to measure covalent or ionic radius. Their atoms are held together by weak van der Waals' forces of attraction. The van der Waals' radius is half of the distance between the centres of nuclei of atoms. Noble gases held by weak van der Waals' forces of attraction.

Variation of Atomic Radii in the Periodic Table

Variation in a Period	Variation in a Group
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.	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 upto which it has an influence in ionic bond.

  The ionic radii share the same trends as atomic radius.

  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. Among these species, the cation with greater positive charge will have a smaller radius because of the greater attraction of the electrons to the nucleus. However, the anion with the greater negative charge will have the larger radius as the net repulsion of the electrons outweighs the nuclear charge.

Topic 2

Periodic Trends in Ionization Enthalpy, Electron Gain Enthalpy, Electronegativity and Valence Electrons

» Revision Notes

- **Ionization enthalpy :** It is defined as : The minimum amount of energy required to remove an electron from an isolated gaseous atom in its ground state.
- **Factors Affecting Ionization Enthalpy :**

  (i) Size of the atom : The ionization enthalpy depends upon the distance between the electron and the nucleus, *i.e.*, size of the atom.

  (ii) Charge on the nucleus : The attractive force between the nucleus and the electron increases with the increase in nuclear charge. This is because, the force of attraction is directly proportional to the product of charges on the nucleus and the electron.

  (iii) 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.

  (iv) Penetration effect of electrons : *s*-electrons are more penetrating towards the nucleus than *p*-electrons and the penetration power decrease in a given shell in the order :

  $$s > p > d > f$$

  For the same shell, the ionisation enthalpy would be more to remove *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 :** Half-filled and completely filled shells have extra stability associated with them and therefore, have high ionization enthalpies. The elements like Be ($1s^2, 2s^2$) and Mg ($1s^2, 2s^2, 2p^6, 3s^2$) have completely filled orbitals and their ionization enthalpies are large.

Variation of Ionisation enthalpy in the Periodic Table

Variation Down a Group	Variation Along a Period
Within a group there is a gradual decrease in ionisation enthalpy on moving from top to bottom. The decrease in ionisation enthalpy down a group can be explained in terms of net effect of the following factors : • In going from top to bottom in a group, the nuclear charge increases. • 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 no. of inner electrons that outweighs the increasing nuclear charge and removal of the outermost electron requires less energy down a group.	In general the ionisation enthalpy increases with increasing atomic number in a period. In general increase along a period can be explained on the basis of atomic size and effective nuclear charge as : • On moving across a period from left to right the effective nuclear charge increases. • The atomic size decreases along a period though the main energy level remains the same.

- **Electron Gain Enthalpy (Enthalpy ΔH_{eg}) :** It is defined as the enthalpy change when a neutral isolated gaseous atom takes up extra electrons to form an anion.

Variation of Electron Gain Enthalpy in the Periodic Table

Variation in a Group	Variation in a Period
Electron gain enthalpy generally decreases in going from top to bottom in a group because with increase in size, the electron gain enthalpy decreases as the nuclear attraction decreases.	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 :**
  - **(i) Nuclear charge :** The electron gain enthalpy become more negative as the nuclear charge increases. This is due to greater attraction for the incoming electron if nuclear charge is high.
  - **(ii) Size of the atom :** With the increase in size of the atom, the distance between the nucleus and the incoming electron increases and this results in lesser attraction.

    Consequently, the electron gain enthalpy become less negative with increase in size of the atom of the element.
  - **(iii) Electronic configuration :** The elements having stable electronic configuration of half-filled and completely filled valence subshells show very small tendency to accept additional electron and thus electron gain enthalpies are less negative.
- Some important features of electron gain enthalpies of elements are :
- Halogens have the highest negative electron gain enthalpies. This is due to the fact that halogens have the general electronic configuration of ns^2np^5 and have only one electron less than the stable noble gas (ns^2np^6) configuration.
- Electron gain enthalpy values of noble gases are positive while those of Be, Mg, N, and P are almost zero. This is because noble gases have stable electronic configuration of ns^2np^6 and thus they have absolutely no tendency to take an additional electron. Thus, energy is required to force the electron in their atoms and therefore, their electron gain enthalpies are positive.
- Electron gain enthalpy of fluorine is unexpectedly less negative than that of chlorine. 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 2*p*-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 electrons to itself.
- **Measurement of Electronegativity**

Pauling Scale

It two atoms, A and B, having different electronegativity values, get bonded to form a molecule, AB, then the bond between A and B in A–B will have both covalent and ionic properties.

Δ_{A-B} = Observed bond energy – Energy of 100%
covalent or $\Delta_{A-B} = D - E_{A-B}$

where D = Observed bond energy

E_{A-B}=Bond energy of pure covalent bond of A – B.

The value of E_{A-A} and E_{B-B} is $E_{A-B} = \frac{1}{2}[E_{A-A}+E_{B-B}]$

$$= 0.208\sqrt{\Delta}_{A-B} = X_A - X_B$$

Where $X_A > X_B$ or $0.043\times\Delta_{A-B}=(X_A - X_B)^2$

Mulliken Scale

Mulliken suggested that the value of electronegativity of an element as an average of the values of ionisation potential and electron affinity of the element.

$$X_m = \frac{\text{LP.}+\text{E.A}}{2}\ (\text{in eV})$$

Where X_m = Electronegativity value as given by Mulliken

$$X_p = \frac{X_m}{2.8} = \frac{\text{LP.}+\text{E.A}}{5.6}$$

Where X_p = Electronegativity value as given by pauling

$$X_p = 0.336\ (X_m - 0.615)$$

Allred–Roschov's Scale

$$X_{AR} = \frac{Z_{eff}.e^2}{r^2} \quad X_p = 0.359\frac{Z_{eff}.e^2 + 0.744}{r^2}$$

$Z_{eff} = Z - \sigma$ where Z = Nuclear charge

σ = Shielding constant

or $X_p = 0.359X_{AR}+0.744$

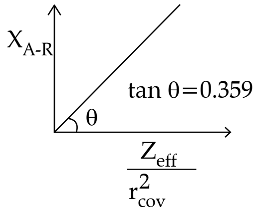
Sanderson's Scale

In the Sanderson scale, the stability ratio of an atom itself has been regarded as its electronegativity.

$$X_s \text{ or S.R.} = \frac{\text{Average electron density of an atom}}{\text{Electron density of the isoelectronic inert gas}}$$

This is related to Pauling scale as follows

$$\sqrt{X_p} = \frac{0.2}{\text{S.R.(or } X_S)} + 0.77$$

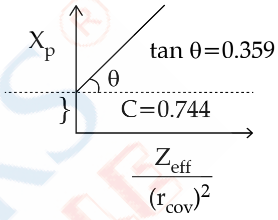


Force can be related with the electronegativity value in the following ways

$$X_{A\text{-}R} = \frac{0.359 \times Z_{eff}}{r^2_{cov}}$$

$$X_p = X_{A\text{-}R} + 0.744$$

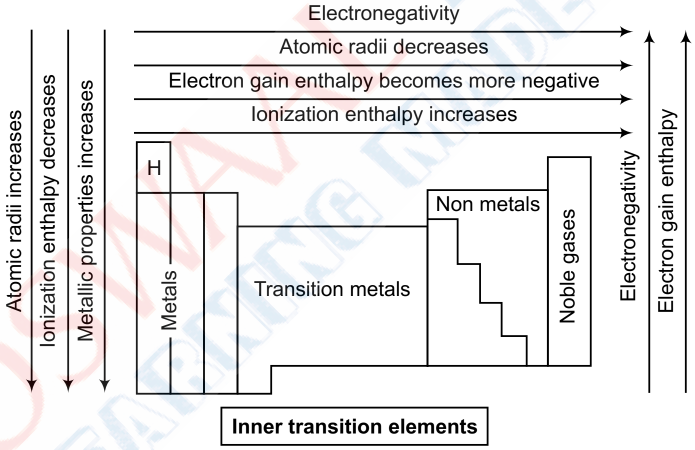
$$X_p = \frac{0.359 \times Z_{eff}}{r^2_{cov}} + 0.744$$



Variation of Electronegativity in the Periodic Table

Variation in a Group	Variation in a Period
Electronegativity decreases on moving down a group because of decrease in effective nuclear charge.	Electronegativity generally increasing on moving across a period because of increase in effective nuclear charge.

- Summary of the trends in the periodic properties of elements in the periodic table :



- **Valence :** The electrons present in the outermost shell of an atom are called valence electrons and the numbers 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. In a period, the number of valence electrons increases (mostly for light metal/elements) as we move from left to right side. However, in a group this periodic trend is constant.

KNOW THE TERMS

- **Coinage Metals :** Group 11 elements like Cu, Ag, Au are called coinage metals as these metals are used to make coins.
- **Inactive Gases :** Group 18 elements are called inactive gases as they are least reactive than other elements in periodic table and exist as gases.
- **Penetration Power :** It is the power of an orbital to penetrate nuclear charge through it to attract the outermost shell electrons.
- **Periodicity :** The repetition of similar properties after regular intervals is called as periodicity, it is due to the similarity in the outer electronic configuration which gives rise to the periodic properties of the element.

❑❑❑

Chapter 4

Chemical Bonding and Molecular Structure

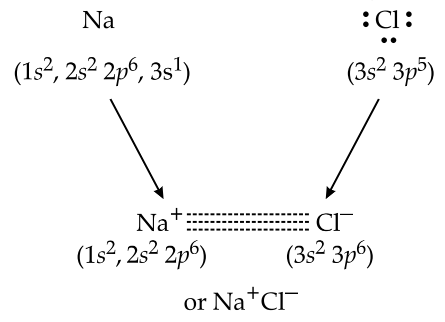
Topic 1

Ionic and Covalent Bonding, Lewis Structure and Polar Character of Covalent Bond

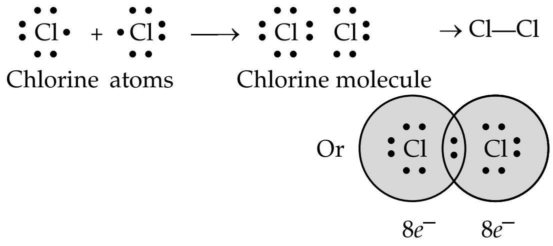
» Revision Notes

- **Chemical Bond :** The attractive force which holds together the various constituent particles (atoms, ions of molecules, etc.) in different chemical species is known as chemical bond.
- **Octet Rule :** According to electronic theory of chemical bonding, octet rule can be defined as the chemical rule by which atoms combine with each other to complete eight electrons in their valence shell to attain noble gas configuration.
- **Limitations of the octet rule :**
    - It cannot be applied to the non-metals after silicon in the periodic table.These elements can ''expand their octet'' and have more than eight valence electrons around the central atom. Examples are PF_5 and SF_6.
    - Molecules with an odd number of electrons such as NO and NO_2 cannot satisfy the octet rule.
    - In some compounds, especially the elements having less than 4 valence electrons, the central atom cannot possibly have eight valence electrons. For example, LiCl, $BeCl_2$ and BCl_2 do not obey the octet rule.
- Atoms can combine either by transfer of valence electrons from one atom to another (gaining or losing) or by sharing of valence electrons in order to have an octet in their valence shells.
- **Types of Bonding**
    - Ionic or Electrovalent Bond
    - Covalent Bond

Ionic bonding is a type of chemical bond that involves the electrostatic attraction between opposite charged ions together. Electrovalent compounds are formed by transfer of electron from a metal to a non-metal.

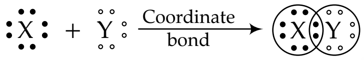


- Ionic compounds have high melting points and high boiling points.
- Ionic compounds have higher enthalpies of fusion and vaporization than molecular compounds.
- Ionic compounds are hard and brittle.
- Ionic compounds conduct electricity when they are dissolved in water or in molten state.
- Ionic 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.



- **Low melting and boiling points :** Covalent compound consists of molecules that are held by weak forces. These can be easily overcome by heat.
- **Non-conductive 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 of 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, toulene etc.
- **Slow rate of reaction :** The reaction of the covalent compounds are quite slow. This reaction is molecular, and the molecular reactions are slow.
- Depending upon the number of 2, 4, or 6 electrons shared between two atoms, a covalent bond is called single, double or triple bond respectively.

➢ **Coordinate bond :** It is a special type of covalent bond in which both the shared electrons between two atoms are donated by one of these atoms.



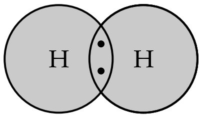
➢ **Lewis Structure of Ionic Compounds :**

(i) $(Na^+)\,(:\overset{..}{\underset{..}{Cl}}:^-)$ (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) $(Ca^{2+})\,(:\overset{..}{\underset{..}{O}}:^{2-})$

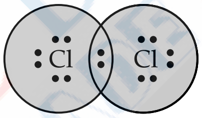
➢ **Lewis Structure of Covalent Compounds :**

(i)



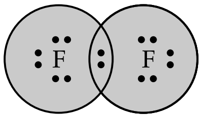
H—H

(ii)



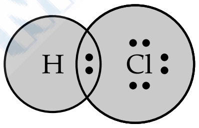
Cl—Cl

(iii)



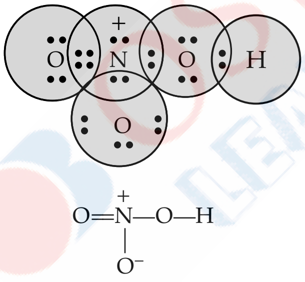
F—F

(iv)



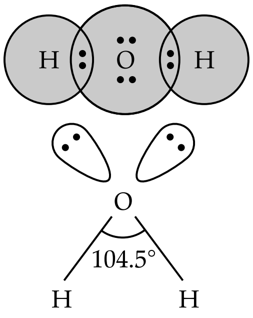
H—Cl

(v)



$O{=}\overset{+}{N}{-}O{-}H$, with O^- on N

(vi)



Bent molecule

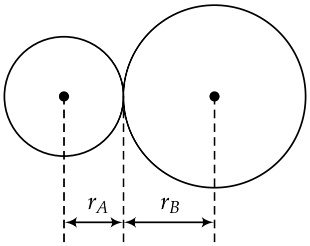
➢ **Formal charge :** It is defined as the difference between the number of valence electrons in an isolated atom and the number of electrons assigned to that atom in a Lewis structure.

➢ **Formal charge (F.C.) on an atom in a Lewis structure :**

= [Total number of valence electrons in the free atom] – [Total number of non-bonding (lone pair) electrons] – (1/2) [Total number of bonding (shared) electrons]

➢ **Bond parameters :**

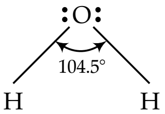
(i) Bond length : Equilibrium distance between the nuclei of two bonded atoms.



$$R = M_A + M_B$$

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

(ii) 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, bond angle of water molecule is 104.5°.



(iii) Bond energy or bond enthalpy : Energy required to break one mole of a bond. The unit of bond enthalpy is KJ mol^{-1}. For example H-H bond enthalpy in hydrogen molecule is 435.8 kJ mol^{-1}.

$$H_2\,(g) \longrightarrow H(g) + H(g);\ \Delta H = 435.8\ kJmol^{-1}$$

(iv) Bond order : It is given by number of bonds between the two atoms in a molecule for example F_2 and N_2. CO and NO^+ have bond order 3.

- 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**

● **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. So, in other words, the shared electron pair will lie exactly midway between the two atoms. 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 :** This type of bond is formed between two atoms of different elements; the shared pair of electrons does not lie exactly midway between the two atoms. In fact it lies more towards the atom which is more electronegative. The atom with higher affinity for electrons develops a slight negative charge and atom with lesser affinity for electrons develop a slight positive charge. For example – HCl, H_2O etc.

- **Polarity of Bond : Dipole Moment :** Dipole moment is defined as : "The product of the magnitude of the charge and the distance of separation between the charges."

$$\text{Dipole moment } (\mu) = \text{Charge } (q) \times \text{Distance of separation } (d)$$

It is usually expressed in Debye units (D)

Dipole moment is also expressed in the units of Cm :

$$1D = 3.33564 \times 10^{-30}\ \text{Cm}.$$

Topic 2

Valence Bond Theory, Resonance, VSEPR Theory and Hybridization

» Revision Notes

- **Resonance :** According to the concept of resonance, whenever a single Lewis structure cannot describe a molecule accurately, a number of structures with similar energy, positions of nuclei, bonding and non-bonding pairs of electrons are taken as the canonical structures of the hybrid which describes the molecule accurately.
- **Conditions for Writing Resonance Structure :** The following are essential conditions for writing resonating structures :
  - The contributing structures should have same atomic positions.
  - The contributing structures should have same number of unpaired electrons.
  - The contributing structures should have nearly same energy.
  - The structures should be so written that negative charge is present on an electronegative atom and positive charge is present on an electropositive atom.
  - In contribution structures, the like charges should not reside on adjacent atoms.
- Resonance energy = Actual bond = Energy of the most stable responding structures.
- **Valence shell electron pair repulsion (VSEPR) Theory :** According to this theory, bonded atoms in a molecule adopt that particular arrangement in space around the central atom which keeps them on the average as for as possible.

➢ **Postulates of VSEPR Theory :**

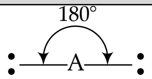
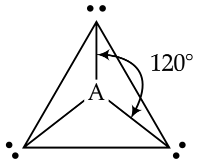
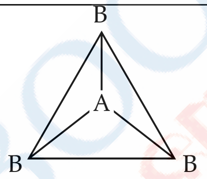
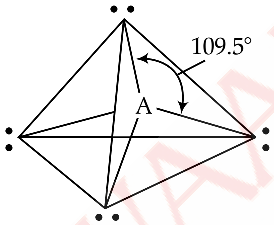
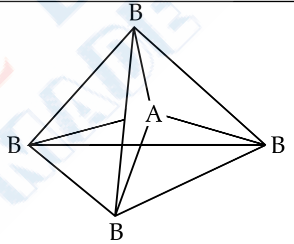
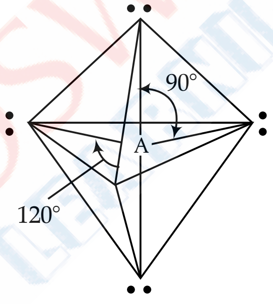
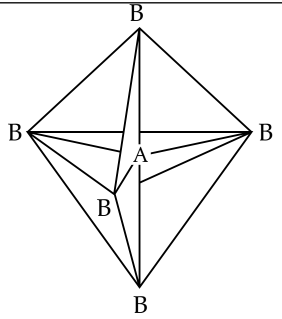
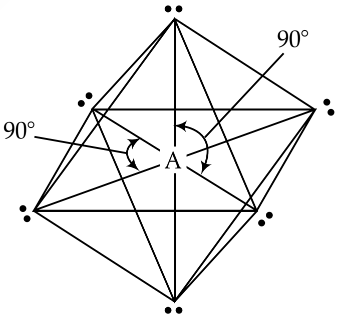
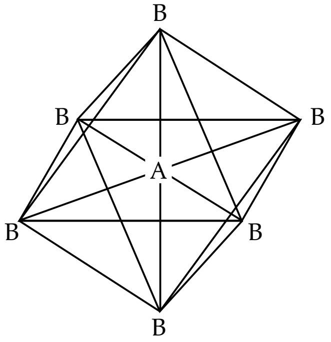
- The geometry of a molecule depends upon the total number of valence shell electron pairs (bonded or non-bonded) around the central atom in the molecule.
- Repulsion between valence shell electron pairs determines molecular shape. In order to minimize electron-electron repulsion or to acquire a state of minimum energy or maximum stability, the valence shell electron pairs keep themselves as far apart as possible.
- In case more than one geometrical arrangements are possible for a given number of bonded and non-bonded pairs, then the most stable arrangement are consistent with the following hypothesis :

(a) The repulsive interactions, decrease in the order :

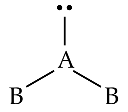
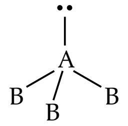
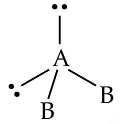
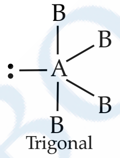
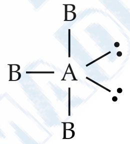
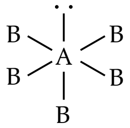
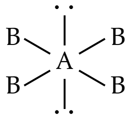
Lone pair–Lone pair > Lone pair–Bond pair > Bond pair–Bond pair.

(b) Repulsive forces decrease sharply with increase in angle between the electron pairs.

➢ Geometry of Molecules in which the Centre Atom has No Lone Pair of Electrons.

Number of electron pairs	Arrangement of electron pairs	Molecular geometry	Examples
2	 Linear	B—A—B Linear	$BeCl_2$, $HgCl_2$
3	 Trigonal planar	 Trigonal planar	BF_3
4	 Tetrahedral	 Tetrahedral	CH_4, NH_4^+
5	 Trigonal bipyramidal	 Trigonal bipyramidal	PCl_5
6	 Octahedral	 Octahedral	SF_6

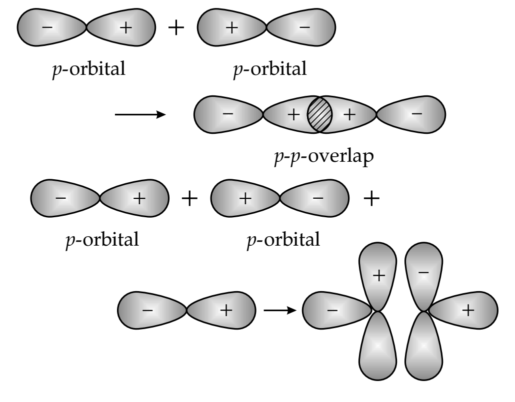
➢ Shape (geometry) of Some Simple Molecules/Ions with Central Ions having One or More Lone Pairs of Electrons (E)

Molecule type	No. of bonding pairs	No. of lone pairs	Arrangement of electron pairs	Shape	Example
AB_2E	2	1	 Trigonal planar	Bent	SO_2, O_3
AB_3E	3	1	 Tetrahedral	Trigonal pyramidal	NH_3
AB_2E_2	2	2	 Tetrahedral	Bent	H_2O
AB_4E	4	1	 Trigonal bi-pyramidal	See saw	SF_4
AB_3E_2	3	2	 Trigonal bi-pyramidal	T-shape	ClF_3
AB_5E	5	1	 Octahedral	Square Pyramidal	BrF_5
AB_4E_2	4	2	 Octahedral	Square Planar	XeF_4

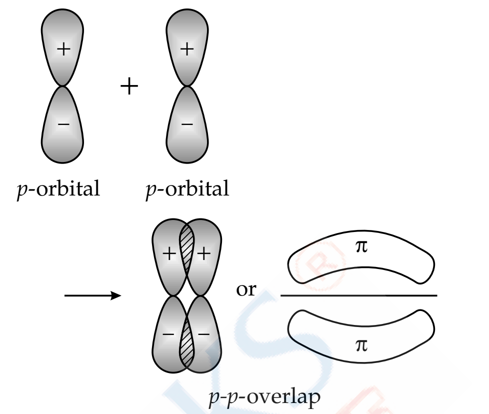
- **Valence Bond Theory :**
  According to V.B.T., a covalent bond is formed between the two atoms by the overlap of half-filled valence atomic orbitals with similar energies of each atom containing one unpaired electron.
  Greater the overlap, stronger is the bond.
- **Types of overlapping and nature of covalent Bond :**

Types of Overlapping and Nature of Covalent Bond

Sigma (σ) bond	Pi (π) bond
● This type of covalent bond is formed by the end to end head on overlap of bonding orbitals along the internuclear axis. The overlap is known as head on overlap or axial overlap. For example, *p-p* overlapping	● This type of covalent bond is formed by the sidewise overlap 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.



For example, p-p overlapping



- **Hybridization :** 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 Hybridization :**
  - The number of hybridised orbitals is equal to the number of the orbitals that get hybridised.
  - The hybridised orbitals are always equivalent in energy and shape.
  - The hybrid orbitals are more effective in forming stable bonds than the pure atomic orbitals.
  - The hybrid orbitals are directed in space in some preferred directions to have stable arrangement. Therefore, the type of hybridization indicates the **geometry of the molecule.**
- **Conditions for Hybridization**
  - Only the orbitals present in the valence shell of the atom are hybridised.
  - The orbitals undergoing hybridization should have only a small difference in energy. The orbitals which differ largely in energy cannot take part in hybridization.
  - Promotion is not essential condition prior to hybridization.
  - It is not essential that only half filled orbitals participate in hybridization. In certain cases, even filled orbitals of valence shell participate in hybridization.

Shape of Molecules/ions	Hybridisation type	Atomic orbitals	Example
Linear	sp	$s + p$	BeF_2
Triangular pyramidal	sp^2	$s + p(2)$	BCl_3
Tetrahedral	sp^3	$s + p_x + p_y + p_z$	CH_4
Square planar	dsp^2	$d + s + p(2)$	$[Ni(CN)_4]^{2-}$, $[Pt(Cl)_4]^{2-}$
Trigonal bipyramidal	sp^3d	$s + p_x + p_y + p_z + d_z^2$	PF_5, PCl_5
Square pyramidal	sp^3d^2	$s + p_x, p_y, p_z + d_{x^2-y^2}, d_{z^2}$	BrF_5
Octahedral	sp^3d^2	$s + p(3) + d(2)\ d_{x^2-y^2}, d_{z^2}$	SF_6, $[CrF_6]^{3-}$
	d^2sp^3	$d_{xy}, d_{x^2 y^2} + s + p(3)$	$[Co(NH_3)_6]^{3+}$
Pentagonal bipyramidal	sp^3d^3	$s + p(3) + d_{xy}, d_{yz}, d_{xz}$	IF_7

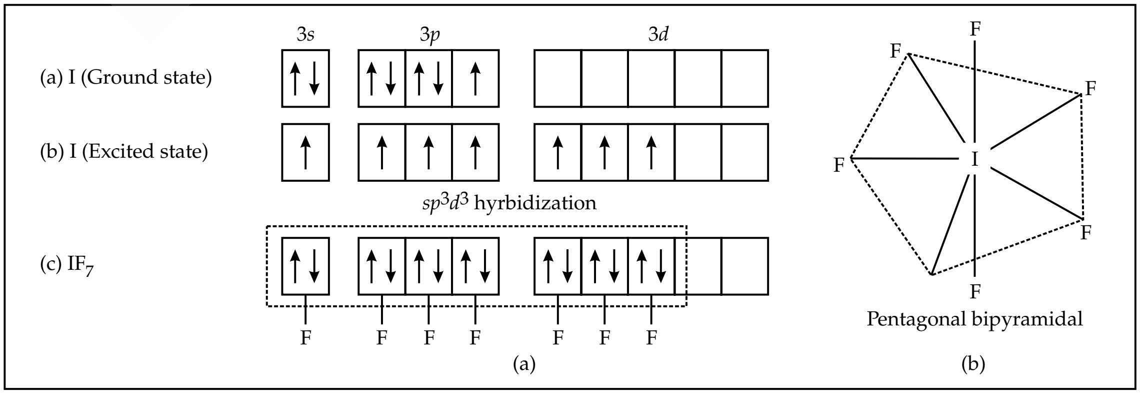


Fig. (a) Formation of IF_7 molecule involving sp^3d^3-hybridization, (b) Pentagonal bipyramidal geometry of IF_7 molecule.

Topic 3

Molecular Orbital Theory and Hydrogen Bond

» Revision Notes

- **Molecular orbital theory :** The basic idea of molecular orbital theory is that atomic orbital of individual atoms combine to form molecular orbitals.
- **Salient features of molecular orbital theory :**
  - Just like one atom, molecules have orbitals of definite energy levels.
  - Molecular orbitals are formed by the combination of atomic orbitals of proper symmetry and comparable energies.
  - 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 orbitals and antibonding molecular orbitals.
  - The bonding molecule has lower energy and hence greater stability whereas corresponding antibonding molecule has more energy and hence lesser stability.

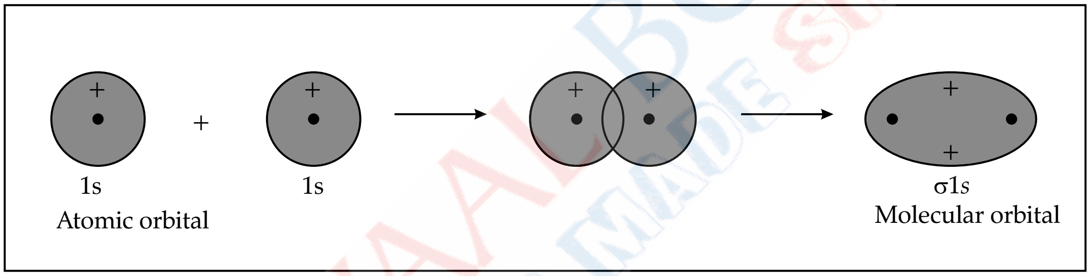


Fig. Formation of bonding molecular orbital

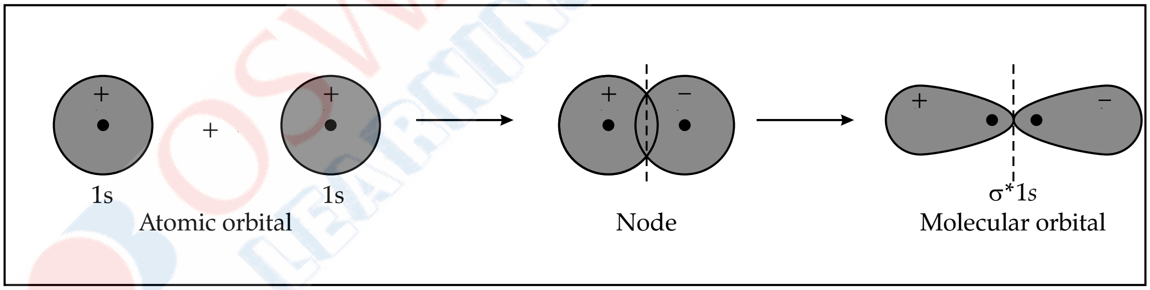


Fig. Formation of antibonding molecular orbital

- The main condition for effective 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 large.
- For homo nuclear, diatomic molecules of second row elements such as Li_2, Be_2, B_2, C_2, N_2, the order of increasing energies for their molecules is

  Energy order 1 :

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

  For molecules O_2 onwards, the increasing order of energies for molecular orbitals in which they are filled is as follows :

  Energy order 2 :

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

- **Hydrogen Bonding :**

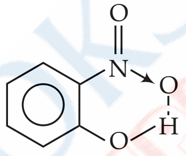
Hydrogen Bonding
(Force between hydrogen atom and an electronegative atom)

Intermolecular

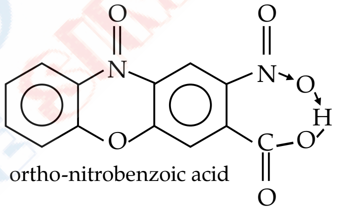
Intermolecular hydrogen bond is formed between two different molecules of the same or different substances.
For example,
(i) hydrogen bond between the molecules of hydrogen fluoride
(ii) hydrogen bond in alcohol or water molecules

Intramolecular

Intramolecular hydrogen bond is formed between the hydrogen atom and the highly electronegative atom (Cl, O, N) present in the same molecule.
For example,

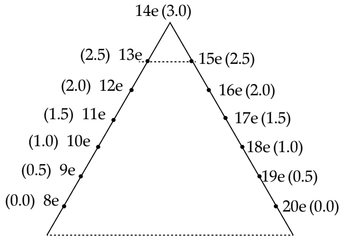


ortho-nitrophenol



ortho-nitrobenzoic acid

Trick of Bond order
e = No. of electrons



KNOW THE TERMS

- **Valence electrons :** Electrons present in the outermost energy level of an atom.
- **Valency :** In a molecule, the number of bonds an atom is formed is known as its valency.
- **Lattice enthalpy :** Energy required to completely separate one mole of a solid ionic compound into gaseous constituent ion.
- **Paramagnetic and diamagnetic :** Presence of unpaired electron shows that molecule is paramagnetic however paired electron shows it is diamagnetic.
- **Covalency :** The number of electrons which an atom contributes towards mutual sharing during the formation of a chemical bond called its covalency in that compound.

❑❑❑

Chapter 5

States of Matter : Gases and Liquids

Topic 1

Three States of Matter, Intermolecular Interactions, Types of Bonding, Melting and Boiling Points

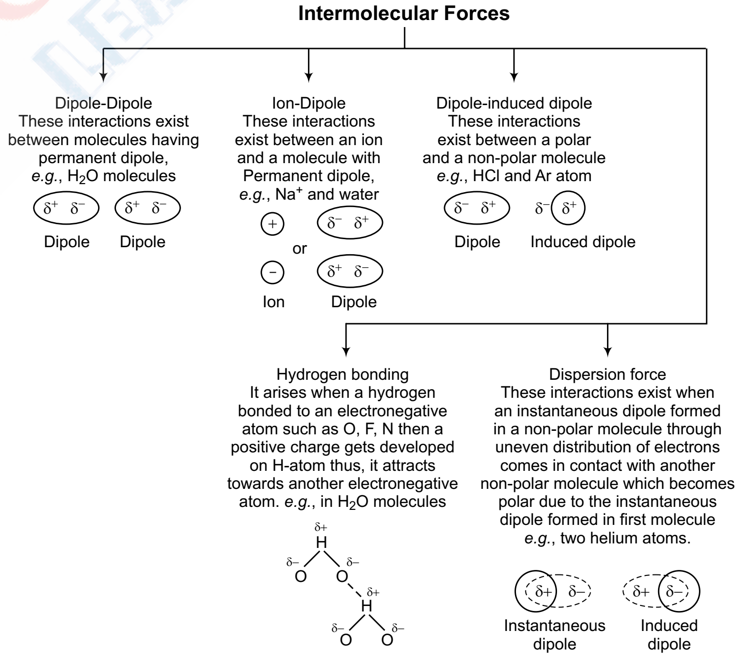
» Revision Notes

- Matter is classified into three states solid, liquid and gas which can be interchanged into each other by changing temperatures.

-

SOLID	LIQUID	GAS
Definite shape, mass and volume.	Definite mass and volume but shape depends upon shape of container.	Definite mass but no definite shape and volume.
High density.	High density but less than solids.	Low density.
Small change in volume occurs with change in temperature and pressure.	Small changes in volume occurs with change in temperature and pressure.	Considerable changes in volume with change in temperature and pressure.
Constituent of solid possess less energy.	Molecules of liquids have high energy.	Molecules of gas are most energetic.
Strongest intermolecular forces.	Intermediate intermolecular forces.	Weakest intermolecular forces.

- The states of matter depends upon its intermolecular forces and thermal energy. Intermolecular forces bind the molecules together, however thermal energy keep them apart.

- 

Intermolecular Forces

Dipole-Dipole
These interactions exist between molecules having permanent dipole, *e.g.*, H_2O molecules

Ion-Dipole
These interactions exist between an ion and a molecule with Permanent dipole, *e.g.*, Na^+ and water

Dipole-induced dipole
These interactions exist between a polar and a non-polar molecule *e.g.*, HCl and Ar atom

Hydrogen bonding
It arises when a hydrogen bonded to an electronegative atom such as O, F, N then a positive charge gets developed on H-atom thus, it attracts towards another electronegative atom. *e.g.*, in H_2O molecules

Dispersion force
These interactions exist when an instantaneous dipole formed in a non-polar molecule through uneven distribution of electrons comes in contact with another non-polar molecule which becomes polar due to the instantaneous dipole formed in first molecule *e.g.*, two helium atoms.

- Melting point of a solid is higher for the solid having stronger bonding thus, ionic solids have higher melting point than the molecular solids.
- Boiling point of a liquid increases when there are greater interactions between liquid molecules. Thus, the liquids having hydrogen bonding have higher boiling point.

Topic 2

Gas Laws, Ideal Behaviour of Gases, Avogadro Number and Ideal Gas Equation

» Revision Notes

- **Gas laws :** The quantitative relationship between any two of the variables (V, P, T, n) when other two are constant.
- **Boyle's law :** At constant temperature, the pressure of a fixed amount (*i.e.*, number of moles n) of gas varies inversely with its volume. This is known as Boyle's law.
- **Boyle's law equation :** (At constant T, n)

$$V \propto \frac{1}{P} \quad \text{or} \quad P_1V_1 = P_2V_2$$

- **Charle's Law :** The volume of fixed mass of a gas is directly proportional to the temperature (in Kelvins) at constant pressure. The volume of a given amount of a gas at constant pressure increases or decreases by a constant fraction (1/273.15).
- **Charle's law equation :** (At constant P, n)

$$V \propto T \quad \text{or} \quad \frac{V_1}{T_1} = \frac{V_2}{T_2}$$

- **Gay Lussac's law :** It states that at constant volume, pressure of a fixed amount of a gas varies directly with the temperature.
- **Gay Lussac's law equation :** (At constant V, n)

$$P \propto T$$

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

- **Avogadro's Law :** Under similar conditions equal volumes of various gases contain equal number of molecules.
- **Avogadro's Law equation :** (At constant T, P)

$$V \propto n$$

- **Ideal Gas :** Ideal gas is a gas that follows all the four gas laws strictly.
- **Ideal Gas Equation :**Ideal gas equation, PV = nRT gives the relationship between parameters and is obtained by combining Boyle's law, Avogadro's Law and Charle's law.

$$PV = \boldsymbol{n}RT$$

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$$

R – Universal gas constant

$$R = \frac{PV}{nT}$$

$$R = \frac{(10^5\,\text{Pa})\,(22.7 \times 10^{-3}\,\text{m}^3)}{(1\,\text{mol})\,(273.15\,\text{K})}$$

$$= 8.314\ \text{Pa m}^3\ \text{K}^{-1}\ \text{mol}^{-1}$$

$$= 8.314\ 10^{-2}\ \text{bar LK}^{-1}\ \text{mol}^{-1}$$

$$= 8.314\ \text{JK}^{-1}\ \text{mol}^{-1}$$

- Dalton's law of partial pressure states that the total pressure exerted by the mixture of non-reactive gases is equal to the sum of partial pressures of individual gases.

$$p_{\text{Total}} = p_1 + p_2 + p_3$$

$$= n_1\frac{RT}{V} + n_2\frac{RT}{V} + n_3\frac{RT}{V} \qquad (p_1, p_2 \text{ and } p_3 \text{ are partial pressure of gasses})$$

- **Graham's law of diffusion :** The rate of diffusion of gases (V/t) is inversely proportional to square root of their densities under similar conditions.

- **Graham's law :** $r \propto \sqrt{\frac{1}{d}}$

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

Topic 3

Kinetic Energy and Molecular Speeds, Deviation from Ideal Behaviour, Liquefaction of Gases, Critical Temperature

» Revision Notes

- **Kinetic gas equation :** $PV = \frac{1}{3} mNu^2$

  Where, P = pressure, V = volume, m = Mass of each molecule of gas, N = total no. of molecules present in volume V, u = root mean square speed of gas

- Kinetic energy per mole $= \frac{3}{2}$ RT

- Average Kinetic energy per molecule $= \frac{3}{2}\frac{RT}{N} = \frac{3}{2}$ KT (where, K = R/N = Boltzmann constant)

  C_{mp} = Most probable velocity $= \sqrt{\frac{2RT}{M}}$

  C_{av} = Average velocity $= \sqrt{\frac{8RT}{\pi M}}$

  C_{rms} = Root mean square velocity $= \sqrt{\frac{3RT}{M}}$

- Under ordinary conditions, real gases show deviation from the ideal gas behaviour. Real gases follow ideal gas behaviour at high temperatures and very low pressures.

- The two main causes of these deviations are the finite size of gas molecules and the existence of attractive inter molecular forces between them. Taking into account of these facts, van der Waal's modified the ideal gas equation and gave the modified equation known as van der Waal's equation.

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

  Where $\frac{a}{V^2}$ is the pressure correction term and b, the volume correction term takes account the finite volume of the gas molecules.

- The deviation from ideal behaviour can be measured in terms of compressibility factor Z.

$$Z = \frac{pV}{nRT} \text{ or } Z = \frac{V_{real}}{V_{ideal}}$$

  If $Z = 1$ then the gas is an ideal gas.
  Z > 1 then the gas is less compressible
  Z < 1 then the gas is more compressible

- **Critical phenomenon :**

  (i) Critical temperature is the temperature above which a gas cannot be liquefied.

$$T_c = 8a/27Rb$$

  (ii) Critical pressure is the minimum pressure required to liquefy the gas at its critical temperature.

$$P_c = a/27b^2$$

  (iii) Critical volume is the volume occupied by one mole of gas at critical temperature and pressure.

Topic 4

Liquid State Vapour Pressure, Viscosity and Surface Tension

» Revision Notes

- **Liquid state :** Vapour pressure is the pressure exerted by the vapours of the liquid in equilibrium with its liquid at a given temperature.
- Boiling point is the temperature at which vapour pressure of a liquid becomes equal to the atmospheric pressure.
- Surface tension is the force which acts at right angle to an imaginary line of unit length at the surface of liquid at rest.
- Viscosity is the force of friction which one part of the liquid offers to another part of the liquid.

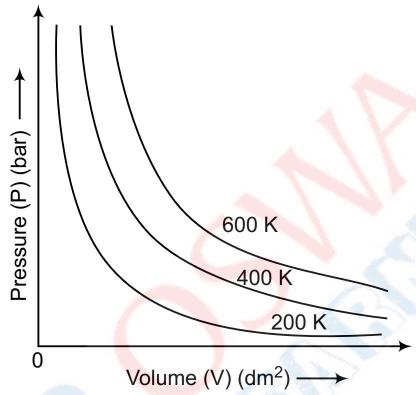
$$F \propto A \text{ (A is the area of contact)}$$

$$F \propto \frac{du}{dz}$$

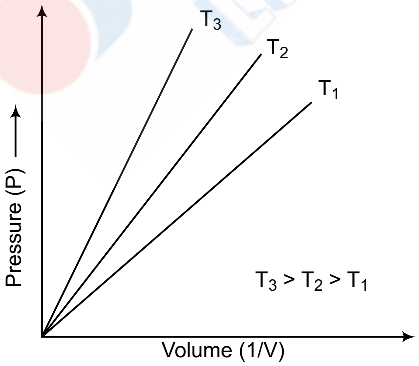
(where, $\frac{du}{dz}$ is velocity gradient : The change is velocity with distance).

- Coefficient of viscosity (η) is the force of friction required to maintain a velocity difference of 1 cm/sec between two parallel layers, 1 cm apart, and each having an area of 1 sq. cm.
- **Important Graphs :**

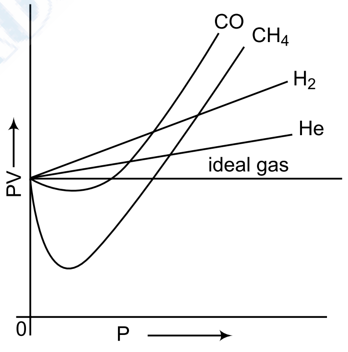
(i) Pressure *vs* Volume of a gas at different temperature



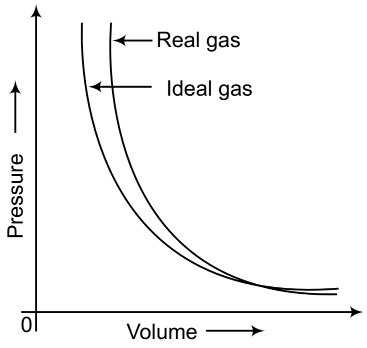
(ii) Pressure *vs* 1/V



(iii) PV *vs* P for real gas and ideal gas



(iv) Pressure *vs* Volume for real and ideal gas



KNOW THE TERMS

- **Isotherm :** Any process at constant temperature.

- **Isobar :** Any process at constant pressure.
- **Isochore :** Any process at constant volume.
- **STP (or NTP) :** It stands for Standard Temperature and Pressure (or Normal Temperature and Pressure). At standard temperature (273.15 K or 0°C) and standard pressure (*i.e.*, 1 bar or 10^5 pascal), volume of an ideal gas or a combination of ideal gases is 22.71098 L mol^{-1}.
- **Aqueous Tension :** Pressure exerted by saturated water vapour is called aqueous tension.
- **Boyle Temperature or Boyle Point :** The temperature at which a real gas obeys ideal gas law over an appreciable range of pressure is called Boyle temperature or Boyle point.

❑❑❑

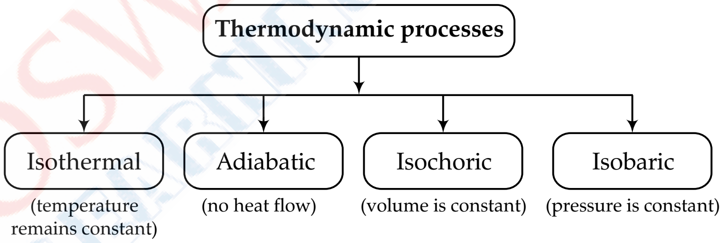
Chapter 6

Thermodynamics

Topic 1

First Law of Thermodynamics–Internal Energy and Enthalpy, Specific Heat and Heat Capacity

» Revision Notes

- **System** : The part of the universe chosen for thermodynamic consideration is called system and the remaining portion is called surroundings.
- **Types of System :**
  - **(i) Open system :** It can exchange both matter and energy with the surrounding.
  - **(ii) Closed system :** It can exchange only energy with the surrounding.
  - **(iii) Isolated system :** It can neither exchange energy not matter with the surrounding.
- **State of a system :** The condition of the system which is described in terms of certain observable properties such as temperature, pressure, etc.
- **State function :** A physical quantity whose value depends only upon the state of a system not upon the path followed.
- 

- **Reversible & irreversible process :**

Reversible	Irreversible
In this process equilibrium is not disturbed.	Equilibrium is obtained only after the completion of process.
Takes infinite time for completion.	Takes finite time for completion.
Work obtained in it is maximum.	Work obtained in it is not maximum.

- **Internal energy** is the total energy stored within the substance or system.

$$\Delta U = U_2 - U_1 = W_{ad}$$

W_{ad} = + ve = work is done on the system and internal energy increases.

W_{ad} = – ve = work is done by the system

- **First Law of Thermodynamics :** First law of thermodynamics is also known as law of conservation of energy which states that energy can neither be created nor be destroyed, although it can be converted from one form to another *i.e.*, total energy of the universe remains constant.

$$\Delta U = q + W$$

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

- For isothermal irreversible change,

$$q = -W = P_{ext}(V_f - V_i)$$

- For isothermal reversible change,

$$q = -W = nRT\ \text{In}\ \frac{V_f}{V_i}$$

$$= 2.303\ nRT \log \frac{V_f}{V_i}$$

- For adiabatic change, $q = 0$

$$\Delta U = W_{ad}$$

- **Enthalpy :** It is the heat content of the system.

$$H = U + P\Delta V$$

- Enthalpy change, $\Delta H = \Delta U + P\Delta V$

$$\Delta H = \Delta U + \Delta nRT$$

$$\Delta H = -\text{ve for exothermic reaction}$$

$$\Delta H = +\text{ve for endothermic reaction}$$

- **Heat capacity :** Amount of heat required to raise the temperature of the system through 1°C.

$$C = \delta q/dT$$

- **Specific heat capacity :** Amount of heat required to raise the temperature of 1 gm. of the substance through 1°C.
- **Molar heat capacity :** Amount of heat required to raise the temperature of 1 mole of the substance through 1°C.

Topic 2

Hess's Law of Constant Heat Summation, Enthalpy of Bond Dissociation, Combustion, Formation, Atomization, Sublimation, Phase Transition, Ionization, Solution and Dilution

» Revision Notes

- **Hess's Law of Constant Heat Summation :** 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.
- **Bond enthalpy (Δ_{bond} H°) :** The average amount of energy required to break one mole of the bonds of a particular type in gaseous molecules.
- **Standard enthalpy of combustion (Δ_CH°) :** It is the enthalpy change occur during the combustion of the mole of the substances in excess of oxygen. $\Delta_C H°$ is always less than zero.
- **Standard enthalpy of formation (Δ_fH°) :** It is enthalpy change accompanying the formation of 1 mole of the substance form its constituent elements in their standard state.

$$\Delta_f H° \text{ can be } > 0 \text{ or } < 0$$

- **Enthalpy of solution (Δ_{sol}H°) :** It is enthalpy change when one mole of it dissolves in a specified amount of solvent.
- **Enthalpy of atomization :** It is the enthalpy change accompanying the dissociation of 1 mole of substance into gaseous atoms.
- **Standard enthalpy of sublimation, (Δ_{sub} H°) :** 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 fusion (Δ_{fusion} H°) :** It is enthalpy change during the fusion of one mole solid at its melting point.
- **Standard enthalpy of vaporisation (Δ_{vap} H°) :** It is the enthalpy change during the vaporisation of 1 mole of liquid at its boiling point and under standard pressure (1 bar).
- **Enthalpy of dilution :** It is the enthalpy change associated with the dilution process of a component in a solution at a constant pressure.
- **Enthalpy of hydration :** It is the enthalpy change during the hydration of 1 mole of anhydrous salt by combining with specific number of moles of water.
- **Enthalpy of neutralisation (Δ_n H) :** It is the enthalpy change during neutralization of 1 gm. equivalent of acid with 1 gm. equivalent of a base in dilute aqueous solution.

Topic 3

Entropy, Second Law of Thermodynamics, Gibbs Energy, Third Law of Thermodynamics

» Revision Notes

- Entropy is thermodynamic property which is a measure of disorder. It is related to heat absorbed at a constant temperature by the system in a reversible process as

$$\frac{-q_{rev}}{T}$$

For a spontaneous change, total entropy change is positive.

$$\Delta S = \frac{q_{rev}}{T}$$

$\Delta S_{total} = \Delta S_{system} + \Delta S_{surr} > 0$

ΔS_{total} = +ve = spontaneous process

ΔS_{total} = –ve = non-spontaneous process

ΔS_{total} = 0, the process is in equilibrium

For a total of one mole of a mixture, $\Delta S_{mix} = -R\Sigma\, xi \text{ In } xi$ [∵ ΔS is always fractional , ΔS always positive]

- **Second Law of Thermodynamics :** The entropy of universe always tends to increase during any spontaneous process.
- Gibbs energy is another thermodynamic property which is a measure of energy stored in a system or a substance that is available for doing useful work. It is related to change in enthalpy and entropy of the system during a process as :

$$\Delta G = \Delta H - T\Delta S$$

- $-\Delta G = W_{non\ expansion} = W_{usefull}$
- $-\Delta G = nFE°$
- $\Delta_r G° = -2.303\ RT \log K$
- $\Delta_r G° = \Delta_r H° - T\Delta_r S° = -RT \ln K$ (K = equilibrium constant)
- If ΔG is negative (<0), the process is spontaneous.
- If ΔG is positive (>0), the process is non-spontaneous.
- In Isothermal process, ΔG = 2.303RTlogV1/V2
- According to Maxwell relation, dG = –SdT + VdP
- **Third Law of Thermodynamics :** The entropy of a perfectly crystalline substance is zero as the temperature approaches absolute zero.

This law can be applied to calculate absolute entropies of pure substances at any temperature.

$$\Delta S = S_T - S_O = S_T$$

$$= \int_0^T \frac{C_p dT}{T} = C_P \ln T = 2.300\ C_P \log T$$

$$\Delta S = nC_p \ln \frac{T_f}{T_i} + nR \ln \frac{P_i}{P_f}$$

- **Effect of temperature on spontaneity of a process :**

Sign of ΔH	Sign of ΔS	Value of T	Spontaneity
–	+	Any	Spontaneous
+	–	Any	Non-spontaneous
–	–	Low	Spontaneous
–	–	High	Non-spontaneous
+	+	Low	Non-spontaneous
+	+	High	Spontaneous

KNOW THE TERMS

- **Thermal process :** This is the process which is carried out at a constant temperature.
- **Adiabatic process :** This is the process in during which heat is gained or lost by the system.
- **Spontaneous process :** A process which has an urge or natural tendency to occur in a particular direction either of its own or after proper initiation under a given set of conditions.
- **Born-Haber Cycle :** It is impossible to determine lattice enthalpies directly by experiment, we use an indirect method where we construct an enthalpy diagram.

❒❒❒

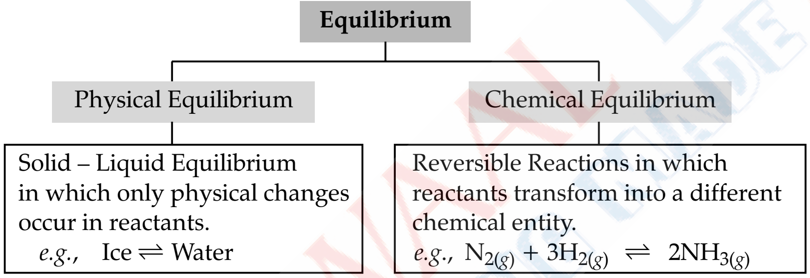
Chapter 7

Equilibrium

Topic 1

Equilibrium Process, Law of Chemical Equilibrium, Equilibrium Constant, Le-Chatelier's Principle

» Revision Notes

- **Equilibrium state :** When rate of formation of a product in a process is in competition with rate of formation of reactant, the state is then termed as "equilibrium state".
- Equilibrium reached in physical process is termed as physical equilibrium.
- Equilibrium achieved in chemical processes is termed as chemical equilibrium.
- 

Equilibrium

Physical Equilibrium

Solid – Liquid Equilibrium in which only physical changes occur in reactants.
e.g., Ice $\rightleftharpoons$ Water

Chemical Equilibrium

Reversible Reactions in which reactants transform into a different chemical entity.
e.g., $N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$

- Comparison between reversible and irreversible

Reversible Reaction	Irreversible Reaction
1. It take place in both the directions, i.e., the product can be again decomposed into reactants. 2. It never go to completion. 3. It attain equilibrium $N_2 + 3H_2 \rightleftharpoons 2NH_3$	1. It take place in only one directions. The product does not decomposes again into reactants. 2. It almost go to completion. 3. It will not attain equilibrium $AgNO_3 + HCl \rightarrow AgCl + HNO_3$

- **Dynamic equilibrium :** The state of equilibrium in which the rate of forward reaction and rate of backward reaction are equal and there is no net change is composition is known as dynamic equilibrium.
- **Law of mass action :** According to this law, the rate of a reaction is directly proportional to the product of the molar concentrations of the reactants, with each concentration term raised to the power equal to the number of times that reactant appears in the balanced chemical equation.

  For a given reaction.

$$aA + bB \rightarrow cC + dD$$

Rate of reaction $\propto [A]^a\,[B]^b$

$= K[A]^a\,[B]^b$

- **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. This is known as the Equilibrium Law or Law of Chemical Equilibrium.

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

Rate of forward reaction, $R_1 = K_1\,[A]^a\,[B]^b$

Rate of backward Reaction, $R_2 = K_2\,[C]^c\,[D]^d$

At equilibrium, rate of forward reaction = Rate of backward reaction so,

$$R_1 = R_2$$

$$\frac{K_1}{K_2} = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

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

- **Equilibrium constant :** It is the ratio of the velocity constant of forward reaction to that of backward reaction. It is denoted by symbol K.
- For a homogeneous gas phase reaction, the molar concentration of a substance is directly proportional to its partial pressure P at constant temperature. Then equilibrium is denoted by K_p.

$$K_p = \frac{(p_C^c)\times(p_D^d)}{(p_A^a)\times(p_B^b)}$$

Le Châtelier's Principle Summary

Variable	Type of Change	Response of System
concentration	increase	shifts to consume some of the addes reactant or product
	decrease	shifts to replace some of the removed reactant or product
temperature	increase	shifts to consume some of the added thermal energy
	decrease	shifts to replace some of the removed thermal energy
volume	increase (decrease in pressure)	shifts toward the side with the larger total amount of gaseous entities
	decrease (increase in pressure)	shifts toward the side with hte smaller total amount of gaseous entities
Variables That Do Not Affect Chemical Equilibria		
catalysts	–	no effect
inert gases	–	no effect

Relation between K_p and K_c :

$$K_p = K_c RT^{\Delta n}$$

- **Le-Chatelier's Principle :** When an equilibrium is subjected to any kind of stress (change in concentration, temperature of (pressure) it shifts in a direction so as to undo the effect of stress.
- Factors affecting equilibrium are :
  - **(a) Effect of concentration :** Increase in concentration of any reaction shifts the equilibrium in the forward direction, *i.e.*, net reaction occurs in the forward direction. However, on decreasing the concentration of any reactant, the reaction moves in backward direction and similar changes in concentration of any product results in opposite changes.
  - **(b) Effect of pressure :** On increasing the pressure, the reaction occurs in that direction in which number of moles of the gas or pressure decreases and vice versa.
  - **(c) Effect of temperature :** On increasing the temperature, the reaction occur in that direction in which some heat can be absorbed *i.e.*, endothermic reaction and vice-versa.
  - **(d) Effect of inert gas :** Addition of inert gas at constant volume does not affect the equilibrium.
  - **(e) Effect of catalyst :** Addition of catalyst does not alter the equilibrium, it just helps in attaining the equilibrium faster.

Topic 2

Ionic Equilibrium, Ionization of Acids and Bases, Strong and Weak Electrolytes, Degree of Ionization, Polybasic Acids, Acid Strength, Concept of pH

» Revision Notes

- The equilibrium established between ions and the unionized molecules. This type of equilibrium involving ions in aqueous solution is called ionic equilibrium.
- **Arrhenius Theory :** Substances producing H^+ ion in aqueous solution are called acids and those producing OH^- ions are called bases.

- **Bronsted-Lowry Theory :** Acids are proton donor. Bases are proton acceptor.
  Lewis Theory : Acid accepts electron pair. Base donates electron pair.
- The acid-base pair that differs only by one proton is called conjugate acid-base pair. If Bronsted acid is a strong acid then its conjugate base is a weak base and vice-versa.
- **Ionisation of weak acids** :

$$HX(aq) + H_2O\,(l) \rightleftharpoons H_3O^+\,(aq) + X^-\,(aq)$$

Initial conc. (M)	C	0	0
Let α be the extent of ionization change	$-C\alpha$	$+C\alpha$	$+C\alpha$
Equilibrium concentration	$C - C\alpha$	$C\alpha$	$C\alpha$

$\therefore$ Dissociation or Ionization constant (K_a)

$$K_a = \frac{C^2\alpha^2}{C\,(1-\alpha)} = \frac{C\alpha^2}{1-\alpha}$$

In terms of molar concentration

$$K_a = \frac{[H^+][X^-]}{[HX]}$$

At a given temperature T, K_a is a measure of the strength of the acid HX, i.e., larger the value of K_a, the stronger is the acid.

pH scale for hydrogen ion concentration is :

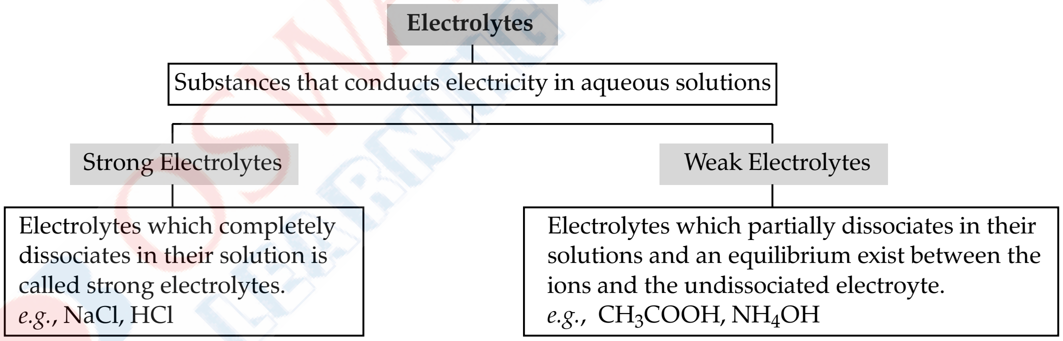
$$pK_a = -\log\,(K_a)$$

- **Ionisation of weak bases** : $MOH_{(aq)} \rightarrow M^+_{(aq)} + OH^-_{(aq)}$

$$K_b = \frac{[M^+][OH^-]}{[MOH]}$$

$$K_b = \frac{(C\alpha)^2}{C\,(1-\alpha)} = \frac{C\alpha^2}{(1-\alpha)}$$

$$pK_b = -\log\,(K_b)$$

- 

Electrolytes

Substances that conducts electricity in aqueous solutions

Strong Electrolytes

Electrolytes which completely dissociates in their solution is called strong electrolytes. *e.g.*, NaCl, HCl

Weak Electrolytes

Electrolytes which partially dissociates in their solutions and an equilibrium exist between the ions and the undissociated electroyte. *e.g.*, CH_3COOH, NH_4OH

- **Degree of ionization :** It is defined as the fraction of number of molecules dissociated into ions and the total number of molecules. It is also called degree of dissociation. It is denoted by α.

$$\alpha = \frac{\text{No. of molecules dissociated}}{\text{Total no. of molecules}}$$

- **Polybasic acids :** Acids having more than one ionizable proton per molecule are called polybasic acids.
- **Acid strength :** It is a measure of H^+ ions produced in an aqueous solution.
- **Factors affecting acid strength :** Depends upon strength and polarity

$$\xrightarrow{\text{Size increases}}$$
$$HF << HCl << HBr << HI$$
$$\xrightarrow[\text{Acid strength increases}]{}$$

$$\xrightarrow{\text{Electronegativity of central atom}}$$
$$CH_4 < NH_3 < H_2O < HF$$
$$\xrightarrow[\text{Acid strength increases}]{}$$

- **pH scale :** Hydronium ion concentration in molarity is more conveniently expressed on a logarithmic scale known as the pH scale. The pH of a solution is defined as the negative logarithm to base 10 of the activity a_{H^+} of hydrogen ion.

$$pH = -\log a_{H^+} = -\log\{[H^+]/\text{mol L}^{-1}\}$$

Acidic solution has $pH<7$
Basic solution has $pH> 7$
Neutral Solution has $pH = 7$
When hydrogen ion concentration, changes by a factor of 10, value of pH changes by 1 unit.

Topic 3

Hydrolysis of Salts, Buffer, Solutions, Henderson Equation, Solubility Product, Common Ion Effect

» Revision Notes

- **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 acids undergo anionic hydrolysis and give basic aqueous solutions.
- **Buffer solution :** A solution which resist the change in its pH value on addition of small amount of acid or base. Buffer solution is generally a mixture of weak acid and its conjugate base or weak base and its conjugate acid.
- **Hendersons Equation :** pH of buffer solution is given by Hendersons- Hasselbalch equation :

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

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

- **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.
- **Common ion effect :** Shift in equilibrium by adding a substance that provides more of an ionic species already present in the dissociation equilibrium.

  For example, in the dissociation of CH_3COOH when a strong electrolyte CH_3COONa is added, common ion CH_3COO^- is furnished and equilibrium shifts to the left and ionization of CH_3COOH is suppressed.

$$CH_3COOH \rightleftharpoons CH_3COO^- + H^+$$
$$CH_3COONa \longrightarrow \underset{\text{Common ion}}{CH_3COO^-} + Na^+$$

KNOW THE TERMS

- **Equilibrium :** It is attained when rate of two opposing processes become equal.
- $\ln K = -\Delta G_0 / RT$

  ΔG_0 is 0, reaction has achieved equilibrium; at this point, there is no longer any free energy left to drive the reaction.
- **pH of solution :** Potency of H^+ in solution. It is negative logarithm of H^+ ion concentration in solution.
- **pOH of solution :** Potency of OH^- ion concentration of the solution.
- **Reaction Quotient :** The reaction quotient, Q (Q_C with molar concentrations and Q_P with partial pressures) is defined in the same way as the equilibrium constant K_C except that the concentrations in Q_C are not necessarily equilibrium values.

❒❒❒

Chapter 8

Redox Reactions

» Revision Notes

- **Oxidation :** A process involving increase in oxidation number by the loss of electrons.

  Or

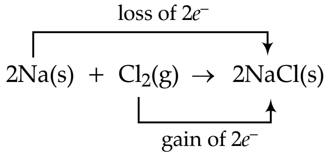
  It can be defined as the addition of oxygen (electronegative element) or removal of hydrogen (electropositive element) in a substance.
- **Reduction :** A process involving decrease in oxidation number by gain of electrons.

  Or

  It can be defined as removal of oxygen (electronegative element) or addition of hydrogen (electropositive element) in a substance.
- **Oxidising agent :** A substance which involves decrease in oxidation number of one or more of its elements. Oxidising agent helps in oxidising the other substance by getting itself reduced.

  $$S + \underset{\substack{\text{Oxidising}\\\text{agent}}}{6HNO_3} \longrightarrow H_2SO_4 + 2H_2O + 6NO_2$$
- **Reducing agent :** A substance which involves increase in oxidation number of one or more of its elements. Reducing agent helps in reducing the other substance by getting itself oxidized.

  $$ZnO + \underset{\substack{\text{Reducing}\\\text{agent}}}{C} \longrightarrow Zn + CO$$
- **Oxidation number :** A residual charge which an atom of the element appears to have when other atoms from the molecule are removed as ions by counting the electrons with more electronegative element.
- Oxidation number of a compound cannot be fractional, because electrons are never shared or transferred in fraction. These are some examples where in a given compound, same element is present in different oxidation states, *e.g.*, Fe_3O_4, Mn_3, O_4, Pb_3O_4, C_3O_2, etc.
- **Rules for assigning oxidation number :**
  - **(a)** Atoms of different elements in elementary state and in allotropic form have oxidation number 0. *e.g.*, N_2, Cl_2, S_8.
  - **(b)** Monoatomic ions have oxidation number same as charge. *e.g.*, $Na^+(1)$, $Mg_2{}^+(2)$, $Cl^-(-1)$.
  - **(c)** Hydrogen with non-metals have oxidation number +1. *e.g.*, H_2O, H_2S and hydrogen with metals have oxidation number –1. *e.g.*, LiH, KH.
  - **(d)** Usually oxygen has oxidation number of -2 (oxide ion e.g CaO, H_2O) but in the compounds of oxygen like peroxides oxygen has the oxidation number of – 1. e.g., H_2O, CaO(–2) and H_2O_2(–1). Oxygen with fluorine have oxidation number +1, +2. *e.g.*, O_2F_2(+1) and OF_2(+2).
  - **(e)** Alkali metal have oxidation number +1. *e.g.*, Li, Na.
  - **(f)** Alkaline earth metals (II A) have oxidation number + 2. *e.g.*, Be, Mg.
  - **(g)** Fluorine (most electronegative) have oxidation number –1. *e.g.*, HF, OF_2, LiF.
- **Redox reaction :** Chemical process involving in which oxidation and reduction occurs simultaneously is called redox reaction. A redox reaction involves transfer of electrons from reducing agent to oxidizing agent.
- In a redox reaction, oxidant is reduced by accepting electrons and reductant is oxidized by losing electrons.



$$2Na(s) + Cl_2(g) \rightarrow 2NaCl(s)$$

- Redox reactions are classified as combination, decomposition, displacement and disproportionation reactions.
- **Types of redox reaction :**

(i) Combination reaction : Two more reactant combine to give a single product A + B → C.

For example : $\overset{0}{C}(s) + \overset{0}{O_2}(g) \xrightarrow{\Delta} \overset{+4}{C}\overset{-2}{O_2}(g)$

$3\overset{0}{Mg}_{(g)} + \overset{0}{N}_{2(g)} \longrightarrow \overset{+2}{Mg_3}\overset{-3}{N}_{2(s)}$

(ii) Decomposition reaction : A single reactant breakdown to give two or more simpler product A → B + C.

For example : $2\overset{+1}{Na}\overset{-1}{H}_{(s)} \longrightarrow \overset{0}{Na}(s) + \overset{0}{H}_{2(g)}$

(iii) Displacement reaction : A more reactive element displaces a less reactive element.

$$X + YZ \longrightarrow XZ + Y$$

(a) Metal displacement : A metal in a compound can be displaced by another metal in the uncombined state.

$$\overset{+2+6-2}{CuSO_4}_{(aq)} + \overset{0}{Zn}_{(s)} \longrightarrow \overset{0}{Cu}_{(s)} + \overset{+2+6-2}{ZnSO_4}_{(aq)}$$

(b) Non-metal displacement : The non-metal displacement redox reactions include hydrogen displacement and a rarely occurring reaction involving oxygen displacement.

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

(iv) Disproportionation reaction : In a disproportionation reaction an element in one oxidation state is simultaneously oxidised and reduced. One of the reacting substances in a disproportionation reaction always contains an element that can exist in at least three oxidation states.

For example : $2\overset{+1}{H_2}\overset{-1}{O_2}(aq) \longrightarrow 2\overset{+1-2}{H_2O}(l) + \overset{0}{O_2}(g)$

- Redox reactions can be balanced by either oxidation number method or half reaction method.
- Balancing of equations of oxidation number method is based upon the fact that loss and gain of electrons in redox process are equal.
- **Balancing redox reaction :**
  - **(a) Oxidation number method :**
    - (i) Select the atom in oxidizing and reducing agents, whose oxidation number increases or decreases and write gain and loss of electrons.
    - (ii) Now cross multiply *i.e.*, oxidizing agent by number of loss of electrons and reducing agent by number of gain of electrons.
    - (iii) Balance the number of atoms on both the sides whose oxidation number change in the reaction.
    - (iv) Balance the charge by adding H^+ ion in acidic medium and OH^- ion in basic medium.
    - (v) Now balance oxygen atom by adding H_2O.
  - **(b) Ion electron method :**
    - (i) Ionic reaction is split into two halves.
    - (ii) Each half is balanced for the number of atoms of each element.
    - (iii) Electrons are added to the side deficient in electrons so as to equalize the charge on both sides.
    - (iv) Both the balanced equations are added.
- **Redox couple :** A redox couple is defined as having together the oxidized and reduced forms of a substance taking part in an oxidation or reduction half reaction.
- Positive and higher electrode potential, E° value means that this redox couple is a greater tendency to get reduced and act a better oxidizing regent.
- More negative value of E° suggest that the redox couple has a greater tendency to get oxidized and act as a better reducing agent.

KNOW THE TERMS

- **Standard electrode potential :** If the concentration of each species taking part in the electrode reaction is unity (if any gas appears in the electrode reaction, it is confined to 1 atmospheric pressure) and further the reaction is carried out at 298 K, then the potential of each electrode is said to be the Standard Electrode Potential.
- **Electrochemical Cell :** A electrochemical cell is an apparatus where chemical energy is converted into electrical energy. *e.g.*, Daniel cell.
- **Salt Bridge :** It is a U-tube filled with a solution of an electrolyte such as KCl or KNO_3 usually solidified by boiling with agar-agar and cooling to a jelly like substance. This allows the conductivity between two solutions of two half cells without extensive mixing of the two.

❑❑❑

Chapter 9

Hydrogen

Topic 1

Position of Hydrogen in the Periodic Table, Preparation and Properties of dihydrogen

» Revision Notes

- Hydrogen is the first element in the periodic table and the lightest element with just one proton and one electron.
- Dihydrogen (H_2) is the most abundant element in the universe (70% of the total mass of the universe) and also a principle element in the solar atmosphere. It occurs in nature as both in free state (in air, natural gases) or in combined state (water, acids, proteins, fats, etc).
- It resembles with both alkali metals and halogens but differs with them in certain aspects. Therefore, it is given a unique position in periodic table.
- **Isotopes :**

  (a) Protium, $_1H^1$ (b) Deuterium, $_1H^2$ or D (c) Tritium, $_1H^3$ or T

  These isotopes show similar chemical properties as they have same electronic configuration but with little difference in their rate of reactions due to different bond enthalpies. However, they show considerable difference in their physical properties due to their large mass differences.
- The predominant form is protium.
- **Preparation :** Hydrogen can be prepared by various methods :

  (i) By the action of water on various metals.

  $$2Na + 2H_2O\ (cold) \longrightarrow 2NaOH + H_2$$

  $$Mg + 2H_2O\ (hot) \longrightarrow Mg(OH)_2 + H_2$$

  $$\underset{(Red\ hot)}{3Fe} + \underset{(Steam)}{4H_2O} \longrightarrow Fe_3O_4 + 4H_2$$

  (ii) By the action of acids and bases on various metals.

  $$Zn + H_2SO_4 \longrightarrow ZnSO_4 + H_{2(g)}$$

  $$2Na + 2HCl \longrightarrow 2NaCl + H_{2(g)}$$

  $$2Al + 2NaOH + 2H_2O \longrightarrow 2NaAlO_2 + 3H_2$$

  (iii) **Manufacture :** On large scale, can be prepared by (a) electrolysis of acidified water (b) from water gas or water-gas shift reaction and (c) from hydrocarbons.

  (a) $2H_2O_{(l)} \xrightarrow[\text{Traces of acid/bases}]{\text{Electrolysis}} 2H_{2(g)} + O_{2(g)}$

  (b) $C_{(s)} + H_2O_{(g)} \xrightarrow{1270\ K} \underbrace{CO_{(g)} + H_{2(g)}}_{\text{water gas or syn gas}} \Rightarrow CO_{(g)} + H_2O_{(g)} \xrightarrow[Fe_2\ (CrO_4)\ \text{catalyst}]{673\ K} CO_{2(g)} + H_{2(g)}$

  (c) $C_nH_{2n+2} + nH_2O \xrightarrow[Ni]{1270\ K} nCO + (2n+1)H_2$

  e.g., $CH_{4(g)} + H_2O_{(g)} \xrightarrow[Ni]{1270\ K} CO_{(g)} + 3H_{2(g)}$

- **Properties of Hydrogen :**

Physical properties :

- It is colourless, odourless and tasteless gas.
- It is highly combustible.
- It is inflammable and does not help in burning.
- It is lighter than air.
- It is insoluble in water.
- It is non-poisonous.

Chemical properties :

(a) Reaction with halogens : $H_{2(g)} + X_{2(g)} \longrightarrow 2HX_{(g)}$ (X = F, Cl, Br, I)

(b) Reaction with dioxygen : $2H_{2(g)} + O_{2(g)} \xrightarrow[\text{Heating}]{\text{Catalyst}} 2H_2O_{(l)}$

(c) Reaction with dinitrogen :

$$H_{2(g)} + N_{2(g)} \xrightarrow[\text{Fe}]{\text{673K, 200 atm}} 2NH_{3(g)}$$

(d) Reaction with metals : $H_{2(g)} + 2M_{(g)} \longrightarrow 2MH_{(s)}$ (M = alkali metal)

(e) Reactions with metal ions and metal oxides :

$$H_{2(g)} + Pd^{2+}{}_{(aq)} \longrightarrow Pd_{(s)} + 2H^+ (aq)$$

$$yH_{2(g)} + M_xO_{y(s)} \longrightarrow xM_{(s)} + yH_2O_{(l)}$$

(f) Reactions with organic compounds :

$$H_2 + CO + RCH = CH_2 \longrightarrow RCH_2CH_2CHO$$

$$H_2 + RCH_2CH_2CHO \longrightarrow RCH_2CH_2CH_2OH$$

- **Uses of Hydrogen :**
  - It is used for hydrogenation of oils.
  - It is used in the manufacture of ammonia and as a fuel.
  - It is used in metallurgy.
  - It is used in oxy-hydrogen torch.
  - It is used as a reducing agent in industries and laboratories.
  - It is used in preparation of metal hydrides.
  - It is used in fuel cells to generate electric energy.

Topic 2

Compounds of Hydrogen [Hydrides, Water, Heavy Water (D_2O), Hydrogen peroxide]

» Revision Notes

- **Hydrides :** Dihydrogen under certain conditions form three types following hydrides :

(a) Ionic hydrides or saline hydrides are the hydrides of *s*-block element. *e.g.*, LiH, NaH, BeH_2, MgH_2.

(b) Covalent or molecular hydrides are molecular compounds with *p*-block elements. *e.g.*, CH_4, NH_3, H_2O and HF. These can be further classified as :

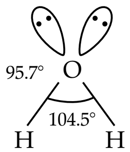
(i) **Electron-deficient hydrides :** *e.g.*, Diborane (B_2H_2).

(ii) **Electron-precise hydrides :** *e.g.*, Methane (CH_4) and other hydrides of group-14 elements.

(iii) **Electron rich hydrides :** Hydrides of group 15-17 elements form these types of hydrides. *e.g.*, NH_3, H_2O, HF etc.

(c) Metallic or non-stoichiometric hydrides are the hydrides of many *d*-block and *f*-block elements. Metals of group 6 (except CrH), 7, 8 and 9 do not form hydride. *e.g.*, $LaH_{2.87}$, $YbH_{2.55}$, $TiH_{1.5\text{-}1.8}$, $ZrH_{1.3\text{-}1.75}$, $VH_{0.56}$, $NiH_{0.6\text{-}0.7}$, $PdH_{0.6\text{-}0.8}$, etc.

- **Structure of water :** Water is a covalent molecule containing two lone pairs. The H—O—H bond angle is 104.5°. Molecule is angular or bent in shape.



- **Physical properties of water :**
  - It is transparent, colourless, odourless and tasteless.
  - It has a high specific heat, thermal conductivity surface tension, dipole moment and dielectric constant due to the presence of extensive hydrogen bonding between water molecules.
  - It is a poor conductor of heat and electricity.
- **Chemical properties of water :**

(i) Amphoteric Nature : Water acts as both as an acid as well as base.

Amphoteric Nature :

$$\underset{\text{Acid}}{H_2O_{(l)}} + \underset{\text{base}}{NH_{3(aq)}} \rightleftharpoons OH^-_{(aq)} + NH_4^+{}_{(aq)}$$

$$\underset{\text{Water}}{H_2O_{(l)}} + \underset{\text{acid}}{H_2S_{(aq)}} \rightleftharpoons H_3O^+_{(aq)} + HS^-_{(aq)}$$

(ii) Reduction Reaction :

$$2H_2O + 2Na \longrightarrow 2NaOH + H_2$$

(iii) Hydrolysis Reaction :

$$SiCl_4 + 2H_2O \longrightarrow SiO_2 + 4HCl$$

$$P_4O_{10(s)} + 6H_2O_{(l)} \longrightarrow 4H_3PO_{4(aq)}$$

$$N_3^-{}_{(s)} + 3H_2O_{(l)} \longrightarrow NH_{3(g)} + 3OH^-_{(aq)}$$

(iv) Water can be reduced to hydrogen by highly electropositive metals.

(v) Water is oxidized to O_2 during photosynthesis and with fluorine.

$$6CO_{2(g)} + 12H_2O_{(l)} \longrightarrow C_6H_{12}O_{6(aq)} + 6H_2O_{(l)} + 6H_2O_{(g)}$$

$$2F_{2(g)} + 2H_2O_{(l)} \longrightarrow 4H^+_{(aq)} + 4F^-_{(aq)} + O_{2(g)}$$

(vi) Hydrates formation : Many salts can be crystallized as hydrate salt from their aqueous solution.

Coordinated water, *e.g.*, $[Cr(H_2O)_6]^{3+}3Cl^-$

Interstitial water, *e.g.*, $BaCl_2.2H_2O$

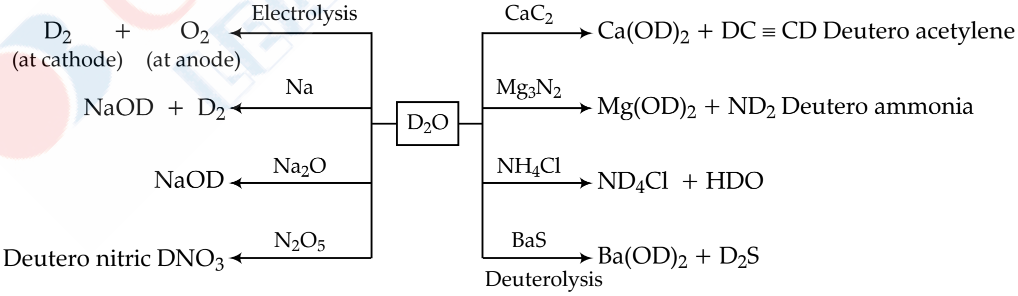
Hydrogen bonded water *e.g.*, $[Cu(H_2O)_4]^{2+}$ SO_4^{2-}, H_2O in $CuSO_4.5H_2O$

- **Heavy water :** Heave water is the form of water consisting of isotope of hydrogen (deuterium).

It is also known as deuterium oxide (D_2O). It is prepared either by prolonged electrolysis or by fractional distillation of ordinary water.

- **Properties of heavy water :**

Heavy water is colourless, odourless, tasteless, liquid and has higher values for all physical constants than the ordinary water.



- **Uses of deutero nitric acid DNO_3 :**
  - It is used as a moderator in nuclear reactor.
  - It is also used as a germicide and bactericide.
- **Hydrogen peroxide :**

Hydrogen peroxide, H_2O_2 is also known as oxygenated water.

Preparation of H_2O_2 :

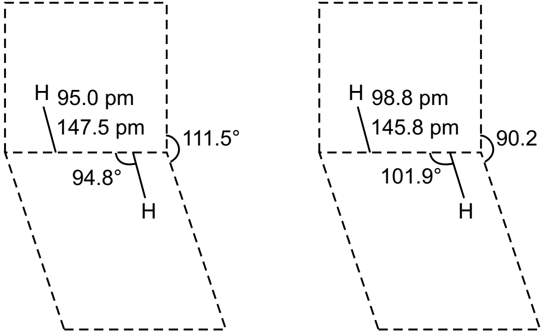
(i) H_2O_2 is prepared by Merck's process as :

$$Na_2O_2 + H_2SO_4 \longrightarrow Na_2SO_4 + H_2O_2$$

(ii) Industrially it is manufactured by the auto oxidation of 2-alkylanthraquinols.

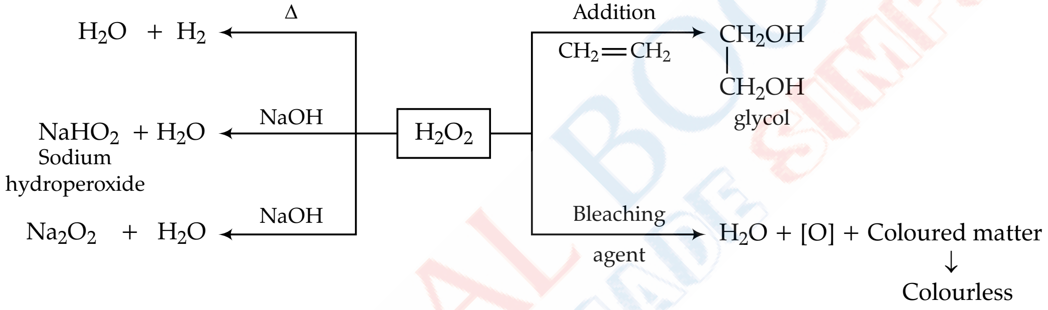
$$\text{2-ethylanthraquinone} \underset{H_2/Pd}{\overset{O_2\text{ (air)}}{\rightleftharpoons}} H_2O_2 + \text{(Oxidised product).}$$

- **Structure of H_2O_2 :**
  (a) H_2O_2 structure (gas phase) dihedral angle 111.5°,
  (b) H_2O_2 (solid phase at 110 K. The dihedral angle is reduced to 90.2°.



(a) Gas phase (b) Solid phase

- **Physical properties of H_2O_2 :**
  Due to the presence of stronger hydrogen bonding as compared to water, it has higher boiling point than water.
- **Chemical properties of H_2O_2 :**



- Oxidising action in acidic medium :

$$2Fe^{2+}_{(aq)} + 2H^+_{(aq)} + H_2O_{2(aq)} \longrightarrow 2Fe^{3+}_{(aq)} + 2H_2O_{(l)}$$
$$PbS_{(s)} + 4H_2O_{2(aq)} \longrightarrow PbSO_4 + 4H_2O_{(l)}$$

- Reducing action in acidic medium :

$$2MnO_4^- + 6H^+ + 5H_2O_2 \longrightarrow 2Mn^{2+} + 8H_2O + 5O_2$$
$$HOCl + H_2O_2 \longrightarrow H_3O^+ + Cl^- + O_2$$

- Oxidising action in basic medium :

$$2Fe^{2+} + H_2O_2 \longrightarrow 2Fe^{3+} + 2OH^-$$
$$Mn^{2+} + H_2O_2 \longrightarrow Mn^{4+} + 2OH^-$$

- Reducing action in basic medium :

$$I_2 + H_2O_2 + 2OH^- \longrightarrow 2I^- + 2H_2O + O_2$$
$$2MnO_4^- + 3H_2O_2 \longrightarrow 2MnO_2 + 3O_2 + 2H_2O + 2OH^-$$

- **Uses of H_2O_2 :**
  - It is employed in the industry as a bleaching agent.
  - It is used as germicide and antiseptic.
  - It is used as a propellant for rockets.
  - It is used for the preparation of various organic and inorganic compounds like H_2SO_5, Na_2O_2, etc.
  - It is used as a hair bleach and mild disinfectant.

KNOW THE TERMS

- **Soft Water :** Water free from soluble salts of calcium and magnesium. It produces lather with soap readily.
- **Hard Water :** Presence of calcium and magnesium salts in the form of hydrogencarbonate, chloride and sulphate in water makes it hard. It does not produce lather with soap.
- **Water Gas or Syn Gas :** The mixture of CO and H_2 is called water gas. As this mixture of CO and H_2 is used for the synthesis of methanol and a number of hydrocarbons, it is also called synthesis gas or 'syngas'. Nowadays 'syngas' is produced from sewage, saw-dust, scrap wood, newspapers etc.
- **Hydrogen Economy :** In space programmes, it is used as a rocket fuel. In fact, it has promising potential for use as a non-polluting fuel of the near future.

❐❐❐

Chapter 10

s-Block Elements

(Alkali and Alkaline Earth Metals)

Topic 1

General Characteristics of Group I and II Elements

» Revision Notes

- ➢ ***s*-Block elements :** *s*-block element are those elements in which the last electron enters in the *s*-orbitals. They contain group I elements (alkali metals) and group II elements (alkaline earth metals). The general electronic configuration of *s*-block elements is [noble gas] ns^1 for alkali metals and [noble gas] ns^2 for alkaline earth metals.

***s*-block elements**

Group I

Element with symbol	Electronic configuration
Lithium, Li	[He] $2s^1$
Sodium, Na	[Ne] $3s^1$
Potassium, K	[Ar] $4s^1$
Rubidium, Rb	[Kr] $5s^1$
Cesium, Cs	[Xe] $6s^1$
Francium, Fr	[Rn] $7s^1$

Group II

Element with symbol	Electronic configuration
Beryllium, Be	[He] $2s^2$
Magnesium, Mg	[Ne] $3s^2$
Calcium, Ca	[Ar] $4s^2$
Strontium, Sr	[Kr] $5s^2$
Barium, Ba	[Xe] $6s^2$
Radium, Ra	[Rn] $7s^2$

- ➢ Group 1 elements show +1 oxidation state and group 2 elements show +2 oxidation state.
- ➢ Group I elements act as strong reducing agents due to their low ionization enthalpies.
- ➢ All alkali metals impart characteristic colour to the flame. *e.g.*, Li-caramine red, Na-golden yellow, K-pale violet, Rb-red violet and Cs-sky blue. Most of the alkaline earth metals also show flame coloration. For example, Ca-Brick red, Sr-Blood red, Ba-Apple green and Ra-Crimson.
- ➢ Sodium is the most abundant element among group I and calcium is the most abundant element among group II.
- ➢ Group II elements have strong metallic bond as compared to group I elements, therefore group II elements are harder and have high melting points as compared to group I elements.
- ➢ **Physical properties :**
  - **(a) Physical appearance :** Group I elements are silvery white, soft and light metals.
    Group II elements are silvery white, lustrous and relatively soft but harder than group I elements.
  - **(b) Melting and boiling points :** Group I elements have low melting and boiling points due to the weak bonding in the crystal lattices of the metals. Group II elements have comparatively higher melting and boiling points.
  - **(c) Density :** Group I elements have lower densities, increases from lithium to caesium. However, potassium is lighter than sodium.
- ➢ **Anomalous properties of lithium :**
  - **(a)** Lithium has small size.

(b) Lithium has high polarizing power.
(c) Lithium is harder and have high melting and boiling point.
(d) Lithium is deliquescent.
(e) It is least reactive and readily reacts with N_2 to form Li_3N.
(f) Lithium has high heat of hydration.

- **Anomalous properties of beryllium :**
  (a) Beryllium has small size and highest ionization energy. It forms predominately covalent compounds which are readily hydrolysed.
  (b) It forms amphoteric oxides and hydroxides.
  (c) It is harder and have high melting and boiling point.
  (d) It has no vacant *d*-orbitals.
  (e) It has high electronegativity.
  (f) It has high charge density and high hydration energy.
- **Diagonal relationship :** Some elements of certain groups in the second period resembles with the certain elements of the next higher group in the third period *i.e.*, resembles diagonally. This is called diagonal relationship.
  (a) **Diagonal relationship between lithium and magnesium :**
    (i) They have almost similar atomic radii and electronegativity.
    (ii) Both of them are harder.
    (iii) LiF_2 is partially soluble in water like MgF_2.
    (iv) LiOH and $Mg(OH)_2$ are both weak bases.
    (v) Bicarbonates of Li and Mg do not exist in solid state.
  (b) **Diagonal relationship between beryllium and aluminium :**
    (i) Both the metals are stable in air.
    (ii) Both of them cannot be decomposed with water.
    (iii) They do not impart any colour to flame.
    (iv) They have similar electronegativity.
    (v) Both form amphoteric oxide and hydroxide.
- **Trends in the properties :**
  (a) **Ionisation enthalpy :** Alkali metals have lowest ionization enthalpy because of their largest size in their respective periods, solitary electron present in the valence shell can be removed by supplying small amount of energy. Ionisation enthalpy decreases from Li to Cs due to increase in atomic size.

  Alkaline metals have highest ionization enthalpy than alkali metals because of increase in nuclear charge. From top to bottom, ionisation enthalpy decreases with the addition of one orbit each time.

  (b) **Atomic and ionic radii :** The alkali metal atoms have the largest sizes in a particular period in the periodic table. Atomic and ionic radii increases form Li to Fr due to the presence of an extra shell of electrons.

  (c) **Hydration enthalpy :**

  The degree of hydration depends upon the size of cation.

  The hydration enthalpies of alkali metal ions are in the order

  $$Li^+ > Na^+ > K^+ > Rb^+ > Cs^+.$$

  The hydration enthalpies of alkaline earth metal ions are in the order.

  $$Be^{2+} > Mg^{2+} > Ca^{2+} > Sr^{2+} > Ba^{2+}$$

  (d) **Melting and boiling point :** Alkali metals show low mp and bp and decreases with increase atomic number.

  The melting and boiling point of alkaline earth metals are higher than those of alkali metals.

Topic 2

Preparation, Properties and Biological Importance of Alkali and Alkaline Earth Metal Compounds

» Revision Notes

- **Trends in chemical reactivity** :

  As the ionization energy decreases, their reactivity also increases. Therefore, alkali metals are highly reactive. The reactivity of alkali metals increases from Li to Cs.

  The alkaline earth metals are less reactive than alkali metals. The reactivity of alkaline earth metals increases on going down the group.

(a) Reactivity with Oxygen :

- The alkali metals are tarnished in acid due to the formation of oxide at their surface and hence they are stored in kerosene oil.

$$4Li + O_2 \xrightarrow[\text{oil}]{\text{Burnt in}} 2Li_2O$$

Sodium forms sodium peroxide (Na_2O_2) and other alkali metals form super oxides [MO_2 where, M = K, Rb, Cs)].

- The alkaline earth metals react slowly with oxygen to from oxides which are basic in nature.

$$2BaO + O_2 \xrightarrow{773\text{ K}} 2BaO_2$$

(b) Reactivity with Water :

- Alkali metals react readily and vigorously with water forming hydroxide with the liberation of hydrogen.

$$2M + 2H_2O \longrightarrow 2MOH + H_2\uparrow \qquad [M = Li, Na, K, Rb, Cs]$$

- Alkaline earth metals are less reactive with water. Be do not react with water. Mg reacts only with hot water and Ca, Sr and Ba reacts with cold water.

(c) Reactivity with Hydrogen :

- Alkali metals reacts with hydrogen and form ionic hydride.

$$2M + H_2 \longrightarrow 2MH \qquad [M = Li, Na, K, Rb, Cs]$$

- Except Be, all other alkaline earth metals combine with H_2 upon heating to form hydrides.

$$Ca + H_2 \xrightarrow{\Delta} CaH_2$$

(d) Reactivity with Halogens :

- Alkali metals react with halogens to form metal halide.

$$2M + X_2 \longrightarrow 2MX$$

- All the alkaline earth metals react with halogens at elevated temperature forming halides.

$$M + X_2 \longrightarrow MX_2 \qquad [X = F, Cl, Br, I]$$

➢ **Preparation and properties of some important compounds :**

1. Sodium Carbonate :

The various form of sodium carbonate are Na_2CO_3 (soda ash), $Na_2CO_3.H_2O$ (monohydrate) and $Na_2CO_3.10H_2O$ Washing soda also called sodium carbonate decahydrate. Sodium bicarbonate is known as baking soda.

Sodium carbonate is prepared by Solvay process as :

$$2NH_3 + H_2O + CO_2 \longrightarrow (NH_4)_2CO_3$$
$$(NH_4)_2CO_3 + H_2O + CO_2 \longrightarrow 2NH_4HCO_3$$
$$NH_4HCO_3 + NaCl \longrightarrow NaHCO_3 + NH_4Cl$$
$$2NaHCO_3 \xrightarrow{\Delta, 150°C} Na_2CO_3 + H_2O + CO_2$$

Properties :

(i) It is a white crystalline solid.
(ii) It is readily soluble in water.
(iii) On heating, the dehydrate loses its water of crystallisation and forms monohydrate
Above 373 K, it becomes soda ash white coloured anhydrous powder.

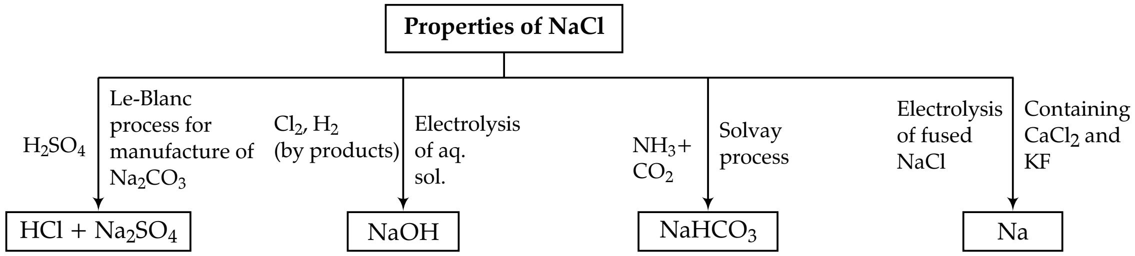
$$Na_2CO_3.H_2O \xrightarrow{> 373\text{ K}} Na_2CO_3 + H_2O$$

Uses :

(i) It is used in laundries as washing soda and also used as water softener.
(ii) It is used in the manufacturing of glass, caustic soda, etc.
(iii) It is used in paper, paints and textile industries.

2. Sodium Chloride :

Generally, NaCl is obtained by evaporation of sea water in sun. However, NaCl so obtained contains impurities like $CaSO_4$, $CaCl_2$, $MgCl_2$, etc. Pure sodium chloride is prepared by passing HCl gas into saturated solution of commercial salt.



Uses :

(i) It is used as table salt.

(ii) It is used in preparation of Na_2CO_3, NaOH, Na_2O_2, etc.

3. **Sodium Hydroxide :**

It is prepared by electrolysis of brine in Castner Kellner cell.

A brine solution is electrolysed using a mercury cathode and a carbon anode. Sodium metal discharged at cathode combines with mercury to form sodium amalgam chlorine gas is evolved at the anode.

Cathode : $Na^+ + e^- \xrightarrow{Hg} \text{Na-amalgam}$

Anode : $Cl^- \longrightarrow \frac{1}{2}Cl_2 + e^-$

The amalgam is treated with water to give hydrogen gas and sodium hydroxide.

$$2\text{Na-amalgam} + 2H_2O \rightarrow 2NaOH + 2Hg + H_2$$

$$2NaCl + 2H_2O \rightarrow 2NaOH + Cl_2 + H_2$$

Properties :

$$NaOH \xrightarrow{CO_2} Na_2CO_3$$

$$NaOH \xrightarrow{SiO_2} Na_2SiO_3$$

$$NaOH \xrightarrow{CO} HCOONa$$

Uses :

(i) It is used as a laboratory reagent

(ii) It is used in the manufacturing of dyes, soap, paper, etc.

(iii) It is used in textile industry.

iv) Used in preparations of fats and oils.

4. **Sodium Hydrogencarbonate :**

Sodium hydrogencarbonate or sodium bicarbonate is obtained as an intermediate compound in Solvay process. It is also called baking soda. It is prepared as :

$$Na_2CO_3 + CO_2 + H_2O \rightarrow 2NaHCO_3.$$

Properties :

It decomposes on heating and produces, bubbles of CO_2 which helps in making the cakes and pastries fluffy.

$$2NaHCO_3 \xrightarrow{\Delta,\,100°C} Na_2CO_3 + H_2O + CO_2$$

Uses :

(i) It is used in preparing cakes, pastries as a baking powder.

(ii) It is used as antacid and mild antiseptic.

➢ **Biological importance of sodium and potassium :**

- Sodium and potassium cations plays an important role in biological fluid.
- They are present in the ratio of 7 : 1 in human beings.
- These ions accumulate in cells and creates a concentration gradient and potential in the membrane.
- These ions participate in transmission of nerve signal, in regulating flow of water across cell membrane.
- These ions activate many enzymes.

Topic 3

Industrial Use of Lime and Limestone, Biological Significance of Ca^{2+}, Mg^{2+} Ions

» Revision Notes

➢ Calcium oxide (CaO) is known as quick lime.

➢ Calcium hydroxide [$Ca(OH)_2$] is known as slaked lime.

➢ The aqueous solution of calcium hydroxide is known is lime water.

➢ Hemihydrate of calcium sulphate ($CaSO_4$. ½ H_2O) is known as plaster of paris.

➢ **Industrial use of lime :**

(i) Lime is used in chemical industries in the processes of purifying metals, neutralization, precipitation, hydrolysis, dehydration, exothermic reactions, coagulation, and saponification.

(ii) Lime is used to purify sugar from other sources such as maple.

(iii) It is used in glass products.
(iv) It is used in construction and building materials.
(v) It is used to reconstitute caustic soda from Na_2CO_3.

- **Industrial use of limestone :**
  (i) Limestone is used for roadbeds, buildings and landscape construction and cement manufacture.
  (ii) It is used as façade on skyscrapers but only in thin sheets rather than solid blocks.
  (iii) Powder of limestone is used to neutralize soil that is 100% acidic.
  (iv) Lumps of limestone is used in buildings.
- **Biological importance of magnesium :**
  (a) It is present in chlorophyll and plays a vital role in photosynthetic activity.
  (b) Magnesium ions are essential for many enzymes and proteins.
  (c) Magnesium ions binds to DNA molecules to stabilize its structure.
  (d) ATP molecules bind to these ions to become biologically active.
  (e) In nucleotides, the triple phosphate moiety of the compound is invariably stabilized by association with Mg^{2+} in all enzymic process.
- **Biological importance of Calcium :**
  (a) Calcium is present in bones and teeth
  (b) Calcium ions are required in blood clotting.
  (c) Blood is a large tank of this mineral.
  (d) Calcium ions are essential to trigger the contraction of muscles.
  (e) It is also required for the regular beating of heart.

❑❑❑

Chapter 11

Some p-Block Elements

Topic 1

General Characteristics of Group-13 Elements

» Revision Notes

- ➢ ***p*-Block Elements :** *p*-block elements are those elements in which the last electron enters in the outermost *p*-orbital.

***p*-block elements**

Group 13

Element with symbol	Electronic configuration
Boron, B	[He] $2s^1p^1$
Aluminum, Al	[Ne] $3s^13p^1$
Gallium, Ga	[Ax] $3d^{10}\ 4s^2\ 4p^1$
Indium, In	[Kr] $4d^{10}\ 5s^2\ 5p^1$
Thallium, Tl	[Xe] $4f^{14}\ 5d^{10}\ 6s^2\ 6p^1$

Group 14

Element with symbol	Electronic configuration
Carbon, C	[He] $2s^1p^1$
Silicon, Si	[Ne] $3s^13p^1$
Germanium, Ge	[Ax] $3d^{10}\ 4s^2\ 4p^1$
Tin, Sn	[Kr] $4d^{10}\ 5s^2\ 5p^1$
Lead, Pb	[Xe] $4f^{14}\ 5d^{10}\ 6s^2\ 6p^1$

- ➢ General electronic configuration of elements of group 13 is $ns^2\ np^{1-6}$.
- ➢ Group 13 elements shows +3 oxidation state.
- ➢ Aluminium is the third most abundant element (after oxygen and silicon).
- ➢ Boron is non-metallic in nature. It has high melting point.
- ➢ The tendency to behave as Lewis acid decreases with the increase in size down the group.

Element	Increasing trends	Decreasing trends	Exceptions
B	• Atomic Radii (M) • Ionic Radii	• Ionisation energies	• Atomic size of Ga < Al • IE_1 of Tl>Al
Al	• Inert pair effect • Tendency to show +1 oxidation state.	• Melting/Boiling Point	• IE_1 of Ga ≈ Al
Ca	• Tendency to form ionic compounds • Electropositive character	• Tendency to show +3 oxidation state	
In	• Lewis acid strength of	• Tendency to form covalent compounds	
Tl	• Trihalides of B increases from $BF_3 \rightarrow BBr_3$		

Topic 2

Compounds of Boron and Aluminium, their Properties and Uses

» Revision Notes

- **Trends in chemical reactivity :**
  - These elements are less reactive than group 1 and 2 elements.
  - All the elements of group 13 forms an ionic compound except boron. Boron forms covalent compounds.
  - **Reaction with oxygen :**

    Boron forms a mixture of oxides and nitride when heated at 700°C in air.

    $$4B + 3O_2 + N_2 \xrightarrow[700°C]{\Delta} 2B_2O_3 + 2BN$$

  - Oxygen does not have any effect on aluminium. However, in the presence of most air, a thin layer of oxide is formed on the surface of aluminium.
  - **Reaction with water :**

    Except boron, group B elements decompose boiling water to give hydrogen gas.

  - **Reaction with halogens :**

    Group 13 elements react with halogens to form trihalides except thallium.

    $$2E + 3X_2 \longrightarrow 2EX_3 \ (X = F, Cl, Br, I)$$

  - **Reaction with acids :** Boron does not react with acids and alkalies even at moderate temperature, but aluminium dissolves in mineral acids and aqueous alkali and thus, show amphoteric character.
- **Anomalous properties of boron :**

  (a) It has small size.

  (b) It has high ionization energy.

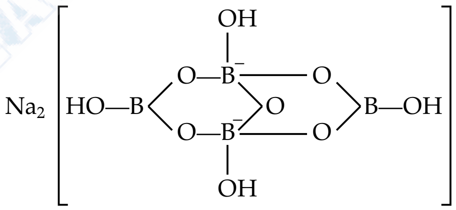
  (c) It has high electronegativity.

  (d) It has vacant *d*-orbitals.

- **Some Important Compounds :**

  Borax, $Na_2B_4O_7.10H_2O$ is represented as $Na_2[B_4O_5(OH)_4].8H_2O$.

- **Structure :**



- When borax is heated, it first loses water molecules and swells up. On further heating, it turns into a transparent liquid which solidifies into glass like material known as borax bead.

$$Na_2B_4O_7.10H_2O \xrightarrow{\Delta} Na_2B_4O_7 \xrightarrow{\Delta} \underset{\text{Sodium metaborate}}{2NaBO_2} + \underset{\text{Boric anhydride}}{B_2O_3}$$

- **Uses :**

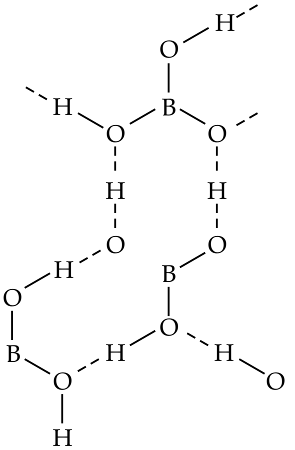
  (a) Borax is used as an antiseptic.

  (b) It is used in the manufacturing of soaps and washing powders.

  (c) It is used as a cleansing agent.

  (d) It is used in the manufacturing of optical glass.

- **Boric Acid :** Boric acid is represented as H_3BO_3. It is also called orthoboric acid.
- **Structure :** Orthoboric acid has a layer structure with planar BO_3 units which are joined by hydrogen bonds.



- **Preparation :** H_3BO_3 is prepared by acidifying an aqueous solution of borax.

$$Na_2B_4O_7 + 2HCl + 5H_2O \longrightarrow 2NaCl + \underset{\text{Boric acid}}{4B(OH)_3}$$

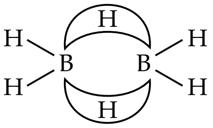
- Boric acid is Lewis acid and not protic acid.

$$B(OH)_3 + 2HOH \longrightarrow [B(OH)_4]^- + H_3O^+$$

- **Effect of heating :**

$$H_3BO_3 \xrightarrow{\Delta} \underset{\text{Metaboric acid}}{HBO_2} \xrightarrow{\Delta} \underset{\text{Boric oxide}}{B_2O_3}$$

- **Uses :**
  (a) It is used in food industries as a food preservative.
  (b) It is used in the manufacture of borax.
  (c) It is used for making borosilicate glass.
- **Boron Hydride :** Boron forms a number of hydrides. The most important hydride of boron is diborane, B_2H_6.
- Diborane is a colour less, highly toxic gas that catches fire immediately on exposure to air.
- **Structure :** In diborane, each boron atom is bonded with two terminal hydrogen atoms. Two other hydrogen atom form between two boron atoms and are known as bridging hydrogen atoms. These bonds are three-centred two electron bonds.



- **Preparation :** B_2H_6 is prepared as :
  (a) $4BF_3 + 3LiAlH_4 \longrightarrow 2B_2H_6 + 3LiF + 3AlF_3$
  (b) $2NaBH_4 + I_2 \longrightarrow B_2H_6 + 2NaI + H_2$ (Laboratory method)
  (c) $2BF_3 + 6NaH \xrightarrow{450\text{ K}} B_2H_6 + 6NaF$ (Industrial method)
- **Reaction of diborane :**
  (a) $B_2H_{6(g)} + 6H_2O_{(l)} \longrightarrow \underset{\text{Boric acid}}{2B(OH)_{3(aq)}} + 6H_{2(g)}$
  (b) $B_2H_6 + 2NMe_3 \longrightarrow 2BH_3.NMe_3$
  $B_2H_6 + 2CO \longrightarrow 2BH_3.CO$
  $3B_2H_6 + 6NH_3 \longrightarrow 3[BH_2(NH_3)_2]^+ [BH_4]^-$
  $\xrightarrow{\Delta} 2B_3N_3H_6 + 12H_2$ (Borazine)
- **Uses :**
  (a) It is used as a reducing agent.
  (b) It is used for making high energy fuels.

- **Reaction of aluminium with acids :**
  - **(a)** $2Al_{(s)} + 6HCl_{(aq)} \longrightarrow 2AlCl_{3(aq)} + 3H_{2(aq)}$
  - **(b)** $2Al_{(s)} + 3H_2SO_{4(aq)} \longrightarrow Al_2(SO_4)_{3(aq)} + 3H_{2(g)}$
  - **(c)** $2Al + 6H_2SO_4\,(\text{conc.}) \xrightarrow{\Delta} Al_2(SO_4)_3 + 2SO_2\uparrow + 6H_2O$
- **Reaction of aluminium with alkalies :**
  - **(a)** $2Al_{(s)} + 2NaOH_{(aq)} + 6H_2O \longrightarrow 2Na[Al(OH)_4]_{(aq)} + 3H_{2(g)}$
  - **(b)** $2Al + 2NaOH + 2H_2O \longrightarrow \underset{\text{Sodium meta aluminate (soluble)}}{2NaAlO_2} + 3H_2$
  - **(c)** $2Al + 6NaOH \longrightarrow \underset{\text{Sodium aluminate}}{2Na_3.AlO_3} + 3H_2\uparrow$
- **Uses :**
  - **(a)** Aluminium is used in making pipe, tubes, rods, wires, plates or foil etc.
  - **(b)** It is used as a conductor for transmission of electricity.
  - **(c)** It is also used in the alumino thermite process.

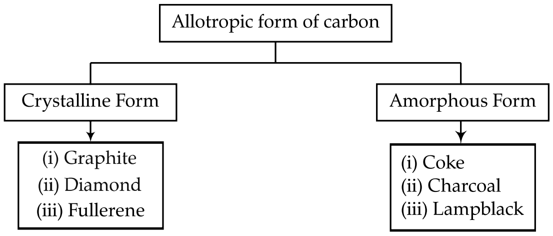
Topic 3

Trends in Periodic Properties of Group 14 Elements

» Revision Notes

- General electronic configuration of elements of group 14 is ns^2np^2.
- Carbon and silicon mostly show +4 oxidation state while other elements show both +2 and +4 oxidation states.
- Atomic radii increases down the group.
- Ionisation enthalpy decreases down the group.

Element	Increasing Trends	Decreasing Trends	Exceptions
C	• Atomic radii • Inert pair effect	• Ionisation energy • Electronegativity	• IE of Pb > Sn • IE of Ge ≈ Sn
Si	• Metallic character	• Non-metallic character	• Only C has ability to form $p\pi - p\pi$ bonding.
Ge	• Tendency of +2 oxidation	• Tendency of +4 oxidation state	• The order of catenation is C >> Si > Ge ≈ Sn
Sn	• Tendency of forming ionic compounds	• Tendency of forming covalent compounds	• All elements except Pb show catenation
Pb	• Reducing character of hydrides (MH_4)	• Thermal stability of hydrides • M-M bond strength • Tendency of catenation	• Carbon shows allotropy due to catenation and $p\pi$-$p\pi$ bond formation

- **Anomalous behaviour of carbon :** Carbon shows anomalous behaviour because of its smaller size, high electro negativity absence of *d*-orbital and high tendency of catenation.
- **Catenation :** Catenation is the property of an element in which elements form long chains or rings by self-linking of their own atoms.
- 

(i) Graphite :

- Graphite is soft and slippery with density of 2.3 g/ml.
- It is black coloured, opaque and has hexagonal crystal.
- It is good conductor of electricity.
- In graphite, carbon atoms are bonded together in flat layers by strong covalent bonds in a regular hexagon. These layers are held together by much weaker van der Waal's forces, therefore, the crystals of graphite are soft and slippery.

Uses :

- It is used in steel manufacture refractories pencils, high temperature crucibles.

(ii) Diamond :

- Diamond is the hardest substance known and its density is 3.5 g/ml.
- Its crystal are octahedral, colourless and transparent.
- It is non-conductor of electricity.
- In diamond, each carbon atom is covalently bonded to four other carbon atoms along four corners of regular tetrahedran. This pattern extends in three dimensions.
- Diamond is hard due to strong covalent bonds present in it.

Uses :

- It is used in gemstone, cutting, drilling, grinding, polishing industry.

(iii) Fullerene :

- Fullerene are highly soluble in non-polar solvents.
- In fullerene C atom are arranged in a spherical or elliptical structure.

Topic 4

Physical and Chemical Properties and Uses of Group 14 Elements and their Compounds

» Revision Notes

- **Oxides of Carbon :** Two important oxides of carbon are carbon monoxide (CO) and carbon dioxide (CO_2).
- **Carbon monoxide (CO) :** Carbon monoxide is a powerful reducing agent.
- **Preparation :**

(i) $2C_{(s)} + O_{2(g)} \longrightarrow 2CO_{(g)}$

(ii) $HCOOH \xrightarrow{\Delta} H_2O + CO$

(iii) $C_{(s)} + H_2O_{(g)} \xrightarrow{473\text{-}1273\ K} \underbrace{CO_{(g)} + H_{2(g)}}_{\text{Water gas}}$

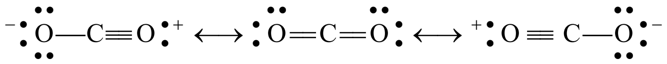
(iv) $2C_{(s)} + O_{2(g)} + 4N_{2(g)} \xrightarrow{1273\ K} \underbrace{2CO_{(g)} + 4N_{2(g)}}_{\text{Producer gas}}$

- CO molecule (: C ≡ O:) has a lone pair on carbon therefore acts as a donor and form metal carbonyls.

Uses :

- It is used in the extraction of many metals from their oxide ores.
- It is used as reducing agent.

- **Carbon dioxide (CO_2) :**
- **Structure :**



$$^{-}:\ddot{O}-C\equiv O:^{+} \longleftrightarrow :\ddot{O}=C=\ddot{O}: \longleftrightarrow {}^{+}:O\equiv C-\ddot{O}:^{-}$$

- **Preparation :**

(i) $C_{(s)} + O_{2(g)} \xrightarrow{\Delta} CO_{2(g)}$

(ii) $CH_{4(s)} + 2O_{2(g)} \xrightarrow{\Delta} CO_{2(g)} + 2H_2O_{(g)}$

(iii) $CaCO_{3(s)} + 2HCl_{(aq)} \xrightarrow{\Delta} CaCl_{2(g)} + CO_{2(g)} + H_2O_{(g)}$

(iv) $CaCO_{3(s)} \longrightarrow CaO_{(s)} + CO_{2(g)}$

➢ **Uses :**

(a) It is used in manufacturing of washing soda.

(b) It is used as fire extinguisher.

➢ **Some important compounds of silicon :**

(i) **Silicon tetrachloride ($SiCl_4$) :** It is a colourless, fuming liquid and its boiling point is 56.8°C.

➢ **Preparation :** $Si_{(s)} + 2Cl_{(g)} \xrightarrow{\Delta} SiCl_{4(l)}$

$$SiC_{(s)} + 4Cl_{2(g)} \xrightarrow{\Delta} SiCl_{4(l)} + CCl_{4(l)}$$

$$SiO + 2C + 2Cl_2 \xrightarrow{\Delta} SiCl_4 + 2CO$$

➢ **Uses :**

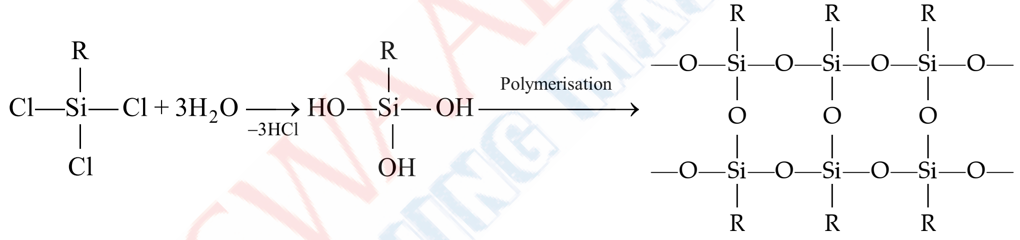
It is used in the preparation of silica and silicones.

(ii) **Silicones :**

- Silicones are organosilicon polymers with $(R_2SiO)_n$ repeating units.
- Silicones have high thermal stability, high dielectric strength and resistance to oxidation and chemicals.
- Silicones are water repellent and antifoaming agents.

Preparation :

The hydrolysis of alkyl trichlorosilicon, $RSiCl_3$, gives cross-linked polymers as :



Uses :

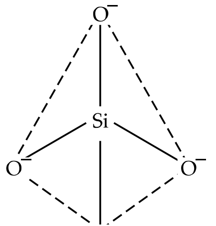
- Silicones are used as sealant, greases, electric insulators and for water proofing of fabrics.
- They are also used in surgical and cosmetic plants as being bio-compatible.

(iii) Silicates :

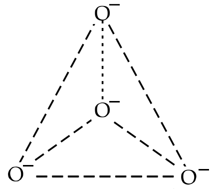
- Silicates exist in nature as feldspar, zeolites, mica and asbestos.
- Glass and cement are man-made silicates.

Structure :

Silicates have SiO_4^{4-} as basic structural unit in which silicon atom is bonded to four oxygen atoms in tetrahedron fashion.



Tetrahedral structure of SiO_4^{4-} anion



Representation of SiO_4^{4-} unit

(iv) Zeolites :

- Replacement of few silicon atom of silicon dioxide by aluminium result in negative charge which is balance by cations Na^+, K^+ or Ca^{2+} to form zeolites.
- Zeolites are used in cracking and isomerisation of hydrocarbons.

KNOW THE TERMS

- ***p*-Block :** In the periodic table is unique in terms of having all types of elements – metals, non-metals and metalloids.
- **Inert pair effect :** The occurrence of oxidation states two unit less than the group oxidation states are attributed to the 'inert pair effect'.
- **Diborane :** Diborane contains two bridging hydrogen atoms between two boron atoms; these bridge bonds are considered to be three-centre two-electron bonds.

❒❒❒

Chapter 12

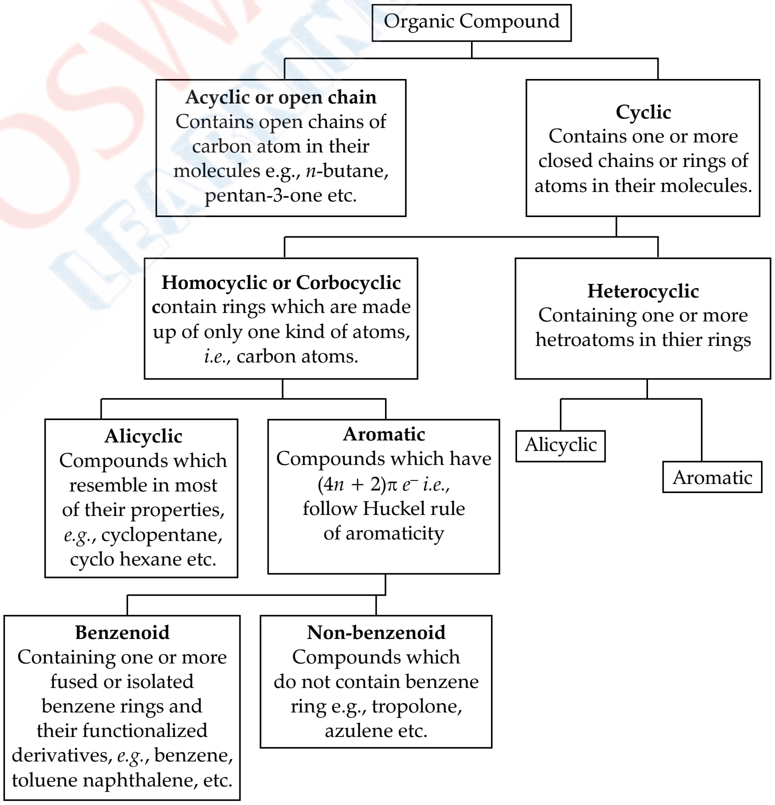
Organic Chemistry Some Basic Principles and Techniques

Topic 1

Introduction, Classification and IUPAC Nomenclature

» Revision Notes

- **Introduction :** Organic compounds are the hydrocarbons and their derivatives and organic chemistry is that branch of chemistry that deals with the study of these compounds.
- **Catenation :** The self linking property of carbon is known as catenation. Carbon is always tetra-covalent, *i.e.*, it forms 4 covalent bonds with other atoms.
- The formation and the shapes of molecules like methane (CH_4), ethene (C_2H_4), ethyne (C_2H_2) are explained in terms of the use of sp^3, sp^2 and sp hybrid orbitals by carbon atoms in the respective molecules.
- **Functional Groups :** A functional group may be defined as an atom or a group of atoms present in a molecule which largely determines the chemical properties.
- **Classification of Organic Compounds**



Organic Compound

Acyclic or open chain Contains open chains of carbon atom in their molecules e.g., *n*-butane, pentan-3-one etc.

Cyclic Contains one or more closed chains or rings of atoms in their molecules.

Homocyclic or Corbocyclic contain rings which are made up of only one kind of atoms, *i.e.*, carbon atoms.

Heterocyclic Containing one or more hetroatoms in thier rings

Alicyclic Compounds which resemble in most of their properties, *e.g.*, cyclopentane, cyclo hexane etc.

Aromatic Compounds which have $(4n + 2)\pi\ e^-$ *i.e.*, follow Huckel rule of aromaticity

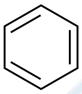
Alicyclic

Aromatic

Benzenoid Containing one or more fused or isolated benzene rings and their functionalized derivatives, *e.g.*, benzene, toluene naphthalene, etc.

Non-benzenoid Compounds which do not contain benzene ring e.g., tropolone, azulene etc.

- **IUPAC Nomenclature**

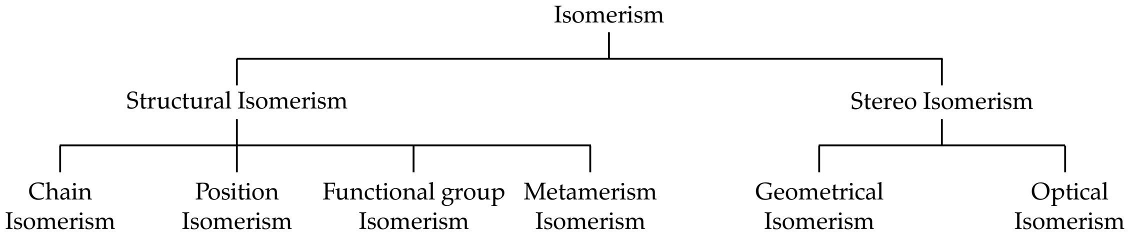
Class of Compounds	Functional group structure	IUPAC group Prefix	IUPAC group Suffix	Example
Alkanes	—	—	-ane	Butane → $[CH_3(CH_2)_2CH_3]$
Alkene	$>C=C<$	—	-ene	But-1-ene $CH_2{=}CHCH_2CH_3$
Alkynes	$—C\equiv C—$	—	-yne	But-1-yne $CH{\equiv}CCH_2CH_3$
Arenes	—	—	—	Benzene 
Halides	—X (X=F, Cl, Br, I)	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	Pentanitrile $CH_3CH_2CH_2CH_2CN$
Ethers	—R—O—R	alkoxy-	—	Ethoxyethane $CH_3CH_2OCH_2CH_3$
Carboxylic acids	—COOH	corboxy	-oic acid	Butanoic acid $CH_3(CH_2)_2COOH$
Esters	—COOR	alkoxy carbonyl	-oate	Methyl propanoate $CH_3CH_2COOCH_3$
Acyl halides	—COX	halo carbonyl	-oyl halide	Butanoyl chloride $CH_3(CH_2)_2COCl$
Amines	$—NH_2$, $>NH$, $>N—$,	amino	-amine	Butan-2-amine $CH_3CHNH_2CH_2CH_3$
Amides	$—CONH_2$, $—CONHR_2$, $—CONR_2$	-carbamoyl	-amide	Butanamide $CH_3(CH_2)_2CONH_2$
Nitro compounds	$—NO_2$	nitro	—	1-Nitorbutane $CH_3(CH_2)_3NO_2$
Sulphonic acids	$—SO_3H$	sulpho	Sulphonic acid	Methyl Sulphonic acid CH_3SO_3H

Topic 2

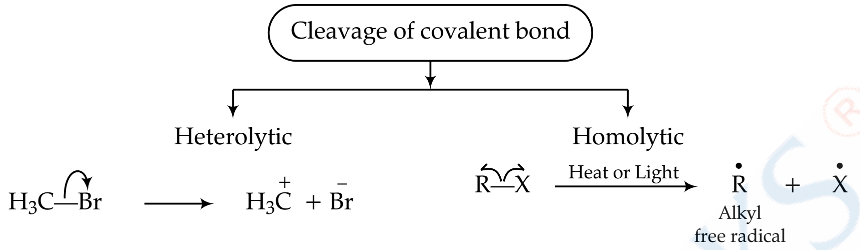
Isomerism, Electron Displacement Effects and Reaction Intermediates

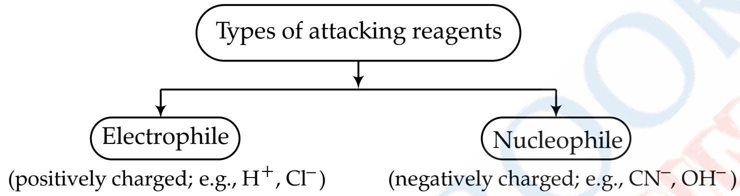
» Revision Notes

- **Isomerism :** Two or more compounds having the same molecular formula but different chemical and physical properties are called isomers and the phenomenon is knows as isomerism.



- **Chain isomerism :** When two or more compounds having same molecular formula but different carbon skeletons.
- **Position isomerism :** Compounds which have the same structure of carbon chain but differ in position of double or triple bonds or functional group.
- **Functional isomerism :** Compounds which have the same molecular formula but different functional group.
- **Metamerism :** It is due to the presence of different alkyl groups on either side of functional group in the molecule.
- **Cleavage of Covalent bond :**





- **Electron displacement effect :**

(i) Inductive Effect : Electron displacement along a carbon chain due to presence of an attached substituent.

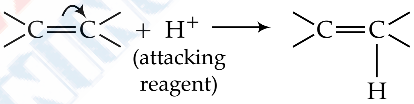
$$\overset{++\delta}{CH_3} \rightarrow\!\!-\!\!- \overset{+\delta}{CH_2} \rightarrow\!\!-\!\!- \overset{-\delta}{Cl}$$

→ +I effect group pushes the electron towards the carbon chain.

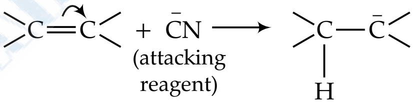
→ –I effect group pulls the electron form the carbon Chain.

(ii) Electromeric effect : Temporary displacement of π electrons.

(a) +E effect—

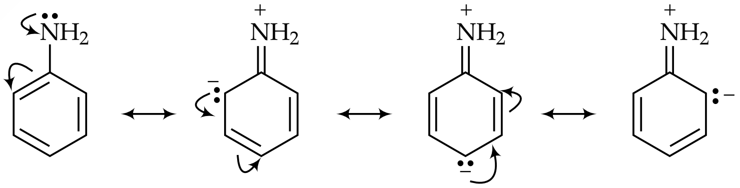


(b) –E effect—

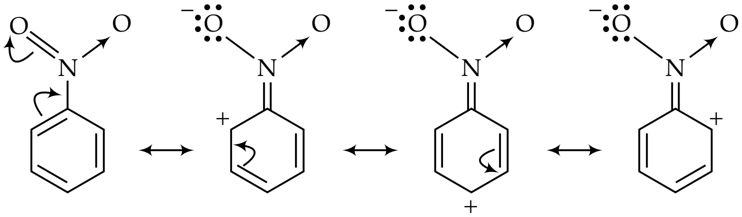


(iii) Resonance effect : Permanent polarization effect (delocalization of pi-electron)

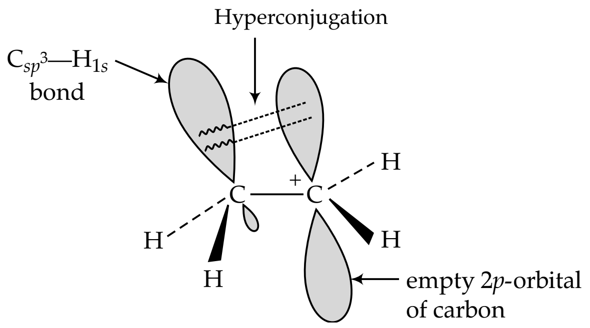
(a) +R effect—



(b) –R effect—



(iv) Hyperconjugation : Conjugation between the σ electrons of a single carbon hydrogen bond and π electrons of the adjacent multiple bond.



Topic 3

Types of Organic Reaction, Purification of Organic Compounds and Their Qualitative and Quantitative Analysis

» Revision Notes

- **Types of Organic Reactions :** Organic reactions can be classified into the following categories :

  (i) Substitution reactions (ii) Addition reactions

  (iii) Elimination reactions (iv) Rearrangement reactions

- Some important methods for determination of elements qualitatively and quantitatively

  (i) Qualitatively ⇒ Lassaigne's test — For nitrogen, sulphur, halogens and phosphorus.

  (ii) Quantitatively ⇒ For nitrogen — Dumas method, Kjeldahl's method

  For halogens — Carius method.

- Lassaigne's test for nitrogen

$$6CN^- + Fe^{2+} \longrightarrow [Fe(CN)_6]^{4-}$$

$$3[Fe(CN)_6]^{4-} + 4Fe^{3+} \xrightarrow{xH_2O} \underset{\text{Prussian blue}}{Fe_4[Fe(CN)_6]_3.xH_2O}$$

- Lassaigne's test for sulphur

$$[Fe(CN)_5NO]^{2-} + S^{2-} \longrightarrow \underset{\text{Violet}}{[Fe(CN)_5\,NOS]^{4-}}$$

- Lassaigne's test when both sulphur and nitrogen are present,

$$SCN^- + Fe^{3+} \longrightarrow \underset{\text{Blood Red}}{[Fe(SCN)]^{2+}}$$

- Lassaigne's test for halogens

$$X^- + Ag^+ \longrightarrow AgX\downarrow \qquad (X^- = Cl^-, Br^- \text{ or } I^-)$$

(i) When white precipitate of AgX is formed which is soluble in ammonium hydroxide indicates that X^- is Cl^-.

(ii) When pale yellow precipitate of AgX is formed, which is sparingly soluble in ammonium hydroxide indicates that X^-, is Br^-.

(iii) When yellow precipitate of AgX is formed, which is insoluble in ammonium hydroxide indicates that X^- is I^-.

- Lassaigne's test for phosphors

$$Na_3PO_4 + 3HNO_3 \longrightarrow H_3PO_4 + 3NaNO_3$$

$$H_3PO_4 + 12(NH_4)_2\,MoO_4 + 21HNO_3 \longrightarrow (NH_4)_3\,PO_4.\,12MoO_3 + 21NH_4NO_3 + 12H_2O$$

- **Purification Techniques :** The common techniques used for purification are :

  (i) Filtration : Separates insoluble solid part of mixture from soluble component in a given solvent.

  (ii) Crystallisation : Organic compounds sparingly soluble in a solvent and soluble completely at higher temperature are the compounds which are purified by this method. A saturated solution of this type of compound is prepared at high temperature and filtered while hot thus, insoluble impurities are removed and pure solute comes out of solvent at lower temperature.

  (iii) Fractional crystallization : This method is used to separate two compounds that are soluble in a solvent but to different extent. Then at certain temperature only one solute comes out of solvent while other remains in the solution. Then to obtain second one cool the solution to the desired temperature.

  (iv) Sublimation : When a sublimable substance is mixed with a non-volatile substance then they are simply separated by sublimation as sublimable substance vaporises remaining behind non-volatile substance only.

  (v) Distillation : Liquids can be separated by this method. The liquid is heated to vaporize and then condense these vapours to get pure liquid.

(vi) Chromatography : This technique is used to separate a mixture by distributing components between two phases, one stationary phase and other is the mobile phase.

KNOW THE TERMS

- **Sublimable :** A solid substance which changes directly into gaseous state without going through its liquid state is called sublimable substance.
- **Fractional distillation :** It is repeated and successive distillation used to separate liquids having very close boiling points.
- **Adsorption Chromatography :** Different components of mixture have different affinity for the absorbent using this fact. This method of chromatography separate components of mixture.
- **Homologous series :** A group or a series of organic compounds each containing a characteristic functional group forms a homologous series and the members of the series are called homologues.

❑❑❑

Chapter 13

Hydrocarbons

Topic 1

Alkanes and Alkenes

» Revision Notes

- **Alkanes : :** Alkanes are saturated open chain hydrocarbons containing carbon - carbon single bonds.

  General Formula : C_nH_{2n+2}

  Nomenclature and 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°).

  Preparation : (i) From unsaturated hydrocarbons

$$\underset{\text{Ethene}}{CH_2{=\!=}CH_2} + H_2 \xrightarrow[\text{or Pt or Pd}]{\text{Raney Ni}} \underset{\text{Ethane}}{CH_3CH_3}$$

(ii) Wurtz reaction

$$R{-\!-}X + 2Na + X{-\!-}R \xrightarrow[\text{ether}]{\text{Dry}} R{-\!-}R + 2NaX$$

(iii) Reduction of alkyl halides

$$R{-\!-}X \xrightarrow{\text{Zn/HCl}} R{-\!-}H + HX$$

(iv) Decarboxylation

$$R{-\!-}COONa + 2H_2O \xrightarrow{\text{CaO, 630 K}} R{-\!-}H + Na_2CO_3$$

(v) Kolbe's electrolytic method

$$2RCOONa + 2H_2O \xrightarrow{\text{Electrolysis}} R{-\!-}R + 2NaOH + H_2 + 2CO_2$$

Physical Properties :

(i) Alkanes are almost non-polar molecules because of the covalent nature of C-C and C-H bonds.

(ii) 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.

(iii) They are colourless and odourless.

(iv) Boiling point (b.p.) of different alkanes are increasing with their molecular mass.

Chemical Properties :

(i) Halogenation (order of reactivity $F_2 > Cl_2 > Br_2 > I_2$)

$$CH_4 + Cl_2 \xrightarrow[\text{520-670 K}]{h\nu} \underset{\text{Chloromethane}}{CH_3Cl} + HCl$$

(ii) Nitration

$$CH_3{-\!-}H + HNO_3 \longrightarrow CH_3{-\!-}NO_2 + H_2O$$

(iii) Combustion :

$$CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O$$

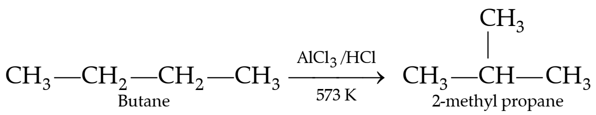
The general combustion equation for any alkane is :

$$C_nH_{2n+2} + \left(3n + \frac{1}{2}\right) O_2 \longrightarrow nCO_2 + (n+1)\,H_2O$$

(iv) Oxidation : Alkanes on heating with a regulated supply of dioxygen or air at high pressure and in the presence of suitable catalysts give a variety of oxidation products.

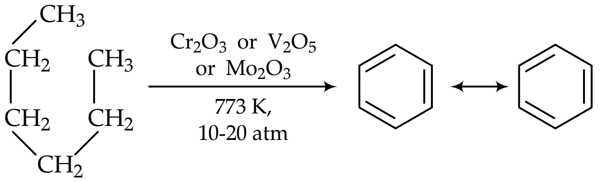
$$2CH_4 + O_2 \longrightarrow 2CH_3OH$$

(v) Isomerization

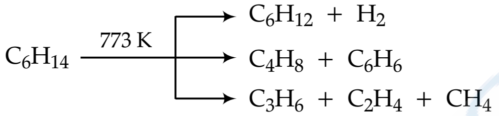


$$\underset{\text{Butane}}{CH_3-CH_2-CH_2-CH_3} \xrightarrow[573\text{ K}]{AlCl_3/HCl} \underset{\text{2-methyl propane}}{CH_3-\overset{\overset{CH_3}{|}}{CH}-CH_3}$$

(vi) Aromatization



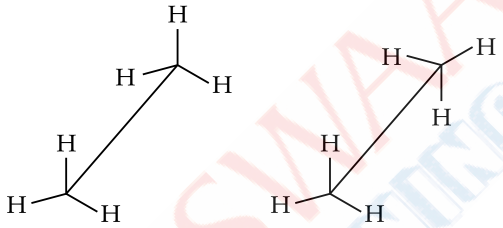
(vii) Pyrolysis



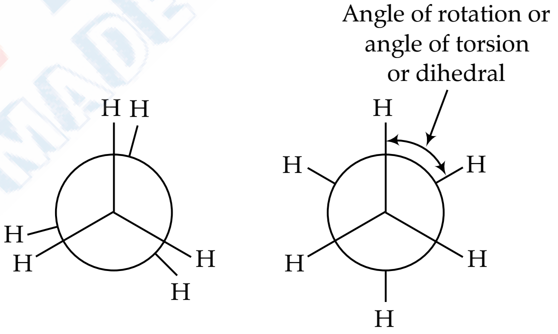
$$C_6H_{14} \xrightarrow{773\text{ K}} \begin{cases} C_6H_{12} + H_2 \\ C_4H_8 + C_6H_6 \\ C_3H_6 + C_2H_4 + CH_4 \end{cases}$$

- **Conformations :** The rotation results into different spatial arrangements of atoms in space which can change into one another. Such spatial arrangements of atoms which can be converted into one another by rotation around a C-C single bond are called conformations or conformers or rotamers.

(i) Sawhorse projection **(ii)** Newman projection



(i) Eclipsed (ii) Staggered



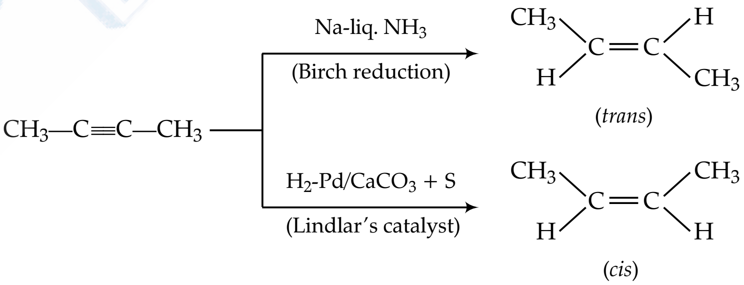
(i) Eclipsed (ii) Staggered

- **Alkene :** Alkenes show both structural isomerism and geometrical isomerism.

General formula : C_nH_{2n}

Preparation :

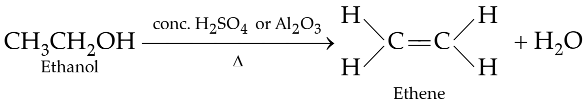
(i) By partial reduction of alkynes



(ii) From alkyl halide (Dehydrohalogenation)

$$CH_3CH_2I + KOH\ (alc.) \xrightarrow{353\text{-}363\text{ K}} \underset{\text{Ethene}}{CH_2{=}CH_2} + KI + H_2O$$

(iii) From alcohols



$$\underset{\text{Ethanol}}{CH_3CH_2OH} \xrightarrow[\Delta]{\text{conc. } H_2SO_4 \text{ or } Al_2O_3} \underset{\text{Ethene}}{H_2C{=}CH_2} + H_2O$$

Physical Properties :

(i) All alkenes are colourless and odourless, insoluble in water but fairly soluble in non-polar solvents like benzene, petroleum, ether.

(ii) They show a regular increase in boiling point with increase in size, *i.e.*, every $-CH_2$ group added increases boiling point by 20–30 K.

Chemical Properties :

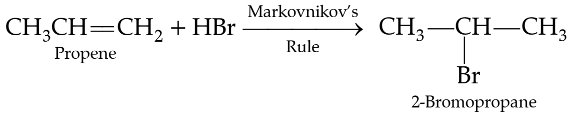
(i) Addition of halogen halides

(a) Symmetrical alkenes

$$\underset{\text{Ethene}}{CH_2{=}CH_2} + HBr \longrightarrow \underset{\text{1-Bromoethane}}{CH_3CH_2Br}$$

Markovnikov rule : The rule states that negative part of the addendum (adding molecule) gets attached to that carbon atom which possesses lesser number of hydrogen atoms.

(b) Unsymmetrical alkenes

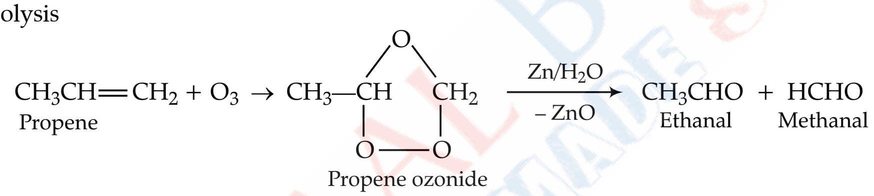


$$\underset{\text{Propene}}{CH_3CH{=}CH_2} + HBr \xrightarrow[\text{Rule}]{\text{Markovnikov's}} \underset{\text{2-Bromopropane}}{CH_3{-}\underset{\large Br}{\underset{|}{C}H}{-}CH_3}$$

$$\underset{\text{Propene}}{CH_3CH{=}CH_2} + HBr \xrightarrow[\text{AntiMarkovnikov's rule}]{\text{Peroxide}} \underset{\text{1-Bromopropane}}{CH_3{-}CH_2{-}CH_2{-}Br}$$

In the presence of peroxide, addition of HBr to unsymmetrical alkenes like propene takes place contrary to the Markovnikov rule.

(ii) Ozonolysis



(iii) Polymerisation

$$n(CH_2{=}CH_2) \xrightarrow[\text{Catalyst}]{\text{High temp./pressure}} \underset{\text{Polythene}}{-\!\!\!\!\!(CH_2{-}CH_2)\!\!\!\!\!-_n}$$

(iv) Addition of hydrogen : Alkenes add up one molecule of dihydrogen gas in the presence of finely divided nickel, palladium or platinum to form alkanes.

(v) Addition of halogen :

$$CH_2{=}CH_2 + Br_2 \longrightarrow CH_2BrCH_2Br$$

(vi) Addition of water : Alkenes react with water to form alcohols, in accordance with the Markovnikov rule.

Topic 2

Alkynes

» Revision Notes

➢ **Alkynes :**

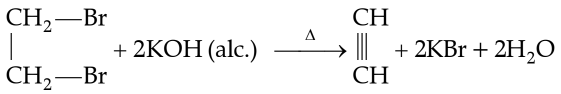
General formula : C_nH_{2n-2}

Preparation :

(i) By action of water on calcium carbide

$$CaC_2 + 2H_2O \longrightarrow HC{\equiv}CH + Ca(OH)_2$$

(ii) By dehydrohalogenation of dihaloalkanes



$$\begin{array}{l} CH_2{-}Br \\ | \\ CH_2{-}Br \end{array} + 2KOH\,(\text{alc.}) \xrightarrow{\Delta} \begin{array}{c} CH \\ ||| \\ CH \end{array} + 2KBr + 2H_2O$$

(iii) Berthelot synthesis

$$2C + H_2 \xrightarrow[\text{3270 K}]{\text{Electric arc}} HC{\equiv}CH$$

Physical Properties :

(i) All alkynes are colourless. Ethyene has characteristic odour.

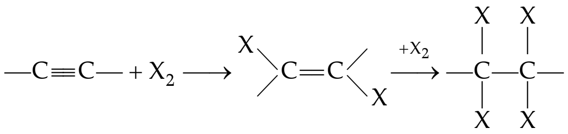
(ii) They are lighter than water and immiscible with water but soluble in organic solvents like ethers, carbon tetrachloride and benzene.

Chemical Properties :

(i) Acidic Character of Alkyne : Sodium metal and sodamide ($NaNH_2$) are strong bases. They react with ethyne to form sodium acetylide with the liberation of dihydrogen gas.

These reactions have not been observed in case of ethene and ethane thus indicating that ethyne is acidic in nature in comparison to ethene and ethane.

(ii) Electrophilic addition reaction



$$—C\equiv C— + X_2 \longrightarrow \text{XC=CX} \xrightarrow{+X_2} —CX_2—CX_2—$$

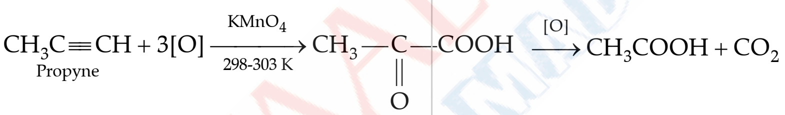
(iii) Addition of halogen halide

$$HC\equiv CH \xrightarrow{HCl} \underset{\text{Chloroethene}}{CH_2=CHCl} \xrightarrow{HCl} \underset{\text{1, 1-Dichloroethane}}{CH_3—CHCl_2}$$

(iv) Nucleophilic addition reactions

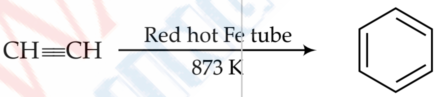
$$HC\equiv CH + CH_3OH \xrightarrow[433\text{-}473\text{ K}]{CH_3O^-K^+} CH_2=CH—OCH_3$$

(v) Oxidation with cold dilute $KMnO_4$



$$\underset{\text{Propyne}}{CH_3C\equiv CH} + 3[O] \xrightarrow[298\text{-}303\text{ K}]{KMnO_4} CH_3—\underset{\underset{O}{\|}}{C}—COOH \xrightarrow{[O]} CH_3COOH + CO_2$$

(vi) Polymerization



$$CH\equiv CH \xrightarrow[873\text{ K}]{\text{Red hot Fe tube}}$$

(vii) Addition of water : One molecule of water adds to alkynes on warming with mercuric sulphate and dilute sulphuric acid at 333 K to form carbonyl compounds.

Topic 3

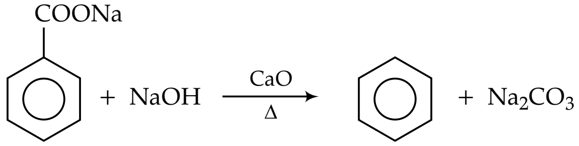
Aromatic Hydrocarbons

» Revision Notes

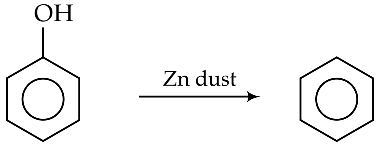
- **Aromatic Hydrocarbon :** These hydrocarbons are also known as 'arenes'. Since most of them possess pleasant odour. Most of such compounds were found to contain benzene ring.
- **Resonance :** The six π-electrons are thus delocalised and can move freely about the six carbon nuclei, The delocalised π-electron cloud is attracted more strongly by the nuclei of the carbon atoms than the electron cloud localised between two carbon atoms. Therefore, presence of delocalised π-electrons in benzene makes it more stable.
- Aromaticity, the property of being aromatic is possessed by compounds having specific electronic structure characterised by Hückel $(4n+2)p$ electron rule. The nature of groups or substituents attached to benzene ring is responsible for activation or deactivation of the benzene ring towards further electrophilic substitution and also for orientation of the incoming group.
- **Benzene :** Aromatic compounds containing benzene ring are known as benzenoids and those not containing a benzene ring are known as non-benzenoids.

Preparation :

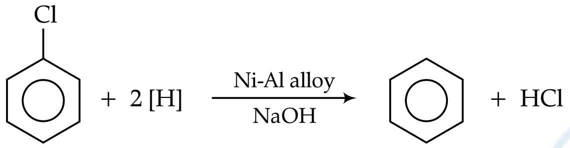
(i) From Sodium benzoate



(ii) From phenol



(iii) From chlorobenzene



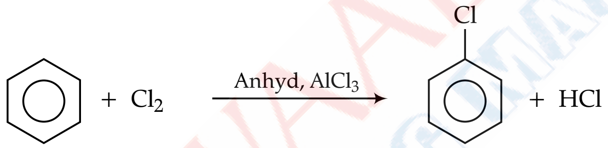
Physical Properties :

(i) Aromatic hydrocarbons are non-polar molecules and are usually colourless liquids or solids with a characteristic aroma.

(ii) Aromatic hydrocarbons are immiscible with water but are readily miscible with organic solvents.

Chemical Properties :

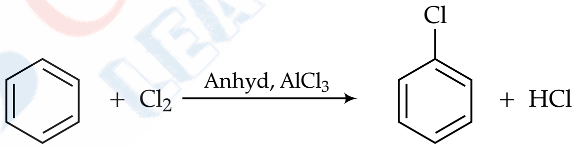
(i) Electrophilic substitution



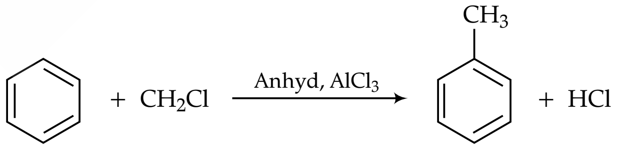
Chlorobenzene

(ii) Addition reaction

(iii) Friedal craft reactions

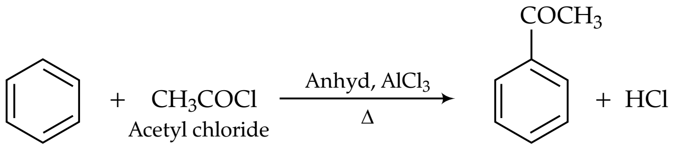


Chlorobenzene



Toluene

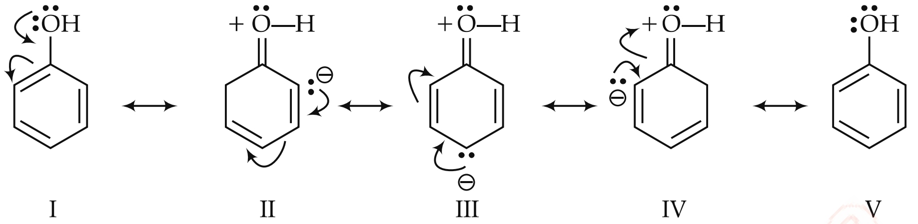
(iv) Friedal craft acylation



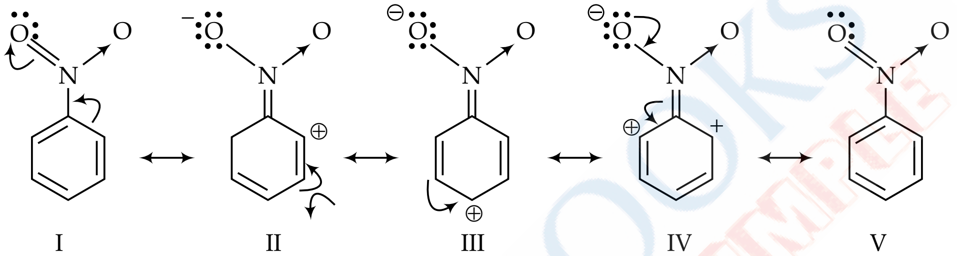
Acetophenone

(iv) Sulphonation : The replacement of a hydrogen atom by a sulphonic acid group in a ring is called sulphonation. It is carried out by heating benzene with fuming sulphuric acid.

- **Directive influence**
  - **(i)** Orthopara direction group (ring activator)
    e.g., NH_2, —NHR, —$NHCOCH_3$, —OCH_3, —CH_3, —C_2H_3. etc.



  - **(ii)** Meta directing group (ring deactivator)
    e.g., NO_2, —CN, —CHO, —COR, —COOH, —COOR, —SO_3H, etc.



- **Carcinogenicity and toxicity :** Benzene and polynuclear hydrocarbons containing more than two benzene rings fused together are toxic and said to possess cancer producing (carcinogenic) property.

KNOW THE TERMS

- **Hydrogenation :** Dihydrogen gas adds to alkenes and alkynes in the presence of finely divided catalysts like platinum, palladium or nickel to form alkanes. This process is called hydrogenation.
- **Pyrolysis :** Higher alkanes on heating to higher temperature decompose into lower alkanes, alkenes etc. Such a decomposition reaction into smaller fragments by the application of heat is called pyrolysis or cracking.
- **Peroxide or Kharash effect :** In the presence of peroxide, addition of HBr to unsymmetrical alkenes like propene takes place contrary to the Markovnikov rule.

Chapter 14

Environmental Chemistry

» Revision Notes

- Environmental chemistry is the branch of science which deals with the chemical phenomena occurring in the environments, *i.e.*, study of origin, transport, reactions, effects and fates of chemical species in the environment.
- Environmental pollution is the effect of undesirable changes in our surroundings that have harmful effects on plant, animals and human beings.
- **Environmental Pollutants :**
  - **(i) Primary pollutants :** Those pollutants which after their formation enter into the environment and remain as such. *e.g.*, NO, SO_2 , NO_2, etc.
  - **(ii) Secondary pollutants :** Those pollutants which are formed by chemical reactions between the primary pollutants. *e.g.*, PAN (peroxyacetyl nitrates)
- **Atmospheric pollution :** Atmospheric pollution is generally studied as tropospheric and stratospheric pollution. The presence of ozone in the stratosphere prevents about 99.5 per cent of the sun's harmful ultraviolet (UV) radiations from reaching the earth's surface and thereby protecting humans and other animals from its effect.
- **Air Pollution :**

  Tropospheric pollution : The major gaseous and particulate pollutants present in the troposphere:

  1. **Gaseous air pollutants :** These are oxides of sulphur, nitrogen and carbon, hydrogen sulphide, hydrocarbons, ozone and other oxidants.
  2. **Particulate pollutants :** These are dust, mist, fumes, smoke, smog etc.

  Major pollutants : Carbon monoxide (CO), hydrocarbons (C_xH_y), oxides of nitrogen (NO_x), oxides of sulphur (SO_x) and particulates.
- **Oxides of Carbon :**

  Carbon monoxide : Carbon monoxide (CO) is one of the most serious air pollutants. It is a colourless and odourless gas, highly poisonous to living beings because of its ability to block the delivery of oxygen to the organs and tissues. It is produced as a result of incomplete combustion of carbon.

  Carbon monoxide is mainly released into the air by automobile exhaust. Other sources, which produce CO, involve incomplete combustion of coal, firewood, petrol, etc.
- **Global warming and green house effect :** Some of the heat is trapped by gases such as carbon dioxide, methane, ozone, chlorofluorocarbon compounds (CFCs) and water vapour in the atmosphere. Thus, they add to the heating of the atmosphere. This causes global warming.

  Carbon dioxide, other greenhouse gases are methane, water vapour, nitrous oxide, CFCs and ozone.
- **Acid Rain :** When the pH of the rain water drops below 5.6, it is called acid rain. Acid rain refers to the ways in which acid from the atmosphere is deposited on the earth's surface.
- **Smog :** The word smog is derived from smoke and fog. This is the most common example of air pollution that occurs in many cities throughout the world. There are two types of smog:
  - **(a)** Classical smog occurs in cool humid climate. It is a mixture of smoke, fog and sulphur dioxide.
  - **(b)** Photochemical smog occurs in warm, dry and sunny climate

Photochemical Smog :

It is formed when NO_2 and hydrocarbon present in air interact with sunlight in a chain reaction the reactions are as follows :

$$NO_2 \xrightarrow{h\nu} NO + O$$

$$O + O_2 \rightleftharpoons O_3$$

$$O_3 + NO \longrightarrow NO_2 + O_2$$

Ozone hole : The depletion of ozone layer commonly known as ozone hole over the South Pole.

Ozone is a toxic gas and both NO_2 and O_3 are strong oxidising agents. They react with unburnt hydrocarbons in the polluted air to produce chemicals such as formaldehyde, acrolein and peroxyacetyl nitrate (PAN).

$$3CH_4 + 2O_3 \longrightarrow \underset{\text{formaldehyde}}{3CH_2{=}O} + 3H_2O$$

$$RCO_3^{\bullet} + NO_3 \longrightarrow RCO_3NO_2$$

Depletion of ozone layer by chlorofluorocarbons (CFC) :

Once CFCs are released in the atmosphere, they mix with the normal atmospheric gases and reach the statosphere. Where, they get broken down by UV rays, releasing chlorine free radicals which causes the breakdown of ozone.

$$CF_2Cl_2 \xrightarrow{h\nu} \dot{C}F_2Cl + Cl^{\bullet}$$

$$CFCl_3 \xrightarrow{h\nu} \dot{C}FCl_2 + Cl^{\bullet}$$

$$Cl^{\bullet} + O_3 \longrightarrow ClO^{\bullet} + O_2$$

$$ClO^{\bullet} + O \longrightarrow Cl^{\bullet} + O_2$$

(PAN)

- **Water Pollution :**

  Major Sources : Sewage and domestic wastes, industrial effluents, agricultural discharge, siltation, thermal pollutant, radioactive discharges and polychlorinated biphenyls (PCBs)

  Biochemical oxygen demand (BOD) : The total amount of oxygen consumed by microorganisms (bacteria) in decomposing the waste (organic matter) present in certain volume of a sample of water is called Biochemical Oxygen Demand (BOD) of water.

  Chemical oxygen demand (COD) : The total amount of oxygen consumed by chemicals (like $K_2Cr_2O_7$ in presence of dilute H_2SO_4) in decomposing the waste present in certain volume of sample of water is called Chemical Oxygen Demand (COD).

- **Soil Pollution :**

  Major Sources : Industrial wastes, urban wastes, agricultural pollutants (like fertilizers, pesticides, soil conditioners, farm wastes) and radioactive pollutants.

- **Strategy for controlling environmental pollution :**

  (i) Waste management of household waste.

  (ii) Management of Industrial waste :

  (a) Recycling
  (b) Burning and Incineration
  (c) Sewage treatment
  (d) Digesting
  (e) Dumping

  Two programmes are being implemented under the broad umbrella of the Swachh Bharat Abhiyan. These are Swachh Bharat Mission–Urban (SBM–U) and Swachh Bharat Mission–Gramin (SBM–G).

- **Green Chemistry :** It is a way of thinking or utilising the existing knowledge and principles of chemistry and other sciences to reduce the adverse impact on environment. Producing the chemical of our daily needs using such reactions and chemical process which neither use toxic chemical, nor emit such chemicals into the atmosphere, *e.g.*,

$$CH_2{=}CH_2 + O_2 \xrightarrow[\text{in water}]{\text{Pd (II)/Cu (II)}} CH_3CHO \quad (90\% \text{ Yield})$$

- **Green Chemistry in Day to Day Life :**

  (a) Dry cleaning of clothes by the use of hydrogen peroxide.

  (b) Bleaching of paper by the hydrogen peroxide with suitable catalyst.

(c) In synthesis of chemicals

$$CH_2{=}CH_2 + O_2 \xrightarrow[\text{Pd (II)/Cu (II)}\atop\text{in water}]{\text{Catalyst}} CH_3CHO \ \ (90\%)$$

(d) Power of kernel of tarmind seeds has been found to be an effective material to make municipal and industrial waste water clean.

KNOW THE TERMS

- **Smog :** It is the phenomenon which occurs due to the condensation of fog on the carbon particles present in the smoke.
- **Greenhouse effect :** The energy trapping phenomenon by infrared active gaseous molecules present in the atmosphere.
- **Global warming :** The steady increases of temperature of the earth due to radiations form sun locked in the earth's atmosphere.
- **Eutrophication :** The process in which nutrient enriched water bodies support a dense plant population, which kills animal life by depriving it of oxygen and results in subsequent loss of biodiversity is known as Eutrophication.

❐❐❐

Chapter 15

Solid State

Topic 1

Crystal Lattices and Unit Cells, Number of Atoms in a Unit Cell, Closed Packed Structure and Packing Efficiency.

» Revision Notes

- Solids are the chemical substances which are characterised by definite shape, volume and rigidity.

  The solids are of two types : crystalline and amorphous solids.

  Crystalline solids : The constituent particles are arranged in regular fashion containing short range as well as long range order. They are anisotropic.

  Amorphous solids : The constituent particles are arranged in any regular fashion have short range order only. They are isotropic.

- **Unit Cell and its Type**

  Unit Cell : The smallest 3-D portion of a complete space lattice which when repeated over and again in different direction produces the complete unit cell.

- **Types of Unit Cell :**

  (a) Simple Unit Cell : Constituent particles are all present only at the corners :

  $$Z = \frac{1}{8} \times 8 = 1$$

  (b) Face Centred (fcc) : Particles are present not only at corners but also at the face centre of each face of the unit cell

  $$Z = \frac{1}{8} \times 8 + 6 \times \frac{1}{2} = 4$$

  (c) End-centred : Particles are at corners and at the centres of any two opposite foces.

  $$Z = 8 \times \frac{1}{8} + 2 \times \frac{1}{2} = 2$$

  (d) Body Centred : Particles are at the corners and one particle at the centre within the body of unit cell.

  $$Z = 8 \times \frac{1}{8} + 1 \times 1 = 2$$

- **Packing Efficiency or Packing Fractions**

  The ratio of the volume of the unit cell that is occupied by the spheres to the volume of the unit cell.

Unit Cell	Packing efficiency
Simple cubic unit cell	52.4 %
Face centred cubic (hcp and ccp)	74 %
Body centred	68 %

- **Coordination Number :** It is defined as the number of particles immediately adjacent to each particle in the crystal lattice.

- In simple cubic lattice, CN is 6, in body centred lattice, CN is 8 and in face centred cubic lattice, CN is 12.

Topic 2

Calculations Involving Unit Cell Dimensions

» Revision Notes

- **Radius Ratio Rules :** $\left(r = \frac{r+}{r-}\right)$

Radius Ratio	Co-ordination number	Structural arrangement	Structure type
0.155 – 0.225	3	Planar triangular	–
0.225 – 0.414	4	Tetrahedral	Sphalerite, ZnS
0.414 – 0.732	6	Octahedral	Sodium chloride (Rock Salt)
0.732 – 1	8	Body-centred cubic	Caesium chloride

- **Calculation of Density (d or ρ) :**

$$\rho = \frac{zM}{a^3 N_A}$$

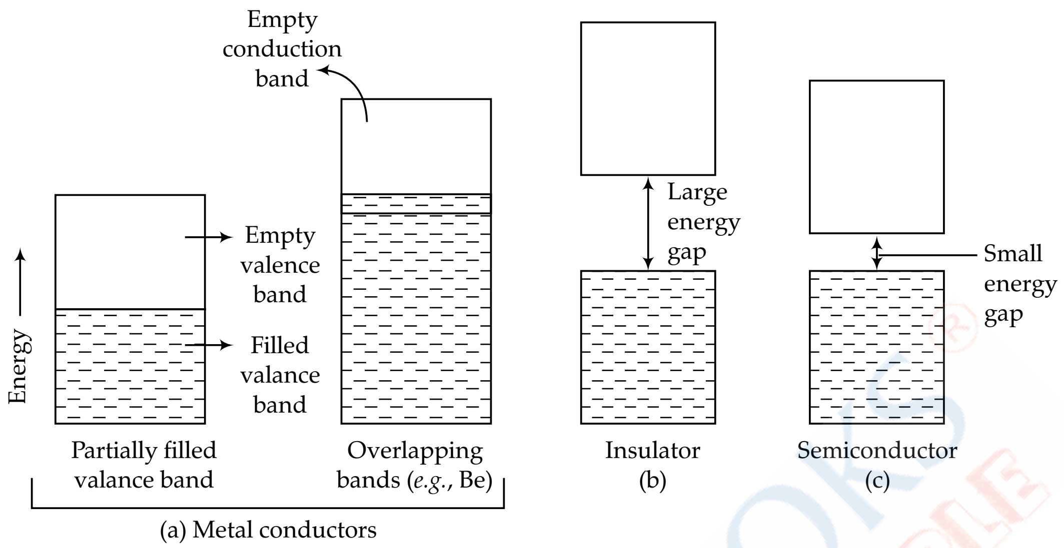
where, a = edge length in pm
M = molar mass in g mol^{-1}
z = No. of atoms in unit cell
N_A = Avogadro's number.

Topic 3

Imperfections in Solids, Electrical and Magnetic Properties of Solids

» Revision Notes

- Point defects are the irregularities or deviations from ideal arrangement around a point or an atom in a crystalline substance. It can be classified into three types :
  (1) Stoichiometric defects
  (2) Impurity defects
  (3) Non-stoichiometric defects
- **Defects in Solids :**
  Frenkel defect : When an ion (usually cation) is missing from its lattice site and it occupies the interstitial site. *e.g.*, in AgCl, AgBr, ZnS, etc.
  Schotky defect : When equal number of cations and anions are missing from the lattice site. *e.g.*, in NaCl, CsCl, etc.
- **Metal Excess by anion vacancies :**
  A negative ion may be missing from the lattice site leaving a hole which is occupied by an electron. The electrons thus trapped in the anion vacancies are called F-centres.
- **Semiconductors :** Electronic conductors having electrical conductivity in the range of 10^4–10^7 Ω^{-1} cm^{-1} are known as semiconductors. Examples Si, Ge, Sn (grey), Cu_2O, SiC and GaAs.
- **Electrical properties in solids :**
  (i) Doping with electron rich impurities : When group 14 elements like silicon is doped with group 15 elements like Phosphorus, *n*-type semiconductors are formed.
  (ii) Doping with electron deficit impurities : When group 14 elements are doped with group 13 elements like B, Al, Ga than *p*-type semiconductors are formed.
  (iii) Band theory : The band formed from atomic orbitals of lower energy is called valence band.
  The band formed from empty or partially filled atomic orbitals of higher energy is called conduction band.



➢ **Magnetic properties in solid :**

(i) Diamagnetic substances : Substances which weakly repelled by the external magnetic field. *e.g.*, TiO_2, H_2O, benzene, etc.

(ii) Paramagnetic Substances : Substances which are attracted by the external magnetic field are called paramagnetic substances. *e.g.*, O_2, Cu^{2+}, Fe^{+3}, etc.

(iii) Ferromagnetic Substances : Substances which show permanent magnetism even in the absence of magnetic field are called ferromagnetic substances, *e.g.*, Fe, Ni, Co, etc.
All domains in same direction : ↑↑↑↑↑↑↑↑

(iv) Anti-ferromagnetic Substances : Substances which possess zero net magnetic moment. *e.g.*, MnO
Alternate arrangement of domains : ↑↓↑↓↑↓↑↓↑↓

(v) Ferrimagnetic Substance : Substances which possess small net magnetic moment. *e.g.*, $FeSO_4$
Direction of domains : ↑↑↓↑↑↑↑↓↑↑↓↑↑↑

❑❑❑

Chapter 16

Solutions

Topic 1

Types of Solutions, Methods of Expressing Concentration, Vapour Pressure of Liquid Solution (Raoult's Law), Ideal and Non-Ideal Solutions

» Revision Notes

- **Solution :** Solution is a homogeneous mixture of two or more substances in same or different physical phases. The substances forming the solution are called components of the solution.
- Depending upon the amount of solute dissolved in a solvent we have the following types of solutions :
  - **(i) Unsaturated solution :** Solution in which more solute can be dissolved without raising temperature is called an unsaturated solution.
  - **(ii) Saturated solution :** A solution in which no solute can be dissolved further at a given temperature is called a saturated solution.
  - **(iii) Supersaturated solution :** A solution which contains more solute than that would be necessary to saturate it at a given temperature is called a supersaturated solution.
- **Expressing concentration of solutions**

(i) Molarity $= \dfrac{\text{Number of moles of solute}}{\text{Volume of solution in liters}} = \dfrac{\text{W}}{\text{Molar Mass}} \times \dfrac{1000}{\text{V}}$

(ii) Normality $= \dfrac{\text{Number of gram equivalents of solute}}{\text{Volume of solution of liters}}$

$$= \frac{\text{W}}{\text{Eq. mass of solute}} \times \frac{100}{\text{M}}$$

Normality of a solution = Molarity $\times \dfrac{\text{Molecular mass}}{\text{Equivalent mass}}$

(iii) Molality $= \dfrac{\text{Number of moles of solute}}{\text{Mass of solvent in kg}} = \dfrac{\text{W}_B}{\text{M}_B} \times \dfrac{1000}{\text{W}_A}$

where, A = solvent, B = solute

(iv) Mole Fraction : Mole fraction of a constituent is the fraction obtained by dividing number of moles of that constituent by the total number of moles of all the constituents present in the solution.

$$x_1 = \frac{n_1}{n_1 + n_2 + n_3 + \ldots + n_i}$$

- **Henry's Law :** The solubility of a gas in a liquid at a particular temperature is directly proportional to the pressure of gas in equilibrium with the liquid at room temperature.

$$x_A = \text{K}_H \, \text{P}_A$$

- **Relative lowering of vapour pressure (Raoult's law) :**

The relative lowering of vapour pressure of a solution containing a non-volatile solute is equal to the mole fraction of the solute in the solution.

$$\frac{p^{\circ} - p_{\text{solution}}}{p^{\circ}_{\text{solution}}} = \frac{n_2}{n_1 + n_2}$$

- **Ideal and non-ideal solution :**

  For ideal solution : $\Delta H_{mix} = 0, \Delta V_{mix} = 0$

  For Non-ideal solution : $\Delta H_{mix} \neq 0, \Delta V_{mix} \neq 0$

  (i) Positive deviation : A-B interaction < A-A or B-B interactions

  (ii) Negative deviation : A-B interaction > A-A or B-B interactions

Topic 2

Colligative Properties and Determination of Molar Mass and Abnormal Molar Masses

» Revision Notes

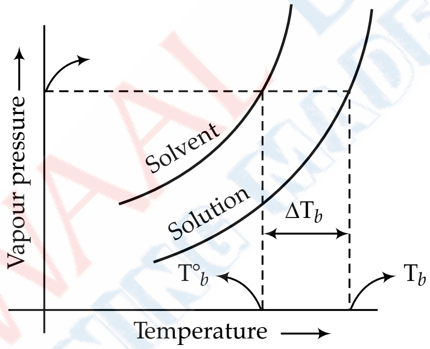
- **Colligative Properties :** Depends only on the number of the solutes particle.

  Osmotic Pressure : The net spontaneous flow of the solvent molecules from the solvent to the solution or from a less concentrated solution to a more concentrated solution through a semi-permeable membrane is called osmosis.

  $$\pi V = nRT \text{ where } \pi = \text{osmotic pressure.}$$

  Elevation in boiling point (ΔT_b) : Boiling point of solution is greater than that of pure solvent and is given by

  $$\Delta T_b = K_b \times m$$

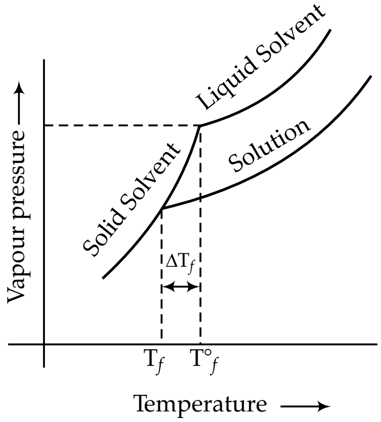


  where, $\Delta T_b = T_b - T_b^\circ$

  $$\Delta T_b = \frac{K_b \times W_2 \times 1000}{M_2 \times W_1}$$

  Depression in freezing point (ΔT_f) : Freezing point of solution is smaller than that of pure solvent and is given by

  $$\Delta T_f = k_f \times m$$



  where $\Delta T_f = T_f^\circ - T_f$

  $$\Delta T_f = \frac{K_f \times W_2 \times 1000}{M_2 \times W_1}$$

- **Van't Hoff Factor :** Ratio of the experimental value of the colligative property to the calculated value of the colligative property

$$i = \frac{\text{Experimental value of colligative property}}{\text{Calculated value of colligative property}}$$

$$= \frac{\text{Observed value of colligative property}}{\text{Normal value of the same property}}$$

Thus, the modified colligative properties are :

Relative lowering of vapour pressure

$$\frac{p^\circ - p_s}{p^\circ} = ix_2$$

Elevation in boiling point, $\Delta T_b = ik_b m$

Depression in freezing point, $\Delta T_f = ik_f m$

Osmotic pressure, $\pi = i\frac{n}{V}RT$

- **Degree of dissociation** (α)

Fraction of total substance that undergoes dissociation.

$$\alpha = \frac{\text{Number of moles dissociated}}{\text{Total number of moles taken}}$$

For strong electrolyte

$$\alpha = \frac{i-1}{n-1}$$ (where, n is number of ions formed)

For weak electrolyte

$$\alpha = (1-i)\frac{n}{n-1}$$

KNOW THE TERMS

- **Formality (F) :** It is the number of formula weights of solute present per litre of the solution.

Formality $= \frac{\text{Moles of substance added to solution}}{\text{Volume of solution (in litres)}}$

- **Azeotropic mixture :** A mixture of two liquids which boils at a particular temperature like pure liquid and distilled over in the same composition is known as constant boiling mixtures. These are formed by non ideal solutions.
- **Reverse osmosis :** When the external pressure applied on the solution is more than osmotic pressure, the solvent, flows form the solution to the pure solvent, which is called reverse osmosis.

❑❑❑

Chapter 17

Electrochemistry

Topic 1

Conductance of Electrolytic Solutions

» Revision Notes

- **Electrochemistry :** Electrochemistry is the study of production of electricity from energy released during spontaneous chemical reactions and the use of electrical energy bring about non-spontaneous chemical transformations.
- **Electrical Resistance and Conductance :**

$$R = \frac{V}{I} \quad \text{and} \quad G = \frac{1}{R} \qquad (G = \text{Conductance}, \Omega^{-1} \text{ or S})$$

$$R = \rho\frac{I}{a} \qquad (\rho = \text{resistivity})$$

and

$$\kappa = \frac{l}{\rho} \qquad (\kappa = \text{conductivity})$$

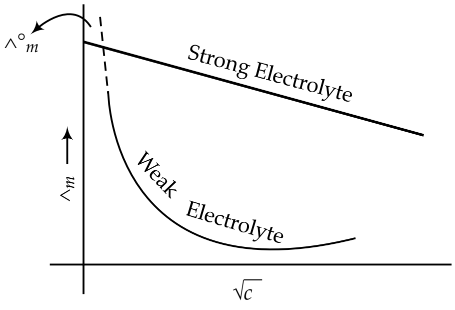
$$\kappa = G\frac{l}{a}$$

- **Equivalent Conductivity :** Conductance of all the ions produced from one gram equivalent of the electrolyte dissolved in V cm^3 of the solution when the distance between the electrodes is one cm and the area of the electrodes is so large that whole of the solution is contained between them. It is represented by Λ_{eq}.

$$\Lambda_{eq} = \kappa_v \times V$$

$$\Lambda_{eq} = \kappa_c \times \frac{1000}{c_{eq}} = \kappa_c \times \frac{1000}{\text{Normality}}$$

- **Molar Conductivity :** $\Lambda_m = \kappa_v \times V = \kappa_c \times \frac{1{,}000}{c} = \kappa_c \times \frac{1{,}000}{\text{Molarity}}$
- Variation of molar conductivity of a strong electrolyte and weak electrolyte



- **Kohlrausch's Law :** The limiting molar conductivity of an electrolyte (*i.e.*, molar conductivity at infinite dilution) is the sum of the limiting ionic conductivities of the cation and the anion, each multiplied with the number of ions present in one formula unit of electrolyte.

$$\overset{\circ}{\Lambda}_m \text{ for } A_xB_y = x\lambda_{(A)}^{0y+} + y\lambda_{(B)}^{0x-}$$

Where λ°_A and λ°_B is the limiting ionic conductivity of the cation and anion.

e.g., $\Lambda^\circ_{(CH_3COOH)} = \lambda^\circ_{CH_3COO} + \lambda^\circ_{H^+}$

- **Cell Representation of an electrochemical cell :**

Ionic form : $Zn_{(s)} + Cu^{+2}_{(aq)} \longrightarrow Zn^{+2}_{(aq)} + Cu_{(s)}$

Two half reactions $Zn_{(s)} \longrightarrow Zn^{2+} + 2e^-$ (Oxidation half anode)

$Cu^{+2} + 2e^- \longrightarrow Cu(s)$ (Reduction half cathode)

Cell : $Zn/Zn^{2+}(c_1)||Cu^{2+}(c_2)/Cu$

In general,	**Metal/Metal ion (conc.)**	||	**Metal ion (conc.)/Metal**
	– Oxidation occurs – Anode – Negative pole	Salt Bridge	– Reduction occurs – Cathode – Positive pole

Standard Electrode potential (E°)

$$E^\circ = E^\circ_{Cathode} - E^\circ_{anode}$$

or, $$E^\circ_{cell} = E^\circ_{right} - E^\circ_{left}$$

Topic 2

Electrolytic Cells and Electrolysis

» Revision Notes

- **Faraday's Laws of Electrolysis :**

First law : The mass of any substance deposited or liberated at any electrode is directly proportional to the quantity of electricity passed through the electrolyte.

$W \propto Q \Rightarrow W = ZQ$ (Z = electrochemical equivalent)

$W = Zit$ $\left(Z = \frac{\text{Eq. wt.}}{96500}\right)$

Second Law : When some quantity of electricity is passed through solutions of different electrolytes connected in series, the weight of substances produced at the electrodes are directly proportional to their equivalent weights.

$$\frac{\text{Weight of } M_1 \text{ deposited}}{\text{Weight to } M_2 \text{ deposited}} = \frac{\text{Equivalent weight of } M_1}{\text{Equivalent weight of } M_2}$$

Topic 3

Electrochemical Cells, Galvanic Cells and Nernst Equation

» Revision Notes

- **Nernst equation :**

For a cell reaction $aA + bB \rightleftharpoons xX + yY$

- **Nernst equation at 298 K :** $E_{cell} = E^\circ_{cell} - \frac{0.0591}{n} \log\frac{[X]^x[Y]^y}{[A]^a[B]^b}$

- **Gibbs's Free energy and cell potential (EMF) :**

$$-\Delta rG^\circ = nFE^\circ_{cell} = 2.303\ RT \log K_{eq.}$$

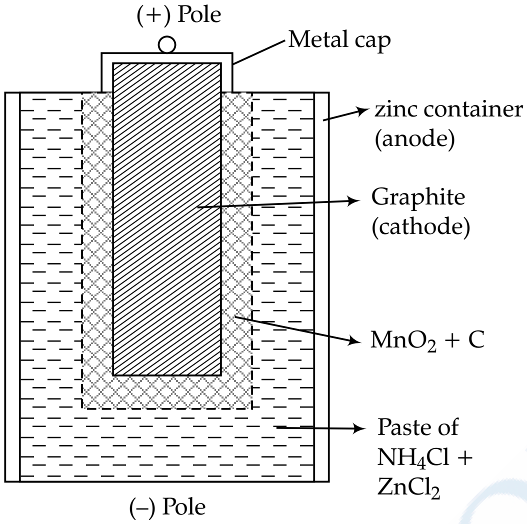
- **Some Commercial Cells (Batteries) :**
  - **Dry Cell**

Reaction at anode :

$$Zn_{(s)} \longrightarrow Zn^{2+}_{(aq)} + 2e^-$$

At cathode :

$$2MnO_{2(s)} + 2NH_4{}^+_{(aq)} + 2e^- \longrightarrow Mn_2O_{3(s)} + 2NH_3 + H_2O$$

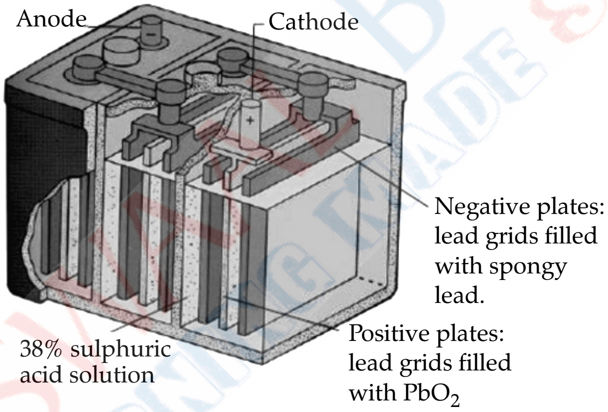


- **Lead Storage Battery :** The cell reactions take place when battery is discharged.

Reaction at anode : $Pb_{(s)} + SO_{4\,(aq)}^{-2} \longrightarrow PbSO_{4(s)} + 2e^-$

At cathode : $PbO_2 + SO_4^{-2} + 4H^+ + 2e^- \longrightarrow PbSO_{4(s)} + 2H_2O_{(l)}$

Overall reaction : $Pb_{(s)} + PbO_{2(s)} + 4H^+_{(aq)} + 2SO_4^{-2} \longrightarrow 2PbSO_{4(s)} + 2H_2O_{(l)}$



Lead Storage Battery

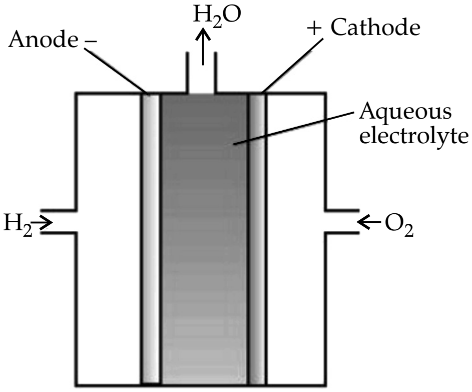
During charging, electrode reaction is reversed.

- **Fuel Cell :**

At anode : $2H_{2(g)} + 4OH^-_{(aq)} \longrightarrow 4H_2O_{(l)} + 4e^-$

At cathode : $O_{2(g)} + 2H_2O_{(l)} + 4e^- \longrightarrow 4OH^-_{(aq)}$

Overall reaction : $2H_{2(g)} + O_{2(g)} \longrightarrow 2H_2O_{(l)}$



Fuel Cell

Corrosion : The process of slowly eating away of the metal due to attack of the atmospheric gases on the surface of the metal resulting into the formation of compounds such as oxides, sulphides, carbonates, sulphates etc. is called corrosion.

Reaction involved :

$$H_2O + CO_2 \longrightarrow H_2CO_3$$

$$H_2CO_3 \rightleftharpoons 2H^+ + CO_3^{-2}$$

$$Fe \longrightarrow Fe^{+2} + 2e^- \; (E^\circ_{ox} = 0.44V)$$

$$O_2 + 4H^+ + 4e^- \longrightarrow 2H_2O \; (E^\circ_{red} = 1.23\ V)$$

$$2Fe_{(s)} + O_{2(g)} + 4H^+ \longrightarrow 2Fe^{+2} + 2H_2O \; (E^\circ_{Cell} = 1.67\ V)$$

$$4Fe^{+2} + O_2 + 4H_2O \longrightarrow 2Fe_2O_3 + 8H^+_{(aq)}$$

$$Fe_2O_3 + xH_2O \longrightarrow \underset{\substack{\text{Hydrated ferric} \\ \text{oxide (Rust)}}}{Fe_2O_3 . xH_2O}$$

❐❐❐

Chapter 18

Chemical Kinetics

Topic 1

Rate of Chemical Reaction, Factors influencing Rate of Reaction and Integrated Rate Equations

» Revision Notes

- **Rate of Reaction :** Change in the concentration of any one of the reactant or products per unit time. Units is mol L^{-1} s^{-1}

$$R \longrightarrow P$$

$$\text{Rate of reaction } = -\frac{\Delta[R]}{\Delta t} = +\frac{\Delta[P]}{\Delta t}$$

- **Rate Law Expression :** Rate law or rate expression is the expression in which reaction rate is given in terms of molar concentration of reactants with each term raised to some power, which may or may not be same as the stoichiometric coefficient of the reacting species in a balanced chemical equation. For general reaction,

$$aA + bB \longrightarrow \text{Products}$$

$$R = K\,[A]^a\,[B]^b$$

$$\frac{-d[R]}{dt} = k\,[A]^x\,[B]^y$$

  where, x and y may or may not be equal to the stoichiometric coefficients of the reactants and k is the proportionality constant called rate constant.

- **Order :** The sum of the exponents (powers) to which the concentration terms in the rate law equation are raised to express the observed rate of the reaction.
- **Molecularity :** The number of atoms, ions or molecules taking part in an elementary reaction, which must collide with one another simultaneously to bring about a chemical reaction a chemical reaction.
- **Difference between Order and Molecularity of the Reaction :**

S.No.	Order	Molecularity
1.	It is experimental quantity. It can be zero and a fraction also.	It cannot be zero or a non-integer.
2.	It is applicable to elementary as well as complex reactions.	It is applicable for elementary reactions only.
3.	For complex reaction, order is given by the slowest step.	Molecularity is same as order of the overall reaction.

- **Instantaneous rate of reaction :** Rate of reaction at any instant of time is the rate of change of concentration (*i.e.*, change of concentration per unit time) of any one of the reactants or products at that particular instant of time.
- **Pseudo first order reaction :** Such reactions which are not truly of the first order but under certain conditions become reactions of the first order are called pseudo-first order reactions.

  e.g., $CH_3COOC_2H_5 + H_2O \xrightarrow{H^+} CH_3COOH + C_2H_5OH$

- **Integrated Rate Equations :**

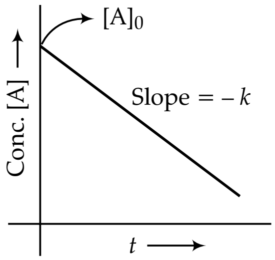
(i) For zero order reaction :

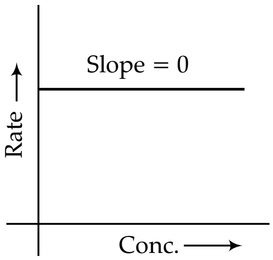
$$A \longrightarrow \text{Products}$$

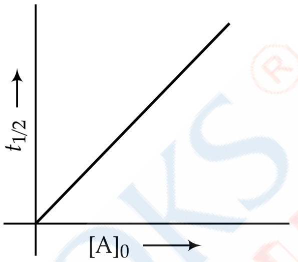
$$\text{Rate } = \frac{d[A]}{dt} = k[A]^0$$

$$k = \frac{1}{t}\{[A]_0 - [A]\} \text{ and } t_{1/2}\,\frac{[A]_0}{2k}$$

Graphs for Zero Order :







(ii) First order reaction

$$A \longrightarrow \text{Products}$$

$t = 0$ a 0

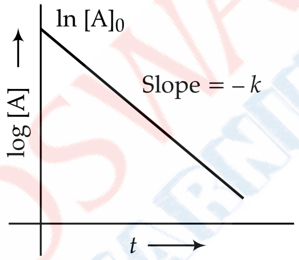
$t = t$ $a - x$ x

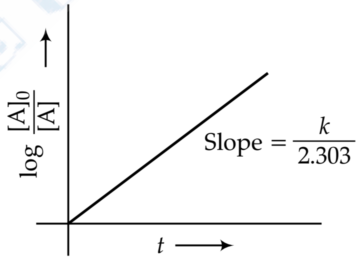
$$\text{Rate } = \frac{dx}{dt} = k(a-x)$$

$$k = \frac{2.303}{t}\log\left(\frac{a}{a-x}\right) \quad \text{or} \quad k = \frac{2.303}{t}\log\frac{[A]_0}{[A]}$$

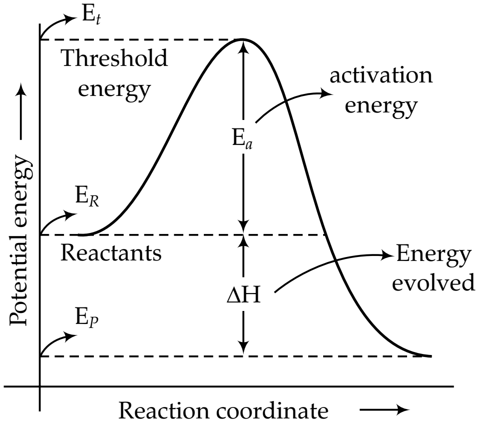
$$\text{or} \quad [A] = [A]_0\, e^{-kt} \quad \text{and} \quad t_{1/2} = \frac{0.693}{k}$$

Graphs for first order reaction :





- **General formula for half-life** ⇒ $t_{1/2} \propto \frac{1}{[A_0]^{n-1}}$
- **Activation Energy :** The minimum extra amount of energy absorbed by the reactant molecules so that their energy becomes equal to threshold energy is called activation energy.



Activation Energy = Threshold energy – Average kinetic energy of reactants

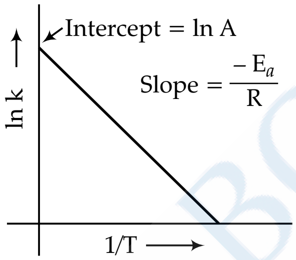
Topic 2

Temperature Dependence of the Rate of Reaction and Collision Theory of Chemical Reactions

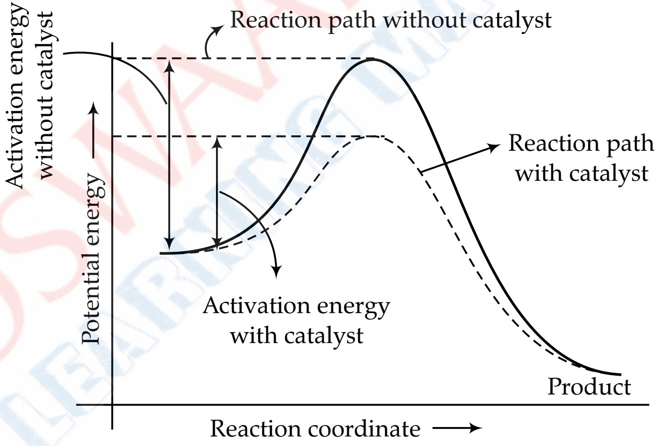
» Revision Notes

- **Arrhenius Equation :** Arrhenius Equation is a mathematical expression to give a quantitative relationship between rate constant and temperature.
- Temperature dependence of the rate of reaction (Arrhenius Equation) : $k = Ae^{-E_a/RT}$ where, k = rate constant and A = pre-exponential factor

$$\log\left(\frac{k_2}{k_1}\right) = \frac{E_a}{2.303\,R}\left(\frac{T_2 - T_1}{T_1T_2}\right)$$



- **Effect of catalyst on the rate of reaction :**
  The presence of catalyst lowers the potential barrier and the reaction follows a new alternate pathway which requires less activation energy.



- **Collision theory of chemical reactions :**
  - The number of collisions that take place per second per unit volume of the reaction mixture is called collision frequency (z).
  - For collision to be effective, the colliding molecules must have energy more than a particular value called threshold energy.
  - The colliding molecules must have proper orientations at the time of collision.
  - Collision theory also has certain drawbacks as it considers atoms/molecules to be hard spheres and ignores their structural aspect.

KNOW THE TERMS

- **Activated complex (Transition state) :** The intermediate with highest energy formed in the graph of a reaction profile.

Chapter 19

Surface Chemistry

Topic 1

Adsorption and Catalysis

» Revision Notes

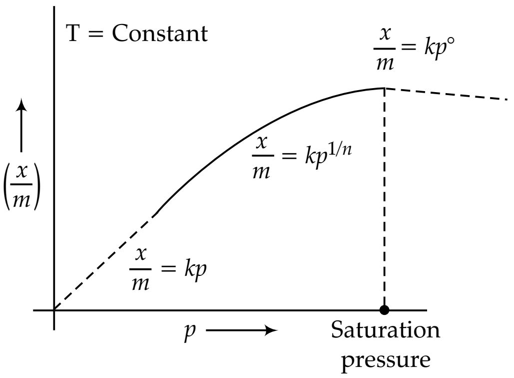
- Surface chemistry deals with the study of the phenomenon occurring at the surface of the boundary separating two bulk phases.
- **Adsorption :** It is the phenomenon of attracting and retaining the molecules of a substance on the surface of the liquid or a solid resulting into the higher concentration of the molecules on the surface.

  It is exothermic, $\Delta H = -\text{ve}$
- **Factors affecting adsorption :**
  - **(i)** Nature and surface area of the absorbent
    - – Greater the surface area, greater will be the volumes of gas adsorbed.
    - – Finely divided substances have larger adsorption power
  - **(ii)** Nature of the gas being adsorbed
    - – Higher the critical temperature of a gas, greater is the amount of that gas adsorbed.
  - **(iii)** Temperature
    - - Adsorption decreases with increase in temperature
  - **(iv)** Pressure
    - – At constant temperature, the adsorption of a gas increases with increase in pressure.
- **Physisorption and chemisorption :**

S.No.	Physisorption	Chemisorption
1.	The forces operating are weak van der Waal forces.	The forces operating are similar to chemical bond.
2.	The heat of adsorption is low.	The heat of adsorption is high.
3.	It forms multimolecular layer.	It forms unimolecular layer.
4.	The process is reversible, i.e., desorption of the gas occurs by increasing the temperature or decreasing the pressure.	The process is irreversible.

- **Freundlich's Adsorption isotherm :**

  A graph between the amount of the gas adsorbed per gram of the adsorbent (x/m) and the equilibrium pressure of the absorbate at constant temperature is called Freundlich adsorption isotherm.



At intermediate range of pressure.

$$\frac{x}{m} = k(p)^{1/n}$$

Or $$\log \frac{x}{m} = \log k + \frac{1}{n} \log p$$

Here, n = positive integer

Power of $\boldsymbol{p}$ *i.e.*, $\frac{1}{n}$ lie between 0 and 1 always.

Topic 2

Colloids and Emulsions

» Revision Notes

- **Colloidal State of Matter :**
  A state in which the size of the particles (1 to 1000 nm) is such that they can pass through filter paper but not through animals or vegetable membrane.

S.No.	Property	True solutions	Colloidal solutions	Suspension
1.	Particle size	Less than 10^{-9} m or 1 nm	Between 10^{-9} to 10^{-6} or 1 nm 1000 nm	More than 10^{-6} m or 1000 nm
2.	Filterability	Pass through ordinary filter paper as wells as animal membrane.	Pass through ordinary filter paper but not through animal membrane.	Do not pass through filter paper and animal membrane.
3.	Settling	Do not settle.	Do not settle.	Settle on standing.
4.	Diffusion	Diffuse quickly.	Diffuse slowly.	Do not diffuse.

- **Lyophilic and Lyophobic Sols**

S.No.	Property	Lyophilic sols	Lyophobic sols
1.	Ease of preparation	Prepared easily by directly mixing with the liquid dispersion.	Cannot be prepared directly. Prepared by special methods only.
2.	Stability	They are quite stable and are not easily precipitated or coagulated.	They are easily precipitated by additions of a small amount of a suitable electrolyte.
3.	Hydration	They are highly hydrated.	They are not much hydrated.
4.	Nature of Substance	These sols are usually formed by the organic substance like starch, gum proteins, etc.	These sols are usually formed by the inorganic materials like metals and their sulphides.

- **Multimolecular Colloids :** When dispersion of a substances in the dispersion medium, a large number of atoms or smaller molecules of the substance (with diameter less than 1 mm) aggregates together to form species having size in the colloidal range, the species formed are called multimolecular colloids.

- **Macromolecualr Colloids :** When certain substances having big size molecules called macromolecules having large molecular masses are dissolved in a suitable liquid, they form a solution in which the molecules of the substance *i.e.*, the dispersed particles have size in the colloidal range.
- **Mechanical properties of Colloids :**
  - **(i) Brownian movement :** Continuous zig-zag movement of the colloidal particles in a colloidal sol.
  - **(ii) Tyndall effect :** Scattering of light by the colloidal particles present in the colloidal gel.
  - **(iii) Electrophoresis :** The movement of colloidal particles under the influence of an electric field is called electrophoresis or cataphoresis.
  - **(iv) Coagulation or precipitation :** It is the process of aggregating together the colloidal particles so as to change them into large sized particles which ultimately settle as precipitate.
- **Hardy Schulze Law :**

  Greater the valency of the coagulating or the flocculating ion, greater is its power to bring about coagulation.
- **Catalysis :** Catalyst is a substance which can change the speed for a chemical reaction without itself undergoing at any change in mass and chemical composition at the end of the reaction.
  - **(i) Homogenous Catalysis :** If the catalyst is present in the same phase as the reactant.

    e.g.,
    $$2SO_{2(g)} + O_{2(g)} \xrightarrow{NO_{(g)}} 2SO_{3(g)}$$
  - **(ii) Heterogenous Catalysis :** If the catalyst is preset in the different phase then that of the reactants.
    $$N_{2(g)} + 3H_{2(g)} \xrightarrow{Fe_{(s)}} 2NH_{3(g)}$$
- **Enzyme as catalyst :** All biological reactions are catalysed by special catalyst called as enzymes, *e.g.*,
  $$C_{12}H_{22}O_{11} + H_2O \xrightarrow{\text{Invertase}} \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Fructose}}{C_6H_{12}O_6}$$
- **Emulsion :** It is a colloidal dispersion in which both the dispersed phase and the dispersion medium are liquid. The two liquids involved are other wise immiscible.

  They are of two types : (i) Oil in water, (ii) Water in oil.

KNOW THE TERMS

- **Adsorbate :** The substance which is adsorbed on the surface is called as adsorbate
- **Adsorbent :** The substance which is adsorbed is called as adsorbent.
- **Adsorption isobar :** A graph drawn between the amount of the gas adsorbed per gram of the adsorbent (x/m) and temperature 'T' at a constant equilibrium pressure of adsorbate gas is known as absorption isobar.
- **Dispersed phase :** The substance distributed in the dispersion medium in the form of colloidal particles.
- **Dispersion medium :** The medium in which the substance is dispersed in the form of colloidal particles.
- **Activity :** By activity of the catalyst we mean its capacity to increase the speed of the chemical reaction.
- **Selectivity :** By selectivity of a catalyst we mean its ability to direct the reaction to form particular products excluding other.

❒❒❒

Chapter 20

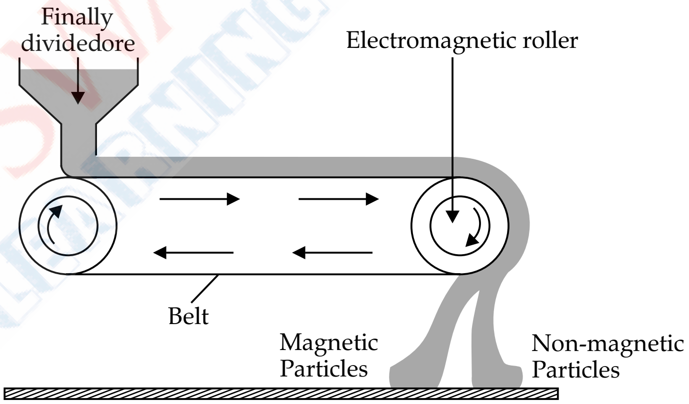
General Principles and Processes of Isolation of Elements

» Revision Notes

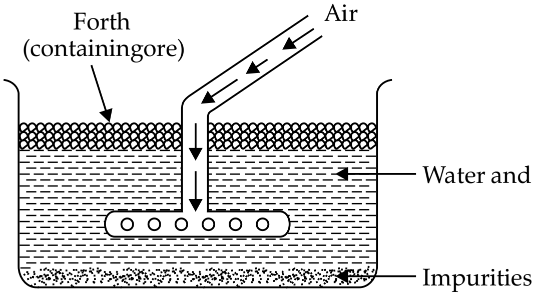
- The process of extracting metals from their ores is called metallurgy.
  - Concentration or Benefaction of the ore.
  - The removal of unwanted earthy and silicones impurities (*i.e.*, gangue or matrix) from the ore is called ore-dressing or concentration of ores.

(i) Hydraulic washing : The process in which earthy particles are freed from the heavier ore particles by washing with water.

(ii) Electromagnetic separation : This method of concentration is employed when either the ore or the impurities associated with it are magnetic in nature.



(iii) Froth floatation : This method is based upon the fact that the surface of sulphide ores is preferentially wetted by oils while that of gangue is preferentially wetted by water.



(iv) Leaching : This process consists in treating the powdered ore with a suitable reagent (such as acids, bases or other chemicals) which can selectively dissolve the ore but not the impurities.

- **Extraction of crude metals- Reduction/Oxidation :**
  - **Calcination :**

    It is the process of converting an ore into its oxide by heating it strongly below its melting point either in absence or limited supply of air.

    e.g.,

$$\underset{\text{Bauxite}}{Al_2O_3.2H_2O} \xrightarrow{\Delta} \underset{\text{Alumina}}{Al_2O_3} + H_2O$$

$$\underset{\text{Limonite}}{Fe_2O_3.3H_2O} \xrightarrow{\Delta} \underset{\text{Ferric oxide}}{Fe_2O_3} + 3H_2O$$

  - **Roasting :** It is the process of converting an ore into its metallic oxide by heating strongly at temperature insufficient to melt in excess of air. *e.g.,*

$$S_8 + 8O_2 \longrightarrow 8SO_2$$
$$2ZnS + 3O_2 \longrightarrow 2ZnO + 2SO_2$$

- **Extraction of Iron :**
  - **Concentration :** The crushed ore is washed in a stream of water when lighter sand and clay particles are washed away while the heavier ore particles settle down.
  - **Calcination :**

$$4FeO + O_2 \longrightarrow 2Fe_2O_3$$

  - Reduction of oxide in blast furnace.
  - At 500 – 800 K

$$3Fe_2O_3 + CO \longrightarrow 2Fe_3O_4 + CO_2$$
$$Fe_3O_4 + 4CO \longrightarrow 3Fe + 4CO_2$$
$$Fe_2O_3 + CO \longrightarrow 2FeO + CO_2$$

  - At 900 – 1500 K

$$C + CO_2 \longrightarrow 2CO$$
$$FeO + CO \longrightarrow Fe + CO_2$$

  - Reaction taking place in blast furnace

$$C + O_2 \longrightarrow CO_2$$
$$CO_2 + C \longrightarrow 2CO$$
$$CaCO_3 \longrightarrow CaO + CO_2$$
$$CaO + SiO_2 \longrightarrow CaSiO_3 \text{ (slag)}$$
$$Fe_2O_3 + CO \xrightarrow{823\text{ K}} 2FeO + CO_2$$
$$Fe_3O_4 + CO \xrightarrow{823\text{ K}} 3FeO + CO_2$$
$$FeO + CO \xrightarrow{1123\text{ K}} Fe + CO_2$$

- **Extraction of copper from cuprous oxide [Copper (I) Oxide]**
  - The sulphide ores are first roasted in a reverberating furnace to convert them into oxides

$$2Cu_2S + 3O_2 \longrightarrow 2Cu_2O + 2SO_2$$

  - The oxide can be reduced by using coke

$$Cu_2O + C \longrightarrow 2Cu + CO$$

    But in actual, sulphide ore is roasted when copper pyrite is converted into a mixture of FeS and Cu_2S which in turn are partly oxidized.

$$\underset{\text{Copper pyrite}}{2CuFeS_2} + O_2 \longrightarrow Cu_2S + 2FeS + SO_2$$
$$2FeS + 3O_2 \longrightarrow 2FeO + 2SO_2$$
$$2Cu_2S + 3O_2 \longrightarrow 2Cu_2O + 2SO_2$$

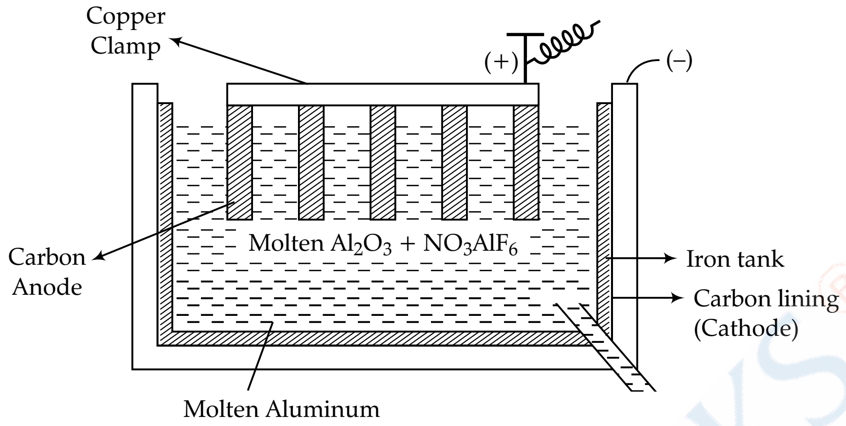
    During smelting FeO is present as impurity is converted into ferrous silicate ($FeSiO_3$)

$$FeO + SiO_2 \longrightarrow FeSiO_3$$

    When whole iron has been removed as a slag some of the cuprous sulphide undergoes oxidation to form cuprous oxide which then react with cuprous sulphide to form copper metal.

$$2Cu_2S + 3O_2 \longrightarrow 2Cu_2O + 2SO_2$$
$$2Cu_2O + Cu_2S \longrightarrow 6Cu + SO_2$$

- **Extraction of Aluminium from Alumina (Hall Heroult Process)**



At cathode : $Al^{+3} + 3e^- \longrightarrow Al_{(l)}$

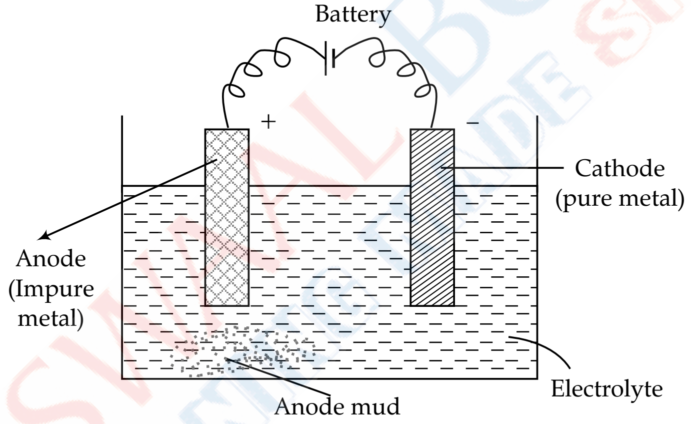
At anode : $C + O^{2-} \longrightarrow CO_{(g)} + 2e^-$

$C + 2O^{2-} \longrightarrow CO_{2(g)} + 4e^-$

- **Electrolytic refining :**

Impure metal = Anode

Pure metal = Cathode



Anode : $M \longrightarrow M^{n+} + ne^-$

Cathode : $M^{n+} + ne^- \longrightarrow M$

- **Zone refining :** Based on principle that the impurities are more soluble in the molten state than in the solid state of the metal.
- **Vapour Phase Refining :**
  - Metal should form a volatile compound with a suitable reagent.
  - Volatile compound should be easily decomposable so that the recovery is easy.
  - **Mond's Process :**

$$Ni + 4CO \xrightarrow{330-350\text{ K}} Ni(CO)_4$$

$$Ni(CO)_4 \xrightarrow{450-470\text{ K}} \underset{\text{Pure Nickel}}{Ni} + 4CO$$

KNOW THE TERMS

- **Depressant :** Substance used to prevent one type of sulphide ore particles from forming the forth with air bubbles.
- **Flux :** A substance that chemically combines with gangue (earthy impurities) which may still be present in the roasted or the calcined ore to form an easily fusible material called the slag.

  Flux + Gangue ⟶ Slag
- **Pyrometallurgy :** The process of extracting the metal by heating the metal oxide with a suitable reducing agent is called pyrometallurgy.

- **Smelting :** The process of extracting a metal by reduction of its oxide with carbon (in form of coke, charcoal or CO) is called smelting.
- **Wrought Iron :** Purest form of commercial iron which contains about 0.2 - 0.5% carbon.
- **Some important alloys :**
  - Brass : Cu (60%), Zn (40%)
  - Bronze : Cu (80%), Zn (10%), Sn (10%)
  - German Silver : Cu (25-30%), Zn (25-30%), Ni (40-50%)
  - Stainless Steel : Fe (73%), Cr (18%), Ni (8%), Carbon (1%)
  - Invar : Fe (64%), Ni (36%)
- **Ellingham Diagram :** For the reduction of a metal oxide with a reducing agent, the plot of ΔG° against temperature is studied, which is called Ellingham diagram.

❒❒❒

Chapter 21

p-Block Elements

Topic 1

Group 15 Elements

» Revision Notes

GROUP 15 ELEMENTS : Nitrogen Family

- **Elements :** Nitrogen (N), Phosphorous (P), Arsenic (As), Antimony (Sb) and Bismuth (Bi)
- **Electronic Configuration :** ns^2np^3 (where $n = 2$ to 6)
- **Chemical Properties :**
  - **Oxidation states :** All the elements of this group show positive oxidation state of +3 and +5 generally.

Compound	NH_3	NH_2NH_2	NH_2OH	N_2	N_2O	NO	N_2O_3	NO_2
Oxidation state of Nitrogen	–3	–2	–1	0	+1	+2	+3	+4

  - Reactivity towards hydrogen to form NH_3, PH_3, AsH_3, SbH_3, BiH_3

(i) Preparation :

$$Mg_3N_2 + 6H_2O \longrightarrow 3Mg(OH)_2 + 2NH_3$$
$$Ca_3P_2 + 6H_2O \longrightarrow 3Ca(OH)_2 + 2PH_3$$
$$Zn_3As_2 + 6HCl \longrightarrow 3ZnCl_2 + 2AsH_3$$
$$Mg_3Sb_2 + 6HCl \longrightarrow 3MgCl_2 + 2SbH_3$$
$$Mg_3Bi_2 + 6HCl \longrightarrow 3MgCl_2 + 2BiH_3$$

(ii) Boiling points : $PH_3 < AsH_3 < NH_3 < SbH_3 < BiH_3$

(iii) Reducing Character : $NH_3 < PH_3 < AsH_3 < BiH_3$

- Reactivity towards oxygen (formation of oxides) :

Nitrogen : N_2O, NO, N_2O_3, N_2O_4, NO_2, N_2O_5

Phosphorus : P_4O_6, P_4O_{10}

Arsenic : As_4O_6, As_4O_{10}

Antimony : Sb_4O_6, Sb_4O_{10}

Bismuth : Bi_2O_3

- Reactivity towards halogen (formation of halides)
- To form MX_3 or MX_5 (where x = F, Cl, Br, I and M = N, P, As, Sb, Bi)

Dinitrogen (N_2)

- **Preparation :** (i) Commercially → By liquefaction and fractional distillation of air

(ii) From ammonium dichromate $(NH_4)_2Cr_2O_7 \xrightarrow{\text{heat}} N_2 + 4H_2O + Cr_2O_3$

Ammonia (NH_3) [sp^3 hybridisation, H-N-H bond angle = 107.8°]

- **Preparation :** (i) By heating ammonium salt with a strong base

$$(NH_4)_2SO_4 + 2NaOH \xrightarrow{\text{heat}} 2NH_3 + 2H_2O + Na_2SO_4$$

(ii) By Haber's process $N_{2(g)} + 3H_{2(g)} \underset{K_2O,\ \text{Molybdenum}}{\overset{\text{Iron oxide, } Al_2O_3}{\rightleftharpoons}} 2NH_{3(g)}$ $(\Delta H_f = -92.4 \text{ kJ mol}^{-1})$

Nitric Acid (HNO_3) [Trigonal planar shape, sp^2 hybridised]

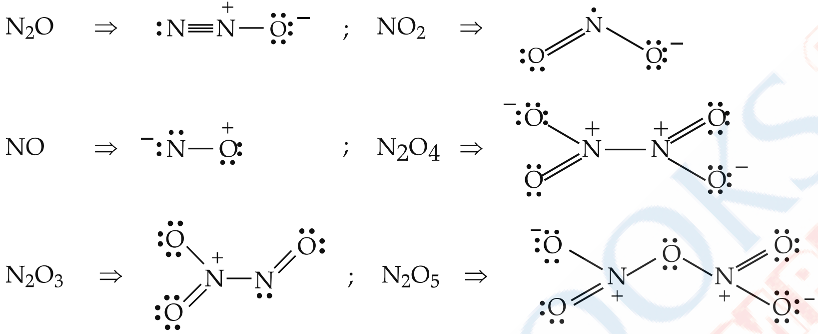
- **Preparation :** (i) In Lab

$$NaNO_3 + H_2SO_4 \xrightarrow{\text{heat}} NaHSO_4 + HNO_3$$

(ii) On commercial scale (Ostwald's Process)

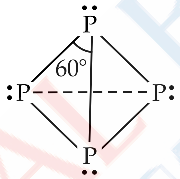
$$4NH_{3(g)} + SO_{2(g)} \xrightarrow[\text{Fe}]{673\text{K, 200 atm}} 4NO_{(g)} + 6H_2O_{(g)}$$

Structure of Some Oxides of Nitrogen :



Allotropic Forms of Phosphorus :

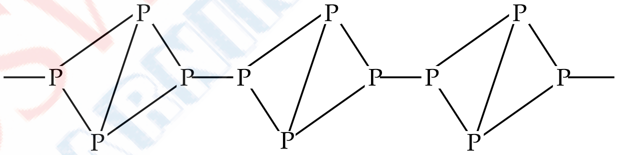
(i) White phosphorus :



- **Preparation :** $Ca_3(PO_4)_2 + 6SiO_2 \xrightarrow{1773\text{ K}} 6CaSiO_3 + P_4O_{10}$

$$P_4O_{10} + 10C \xrightarrow{1773\text{ K}} P_4 + 10CO$$

(ii) Red phosphorus :



- **Preparation :** $P_{4(s)} \xrightarrow[CO_2]{573\text{ K}} P_{4(s)}$

(iii) Black Phosphorus (layered structure)

- **Preparation :** White phosphorus $\xrightarrow[4{,}000\text{-}12{,}000]{473\text{ K}}$ Black phosphorus

Phosphine (PH_3) [Pyramidal structure, sp^3 hybridisation]

- **Preparation :**

(i) $Ca_3P_2 + 6H_2O \longrightarrow 3\,Ca(OH)_2 + 2PH_3$

(ii) $4H_3PO_3 \xrightarrow{\Delta} 3H_3PO_4 + PH_3$

Oxoacids of Phosphorus :

S. No.	Name	Formula	Oxidation	Characteristic bond and their number	Basicity	Method of preparation
1.	**Hyphosphorous acid (photosphosphoric)**	H_3PO_2	+1	One P—OH, two P—H, one P=O	Monobasic	$2P_4 + 3Ba(OH)_2 + 6H_2O \longrightarrow 2PH_3 + 3Ba(H_2PO_2)_2$ $Ba(H_2PO_2)_2 + H_2SO_4 \longrightarrow BaSO_4 + 2H_3PO_2$
2.	**Orthophosphorous acid (Phosphoric acid)**	H_3PO_3	+3	Two P—OH, one P—H, one P=O	Dibasic	$P_4O_6 + 6H_2O \longrightarrow 4H_3PO_3$ $PCl_3 + 3H_2O \longrightarrow H_3PO_3 + 3HCl$

3.	**Pyrophosphorous acid**	$H_4P_2O_5$	+3	Two P—OH, two P—H, two P=O	Dibasic	$5H_3PO_3 + PCl_3 \longrightarrow 3H_4P_2O_5 + 3HCl$
4.	**Hypophosphoric acid**	$H_4P_2O_6$	+4	Four P—OH, two P=O, One P—P	Tetrabasic	$2P(red) + 4NaOCl + 2H_2O \longrightarrow H_4P_2O_6 + 4NaCl$
5.	**Orthophosphoric acid**	H_3PO_4	+5	Three P—OH, one P=O	Tribasic	$P_4O_{10} + 6H_2O \longrightarrow 4H_3PO_4$
6.	**Pyrophosphoric acid**	$H_4P_2O_7$	+5	Four P—OH, two P=O one P—O—P	Tetrabasic	$2H_3PO_4 \xrightarrow{523k} H_4F_2O_7 + H_2O$
7.	**Metaphosphoric acid (exist in polymeric form), e.g., cyclotrimetaphosphoric acid or linear polymetaphosphoric acid**	HPO_3 $(HPO_3)_3$ $(HPO_3)_6$	+5 +5 +5	Three P—OH, three P=O, three P—O—P One P=O, One P—OH, two P—O—P	Tribasic Monobasic	$3H_3PO_3 + 3Br_2 \xrightarrow{\Delta,\ \text{sealed tube}} (HPO_3)_3 + 6HBr$
8.	**Peroxomonophosphoric acid**	H_3PO_5	+5	Two O—H one P=O, one P—O—O—H	Tribasic	$P_4O_{10} + 36\% H_2O_2$
9.	**Peroxydiphosphoric acid**	$H_4P_2O_8$	+5	Four O—H, two P=O, one P—O—O—P	Tetrabasic	Electrolysis of a mixture of $K_2HPO_4 + KF$

Topic 2

Group 16 Elements

» Revision Notes

GROUP 16 ELEMENTS : Oxygen Family

- **Elements :** Oxygen (O), Sulphur (S), Selenium (Se), Tellurium (Te) Polonium (Po)
- **Electronic configuration :** ns^2np^4 (Here n = 2 to 6)
  - — **Properties** :
    - **Oxidation states :** Show oxidation state of – 2 generally.
    - **Trend in chemical reactivity** : O > S > Se > Te > Po
    - **Order of bond angle** : $H_2O > H_2S > H_2Se > H_2Te$
    - **Volatility of hybrids** : $H_2S > H_2Se > H_2Te > H_2O$
    - **Acidic character** : $H_2Te > H_2Se > H_2S > H_2O$

Dioxygen (O_2)

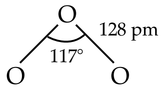
- **Preparation : (i) In Laboratory :** $2KClO_{3(s)} \xrightarrow[420\,K]{MnO_2} 2KCl + 3O_{2(g)}$

  (ii) Commercially : By liquefaction of air (after removing CO_2 and water vapours)

Ozone (O_3)

- **Preparation** : $3O_{2(g)} \xrightleftharpoons{\text{Silent electric discharge}} 2O_{3(g)}$

$O_3 \Rightarrow$



Sulphur Allotropic Form

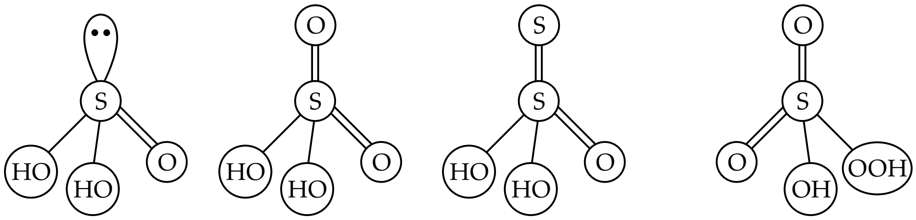
- **Rhombic Sulphur :** Prepared by slowly evaporating the solution of roll sulphur in CS_2 in a China dish.
- **Monoclinic Sulphur** (β–sulphur) **:** Prepared by melting sulphur in a China dish.
- **Cyclo S_6 (Engel's sulphur) :** Prepared by pouring molten sulphur into cold water.

Sulphur dioxide (SO_2) :

- **Preparation :** (i) $S_{8(s)} + 8O_{2(g)} \longrightarrow 8SO_{2(g)}$

  (ii) In laboratory : $Cu_{(s)} + 2H_2SO_{4(l)} \xrightarrow{heat} CuSO_{4(aq)} + SO_{2(g)} + 2H_2O_{(l)}$

- **Oxoacids of sulphur :**

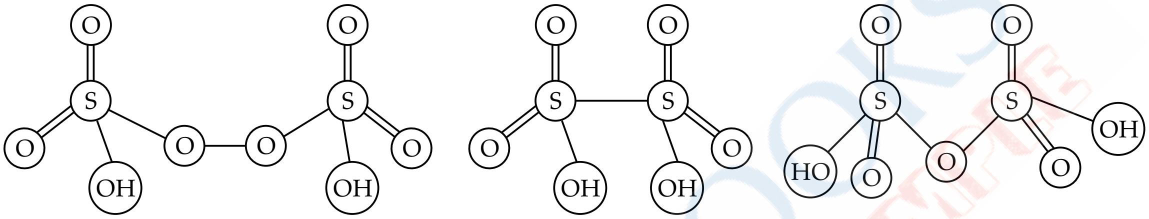


H_2SO_3 (+4) Sulphurous acid

H_2SO_4 (+6) Sulphuric acid

$H_2S_2O_3$ (+6, –2) Thiosulphuric acid

H_2SO_5 (+6) Peroxomonosulphuric acid or Caro's acid



$H_2S_2O_7$ (+6) Peroxodisulphuric acid or Marshall's acid

$H_2S_2O_6$ (+6) Dithionic acid

$H_2S_2O_7$ (+6) Pyrosulphuric acid (oleum)

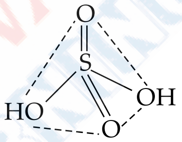
Structures of Some Important Oxoacids of Sulphur.

Sulphuric Acid H_2SO_4

- **Preparation :** By contact the process

$$S_8 + 8O_2 \longrightarrow 8SO_2$$
$$2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)}, \Delta_r H^\circ = -196.6 \text{ kJ mol}^{-1}.$$
$$SO_3 + H_2SO_4 \longrightarrow \underset{\text{(oleum)}}{H_2S_2O_7}$$
$$H_2S_2O_7 + H_2O \longrightarrow 2H_2SO_4$$

- **Structure of H_2SO_4 :**



Tetrahedral
sp^3 hybridised

Tetrahedral structure of H_2SO_4

Topic 3

Group 17 Elements

» Revision Notes

GROUP 17 ELEMENTS : Halogen Family

- **Elements :** Fluorine (F), Chlorine (Cl), Bromine (Br), Iodine (I) Astatine (At)
- **Electronic configuration :** ns^2np^5 (where n = 2 to 6)
- **Properties :**

Enthalpy of dissociation	:	$Cl_2 > Br_2 > F_2 > I_2$
Dipole moments	:	HF > HCl > HBr > HI
Percentage ionic character	:	HI < HBr < HCl < HF
Bond length	:	HF < HCl < HBr < HI
Bond strength	:	HI < HBr < HCl < HF
Thermal stability	:	HI < HBr < HCl < HF
Reducing power	:	HF < HCl < HBr < HI
Acid strength	:	HF < HCl < HBr < HI

Chlorine (Cl_2)

- **Preparation : (i) In laboratory :**

$$2NaCl + 3H_2SO_4 + MnO_2 \longrightarrow 2NaHSO_4 + MnSO_4 + 2H_2O + Cl_2$$

(ii) Deacon's process :

$$4HCl + O_2 \xrightarrow{CuCl_2, 723K} 2Cl_2 + 2H_2O$$

Hydrogen chloride (HCl)

- **Preparation : (i) In laboratory :**

$$NaCl + H_2SO_4 \xrightarrow{420\ K} NaHSO_4 + HCl$$

(ii) $2NH_4Cl + H_2SO_4 \xrightarrow{heat} 2HCl + (NH_4)_2SO_4$

Oxoacids of halogens

- Due to very small size, fluorine can form only 1 oxoacid *i.e.*, HOF. Chlorine form four types of oxoacids viz, hypochlorous acid (HOCl), chlorous acid (HOClO), chloric acid ($HOClO_2$) and perchloric acid ($HOClO_3$). Oxoacids of bromine are HOBr, $HOBrO_2$ and $HOBrO_3$ while iodine forms HOI, $HOIO_2$ and $HOIO_3$ – oxoacids

Inter-halogen Compounds

XX′ ⇒ ClF , BrF, BrCl , ICl, IBr, IF
XX'_3 ⇒ ClF_3, BrF_3, IF_3 $ICl_3(I_2Cl_6)$
XX'_5 ⇒ ClF_5, BrF_5, IF_5
XX'_7 ⇒ IF_7

Shapes of Inter-halogen Compounds

Molecule	No. of bond pairs	No. of lone pairs	Total electron pairs	Shape
XX'_3	3	2	5	T-shaped
XX'_5	5	1	6	Distorted octahedral or square pyramidal
XX_7	7	0	7	Pentagonal bipyramid

Topic 4

Group 18 Elements

» Revision Notes

GROUP 18 ELEMENTS : Nobel Gases

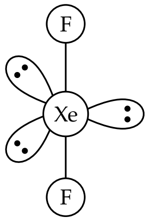
- **Elements :** Helium (He), Neon (Ne), Argon (Ar), Krypton (Kr), Xenon (Xe) and Radon (Rn)
- **Electronic configuration :** $ns^2\ np^6$ (Here, $n = 1$ to 6)
- **Properties :**

The noble gases have high ionization enthalpies.
The electron gain enthalpies of noble gases are positive.
First compounds prepared by Neil Bartlett..

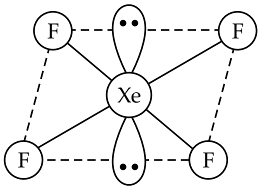
$$O_{2(g)} + PtF_{6(g)} \longrightarrow O_2^+ [PtF_6]^-_{(s)}$$

Shapes and Hybridization of Xenon Compounds :

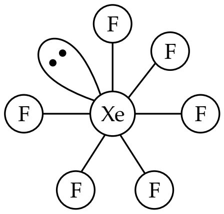
Molecule	Hybridization	Geometry	Shape
XeO_3	sp^3	Tetrahedral	Pyramidal
XeO_4	sp^3	Tetrahedral	Tetrahedral
$XeOF_2$	sp^3d^2	Trigonal bipyramidal	T-shaped
$XeOF_4$	sp^3d^2	Square pyramidal	Square Pyramidal
XeO_2F_2	sp^3d	Trigonal bipyramid	Distorted trigonal bipyramid
XeO_3F_2	sp^3d	Trigonal bipyramid	Trigonal bipyramid
XeO_2F_4	sp^3d^2	Octahedral	Octahedral



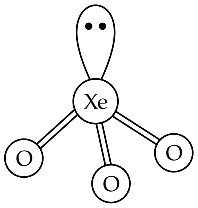
XeF_2
r(Xe—F) = 200 pm
LINEAR



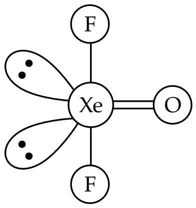
XeF_4
r(Xe—F) = 195 pm
SQUARE PLANAR



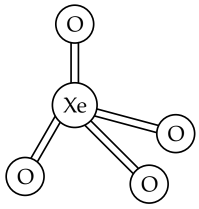
XeF_6
DISTORTED OCTAHEDRAL



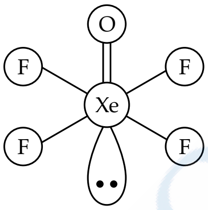
XeO_3
PYRAMIDAL



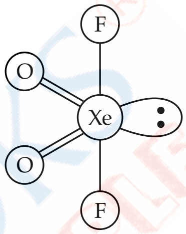
$XeOF_2$
T-SHAPED



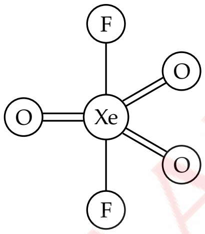
XeO_4
TETRAHEDRAL



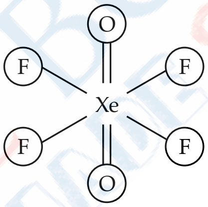
$XeOF_4$
SQUARE PYRAMIDAL



XeO_2F_2
TRIGONAL
BIPYRAMIDAL



XeO_3F_2
TRIGONAL
BIPYRAMIDAL



XeO_2F_4
OCTAHEDRAL

* * *

Chapter 22

d and f-Block Elements

Topic 1

First and Second Transition Series

» Revision Notes

- General electronic configuration = $(n-1)\,d^{1-10}\,ns^{0-2}$
- Electronic configuration of transition metals.

1. First (3*d*) Transition Series (Sc-Zn)

Atomic No.	21	22	23	24	25	26	27	28	29	30
Element	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Cu
Electronic Configuration	$3d^1 4s^2$	$3d^2 4s^2$	$3d^3 4s^2$	$3d^5 4s^1$	$3d^5 4s^2$	$3d^6 4s^2$	$3d^7 4s^2$	$3d^8 4s^2$	$3d^{10} 4s^1$	$3d^{10} 4s^2$

2. Second (4*d*) Transition Series (Y-Cd)

Atomic No.	30	40	41	42	43	44	45	46	47	48
Element	Y	Zr	Nb	Mo	Tc*	Ru	Rh	Pd	Ag	Ca
Electronic Configuration	$4d^1 5s^2$	$4d^2 5s^2$	$4d^4 5s^1$	$4d^5 5s^1$	$4d^6 5s^1$	$4d^7 5s^1$	$4d^8 5s^1$	$4d^{10} 5s^0$	$4d^{10} 5s^1$	$4d^{10} 5s^2$

*Technetium (Tc) is a synthetic transition metal.

3. Third (5*d*) Transition Series (La-Hg) :

Atomic No.	57	72	73	74	75	76	77	78	79	80
Elements	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg
Electronic Configuration	$5d^1 6s^2$	$5d^2 6s^2$	$5d^3 6s^2$	$5d^4 6s^2$	$5d^5 6s^2$	$5d^6 6s^2$	$5d^7 6s^2$	$5d^9 6s^1$	$5d^{10} 6s^1$	$5d^{10} 6s^2$

4. Fourth (6*d*) Transition Series :

Atomic No.	89	104	105	106	107	108	109	110	111	112
Elements	Ac	Ku	Ha	Sg (Unn)	Bh (Uns)	Hs (Uno)	Mt (Une)	Unn	Uuu	Uub
Electronic Configuration	$5d^1 7s^2$	$6d^2 7s^2$	$6d^3 7s^2$	$6d^4 7s^2$	$6d^5 7s^2$	$6d^6 7s^2$	$6d^7 7s^2$	$6d^8 7s^2$	$6d^{10} 7s^1$	$6d^{10} 7s^2$

- **Properties :**
  - **Atomic Radii :** Generally the atomic radii of *d*-block elements in a series decrease with increase in atomic number but the decrease in atomic size is small after midway.
  - **Metallic Character :** Except for mercury which is liquid, all the transition elements have typical metallic structure (hcp, ccp or bcc). They exhibit all the characteristics of metals.
- **Melting and Boiling Points :** The transition metals have very high melting and boiling points. The melting points of the transition metals rise to a maximum and then fall as the atomic number increases. Mn and Tc have abnormally low melting points.
- **Ionisation energies or ionization enthalpies :** First ionization enthalpies of *d*-block elements lie between *s*-block and *p*-block elements. They are higher than those of *s*-block elements and lesser than those of *p*-block elements.
- Trends in the M^{2+}/M standard electrode potential.
  - There is no regular trend in the E° (M^{2+}/M) values This is because their ionization enthalpies ($IE_1 + IE_2$) and sublimation enthalpies do not show any regular trend.
- **Oxidation States :** All transition elements except the first and last member of the series, exhibit a number of oxidation states.

Sc → +3

Ti → +2, +3, +4

V → +2, +3, +4, +5

Cr → +2, +3, +4, +5, +6,

Mn → +2, +3, +4, +5, +6, +7

Fe → +2, +3, +4, +6

Co → +2, +3, +4

Ni → +2, +3, +4

Cu → +1, +2

Zn → +2

- **Coloured Ions :** Most of the transition metal compounds (ionic as well as covalent) are coloured both in the solid and in aqueous solution in contrast to the compounds of *s* and *p*-block elements.

Ion	Configuration	Colour
Sc^{3+}	$3d^0$	Colourless
Ti^{4+}	$3d^0$	Colourless
Ti^{3+}	$3d^1$	Purple
V^{4+}	$3d^1$	Blue
V^{3+}	$3d^2$	Green
V^{2+}	$3d^3$	Violet
Cr^{3+}	$3d^3$	Violet
Mn^{3+}	$3d^4$	Violet
Cr^{2+}	$3d^4$	Blue
Mn^{2+}	$3d^5$	Pink
Fe^{3+}	$3d^5$	Yellow
Fe^{2+}	$3d^6$	Green
Co^{3+}	$3d^6$	Blue
Co^{2+}	$3d^7$	Pink
Ni^{2+}	$3d^8$	Green
Cu^{2+}	$3d^9$	Blue
Zn^{2+}	$3d^{10}$	Colourless

- **Magnetic properties :** In case of transition metals as they contain unpaired electrons in $(n-1)d$ orbitals, most of the transition metal ions and their compounds are paramagnetic.

Magnetic moment is calculated by spin only formula viz.

$$\mu = \sqrt{n(n+2)}\text{ B.M.}$$

where, n = number of unpaired electrons

Topic 2

Important Compounds of Transition Series ($KMnO_4$ and $K_2Cr_2O_7$)

» Revision Notes

➢ Some Important Compounds of Transition Elements

I. $K_2Cr_2O_7$ (Potassium dichromate)

Preparation from chromite ($FeO.Cr_2O_3$)

$4FeO.Cr_2O_3 + O_2 \longrightarrow 2Fe_2O_3 + 4Cr_2O_3$

$[4Na_2CO_3 + 2Cr_2O_3 + 3O_2 \longrightarrow 4Na_2Cr_2O_4 + 4CO_2] \times 2$

$4FeO.Cr_2O_3 + 8Na_2CO_3 + 7O_2 \longrightarrow 8Na_2Cr_2O_4 + 2Fe_2O_3 + 8CO_2$

$2Na_2CrO_4 + 8H_2SO_4 \longrightarrow Na_2Cr_2O_7 + Na_2SO_4 + H_2O$

$Na_2Cr_2O_7 + KCl \longrightarrow K_2Cr_2O_7 + 2NaCl$

Properties :

Oxidising Properties :

(a) Liberates I_2 from KI

$K_2Cr_2O_7 + 7H_2SO_4 + 6KI \longrightarrow 4K_2SO_4 + Cr_2(SO_4)_3 + 3I_2 + 7H_2O$

(b) Oxidises ferrous salts to ferric salts :

$K_2Cr_2O_7 + 7H_2SO_4 \longrightarrow K_2SO_4 + Cr_2(SO_4)_3 + 3Fe_2(SO_4)_3 + 2H_2O + 6FeSO_4$

(c) Oxidises H_2S to sulphur :

$K_2Cr_2O_7 + 4_2SO_4 + 3H_2S \longrightarrow K_2SO_4 + Cr_2(SO_4)_3 + 7H_2O + 3S$

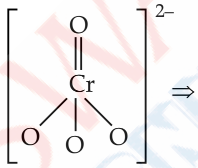
(d) Oxidises sulphites to sulphates :

$K_2Cr_2O_7 + 7H_2SO_4 + 3Na_2SO_3 \longrightarrow K_2SO_4 + Cr_2(SO_4)_3 + 4H_2O + 3Na_2SO_4$

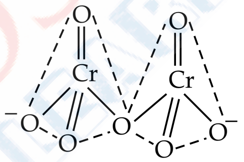
(e) Oxidises nitrites to nitrates :

$K_2Cr_2O_7 + 4H_2SO_4 + 3NaNO_2 \longrightarrow K_2SO_4 + Cr_2(SO_4)_3 + 3NaNO_3 + 4H_2O$

Structures :



⇒ Chromate ion-tetrahedral structure



⇒ Dichromate ion-two tetrahedral sharing one oxygen atom.

II. Potassium Permanganate ($KMnO_4$)

Preparation : From Pyrolusite (MnO_2)

$2MnO_2 + 4KOH + O_2 \longrightarrow 2K_2MnO_4 + 2H_2O$

$2MnO_2 + 2K_2CO_3 + O_2 \longrightarrow 2K_2MnO_4 + 2CO_2$

$MnO_2 + 4KOH + KNO_3 \longrightarrow K_2MnO_4 + KNO_2 + H_2O$

$K_2MnO_4 + 2CO_2 \longrightarrow 2KMnO_4 + MnO_2\downarrow + 2K_2CO_3$

Properties :

Oxidising Properties :

(a) Oxidising H_2S to S

$2KMnO_4 + 3H_2SO_4 + 5H_2S \longrightarrow K_2SO_4 + 2MnSO_4 + 3H_2O + 5S$

(b) Oxidises sulphur dioxide to sulphuric acid

$2KMnO_4 + 5SO_2 + 2H_2O \longrightarrow K_2SO_4 + 2MSO_4 + 3H_2SO_4$

(c) Oxidises oxalates to CO_2

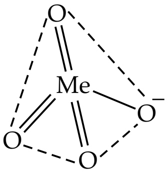
$2KMnO_4 + 3H_2SO_4 + 5C_2H_2O_4 \longrightarrow K_2SO_4 + 2MnSO_4 + 8H_2O + 10CO_2$

(d) Oxidises HX to X_2. where, X = Cl, Br, I

$2KMnO_4 + 3H_2SO_4 + 10HX \longrightarrow K_2SO_4 + 2MnSO_4 + 8H_2O + 5X_2$

Structure :

MnO_4^- ⇒



sp^3, tetrahedral

Topic 3

Inner Transition Elements (Lanthanoids and Actinoids)

» Revision Notes

➢ **Lanthanoids**

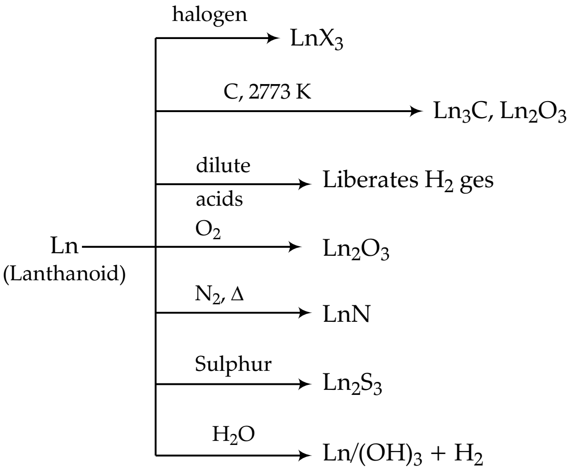
Name of the Element	Symbol (Ln)	At. No. (Z)	Electronic configuration	Oxidation states	F.C. outside [Xe] core		
					Ln^{2+}	Ln^{3+}	Ln^{4+}
Lanthanum	La	57	[Xe] $5d^1\,6s^2$	+3	$5d^1$	$4f^0$	
Cerium	Ce	58	[Xe] $4f^1\,5d^1\,6s^2$	+3, +4	$4f^2$	$4f^1$	$4f^0$
Praseodymium	Pr	59	[Xe] $4f^3\,5d^0\,6s^2$	+3, +4	$4f^3$	$4f^2$	$4f^1$
Neodymium	Nd	60	[Xe] $4f^4\,5d^0\,6s^2$	+2 +3, +4	$4f^4$	$4f^3$	$4f^2$
Promethium*	Pm	61	[Xe] $4f^5\,5d^0\,6s^2$	+3	$4f^5$	$4f^4$	
Samarium	Sm	62	[Xe] $4f^6\,5d^0\,6s^2$	+2, +3	$4f^6$	$4f^5$	
Europium	Eu	63	[Xe] $4f^7\,5d^0\,6s^2$	+2, +3	$4f^7$	$4f^6$	
Gasdonium	Gd	64	[Xe] $4f^7\,5d^1\,6s^2$	+3	$4f^7\,5d^1$	$4f^7$	
Fermium	Tb	65	[Xe] $4f^9\,5d^0\,6s^2$	+3, +4	$4f^9$	$4f^8$	$4f^7$
Dysprosium	Dy	66	[Xe] $4f^{10}\,5d^0\,6s^2$	+3, +4	$4f^{10}$	$4f^9$	$4f^8$
Holmium	Ho	67	[Xe] $4f^{11}\,5d^0\,6s^2$	+3	$4f^{11}$	$4f^{10}$	
Erbium	Er	68	[Xe] $4f^{12}\,5d^0\,6s^2$	+3	$4f^{12}$	$4f^{11}$	
Thulium	Tm	69	[Xe] $4f^{13}\,5d^0\,6s^2$	+2, +3	$4f^{13}$	$4f^{12}$	
Ytterbium	Yb	70	[Xe] $4f^{14}\,5d^0\,6s^2$	+2, +3	$4f^{14}$	$4f^{13}$	
Lutetium	Lu	71	[Xe] $4f^{14}\,5d^1\,6s^2$	+3	$4f^{14}\,5d^1$	$4f^{14}$	

➢ **Lanthanoid contraction :**

The regular decrease in the size of the atoms and ions with increasing atomic number is known as lanthanoid contraction.

Due to this Zirconium (Zr) and Hafnium (Hf) have nearly same size.

➢ **Chemical behaviour :**



- **Actinoids :**

Name of the Element	Symbol (M)	At. No. (Z)	Electronic configuration	Oxidation states	E.C. outside [Rn] core	
					M^{3+}	M^{4+}
Actinium	Ac	89	[Rn] $6d^1\,7s^2$	+3	$5f^0$	
Thorium	Th	90	[Rn] $6d^2\,7s^2$	(+3), +4	$5f^1$	$5f^0$
Protactinium	Pa	91	[Rn] $5f^2\,6d^1\,7s^2$	+3, +4, +5	$5f^2$	$5f^1$
Uranium	U	92	[Rn] $5f^4\,6d^0\,7s^2$	+3, +4, +5, +6	$5f^3$	$5f^2$
Neptunium	Np	93	[Rn] $5f^4\,6d^1\,7s^2$	+3, +4, +5, +6, +7	$5f^4$	$5f^3$
Plutonium	Pu	94	[Rn] $5f^6\,6d^0\,7s^2$	+3, +4, +5, +6, +7	$5f^5$	$5f^4$
Americium	Am	95	[Rn] $5f^7\,6d^0\,7s^2$	+3, (+4), +5, +6	$5f^6$	$5f^5$
Curium	Cm	96	[Rn] $5f^7\,6d^1\,7s^2$	+3, (+4)	$5f^7$	$5f^7$
Berkelium	Bk	97	[Rn] $5f^9\,6d^0\,7s^2$	+3, +4	$5f^8$	$5f^7$
Californium	Cf	98	[Rn] $5f^{10}\,6d^0\,7s^2$	+3	$5f^9$	$5f^8$
Einsteinium	Es	99	[Rn] $5f^{11}\,6d^0\,7s^2$	+3	$5f^{10}$	$5f^9$
Fermium	Fm	100	[Rn] $5f^{12}\,6d^0\,7s^2$	+3	$5f^{11}$	$5f^{10}$
Mendelevium	Md	101	[Rn] $5f^{13}\,6d^0\,7s^2$	+3	$5f^{12}$	$5f^{11}$
Nobelium	No	102	[Rn] $5f^{14}\,6d^0\,7s^2$	+3	$5f^{13}$	$5f^{12}$
Lawrencium	Lr	103	[Rn] $5f^{14}\,6d^1\,7s^2$	+3	$5f^{14}$	$5f^{13}$

Note : Oxidation states given in brackets are less stable.

- **Chemical behaviour :**

  They react with boiling water to give a mixture of oxide and hydride.
  They combine with most of the non-metals at moderate temperature.
  Alkalies have no action on them.

KNOW THE TERMS

- **Alloy :** They are homogeneous solid solutions of two or more metals obtained by melting the components and then cooling the melt.
- **Coinage metals :** The elements of group 11 (Cu, Ag and Au)
- **Mohr salt :** $FeSO_4.(NH_4)_2SO_4.6H_2O$

  Used as a primary standard in $KMnO_4$ titration.
- **Mischmetal :** A well known alloy which contains Lanthanoid metal (La (40%), Ca (50%) and other lanthanoids 5%] + Iron 5% and Traces of S, C, Ca and Al.

❑❑❑

Chapter 23

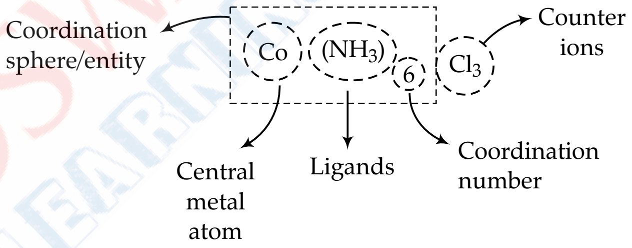
Co-ordination Compounds

Topic 1

Nomenclature and Isomerism

» Revision Notes

- Coordination compounds are those compounds in which the central metal atom is linked to a number of ions or neutral molecules by coordinate bonds. *i.e.*, by donation of lone pair of electrons by these ions or neutral molecules to the central metal atom.
- **Ligand :** The donor atoms, molecules or anions which donate a pair of electrons to the metal atom or ion and form a coordinate bond with it are called ligand.
- The number of coordinating or ligating groups present in a ligand is called the denticity of that ligand.
- **Coordination number :** The total number of unidentate ligands (plus double the number of didentate ligands if any) attached to the central metal ion through coordinate bonds.



- **Naming of coordination compounds :**
  - **(i) Order of naming ions :** The positive ions (cation) whether simple or complex, is named first followed by the negative ion (anion).
  - **(ii) Naming of ligands :**
    Negative ligands (organic or inorganic) end in – o
    Neutral ligands have no special ending
    Positive ligands end in—ium
  - **(iii) Prefixes :** If there are several ligands of the same type, the prefixes like di,tri, tetra, penta and hexa are used.
  - **(iv) Preference order :** All ligands whether negative, natural or positive are named first in the alphabetical order
  - **(v) Naming of the complex ion :** Ligands are named first followed by the metal atom.
  - **(vi) Naming of the geometrical isomers :** In geometrical isomers, the term *cis* is used to designate similar groups at adjacent positions and *trans* to designate similar groups at opposite positions.
- **Isomerism :**
  - **(i) Ionisation isomerism :** Compounds which give different ions in solution although they have same composition are called ionization isomers.
    e.g., $[Pt(NH_3)_4(OH)_2]SO_4$ and $[Pt(NH_3)_4(SO_4)](OH)_2$

(ii) Solvate or hydrate isomerism : This is also known as hydrate isomerism. In this isomerism, water is taken as solvent. It has different number of water molecules in the coordination sphere and outside it.

e.g., $[Co(NH_3)_4(H_2O)]Cl_2$ and $[Co(NH_3)_4Cl_2)]Cl.H_2O$

(iii) Linkage isomerism : When more than one atom in a unidentate ligand may function as a donor

e.g., $[Cr(H_2O)_5(SCN)]^{2+}$ and $[Cr(H_2O)_5(NCS)]^{2+}$

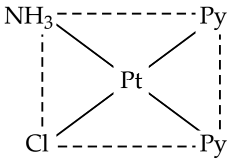
(iv) Coordination isomerism : When anion and cation both are in complex form

e.g., $[Co(NH_3)_6][Cr(CN)_6]$ and $[Cr(NH_3)_6][Co(CN)_6]$

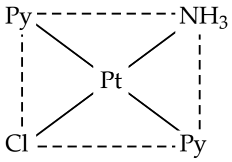
➢ **Geometrical isomerism :**

cis-trans isomerism

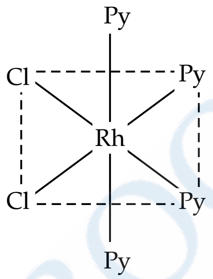
Shown by MA_2B_2, $M(AB)_2$, MA_2BC, MABCD type [C.N = 4] or MA_4B_2, MA_2B_4, $[M(AA)_2B_2]$, $[M(AA)_2BC]$, MA_3B_3 [C.N. = 6]



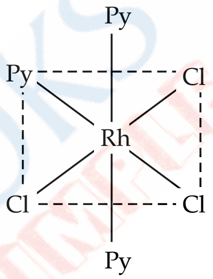
cis



trans



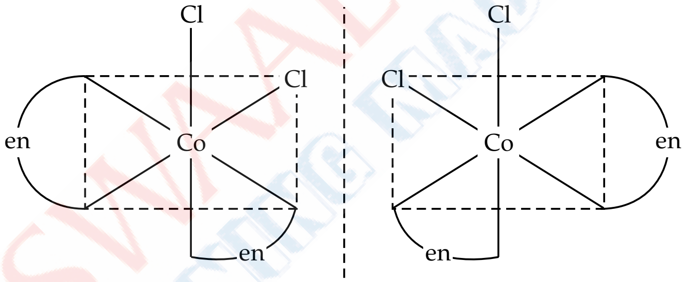
cis-or
fac isomer



trans-or
mer isomer

➢ **Optical isomers :**

Shown by $[M(AA)_3]$, $[M(AA)_2B_2]$ or $[M(AA)_2BC]$, $[M(AA)B_2C_2]$



Topic 2

Bonding in Coordination Compounds (CFSE and Jahn-Teller Effect)

» Revision Notes

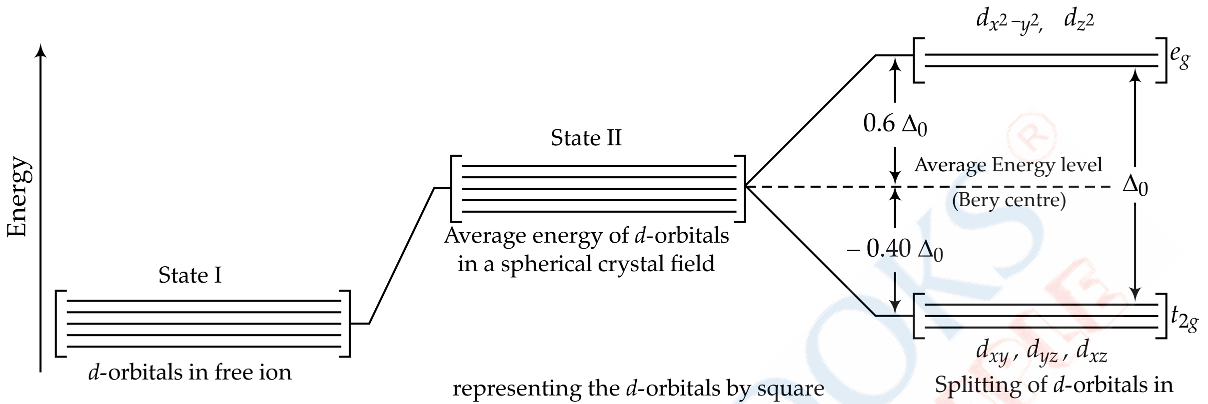
➢ **Werner's theory of co-ordination compounds :**

- **Primary Valencies :** They are those which a metal exhibits in the formation of its simple salts.
- **Secondary Valencies :** Correspond to coordination number (CN) of the metal atom and are satisfied by ligands. These are non-ionisable and directional. Hence, geometry is decided by these valencies.
- Every metal atom has a tendency to satisfy both its primary and secondary valencies.

➢ **Valence Bond (VB) Theory :**

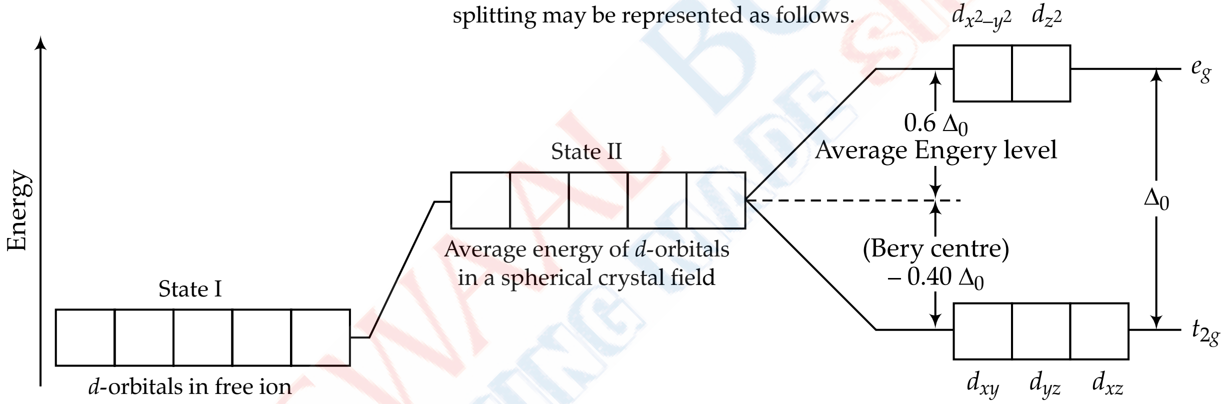
- Metal : Ligand bond arises by the donation of pairs of electrons by ligands to the metal atom/ion.
- In order to accommodate these electrons the metal ion must possess requisite number of vacant orbitals of equal energy.
- Sometimes the unpaired (n – 1) d-electrons pair up as fully as possible prior to hybridization thus making some (n – 1)d orbitals vacant.
- With the approach of the ligands, metal-ligand bonds are then formed by the overlap of these orbitals with those of the ligands *i.e.*, by donation of electron pairs by the ligands to the empty hybridized orbitals.

- **Crystal Field Theory :**
  - There is electrostatic interaction between the metal ion and the ligand.
  - Each ligand is a point of negative charge.
  - It considers the effect of the ligands on the relative energies of the d-orbitals of the central metal atom/ion.
- **Splitting of *d*-orbitals in octahedral crystal field :**



Splitting of *d*-orbitals in an octahedral crystal field

or representing the *d*-orbitals by square boxes and remembering that *d*-orbitals of the free ion are degenerate, the splitting may be represented as follows.



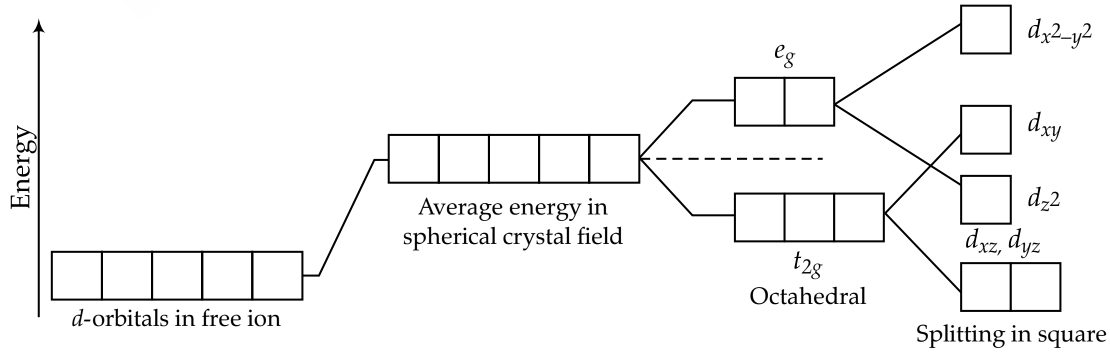
$I^- < Br^- < S^{2-} < SCN^- < Cl^- < F^- < OH^- < C_2O_4^{2-} < O^{2-} < H_2O < NCS^- < NH_3 < en < NO_2^- < CN^- < CO$

Weak field ligand → Increasing order of Δ_0 → Strong field ligand

If $\Delta_0 < P$, 4th electron will enter e_g giving the configuration $t_3^{2g} e_1^{g}$. Ligands for which $\Delta_0 < P$ are called weak field ligands.

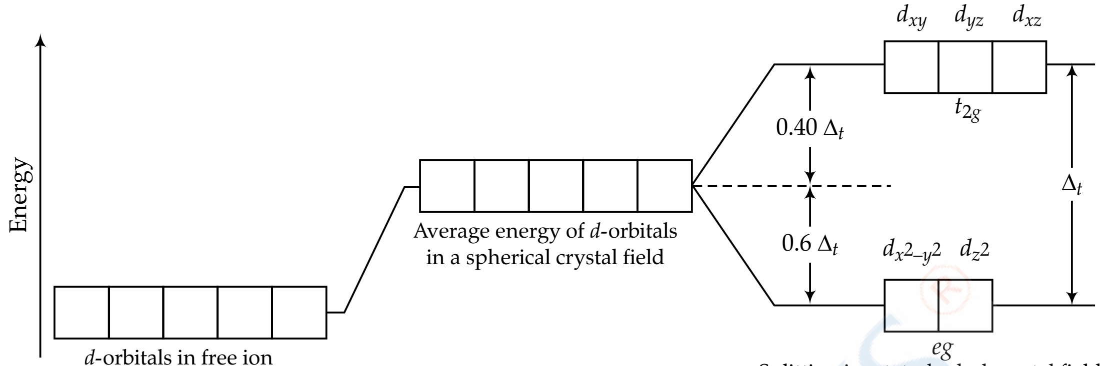
If $\Delta_0 > P$, pairing will occur in the t_{2g} orbitals and e_g orbitls well remain vacant. For $\Delta_0 > P$ ligands are strong field ligands.

- **Splitting of *d*-orbitals in a square planar crystal field :**



Splitting in square planar crystal field

- **Splitting of *d*-orbital in tetrahedral crystal field.**

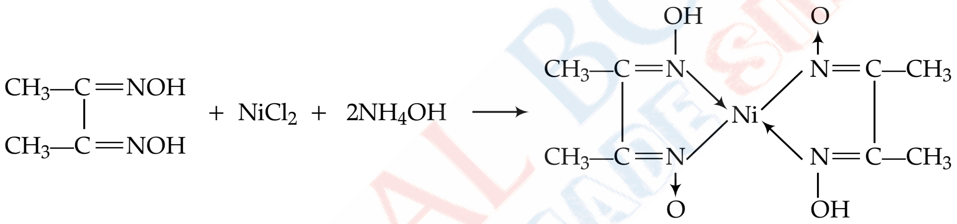


Splitting in a tetrahedral crystal field

- **Jahn-Teller effect :** If the ground electronic configuration of a non linear complex is orbitally degenerate, the complex will distort so as to remove degeneracy and achieve a lower energy, this is called Jahn-Teller effect.
- **Importance and applications of coordination compounds/complexes :**

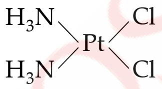
(a) Qualitative Analysis :

1. To detect the presence of Ni^{2+} ion



Nickel dimethyl glyoxime (Ni-DMG)

2. In gravimetric analysis.
3. In volumetric analysis.
4. In biological systems: In chlorophyll, haemoglobin, vitamin B_{12}.
5. Cis-platin complex is useful in treatment of cancer.



⇒ *cis*-platin

KNOW THE TERMS

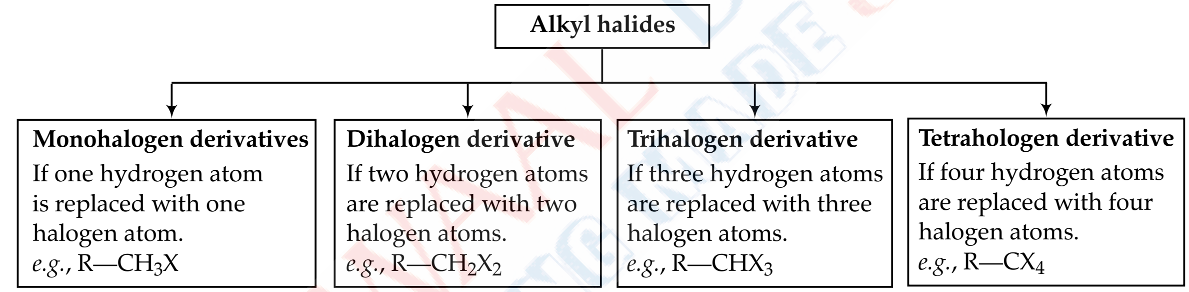
- **Chelation/Chelate ring :** The ligand may contain two donor atoms positioned in such a way that a five or a six membered ring is formed with the metal ion. The ring formed is called chelate ring.
- **Ambidentate Ligands :** Unidentate ligands containing more than one coordinating atoms are called ambidentate ligands.
- **Counter ions :** The ionizable groups which are written outside the brackets are called counter ions.
- **Homoleptic Complex :** Those complexes in which the metal atom or ion is linked to only one type of ligand.
- **Heteroleptic Complex :** Those complexes in which the metal atom or ion is linked to more than one kind of ligands.
- **Chirality :** The molecules or ions which are non-superimposable mirror images of each other are called chiral and this property is called chirality.
- **Spectrochemical Series :** A series in which ligand are arranged in order of increasing magnitude of crystal field splitting, is called spectrochemical series.

Chapter 24

Haloalkanes and Haloarenes

» Revision Notes

- **Haloalkanes :** These are the compounds in which one or more hydrogen atom(s) of alkane is (are) replaced by halogen.
- **Haloarene :** These are the compounds in which one or more hydrogen atom(s) directly bonded to an aromatic ring is(are) replaced by halogen.
- **Classification of Alkyl Halides :** On the basis of number of halogen atoms :



Alkyl halides

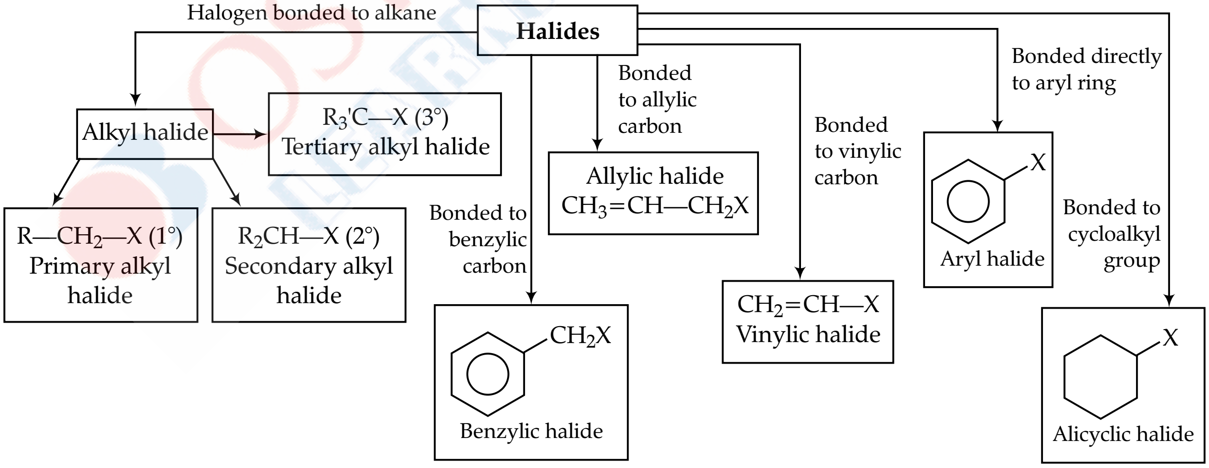
Monohalogen derivatives If one hydrogen atom is replaced with one halogen atom. *e.g.*, $R—CH_3X$

Dihalogen derivative If two hydrogen atoms are replaced with two halogen atoms. *e.g.*, $R—CH_2X_2$

Trihalogen derivative If three hydrogen atoms are replaced with three halogen atoms. *e.g.*, $R—CHX_3$

Tetrahologen derivative If four hydrogen atoms are replaced with four halogen atoms. *e.g.*, $R—CX_4$

On the basis of type of carbon atom to which halogen atom is attached halogen bonded to alkane :

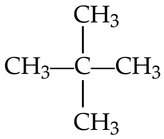


- **Nomenclature :**
  Common Name – Alkyl halide or aryl halide

IUPAC Name – Haloalkane

e.g., CH_3Cl ,

Common Name : Methyl chloride
IUPAC Name : 2-chloromethane

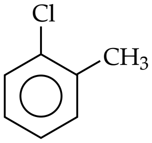


$$CH_3-\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\underset{|}{\overset{|}{C}}}}-CH_3$$

Common Name : Tertiary butyl chloride
IUPAC Name : 2-chloro-2-methyl propane

$CH_2{=}CHCl$,

Common Name : vinyl chloride
IUPAC Name : chloroethene

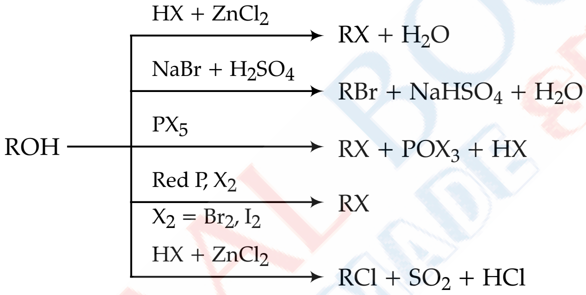


Common Name : o-chlorotoluene
IUPAC Name : 1-chloro-2-methyl benzene

If two different halogen atoms are present in a molecule then write them alphabetically and number the carbon chain so that least possible number is given to the carbon which is bonded to the halogen having written first according to the alphabetical order.

- **Preparation of haloalkanes :**

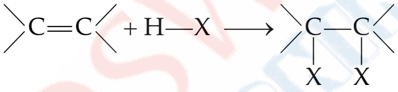
From alcohols :



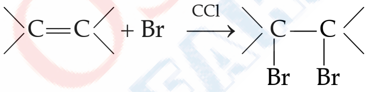
From hydrocarbon :

$$CH_3CH_2CH_2CH_3 \xrightarrow[\text{or heat}]{Cl_2/\text{UV light}} CH_3CH_2CH_2CH_2Cl + CH_3CH_2CHClCH_3$$

From alkene :



(X = Cl, Br, I)



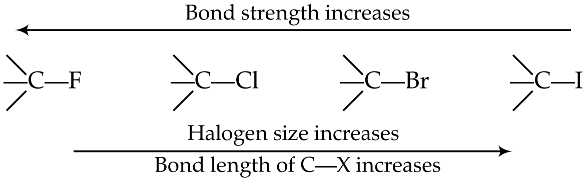
Finkelstein reaction :

$$RX + NaI \xrightarrow{\text{acetone}} R—I + NaX \ (X = Cl, Br)$$

Swarts reaction :

$$RX \xrightarrow{AgF,\ Hg_2F_2,\ CoF_2 \text{ or } SbF_3} RF$$

- **Nature of C—X Bond :** The carbon halogen bond is polarized. This occurs due to electronegativity difference between carbon and halogen. Halogen atoms being more electronegative than carbon atom thus, contains partial negative charge due to which carbon atom have a partial positive charge.



- **Physical Properties :**

M.P. and B.P. : Due to polar nature they have high melting point (M.P.) and boiling point (B.P.). On increasing molecular mass, the van-der Waal's interaction increases thus, M.P. and B.P. increases.

M.P. & B.P. ⇒ RCl < RBr < RI

While on increasing branching the surface area decreases and thus, the van-der Waal's interactions decreases hence, M.P. & B.P. decreases.

Density : R—I > R—Br > R—Cl > R—F

Solubility : Soluble in organic solvents and insoluble in water as they are not capable of breaking extensive H-bonding in water molecules. However, solubility order is :

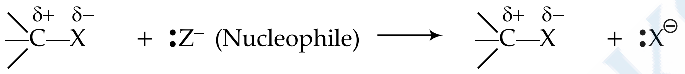
R—F > R—Cl > R—Br > R—I

Alkyl iodide is so much unstable that it decomposes in the presence of sunlight according to the following equation

$$2R-I_{aq}\xrightarrow{h\nu}aq.R-R_{aq}+\underset{\text{violet vapours}}{I_2}$$

- **Chemical Properties :**

  Due to unstable R—X bond in alkyl halide they are reactive and undergo nucleophilic substitution reaction.

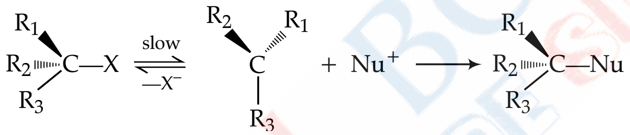


- **Nucleophilic substitution reaction :**

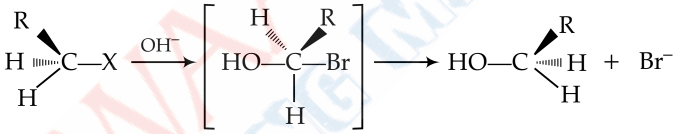
  S_N1 (Nucleophilic substitution unimolecular)

  S_N2 (Nucleophilic substitution bimolecular)

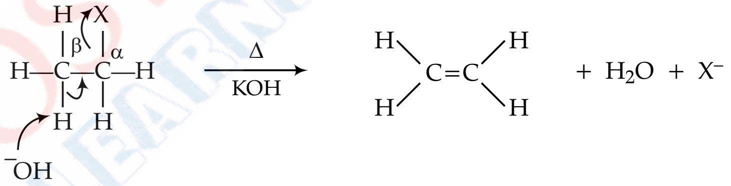
  S_N1 : It is a first order reaction which occurs in two steps. In first step, heterolytic cleavage of C—X bond takes place to form carbonium ion which is a slow step. In second step, nucleophile attacks on carbonium ion which is a fast step. It gives optically inactive product, *i.e.*, racemic mixture.



  S_N2 : It is a second order reaction occurs via formation of transition state in a simultaneous process, *i.e.*, attack of nucleophile and removal of leaving group (halide group) takes place at the same time. In this mechanism, inversion of configuration takes place which is said to be Walden inversion.



- **Elimination reaction :** When alkyl halides heated with KOH (alc.) or KNH_2 they undergo β-elimination of hydrogen and halogen to form alkene.



  Order of reactivity : RCl < RBr < RI

  $RCH_2X < R_2CHX < R_3CX$

  In case of unsymmetric alkyl halides, Saytzeff's rule is followed which says that hydrogen is eliminated preferentially from the carbon atom which has less number of hydrogen atoms, *i.e.*, highly substituted alkene is the major product.

- **Reaction with metals :**

  With Magnesium : $RX + Mg \xrightarrow[\text{Ether}]{\text{Dry}} RMgX$ (Grignard reagent)

  With sodium (Wurtz Reaction) → $RX + 2Na + XR \xrightarrow{\text{Dry ether}} R{-}R + 2NaX$

- **Reduction :** $RX + 2H \xrightarrow[\text{or Zn-Cu}/C_2H_5OH]{\text{Zn/HCl (conc.)}} RH + HX$

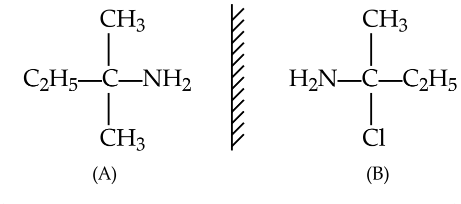
- **Stereoisomerism :** Two or more compounds with same molecular and structural formula but different spatial arrangements of atoms or groups of atom in space exhibits stereoisomerism.

- **Optical Isomerism :** Compounds which differ only in the behavior towards polarized light are optical isomers and the phenomenon is optical isomerism. Alkyl halides show optical isomerism.

  Requirements for the compounds to show optical isomerism are

  - compounds must have a chiral centre, *i.e.*, carbon bonded to four different atoms or groups of atoms.
  - Their mirror images must be non-superimposable. Non-superimposable mirror images are the enantiomers.

Enantiomers rotate the plane polarized light to same magnitude but in opposite direction.



{Both A & B are optically active compounds}

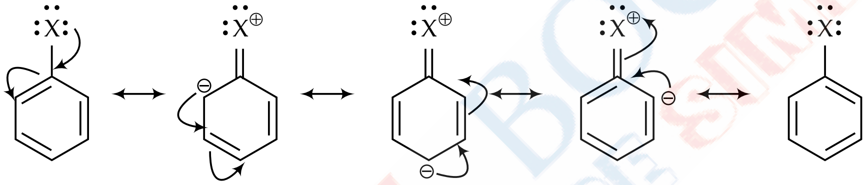
Non-superimposable (Enantiomers)

Diastereomers are the stereoisomers which are not mirror images of each other. They have different physical properties and different magnitude of specific rotation.

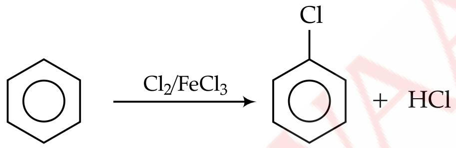
Meso Compounds : These compounds have two or more even number of chiral carbon atoms and have an internal plane of symmetry. They are optically inactive due to internal configuration.

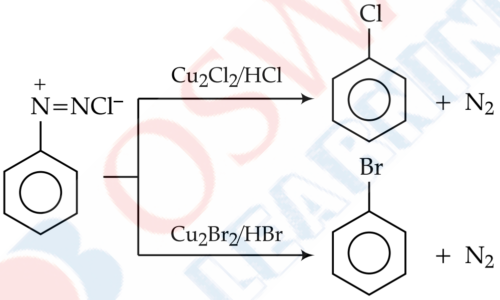
- **Haloarene :** In haloarenes, the carbon atom is sp^2 hybridised through which halogen is attached. Due to sp^2 character, the carbon is more electronegative which results in C—X bond to be shorter than the C—X bond in haloalkane.

Resonance Effect : Due to resonance, C—X bond acquire partial double bond character.



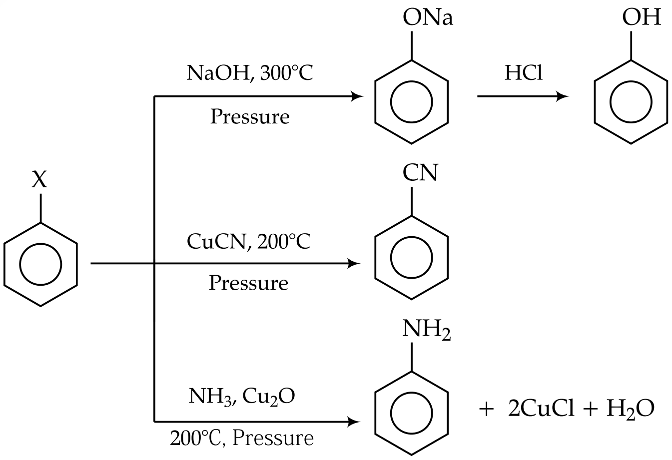
- **Preparation of haloarenes :**



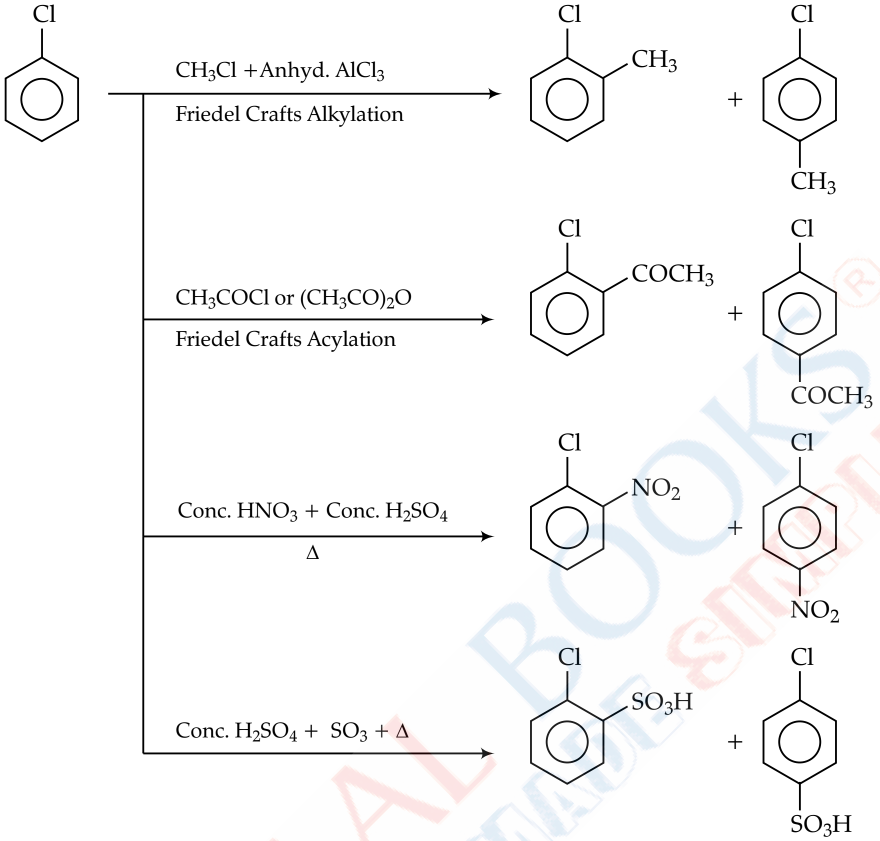


- **Substitution Reaction of Haloarenes :**

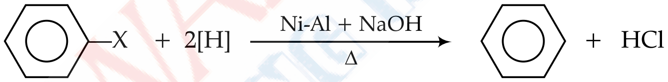
Nucleophilic Substitution Reaction :



Electrophilic Substitution Reaction :

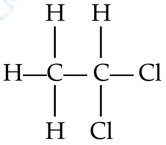


- **Reduction :**



- **Dihalogen compounds :**

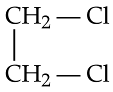
Gem dihalides : Two halogens bonded to same carbon atom. *e.g.*,



$$H-\overset{\overset{H}{|}}{\underset{\underset{H}{|}}{C}}-\overset{\overset{H}{|}}{\underset{\underset{Cl}{|}}{C}}-Cl$$

Ethylidene dichloride
(1, 2-dichloroethane)

Vic dihalide : Two halogens bonded to adjacent carbon atoms.



$$\begin{array}{l} CH_2-Cl \\ | \\ CH_2-Cl \end{array}$$

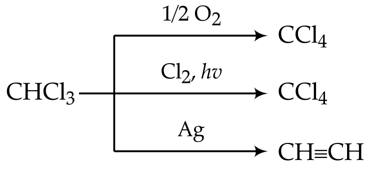
Ethylene chloride
(1, 2-dichloroethane)

- **Polyhalogen Compounds :** Compounds containing more than one halogen atoms.

Chloroform ($CHCl_3$) :

Preparation : $CH_4 + 3Cl_2 \xrightarrow[\text{Sunlight}]{h\nu} CHCl_3 + 3HCl$

Properties :



$$CHCl_3 \xrightarrow{1/2\ O_2} CCl_4$$

$$CHCl_3 \xrightarrow{Cl_2,\ h\nu} CCl_4$$

$$CHCl_3 \xrightarrow{Ag} CH\equiv CH$$

Uses : As solvent for waxes, resins, rubber, fats, etc., as freons in refrigerant.

Environmental Effects : May damage liver and kidney due to metabolise into phosgene.

Iodoform (CHI_3) :

Preparation :

$$CH_3CH_2OH + 6NaOH + 6I_2 \xrightarrow{\text{heat}} CHI_3 + 5NaI + HCOONa + 5H_2O$$

$$CH_3COCH_3 + 4NaOH + 3I_2 \xrightarrow{\text{heat}} CHI_3 + 3NaI + CH_3COONa + 3H_2O$$

Properties : It is insoluble in water and yellow coloured solid.

Uses : As an antiseptic for dressing wounds

Enviromental effects : Causes nausea, vomiting and eye irritation.

Carbon tetrachloride (CCl_4) :

Preparation : $$CS_2 + 3Cl_2 \xrightarrow[\Delta]{AlCl_3} CCl_4 + SCl_2$$

$$CH_4 + 4Cl_2 \xrightarrow{h\nu} CCl_4 + HCl$$

Properties : It is non-polar, somewhat volatile giving off vapours.

Environmental Effects : Causes liver cancer, dizziness, depletion of the ozone layer, etc.

- **Other important Polyhalogen Compounds :**

Freons (Chlorofluorocarbons) :

Uses : As refrigerants in refrigerators and air conditioners due to which it is named as freons.

Environmental effects : Deplete ozone layer.

DDT (Dichlorodiphenyltrichloroethane) :

Uses : As an insecticide for killing mosquitoes and other insects.

Environmental Effects : Not biodegradable, toxic to fishes and stored in fatty tissues of animals when consumed.

KNOW THE TERMS

- **Plane-polarised Light :** Beam of light that oscillates only in one plane.
- **Dextrorotatory :** Substances which rotate the plane polarized light towards right in clockwise direction are dextrorotatory. It is conventionally given positive sign.
- **Laevorotatory :** Substances which rotate the plane polarized light towards left in anticlockwise direction are laevorotatory. It is conventionally given negative sign.
- **Racemic Mixture :** A mixture containing equal amounts of enantiomers does not show any optical activity.
- **Absolute configuration :** The three-dimensional structure of a molecule that has one or more centres of chirality is referred to its absolute configuration.

❒❒❒

Chapter 25

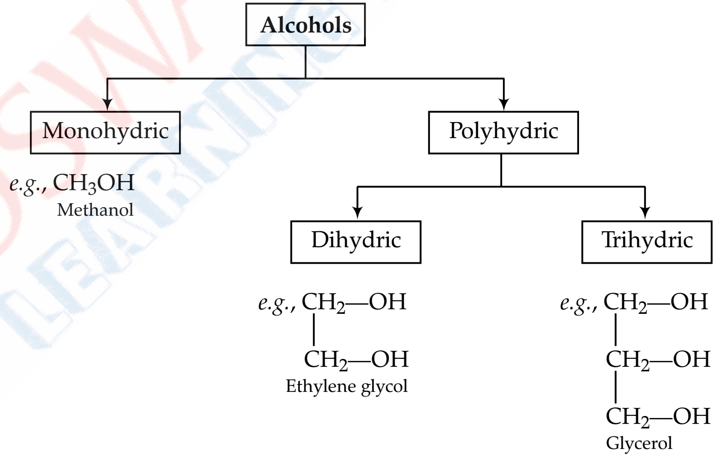
Alcohols, Phenols and Ethers

Topic 1

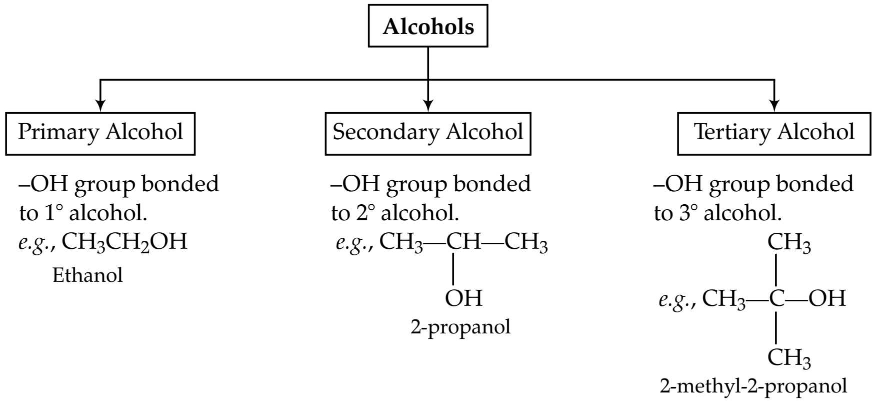
Alcohols

» Revision Notes

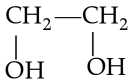
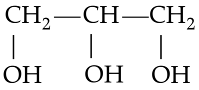
- **Alcohols :** When one hydrogen in alkane is replaced by hydroxyl group to give compound of general formula C_nH_{2n+1} OH is called alcohol.
- **Classification of Alcohols :**
  On the basis of number of alcoholic groups :



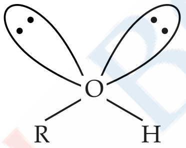
On the basis of alcoholic group attached to which type of carbon :



- **Nomenclature :** In common system → Alkyl alcohol
  In IUPAC system → Alkanol

Formula	Common Name	IUPAC Name
CH_3CH_2OH	Ethyl alcohol	Ethanol
$CH_3CH_2CH_2OH$	*n*-Propyl alcohol	Propan-1-ol
$CH_3CHOHCH_3$	Iso-propyl alcohol	Propan-2-ol
$CH_3CH_2CHOHCH_3$	Sec-Butyl alcohol	Butan-2-ol
$(CH_3)_3C—OH$	Tert. Butyl alcohol	2-Menthyl propan-2-ol
 $\underset{OH}{CH_2}—\underset{OH}{CH_2}$	Ehylene glycol	Ethane-1, 2-diol
 $\underset{OH}{CH_2}—\underset{OH}{CH}—\underset{OH}{CH_2}$	Glycerol or Glycerine	Propane, 1, 2, 3 -triol

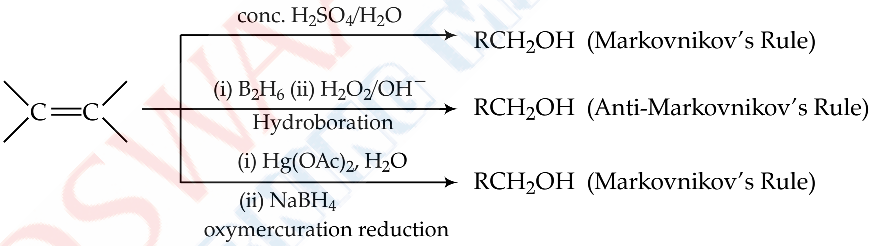
- **Structure :** Oxygen atom of hydroxyl group is attached to alkyl group. As oxygen atom contains two lone pairs of electrons along with two bond pairs of electrons, thus its structure is as follows :



- **Preparation of Alcohols**

From haloalkanes : $R—X + KOH_{(aq)} \longrightarrow ROH + KX$

From alkenes :



From Grignard reagent :

$$\begin{matrix}R_1\\ R_2\end{matrix}\!\!>C=O \xrightarrow[H_2O\,/\,H^+]{R_2'MgX\,/\,Dry\ ether} \begin{matrix}R_1\\ R_2'\\ R_2\end{matrix}\!\!>COH \qquad \left\{\begin{matrix}\text{when } R_1 = R_2 = H \text{ then } 1^\circ \text{ alcohol}\\ \text{when } R_1 = H \text{ then } 2^\circ \text{ alcohol}\\ \text{when } R_1 = R_2 \neq H \text{ then } 3^\circ \text{ alcohol}\end{matrix}\right.$$

From reduction of aldehydes & ketones :

$$RCHO \xrightarrow{H_2/Pt \text{ or } Pd \text{ or } Ni} RCH_2OH\ (1^\circ \text{ alcohol})$$

$$\begin{matrix}R\\ R\end{matrix}\!\!>C=O \xrightarrow[\text{or } Na/C_2H_5OH]{NaBH_4 \text{ or } LiAlH_4} R_2CHOH\ (2^\circ \text{ alcohol})$$

By reduction of carboxylic acid and ester :

$$RCOO \xrightarrow{LiAlH_4} RCH_2OH$$

$$RCOOR' \xrightarrow{LiAlH_4} RCH_2OH + R'OH$$

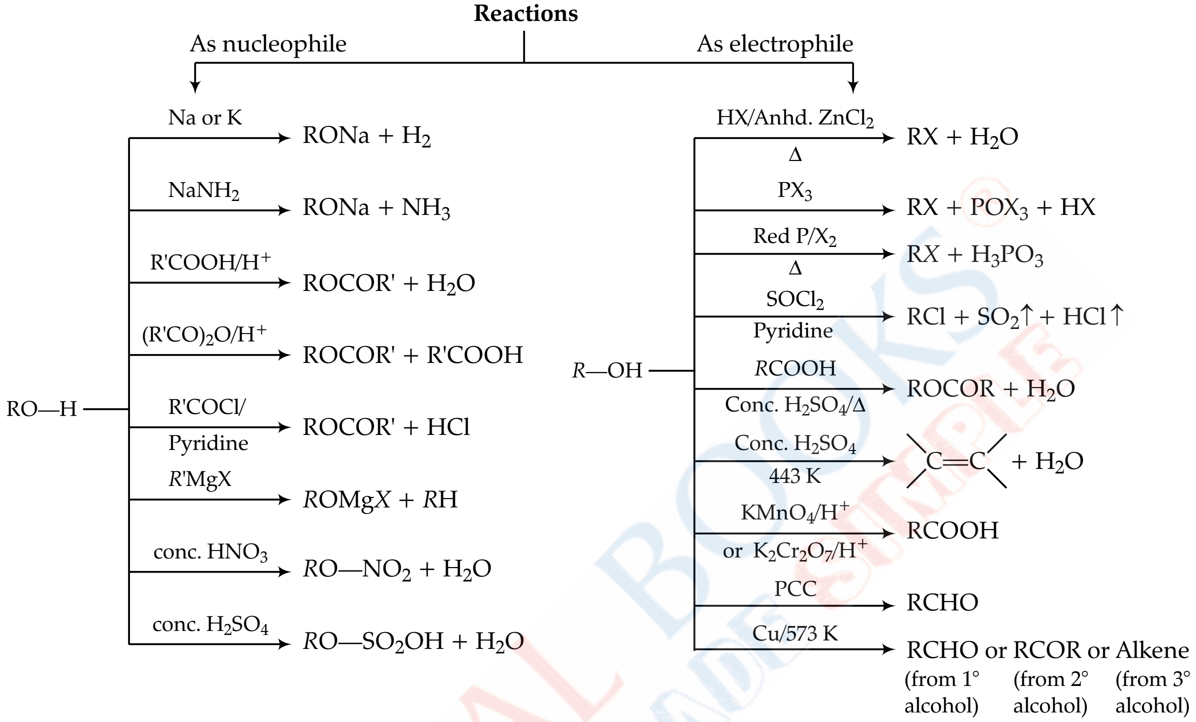
Hydrolysis of ester :

$$RCOOR' + H_2O \xrightarrow[OH^-]{H^+} RCOOH + R'OH$$

- **Physical properties of alcohols :** They are colourless and exist as liquid for lower order alcohols while high order alcohols exist as colourless waxy solids.
  - They are soluble in water due to hydrogen bonding. Solubility decreases with increase in size of alkyl group and increases with increase in branching.

- Their boiling point increases with increase in size of alkyl group due to van der Waal's interactions and decreases with increase in branching.

➢ **Chemical properties :** They act as a nucleophile (RO^-) when O—H bond is broken and act as an electrophile (R^+) when C—O bond is broken.



➢ **Test for 1°, 2° and 3° alcohols :**
Lucas : Lucas reagent is the solution of conc. HCl with anhydrous $ZnCl_2$.
1° alcohol gives no cloudiness with Lucas reagent.
2° alcohol gives no cloudiness in 5 minutes with Lucas reagent.
3° alcohol gives no cloudiness immediately with Lucas reagent.

➢ Some commercially important alcohols are methanol (wood spirit) and ethanol.

- Methanol is produced by catalytic hydrogenation of CO in presence of ZnO – Cr_2O_3 catalyst.

$$CO + 2H_2 \xrightarrow[200-300\text{ atm},\ 573-673\text{K}]{ZnO-Cr_2O_3} CH_3OH$$

It is highly poisonous and used as solvent in paints and varnishes.

- Ethanol is produced by fermentation of sugar.

$$C_{12}H_{22}O_{11} + H_2O \xrightarrow{\text{Invertase}} \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Fructose}}{C_6H_{12}O_6}$$

$$\xrightarrow[\text{Zymase}]{} 2C_2H_5OH + 2CO_2$$

It is used as solvent in paints and used in preparation of carbon compounds.

➢ **Differentiation between methanol and ethanol :**
• **Iodoform Test :** On heating with I_2 and NaOH, methanol gives no reaction but ethanol gives yellow precipitate of iodoform, CHI_3.
• On heating with salicylic acid and conc. H_2SO_4, methanol forms methyl salicylate which has characteristic odour while ethanol gives no specific odour.

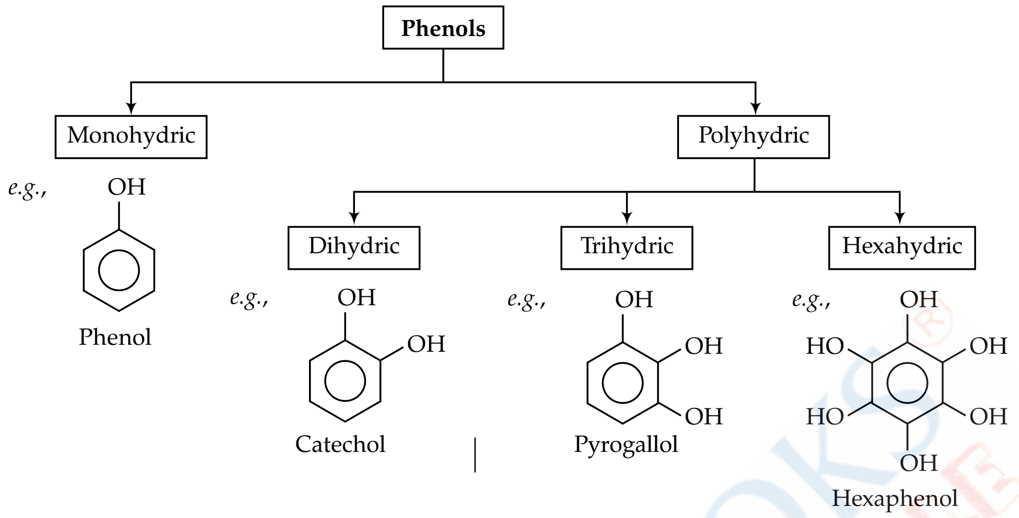
Topic 2

Phenols

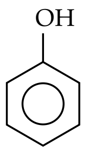
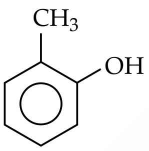
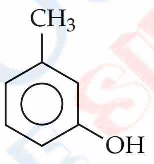
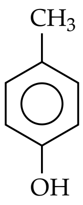
» Revision Notes

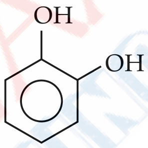
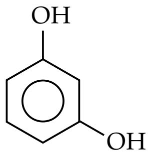
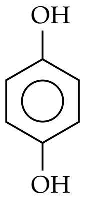
➢ **Phenols :** Compounds in which hydroxy group is directly bonded to aromatic ring.

➢ **Classification :** They are classified as mono and polyhydric phenols.



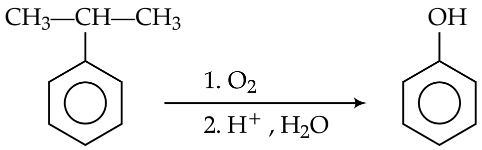
- **Nomenclature :**

				
Common Name :	Phenol	*o*-cresol	*m*-Cresol	*p*-cresol
IUPAC :	Phenol	2-methylphenol	3-methylphenol	4-methylphenol

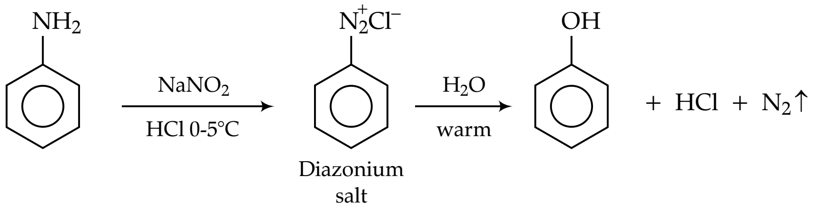
			
Common Name :	Catechol	Resorcinol	Hydroquinone or quinol
IUPAC :	Benzene-1,2-diol	Benzene-1,3-diol	Benzene-1,4-diol

- **Preparation :**

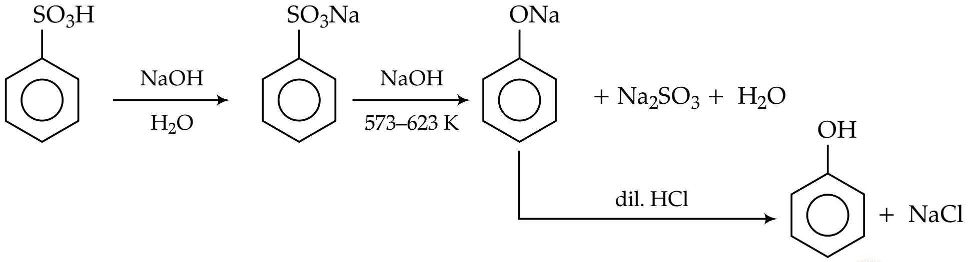
  - **From cumene :**



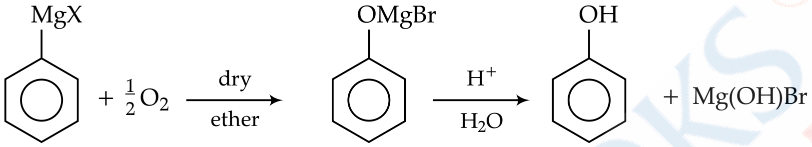
  - **From diazonium salts :**



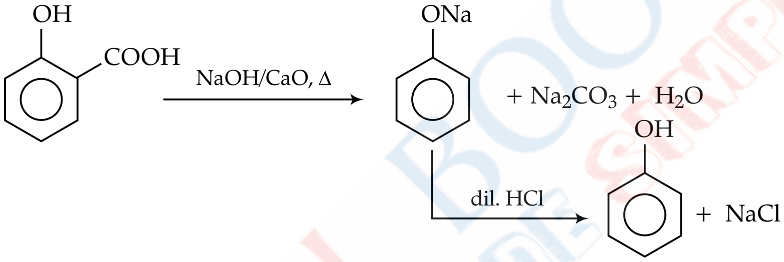
- **From benzenesulphonic acid :**



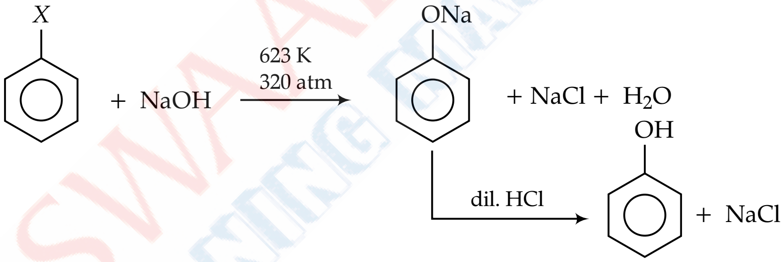
- **From phenyl magnesium bromide (Grignard reagent) :**



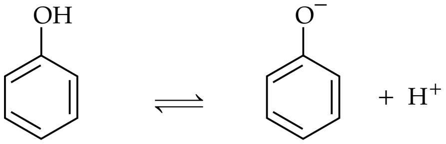
- **From salicylic acid :**

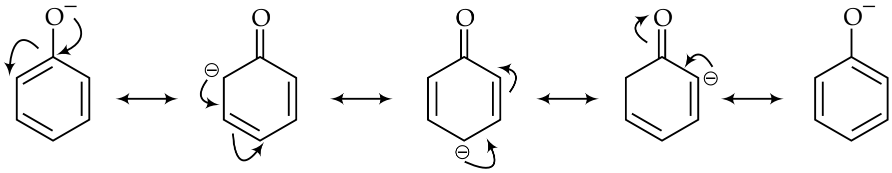


- **From haloarenes (Dow's Process) :**



- **Physical properties :** Colourless, crystalline, characteristic odour, higher boiling point than their corresponding aromatic hydrocarbon and haloarenes due to hydrogen bonding. Soluble in water due to hydrogen bonding but solubility is less than the alcohols due to large hydrocarbon ring.
- **Chemical properties :**
  - **Acidic nature of phenol :** Phenol is acidic in nature due to resonance stabilisation of its conjugate base *i.e.*, phenoxide ion.

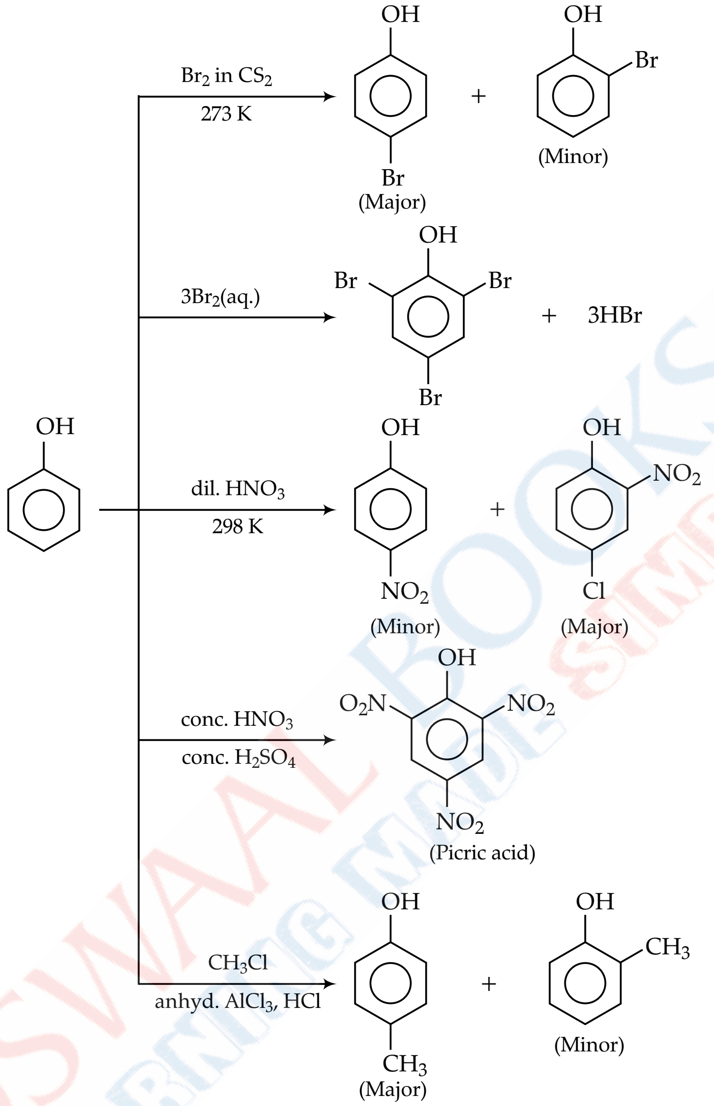




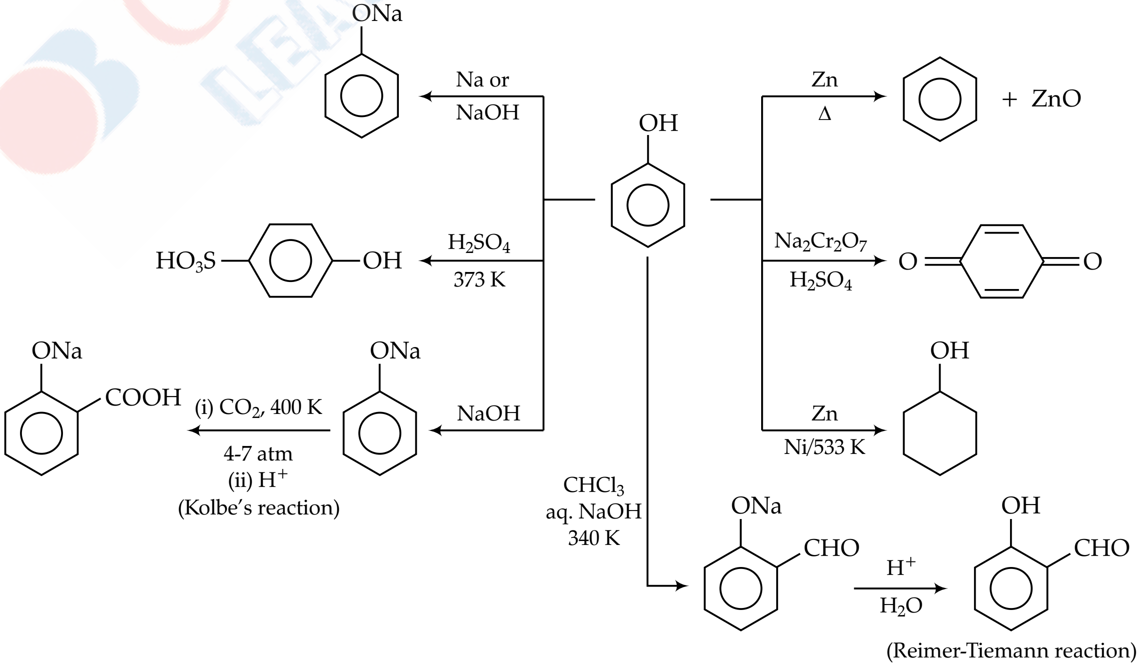
Though phenol is also resonance stabilized but in phenol there is charge separation takes place and positive charge occurs on electronegative atom, oxygen. This makes it less stable than phenoxide ion.

Electron donating group as a substituent in phenol increase the negative charge on phenoxide ion thus, destabilize it and this results in decrease in acidity of phenol. While electron withdrawing group increases the acidity of phenol.

- Electrophilic aromatic substitution.



- **Other reactions :**

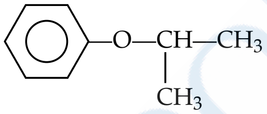


Topic 3

Ethers

» Revision Notes

- **Ethers :** Compounds having general formula R—O—R′ when, R and R′ are same then it is symmetrical ether, otherwise it is unsymmetrical ether.
- **Nomenclature :**
  - **Common system :** Alkyl groups are written alphabetically followed by word ether.
  - **IUPAC system :** It is written as alkoxyalkane. The larger alkyl group attached to oxygen is taken as parent chain while group is written as alkoxy part of ether.

e.g.,	$CH_3—O—CH_2—CH_3$	
Common Name :	Ethyl methyl ether	Isopropyl phenyl ether
IUPAC :	Methoxyethane	Isopropoxy benzene

- **Preparation :**
  - **From alkyl halides (Williamson synthesis) :**

$$R—O—Na + X—R' \longrightarrow R—O—R' + NaX$$

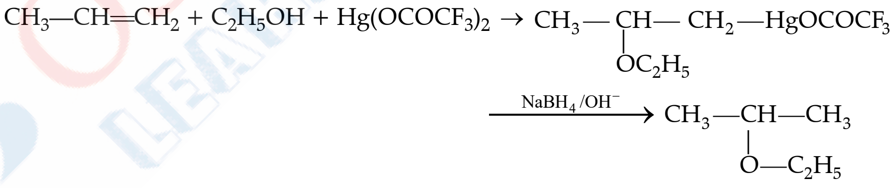
  - **From alcohols by acidic dehydration :**

$$2ROH \xrightarrow[413\text{ K}]{H_2SO_4} ROR + H_2O$$

  - **From alcohols by catalytic dehydration**

$$2C_2H_5OH \xrightarrow[240-260°C]{Al_2O_3} C_2H_5—O—C_2H_5 + H_2O$$

  - **Addition of alcohol to alkene (Alkoxy mercuration- demercuration) :**

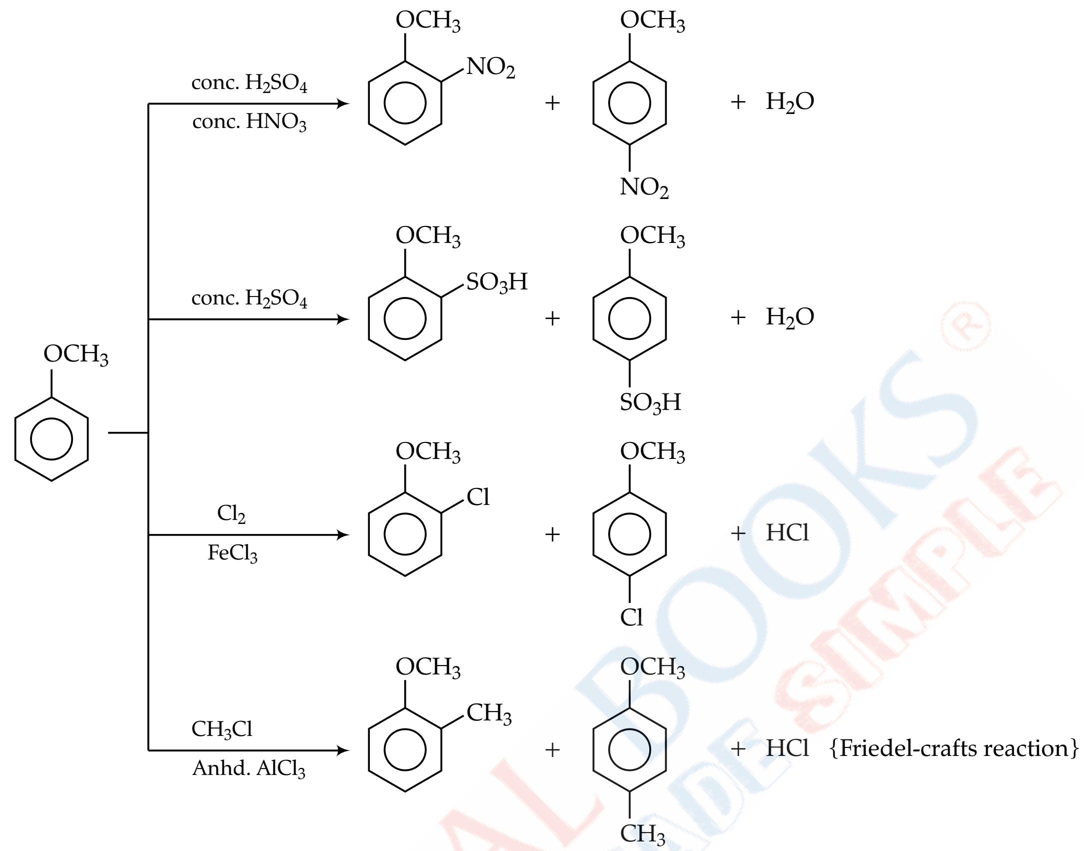


$$CH_3—CH{=}CH_2 + C_2H_5OH + Hg(OCOCF_3)_2 \rightarrow CH_3—\underset{\substack{|\\OC_2H_5}}{CH}—CH_2—HgOCOCF_3 \xrightarrow{NaBH_4/OH^-} CH_3—\underset{\substack{|\\O—C_2H_5}}{CH}—CH_3$$

- **Physical properties :** They are colourless liquids except dimethyl ether and diethyl ether which are gases.
  - They are polar due to bent structure.
  - They have low boiling point due to absence of hydrogen bonding in ethers.
  - They are slightly soluble in water due to hydrogen bonding between ether and water molecules. They are soluble in organic solvents to greater extent.
- **Chemical Properties :**
  - Cleavage by acid

$$C_2H_5OC_2H_5 + HI \xrightarrow{\text{Cold}} C_2H_5I + C_2H_5OH$$

  - Reactivity of hydrogen halide HCl < HBr < HI
  - When 1° or 2° alkyl groups are present in ether then smaller alkyl group forms alkyl iodide.
  - When one of the alkyl group is 3° then it forms tertiary alkyl halide.
  - Substitution in aromatic ethers



- **Uses of Ethers**
  1. Dimethyl ether is used as refrigerant and as a solvent at low temperature.
  2. Diethyl Ether is used as an anaesthesia in surgery.

KNOW THE TERMS

- **Absolute alcohol :** It is 100% ethanol obtained by fractional distillation of 95% ethanol and little amount of benzene.
- **Denatured alcohol :** Commercial alcohol which is mixed with copper sulphate or and pyridine to make it unfit for drinking.
- **Power alcohol :** Mixture of absolute alcohol and petrol in the ratio of 20 : 30. It is used as a substitute of gasoline in automobiles.
- **Rectified spirit :** It contains 95% ethyl alcohol and 45% water. It is an azeotrope (constant boiling mixture) and boils at 74°.

Chapter 26

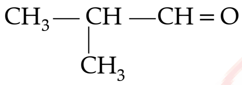
Aldehydes, Ketones and Carboxylic Acids

Topic 1

Aldehydes and Ketones

» Revision Notes

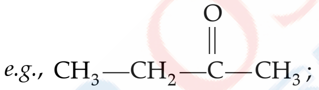
- **Aldehydes and Ketones :** Aldehydes are the compounds in which carbonyl group is either attached to two hydrogen atoms or one hydrogen and one carbon atom of alkyl or aryl group. *e.g.*, —CH_3CHO, HCHO, etc.
  Ketones are the compounds in which carbonyl group is attached to two alkyl or aryl groups. *e.g.*, $CH_3COC_6H_5$, $C_6H_5COC_6H_5$, CH_3COCH_3, etc.
- **Nomenclature :** In IUPAC system in aldehyde the suffix 'e' of alkane is replaced by 'al'. *e.g.*, $CH_3—CH_2—CH{=}O$;
  Propanal



$$\underset{\displaystyle CH_3}{CH_3—\underset{|}{CH}—CH=O}$$

2-methylpropanal

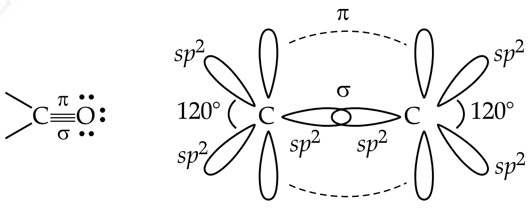
In ketones, the suffix 'e' of alkane is replaced by 'one'.



e.g., $CH_3—CH_2—\overset{\overset{\displaystyle O}{||}}{C}—CH_3$; CH_3COCH_3

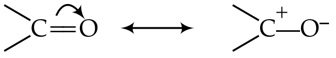
2-Butanone Propanone

- **Nature of carbonyl group :**



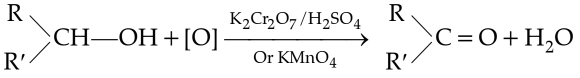
Linear

The carbonyl group is polar due to electronegativity difference between C and O. Oxygen being more electronegative pulls π-electrons move towards itself.



$$>C=O \longleftrightarrow >\overset{+}{C}—O^-$$

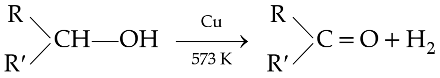
- **Preparation :**
  (i) Preparation of aliphatic aldehydes and ketones
  - **By oxidation of alcohols :**



$$\frac{R}{R'}>CH—OH+[O]\xrightarrow[\text{Or } KMnO_4]{K_2Cr_2O_7/H_2SO_4}\frac{R}{R'}>C=O+H_2O$$

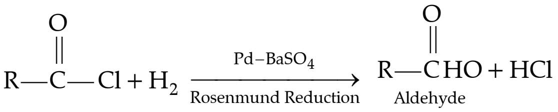
When, R′ = H then 1° alcohol to aldehyde.
R′ = alkyl group then 2° alcohol to ketone.

- **By dehydrogenation of alcohols :**



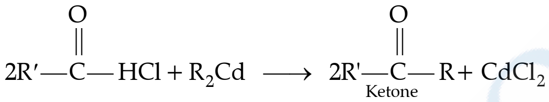
When R′ = H then 1° alcohol to aldehyde.
R′ = alkyl group the 2° alcohol to ketone.

- **By acid chloride**



$$R-\overset{O}{\overset{\|}{C}}-Cl + H_2 \xrightarrow[\text{Rosenmund Reduction}]{Pd-BaSO_4} \underset{\text{Aldehyde}}{R-\overset{O}{\overset{\|}{C}}HO} + HCl$$

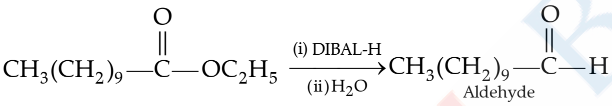
$$2RMgX + CdCl_2 \longrightarrow R_2Cd + 2MgXCl$$



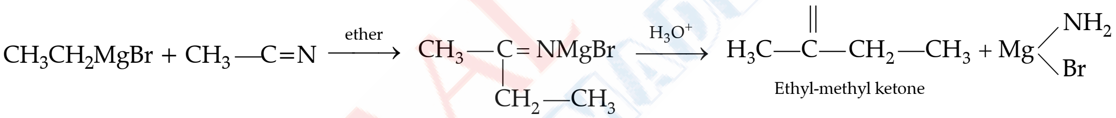
$$2R'-\overset{O}{\overset{\|}{C}}-HCl + R_2Cd \longrightarrow 2R'-\underset{\text{Ketone}}{\overset{O}{\overset{\|}{C}}}-R + CdCl_2$$

➢ **From nitriles and esters**

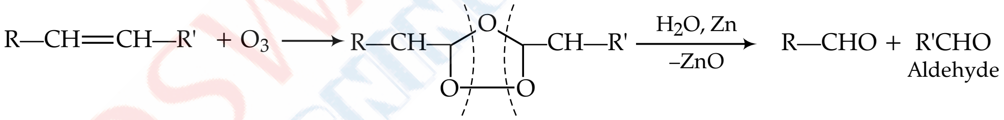
- $R{-}CN \xrightarrow[(ii)H_2O]{(i)\ AlH\ (iBu)_2} \underset{\text{Aldehyde}}{R{-}CHO}$

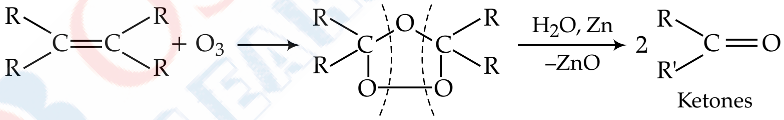


$$CH_3(CH_2)_9-\overset{O}{\overset{\|}{C}}-OC_2H_5 \xrightarrow[(ii)H_2O]{(i)\ DIBAL\text{-}H} \underset{\text{Aldehyde}}{CH_3(CH_2)_9-\overset{O}{\overset{\|}{C}}-H}$$

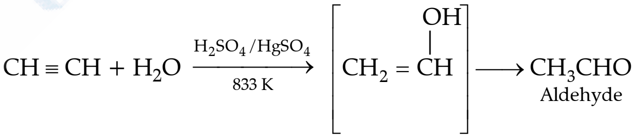


➢ **From hydrocarbons**
- By ozonolysis

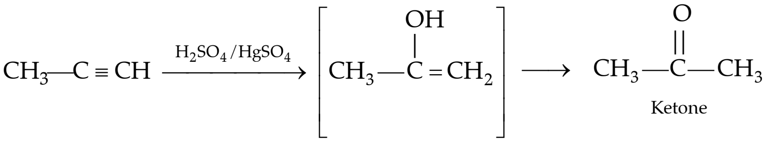




- By hydration

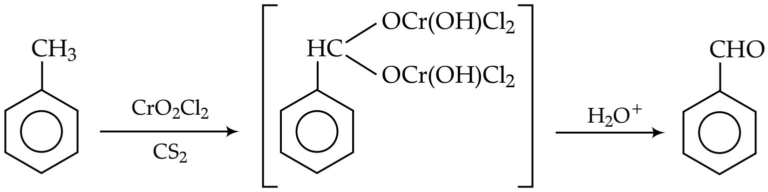


$$CH\equiv CH + H_2O \xrightarrow[833\ K]{H_2SO_4/HgSO_4} \left[CH_2 = \overset{OH}{\overset{|}{C}H}\right] \longrightarrow \underset{\text{Aldehyde}}{CH_3CHO}$$

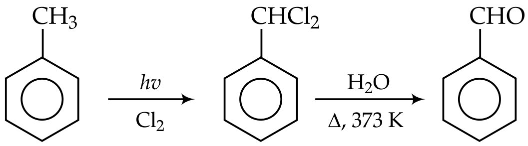


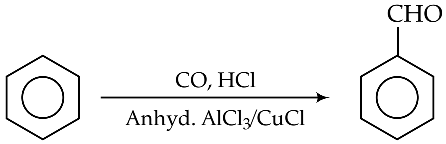
$$CH_3-C\equiv CH \xrightarrow{H_2SO_4/HgSO_4} \left[CH_3-\overset{OH}{\overset{|}{C}} = CH_2\right] \longrightarrow \underset{\text{Ketone}}{CH_3-\overset{O}{\overset{\|}{C}}-CH_3}$$

(ii) Preparation of aromatic aldehydes



(Etard reaction)

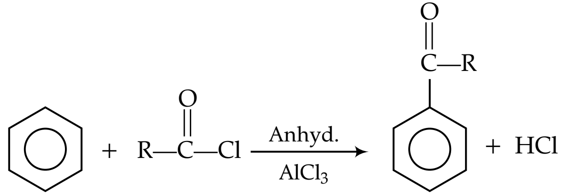




{Gatterman-Koch reaction}

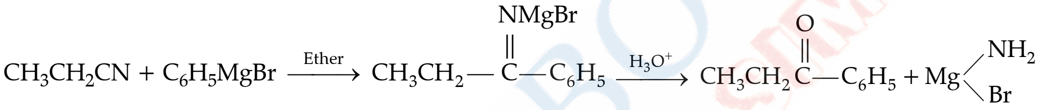
(iii) Preparation of aromatic ketones

- **Friedel crafts acylation**



{R may be alkyl or aryl)

- **From nitriles**



$$CH_3CH_2CN + C_6H_5MgBr \xrightarrow{Ether} CH_3CH_2-\overset{NMgBr}{\overset{\|}{C}}-C_6H_5 \xrightarrow{H_3O^+} CH_3CH_2\overset{O}{\overset{\|}{C}}-C_6H_5 + Mg\begin{matrix}NH_2\\Br\end{matrix}$$

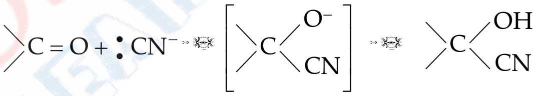
➢ Physical Properties of Aldehydes and Ketones

- Most of the aldehydes are liquid except formaldehyde which is a gas.
- Ketones of lower order are colourless liquids and have pleasant odour.
- Aldehydes and ketones have higher b.p. than corresponding hydrocarbons but lower than the corresponding alcohols due to extensive hydrogen bonding in alcohols.
- The lower member of aldehydes and ketones are soluble in water due to hydrogen bonding while in higher members due to large alkyl groups it is difficult to dissolve in water.

➢ Chemical Properties of Aldehydes & Ketones

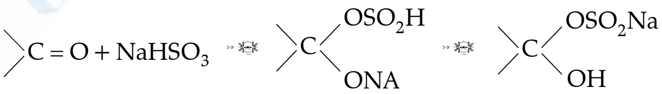
- Nucleophilic addition reaction
  - Addition of HCN

$$HCN + OH^- \rightleftharpoons :CN^- + H_2O$$



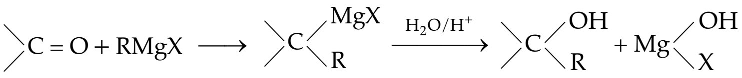
$$>C=O + :CN^- \rightleftharpoons \left[>C\begin{matrix}O^-\\CN\end{matrix}\right] \rightleftharpoons >C\begin{matrix}OH\\CN\end{matrix}$$

  - Addition of $NaHSO_3$



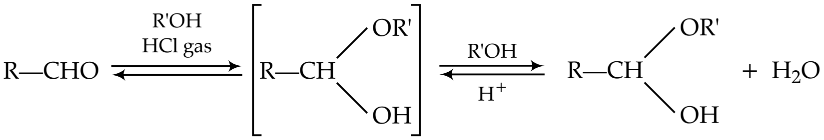
$$>C=O + NaHSO_3 \rightleftharpoons >C\begin{matrix}OSO_2H\\ONA\end{matrix} \rightleftharpoons >C\begin{matrix}OSO_2Na\\OH\end{matrix}$$

  - Addition of Grignard reagent

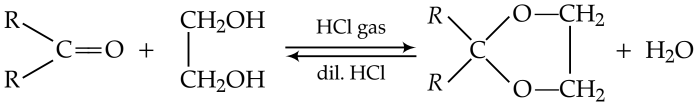


$$>C=O + RMgX \longrightarrow >C\begin{matrix}MgX\\R\end{matrix} \xrightarrow{H_2O/H^+} >C\begin{matrix}OH\\R\end{matrix} + Mg\begin{matrix}OH\\X\end{matrix}$$

  - Addition of Alcohols



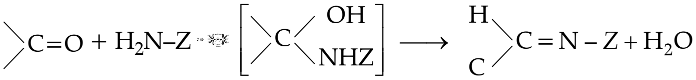
$$R-CHO \underset{}{\overset{R'OH \\ HCl\ gas}{\rightleftharpoons}} \left[R-CH\begin{matrix}OR'\\OH\end{matrix}\right] \underset{H^+}{\overset{R'OH}{\rightleftharpoons}} R-CH\begin{matrix}OR'\\OH\end{matrix} + H_2O$$



Ethylene glycol ketal

Ketones does not react with monohydric alcohol.

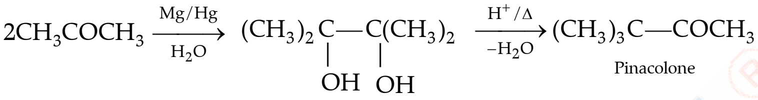
- Addition of ammonia and its derivatives.



$$\rangle C=O + H_2N-Z \rightleftharpoons \left[\rangle C\langle^{OH}_{NHZ}\right] \longrightarrow {}^{H}_{C}\rangle C=N-Z+H_2O$$

Where, Z = Alkyl, aryl, OH, NH_2, C_6H_5NH, $NHCONH_2$, etc.

- Pinacol pinacolone rearrangement

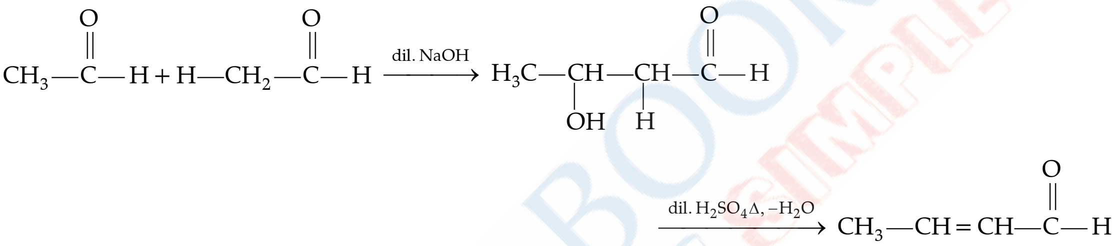


$$2CH_3COCH_3 \xrightarrow[H_2O]{Mg/Hg} (CH_3)_2\underset{OH}{C}-\underset{OH}{C}(CH_3)_2 \xrightarrow[-H_2O]{H^+/\Delta} (CH_3)_3C-COCH_3$$

Pinacolone

Reactivity of α-hydrogen

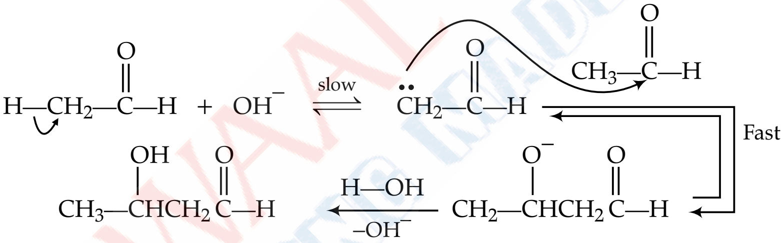
- Condensation reaction
  - **Aldol condensation**



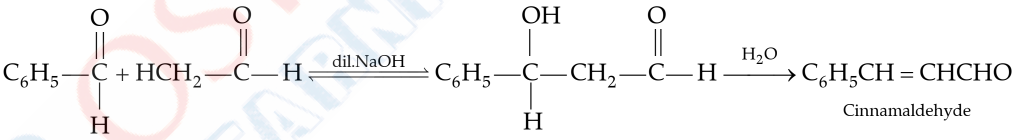
$$CH_3-\overset{\overset{O}{\|}}{C}-H+H-CH_2-\overset{\overset{O}{\|}}{C}-H \xrightarrow{\text{dil. NaOH}} H_3C-\underset{OH}{CH}-\underset{H}{CH}-\overset{\overset{O}{\|}}{C}-H$$

$$\xrightarrow{\text{dil. } H_2SO_4\Delta,\ -H_2O} CH_3-CH=CH-\overset{\overset{O}{\|}}{C}-H$$

Mechanism :



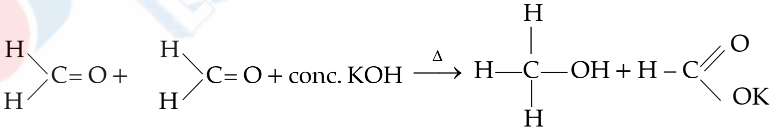
- **Cross Aldol condensation**



$$C_6H_5-\underset{H}{\overset{\overset{O}{\|}}{C}}+HCH_2-\overset{\overset{O}{\|}}{C}-H \xrightleftharpoons{\text{dil.NaOH}} C_6H_5-\underset{H}{\overset{OH}{C}}-CH_2-\overset{\overset{O}{\|}}{C}-H \xrightarrow{H_2O} C_6H_5CH=CHCHO$$

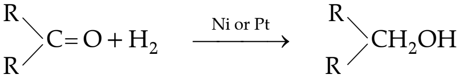
Cinnamaldehyde

- Cannizzaro reaction : It is a self oxidation reduction reaction.

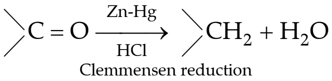


$${}^{H}_{H}\rangle C=O+{}^{H}_{H}\rangle C=O+\text{conc. KOH} \xrightarrow{\Delta} H-\underset{H}{\overset{H}{C}}-OH+H-C\langle^{O}_{OK}$$

- **Reduction**
  - R–CHO + 2[H] $\xrightarrow[\text{or } BH_4]{LiAlH_3}$ RCH_2OH

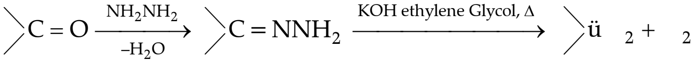


- ${}^{R}_{R}\rangle C=O+H_2 \xrightarrow{\text{Ni or Pt}} {}^{R}_{R}\rangle CH_2OH$



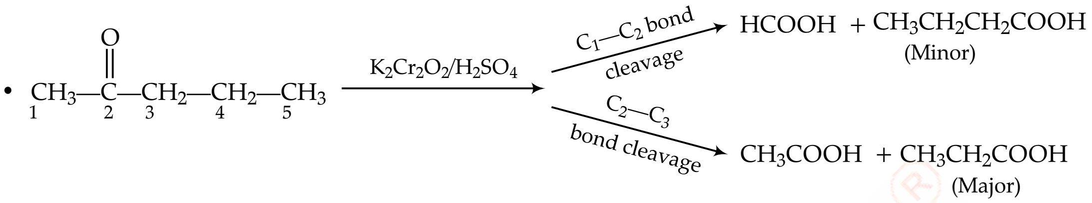
- $\rangle C=O \xrightarrow[HCl]{Zn\text{-}Hg} \rangle CH_2+H_2O$

Clemmensen reduction



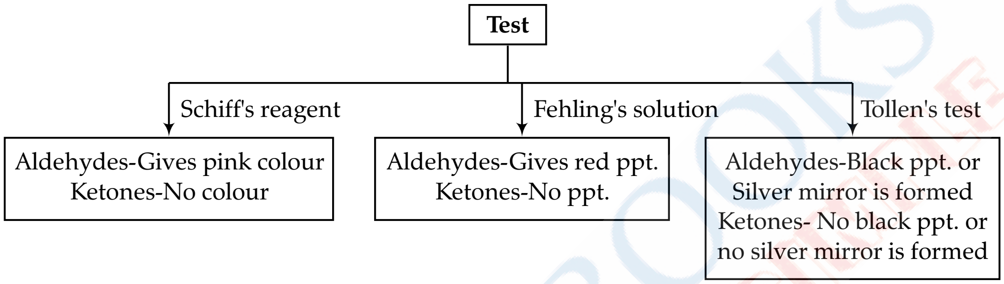
- $\rangle C=O \xrightarrow[-H_2O]{NH_2NH_2} \rangle C=NNH_2 \xrightarrow{\text{KOH ethylene Glycol, }\Delta} \rangle$ü $_2$ + $_2$

- **Oxidation reaction**
  - $\underset{\text{Aldehyde}}{R-CHO} + [O] \xrightarrow[\text{or } KMnO_4/H_2SO_4]{K_2Cr_2O_7/H_2SO_4} \underset{\text{Carboxylic acid}}{R-COOH}$



- $\underset{1}{CH_3}-\underset{2}{\overset{\overset{O}{\|}}{C}}-\underset{3}{CH_2}-\underset{4}{CH_2}-\underset{5}{CH_3} \xrightarrow{K_2Cr_2O_7/H_2SO_4}$

➢ **Tests of aldehydes and ketones**



Topic 2

Carboxylic Acids and their derivatives

» Revision Notes

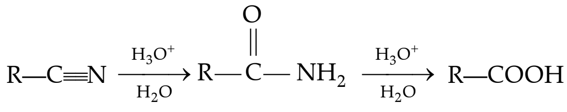
➢ **Carboxylic Acids :** Theses are the compounds with $-\overset{\overset{O}{\|}}{C}-OH$ group

➢ **Nomenclature :** IUPAC system-Replace suffix 'e' of alkane by 'oic acid'
While naming a compound preference will be given to carboxylic carbon.

e.g., $\underset{\text{Methanoic acid}}{HCOOH}$, $\underset{\text{Ethanoic acid}}{CH_3-COOH}$, $\underset{\text{4-methylpentanoic acid}}{CH_3-\underset{\underset{CH_3}{|}}{CH}-CH_2-CH_2-COOH}$

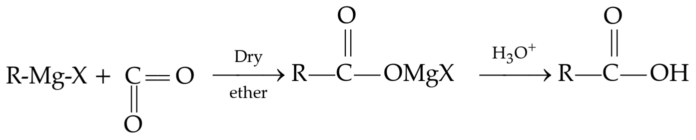
➢ **Preparation :**

- Oxidation of alcohols and aldehydes
  - $R\text{-}CH_2OH \xrightarrow[H_3O^+]{\text{Alk. } KMnO_4} RCOOH$
  - $R\text{-}CHO \xrightarrow[H_3SO_4]{K_2Cr_2O_7} RCOOH$
- From ketones
  - $RCOH_3 \xrightarrow[H_2O]{X_2/NaOH} RCOOH$
- From cyanides and amides



$$R-C\equiv N \xrightarrow[H_2O]{H_3O^+} R-\overset{\overset{O}{\|}}{C}-NH_2 \xrightarrow[H_2O]{H_3O^+} R-COOH$$

- From Grignard reagent

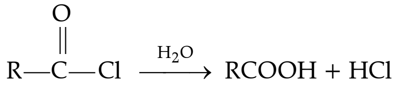


$$R\text{-}Mg\text{-}X + \underset{\underset{O}{\|}}{C}=O \xrightarrow[\text{ether}]{\text{Dry}} R-\overset{\overset{O}{\|}}{C}-OMgX \xrightarrow{H_3O^+} R-\overset{\overset{O}{\|}}{C}-OH$$

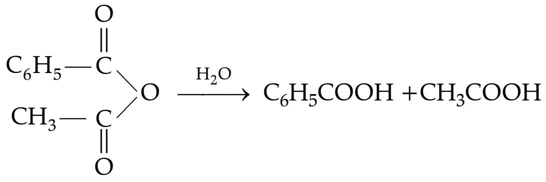
- Form hydrolysis of esters

$$RCOOR' \xrightarrow{H_3O,\ H^+} RCOOH + R'OH$$

- From acid halide and anhydride



$$R-\overset{\overset{\displaystyle O}{\|}}{C}-Cl \xrightarrow{H_2O} RCOOH + HCl$$



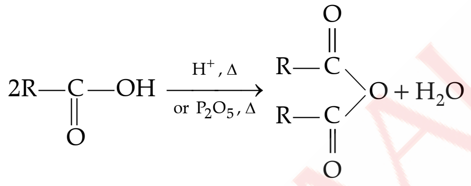
$$\xrightarrow{H_2O} C_6H_5COOH + CH_3COOH$$

➢ Physical Properties :

- Lower members are colourless liquid with pungent smell while higher members are odourless waxy solid.
- First four members are water soluble due to hydrogen bonding while higher acids are insoluble.
- They have higher boiling point due to their ability of form intermolecular hydrogen bonding.

➢ Chemical properties :

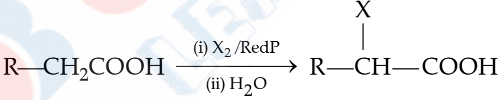
- Cleavage of O—H bond
  - $R—COOH + NaOH \longrightarrow RCOONa + H_2O$
- Cleavage of C—OH bond



$$2R-\underset{\underset{\displaystyle O}{\|}}{C}-OH \xrightarrow[\text{or } P_2O_5,\ \Delta]{H^+,\ \Delta} (RCO)_2O + H_2O$$

- $RCOOH + R'OH \overset{H^+}{\rightleftharpoons} RCOOR' + H_2O$
- $RCOOH + PCl_5 \longrightarrow RCOCl + POCl_3 + HCl$
- $RCOOH + NH_3 \rightleftharpoons RCOONH_4 \xrightarrow[-H_2O]{\Delta} RCONH_2$

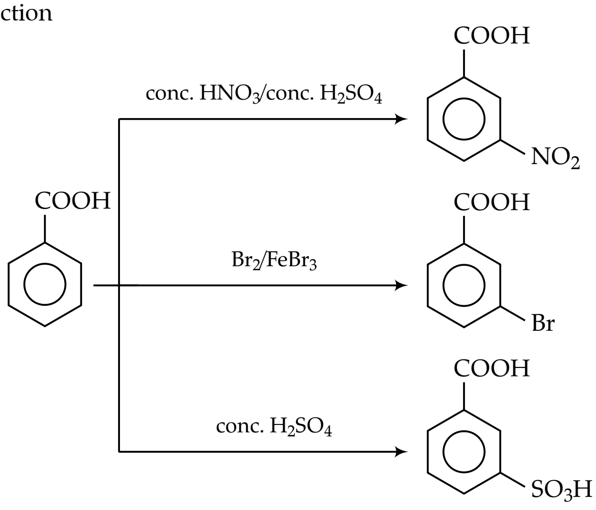
- Reduction
  - $R—COOH \xrightarrow[\text{(ii) } H_2O^+]{\text{(i) } LiAlH_4/\text{ether or } B_2H_6} R—CH_2—OH$
  - $R—COONa \xrightarrow[\Delta]{NaOH + CaO} R—H + Na_2CO_3$



$$R—CH_2COOH \xrightarrow[\text{(ii) } H_2O]{\text{(i) } X_2/\text{RedP}} R-\overset{\overset{\displaystyle X}{|}}{CH}-COOH$$

(Hell-Volhard Zelinsky reaction)

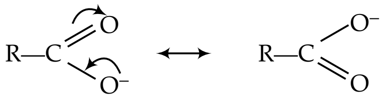
- Ring substitution reaction



- Acidity of carboxylic group

$$RCOOH \rightleftharpoons RCOO^- + H$$

The conjugate base, $RCOO^-$ is resonance stabilized thus, carboxylic acid shows acidic nature.



when R group is electron withdrawing then it disperse the negative charge on oxygen atom of carboxylic group thus, increases acidity by stabilizing R-COO^- species.

When R group is electron donating then it intensify the negative charge on oxygen atom of carboxylic group thus, destabilizing $RCOO^-$ species and hence, decreasing acidity.

- **Uses of carboxylic acids**
  - Methanoic acid is used in leather tanning, dyeing and finishing in textiles, manufacturing of rayon and plastic, as vinegar in cooking.
  - Benzoic acid is used as food preservatives and in perfumery.

KNOW THE TERMS

- **Hydroformlyation :** Reaction of alkenes to give aldehydes by the reaction by the reaction of H_2 and CO.
- **MPV Reduction :** Meerwein Pondorof Venly reduction. In this reaction, ketones are reduced to secondary alcohols with isopropyl alcohol in the presence of aluminium isopropoxide.
- **Oppenauer oxidation :** It is just reverse of MPV reaction in which selectively secondary alcohol gets oxidized to ketones.

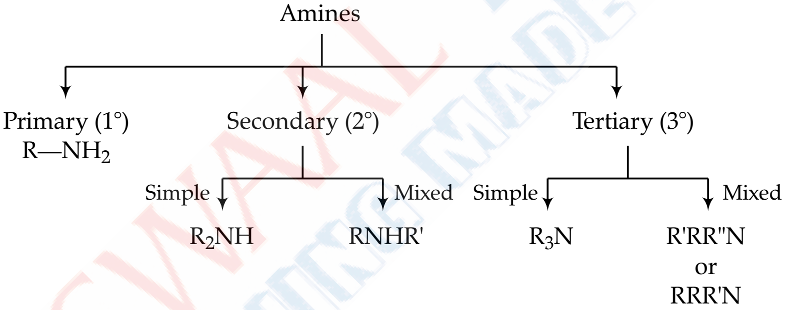
❑❑❑

Chapter 27

Organic Compounds Containing Nitrogen

» Revision Notes

- **Amine :** When hydrogen atom (s) of ammonia is/are replaced by alkyl or aryl groups then it is called amines.
- **Classification :**

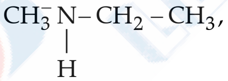


- **Nomenclature :** Replace 'e' of alkane by amine'.

  e.g., $\underset{\text{Ethanamine}}{CH_3CH_2NH_2}$, $\underset{\text{1-Propanamine}}{CH_3CH_2CH_2NH_3}$

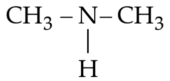
  - Secondary amines are named as N-alkylaminoalkanes and tertiary amines are named as N, N-dialkylaminoalkanes

  For ex-



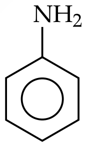
$CH_3-\underset{|}{\overset{}{N}}-CH_2-CH_3$ with H below N: $CH_3-\underset{H}{\underset{|}{N}}-CH_2-CH_3$,

N-methyletharamine

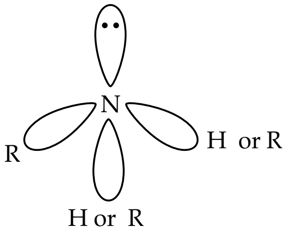


$CH_3-\underset{H}{\underset{|}{N}}-CH_3$

N, N-methyletharamine

  - Aromatic amine,  is named as aniline or benzenamine.

- **Structure :** In amines, N atom is sp^3 hybridised. Among four sp^3 hybridised orbitals one contains lone pair of electrons and other three contain bond pairs of electrons.



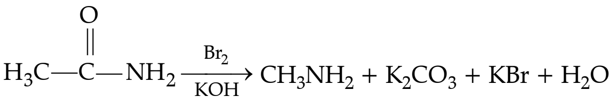
Due to lone pair of electrons it is pyramidal in shape.

- **Preparation :**

- **From alcohols :**

$$\mathrm{CH_3CH_2OH} \xrightarrow[-\mathrm{H_2O}]{\mathrm{NH_3},\Delta} \underset{1^\circ\text{ amine}}{\mathrm{CH_3CH_2NH_2}} \xrightarrow[-\mathrm{H_2O}]{\mathrm{CH_3CH_2OH},\,\Delta} \underset{2^\circ\text{ amine}}{(\mathrm{CH_{ü}CH}\ )\ \mathrm{NH}} \xrightarrow[-\mathrm{H_2O}]{\mathrm{CH_3CH_2OH},\,\Delta} \underset{3^\circ\text{ amine}}{(\mathrm{CH_3CH_2})_3\mathrm{N}}$$

- **Hofmann bromamide reaction :**



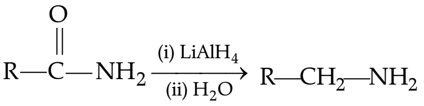
$$\mathrm{H_3C{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}NH_2} \xrightarrow[\mathrm{KOH}]{\mathrm{Br_2}} \mathrm{CH_3NH_2 + K_2CO_3 + KBr + H_2O}$$

- **Reduction of nitro and nitriles :**

$$\mathrm{R{-}NO_2} \xrightarrow[\text{or } \mathrm{H_2/Pt}]{\mathrm{Sn/HCl}} \mathrm{RNH_2},\ \mathrm{R{-}C\equiv N} \xrightarrow[\mathrm{Na(Hg)/C_2H_5OH}]{\mathrm{H_2/Ni}} \mathrm{R{-}CH_2{-}NH_2}$$

- **Hydrolysis of isocyanides to isocyanate :** $\mathrm{R{-}NC} \xrightarrow{\mathrm{H^+/H_2O}} \mathrm{RNH_2}$, $\mathrm{R{-}N{=}C{=}O} \xrightarrow{\mathrm{KOH}} \mathrm{RNH_2}$

- **Reduction of amide :**



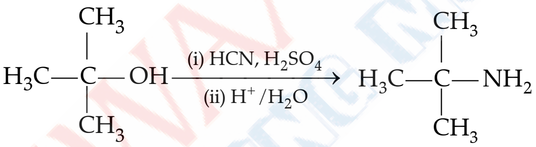
$$\mathrm{R{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}NH_2} \xrightarrow[\text{(ii) } \mathrm{H_2O}]{\text{(i) } \mathrm{LiAlH_4}} \mathrm{R{-}CH_2{-}NH_2}$$

- **Ammonolysis of alkyl halides :** $\mathrm{R{-}X + NH_3} \longrightarrow \underset{1^\circ\text{amine}}{\mathrm{RNH_2}} \xrightarrow{\mathrm{RX}} \underset{2^\circ\text{amine}}{\mathrm{R_2NH}}$

$$\underset{2^\circ\text{amine}}{\mathrm{R_2NH}} \xrightarrow{\mathrm{RX}} \underset{3^\circ\text{amine}}{\mathrm{R_3N}} \xrightarrow{\mathrm{RX}} \underset{\text{Quaternary ammonium salt}}{\mathrm{R_4\overset{+}{N}\overset{-}{X}}}$$

- **Schmidt reaction :** $\mathrm{CH_3COOH} \xrightarrow[\mathrm{H_2SO_4}]{\mathrm{N_3H},\,\Delta} \mathrm{CH_3NH_2 + CO_2 + N_2}$

- **Ritter reaction :**

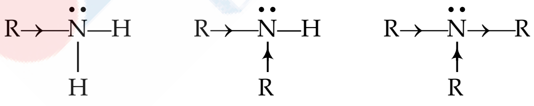


$$\mathrm{H_3C{-}\underset{\underset{\displaystyle CH_3}{|}}{\overset{\overset{\displaystyle CH_3}{|}}{C}}{-}OH} \xrightarrow[\text{(ii) } \mathrm{H^+/H_2O}]{\text{(i) HCN, } \mathrm{H_2SO_4}} \mathrm{H_3C{-}\underset{\underset{\displaystyle CH_3}{|}}{\overset{\overset{\displaystyle CH_3}{|}}{C}}{-}NH_2}$$

➢ **Physical Properties :**

- Lower amines are gases or liquids but higher amines are solids.
- 1° and 2° amines have hydrogen bonded to electronegative atom Nitrogen (N), thus, they have higher boiling point than other organic compounds due to hydrogen bonding.
- Due to hydrogen bonding 1° and 2° amines are water soluble.

➢ **Basic character of amines :**

- They are basic in nature due to available lone pair of electrons on nitrogen.
- 

$$\mathrm{R{\rightarrow}\underset{\underset{\displaystyle H}{|}}{\ddot{N}}{-}H} \qquad \mathrm{R{\rightarrow}\underset{\underset{\displaystyle R}{\uparrow}}{\ddot{N}}{-}H} \qquad \mathrm{R{\rightarrow}\underset{\underset{\displaystyle R}{\uparrow}}{\ddot{N}}{\leftarrow}R}$$

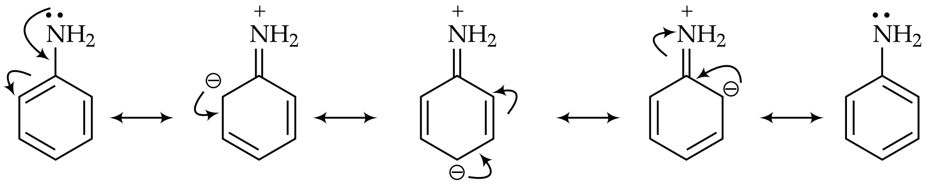
(1° amine) (2° amine) (3° amine)

Due to +I effect of R group expected order of basicity of amine is 3° > 2° > 1° but it is not so due to alkyl groups crowding and thus, lone pair of electrons is not easily available to it. Basicity order depends on the type of alkyl group.

$\mathrm{R = CH_3 : R_2NH > RNH_2 > R_3N > NH_3}$

$\mathrm{R = C_2H_5 : R_2NH > R_3N > RNH_2 > NH_3}$

- Aniline is a weaker base as the lone pair of N is involved in conjugation with π-electrons and thus, less available for protonation..



- **Chemical Properties :**

- Oxidation reactions : $RCH_2NH_2 \xrightarrow{KMnO_4} RC{=}NH \xrightarrow[H^+]{H_2O} RCHO + NH_3$

- **Electrophilic substitution reactions :**

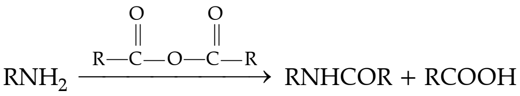
$$RNH_2 \xrightarrow{H_2O} R\overset{+}{N}H_3OH^- \rightleftharpoons RNH_3{}^+ + OH^-$$

$$RNH_2 \xrightarrow{HCl} RNH_3{}^+Cl^-$$

$$RNH_2 \xrightarrow{AgCl} [Ag(RNH_2)_2]^+Cl^-$$

$$RNH_2 \xrightarrow{RCOCl} RNHCOR + HCl$$

$$RNH_2 \xrightarrow[-HI]{RI} \underset{2° \text{ amine}}{R_2NH} \xrightarrow[-HI]{RI} \underset{3° \text{ amine}}{R_3N} \xrightarrow{RI} \underset{\text{Quaternary ammonium salt}}{R_4\overset{+}{N}I^-} \xrightarrow[AgI]{AgOH} R_4N^+OH^-$$

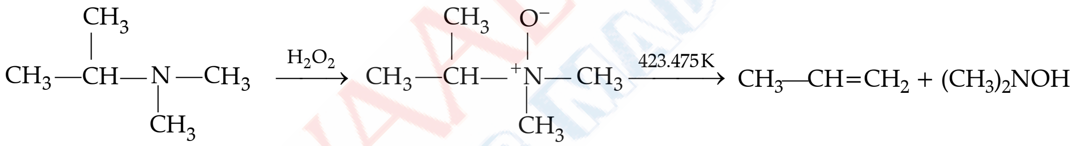


$$RNH_2 \xrightarrow{R-\overset{\overset{O}{||}}{C}-O-\overset{\overset{O}{||}}{C}-R} RNHCOR + RCOOH$$

$$RNH_2 \xrightarrow[\text{Warm}]{CHCl_3,3KOH(alc)} RNC + 3KCl + H_2O \text{ (Carbylamine reaction)}$$

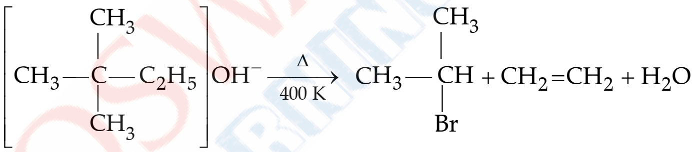
$$RNH_2 \xrightarrow[\Delta]{CS_2,\ HgCl_2} RNC = S + HgS + 2HCl \text{ (Hofmann's mustard oil reaction)}$$

- **Cope elimination :**



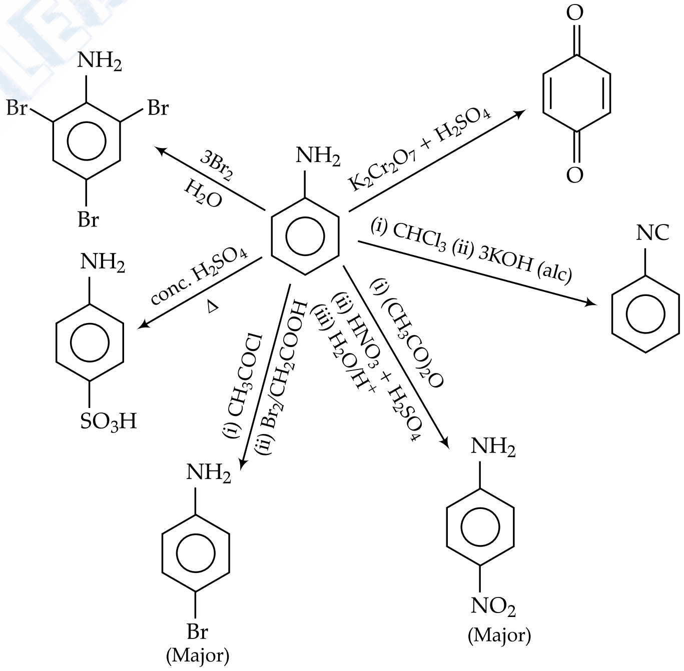
$$CH_3-\overset{\overset{CH_3}{|}}{C}H-\underset{\underset{CH_3}{|}}{N}-CH_3 \xrightarrow{H_2O_2} CH_3-\overset{\overset{CH_3}{|}}{C}H-\overset{\overset{O^-}{|}}{\underset{\underset{CH_3}{|}}{{}^+N}}-CH_3 \xrightarrow{423.475K} CH_3-CH=CH_2 + (CH_3)_2NOH$$

- **Hofmann elimination reaction :**



$$\left[CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-C_2H_5\right]OH^- \xrightarrow[400\ K]{\Delta} CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{Br}{|}}{CH}} + CH_2=CH_2 + H_2O$$

- **Electrophilic substitution reaction of arylamines :**



- **Uses :** Lower aliphatic amines are used as solvents
  - Aromatic amines are used in manufactures of polymers, dyes and in rubber industry.
  - Quaternary ammonium salts are used as detergents.
- **Test for 1°, 2° and 3° amines :**

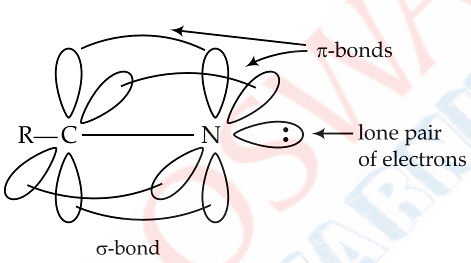
S. No.	Test	1° amine	2° amine	3° amine
1.	Reaction with nitrous acid	Give alcohol with effervescence of N_2 gas	Gives oily nitroso-amine which gives Liebermann's nitroso amine test.	Forms nitrite in cool which is soluble in water and on heating gives nitroso amine.
2.	Hinsberg's reagent	Gives N-alkyl benzene sulphonamide soluble in alkali	Gives N, N-dialkyl benzene sulphonamide insoluble in alkali.	No reaction
3.	Carbylamine test	Forms isocyanide with pungent odour	No reaction	No reaction
4.	Hofmann's mustard oil reaction	Forms isothio cyanate having smell of mustard oil	No reaction	No reaction

- **Cyanides and isocyanides :**

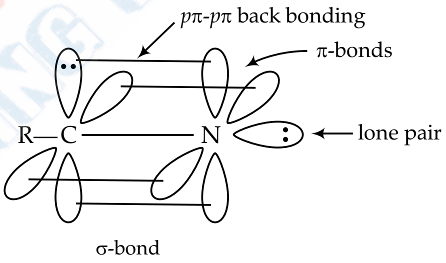
$R{-}C{\equiv}N$ Alkyl cyanide

$R{-}N{\equiv}C$ Alkyl isocyanide

- **Structure :** In cyanides and isocyanides, both carbon and nitrogen are *sp* hybridised.

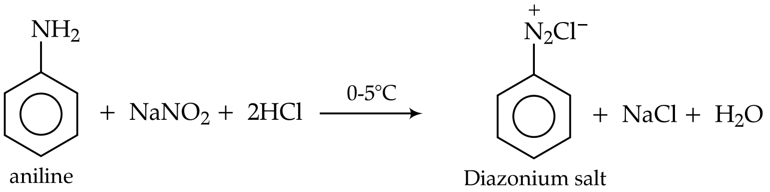


Cyanide



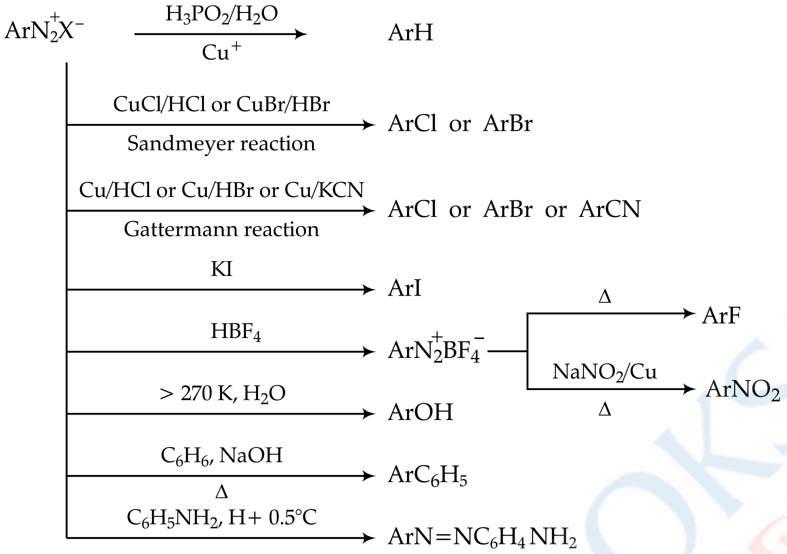
Isocyanide

- **Nomenclature :** Cyanides are named as alkane nitriles, and Isocyanides are named as alkyl isocyanide or alkyl carbylamines.
- **Diazonium salts :** These are the compounds with general formula $ArN_2^+ X^-$ where, Ar is the aryl group and $X^-$is the anion say Cl^-, Br^-, HSO_4^-, NO_3^- etc.
- **Nomenclature :** After the name of parent hydrocarbon add diazonium and the write the name of anion.
- **Preparation :**



Due to dispersal of positive charge over the ring it is stable for shorter period than alkanediazonium salt.

- **Chemical properties :**



- **Importance of diazonium salts in synthetic organic chemistry :**
  - It is used in synthesis of various organic compounds such as alkyl halides.
  - It is used in manufacture of azo dyes.

KNOW THE TERMS

- **Baker-Mulliken Test :** It is a test for nitro compounds in which hydroxyl amines when warmed with Tollen's reagent gives metallic silver.
- **Cope Elimination :** It is used to identify the structure of 3° amines. In which one alkyl group must contain a β-hydrogen. This amine reacts with H_2O_2 to get an amine oxide which on heating gives alkane and a dialkyl hydroxyl amine.

Chapter 28

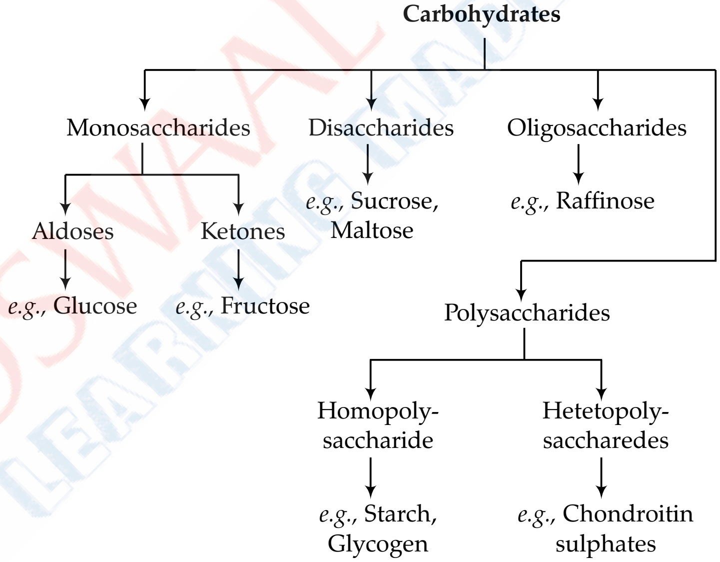
Biomolecules

Topic 1

Carbohydrates

» Revision Notes

- **Biomolecules :** Biomolecules are the organic compounds present as essential constituents of living organism in different cells. *e.g.*, Carbohydarates, proteins, fats, amino acids, etc.
- **Carbohydrates :** Carbohydrates may be defined as optically active polyhydroxy aldehydes or ketones or compound which produce such units on hydrolysis *e.g.*, cellulose, glycogen, starch, etc.
- **Classification of carbohydrates :**



- **Monosaccharides :** Monosaccharide include non-hydrolysable carbohydrates. They are soluble in water. Those containing aldehydic group are called aldoses while containing a ketonic group are called ketoses.
- **Disaccharides :** Those carbohydrates which on hydrolysis yield two molecules of monosaccharides are called disaccharides. They are crystalline, soluble in water and sweet in taste. *e.g.*, Cane sugar, maltose.
- **Oligosaccharides :** Those carbohydrates which yield 2 to 10 monosaccharide molecules on hydrolysis are called oligosaccharides.
- **Polysaccharides :** Those carbohydrates which produces large number of monosaccharide units on hydrolysis are called polysaccharides. They are formed by linking together a large number of monosaccharide units through glycosidic linkage, *e.g.*, starch, glycogen and cellulose.
- **Glucose :** Glucose occurs in nature in free as well as in combined form. It is present in sweet fruits and honey.
- **Preparation of Glucose :**

  (i) From sucrose :

$$\underset{\text{Sucrose}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow{H^+} \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Fructose}}{C_6H_{12}O_6}$$

(ii) From starch :

$$(C_6H_{10}O_5)_n + nH_2O \xrightarrow[393\text{ K, 2-3 bar}]{H^+} \underset{\text{Glucose}}{nC_6H_{12}O_6}$$

- **Fructose :** Fructose is found in free state along with glucose in many fruits and in honey (50%)

Preparation of Fructose :

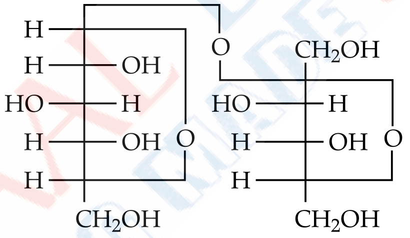
(i) From hydrolysis of cane sugar :

$$\underset{\text{Cane sugar}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow{\text{Dil.}H_2SO_4} \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Fructose}}{C_6H_{12}O_6}$$

(ii) From inulin :

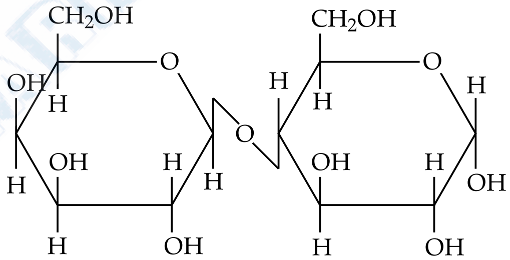
$$\underset{\text{Inulin}}{(C_6H_{10}O_5)_n} + nH_2O \xrightarrow{\text{Dil.}H_2SO_4} \underset{\text{Fructose}}{nC_6H_{12}O_6}$$

- **D and L Configuration :** The conformations of the carbohydrates are determined by the orientation of the hydroxyl group about the asymmetric carbon farthest from the carbonyl. The carbohydrates that are of physiological significance are in the D-conformation. The mirror image conformations, called enantiomers, are in L-conformation.
- **Sucrose :** Its molecular formula is ($C_{12}H_{22}O_{11}$). Sucrose is dextrorotatory in nature. The hydrolysis of sucrose brings a change in the sign of optical rotation from dextro (+) to laevo (–) and is known as inversion. The equimolar mixture of D-(+)-) glucose and D-(–)-) fructose produced on the hydrolysis of sucrose is called invert sugar.
- **Structure of Sucrose :**



Glucose unit Fructose unit

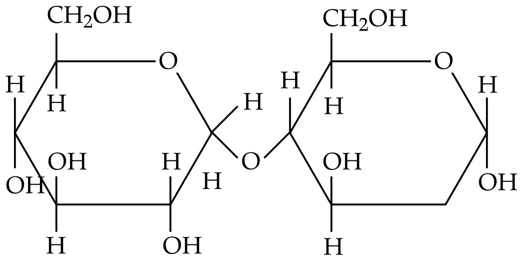
- **Lactose ($C_{12}H_{22}O_{11}$) :** Hydrolysis of lactose produces equimolecular mixture of D-glucose and D-galactose.
- **Structure of Lactose :**



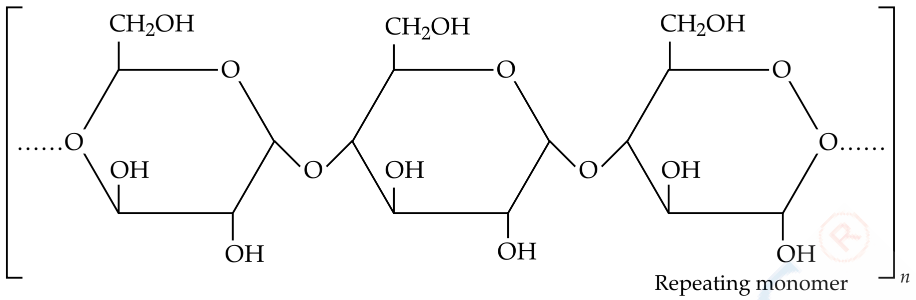
- **Maltose ($C_{12}H_{22}O_{11}$) :** Partial hydrolysis of starch by diastase produces maltose.

$$\underset{\text{Starch}}{2(C_6H_{10}O_5)_n} + nH_2O \xrightarrow{\text{Diastase}} \underset{\text{Maltose}}{nC_{12}H_{22}O_{11}}$$

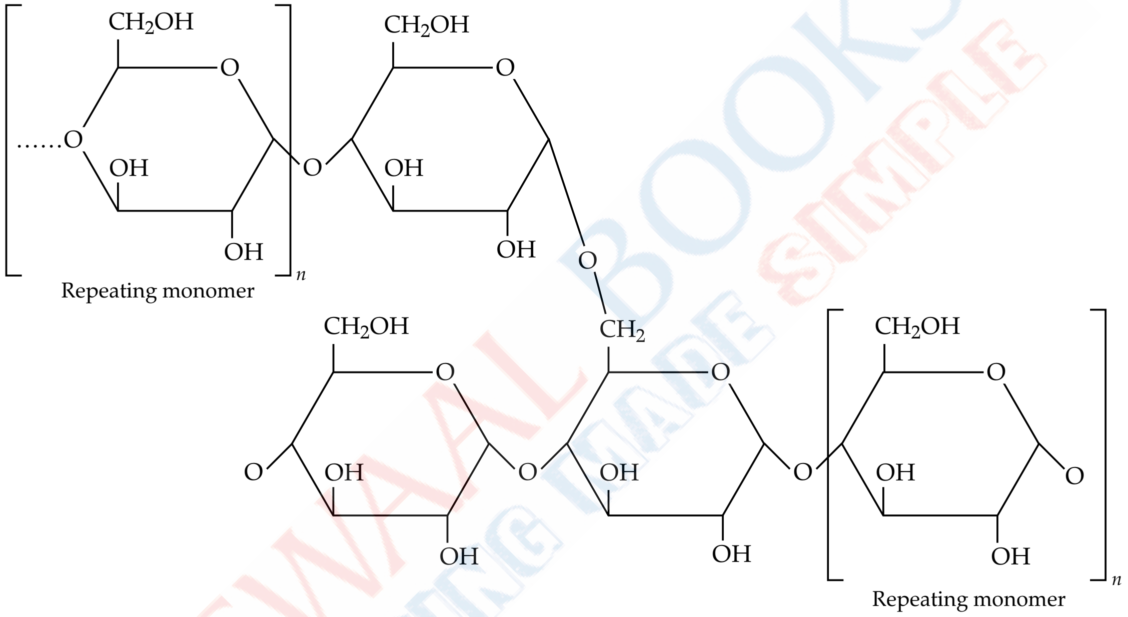
- **Structure of Maltose :**



- **Starch :** Hydrolysis of starch produces glucose. It consists of two components – amylose and amylopectin.
- **Structure of amylose and amylopectin :**



Amylose



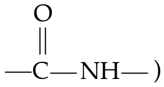
Amylopectin

- **Cellulose :** Hydrolysis of cellulose gives β-D-(+)-glucose. It is the structural material of the cell walls in the plant cells.
- **Glycogen :** Glycogen $(C_6H_{10}O_5)_n$ is present in WBC, liver, muscles in human body. It resembles amylopectin and has a branched structure.
- **Importance of Carbohydrates :**
  (i) They are essential for plants and animals as a source of energy.
  (ii) Honey consists of mixture of carbohydrates which is source of energy.
  (iii) They store energy in the form of starch and cellulose in plants and glycogen in animals and human beings.
  (iv) They are used in textile, paper and alcohol industry.
  (v) They are also found in combination with proteins and lipids.

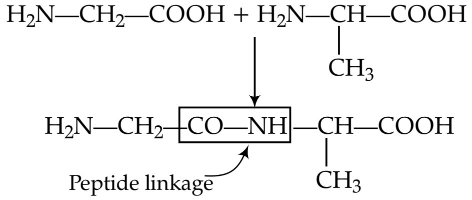
Topic 2

Proteins, Enzymes, Vitamins and Hormones

» Revision Notes

- **Proteins :** Proteins are complex polyamides formed from amino acids. They are essential for proper growth and maintenance of body. They have many peptide ( $—\overset{\overset{\displaystyle O}{\|}}{C}—NH—$) bonds.
- **α-amino acids :** Those amino acids in which $—NH_2$ group and —COOH group are attached to same carbon are called α-amino acids. These are obtained by hydrolysis of proteins *e.g.*, glycine.

- **Peptide bond :** It is a bond between two amino acids by elimination of water.

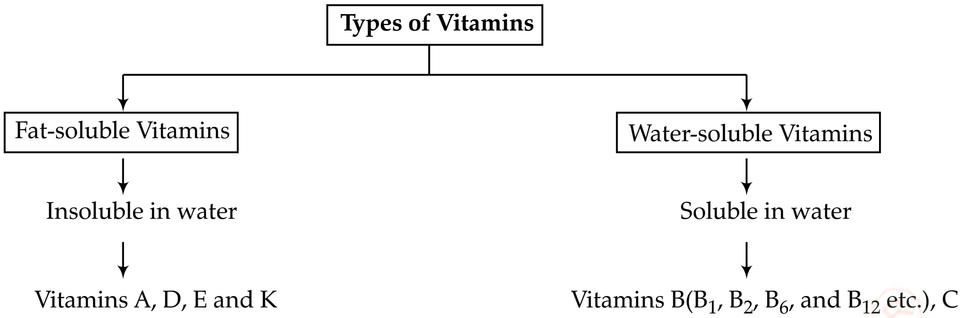


$$\mathrm{H_2N{-}CH_2{-}COOH + H_2N{-}\underset{\underset{\displaystyle CH_3}{|}}{CH}{-}COOH} \;\longrightarrow\; \mathrm{H_2N{-}CH_2{-}\boxed{CO{-}NH}{-}\underset{\underset{\displaystyle CH_3}{|}}{CH}{-}COOH}$$

- **Polypeptides :** Polypeptides are the structures which contain more than 10 amino acids.
- **Classification of Proteins :** On the basis of their properties, proteins are classified into :
  - **(i) Fibrous protein :** They have thread like molecules which tend to lie side by side to form fibers. *e.g.*, keratin, collagen, etc.
  - **(ii) Globular proteins :** They have molecules which are folded into compact units that often approach spheroidal shape, *e.g.*, insulin, albumins, haemoglobin, etc.
- **Structure of Proteins :**
  - **(a) Primary structure :** Here, linear sequence of amino acids are linked together by peptide bonds.
  - **(b) Secondary structure :** α-helix structure maintained by hydrogen bonds or β-pleated sheet structure when R is small group.
  - **(c) Tertiary structure :** Here, the structure is formed by the further folding of the secondary structure by hydrophobic interactions, hydrogen bonds, ionic interactions, van der Waal's forces and disulphide bonds.
  - **(d) Quaternary structure :** Here, the spatial arrangement of two or more polypeptide chains with respect to each other.
- **Denaturation of proteins :** When a protein in its native form, is subjective to change, like change in temperature or pH, the hydrogen bond are disturbed. Due to this, globules unfold and helix get uncoiled and protein loses its biological activity. It is called denaturation of protein, *e.g.*, coagulation of egg-white on boiling, curding of milk, etc.
- **Enzymes :** Enzymes are essential biological catalysts which are needed to catalyse biochemical reactions *e.g.*, maltase, lactase, invertase etc. Almost all enzymes are global proteins.
- **Hormones :** Hormones are the chemical substances produced by ductless glands called endocrine glands such as thyroid, adrenals, etc. They find their way into the blood stream and influence and regulate the functions of the other organs of the body.
- **Various Hormones, gland of secretion and their functions :**

Hormones	Gland	Function
Steroid Hormones		
(a) Testosterone (androgens)	Testes	Responsible for development of male sex organs.
(b) Estrogen and progesterone	Ovary	Influences development of sex organs, maintains pregnancy.
(c) Cortisone	Adrenal cortex	Regulates metabolism of water, minerals salts.
Amine Hormones		
(a) Adrenalin	Adrenal medulla	Increases blood pressure and pulse rates
(b) Thyroxin	Thyroid	Stimulates rate of oxidative metabolism and regulates general growth and development.
Peptide Hormones		
(a) Oxytocin	Posterior pituitary	Causes constitution of some smooth muscles. It causes contraction of uterus during child birth.
(b) Vasopressin	Posterior pituitary	Controls the reabsorption of water in kidneys.
(c) Insulin	Posterior pituitary	Controls blood glucose level.
(d) Glucagon	Pancreas	Increases blood glucose level

- **Vitamins :** Vitamins are group of organic compounds which are required in very small quantity for the healthy growth and functioning of animal organism.



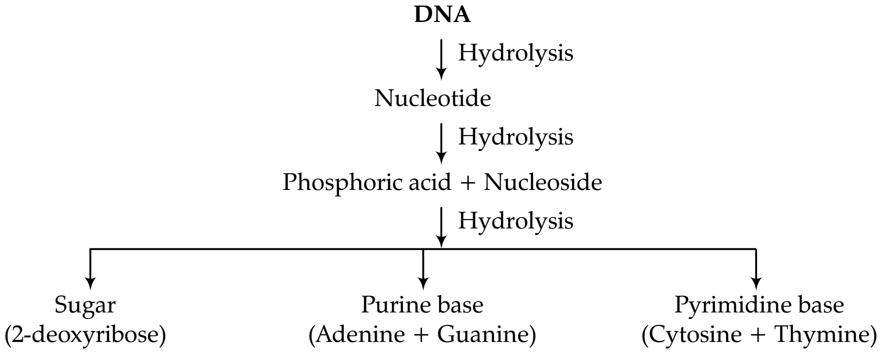
- **Function of Vitamins :**
  - **(i)** Vitamin A is essential for vision and growth. It develops resistance against deceases.
  - **(ii)** Vitamin B_1 is essential for proper functioning of nervous system.
  - **(iii)** Vitamin B_2 is essential for growth of body.
  - **(iv)** Vitamin B_6 is required in blood formation.
  - **(v)** Vitamin B_{12} is also required in blood formation.
  - **(vi)** Vitamin C is required for bones, teeth and healing of wounds, healthy skin,
  - **(vii)** Vitamin D is essential for control of metabolism of calcium and phosphorous in the formation of bones.
  - **(viii)** Vitamin E is required for antisterility or reproduction.
  - **(ix)** Vitamin K helps in clotting of blood.

Topic 3

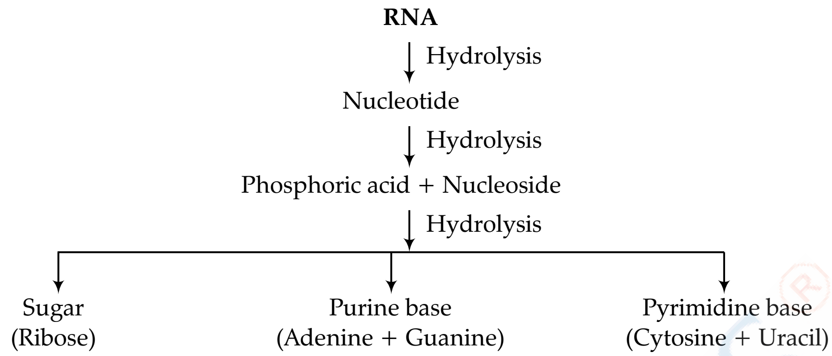
Nucleic Acids, (DNA, RNA)

» Revision Notes

- **Nucleic acids :**
  - **(i)** Nucleic acids are very important constituents (polynucleotide) found in nucleus of cell which help in biosynthesis of protein and act as carriers for transfer of hereditary characters.
  - **(ii)** A molecule formed by the combination of one pentose sugar unit, a purine or pyrimidine base and a phosphate. Nucleotide combine among themselves to many acute polynucleotide.
  - **(iii)** A DNA has a thiamine base but not a uracil base. It contains deoxyribose sugar but not ribose sugar. It has double helix structure.
  - **(iv)** A RNA contains uracil base and ribose sugar. It has single standard structure.
- **DNA :**



- **RNA :**



KNOW THE TERMS

- **Aldoses :** Monosaccharides which contain an aldehyde (—CHO) group are called aldoses.
- **Ketones :** Monosaccharides which contain a Keto (>C=O) group are called ketoses.
- **Invert Sugar :** An equimolar mixture of glucose an fructose which is formed as a result of hydrolysis of sucrose.
- **N-terminal end :** There is a free amino group at one end of molecule of amino acid which is known as N-terminal end.
- **C-terminal end :** There is a free carboxy group at the end of amino acid molecule which is known as C-terminal end.
- **Essential amino acids :** Those amino acids which can be synthesized in the body *e.g.*, glycine, alanine.
- **Non-essential amino acids :** Those amino acids cannot be synthesized by the body and must be obtained by the diet.
- **Mutarotation :** When either of the two forms of glucose is dissolved in water, there is a spontaneous change in specific rotation till the equilibrium value of +52.5°. This is known as mutarotation.

➢

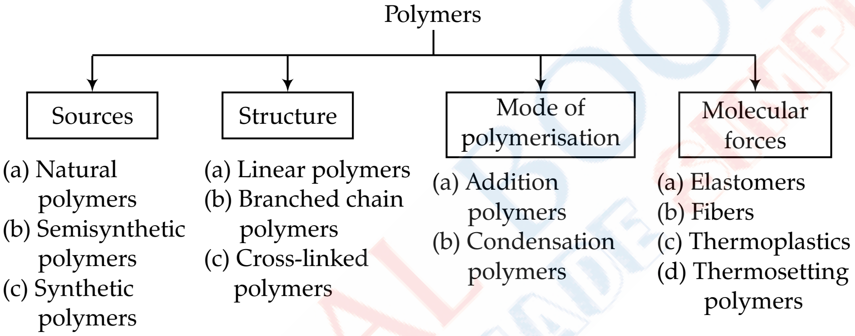
❑❑❑

Chapter 29

Polymers

» Revision Notes

- **Polymers :** Polymers are defined as high molecular mass macromolecules, which consists of repeating structural units derived from the corresponding monomers.
- **Polymerisation :** The process of which monomers are converted into polymers is called polymerization.
- **Classification of Polymers :**

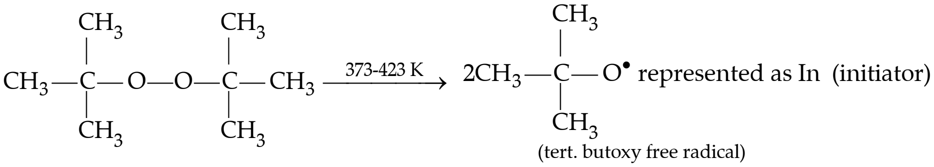


- **Natural polymers :** They are found in nature, mostly in plants and animals. *e.g.*, proteins, natural rubber, etc.
- **Semisynthetic Polymers :** They are obtained by making some modifications in natural polymers by artificial means, *e.g.*, nitrocellulose, cellulose acetate, etc.
- **Synthetic Polymers :** These are man-made polymers prepared in the laboratory, *e.g.*, polythene, Teflon, nylon, etc.
- **Linear Polymers :** These polymers consist of long and straight chains, *e.g.*, high density polythene, nylon, polyvinyl chloride, etc.
- **Branched Chain Polymers :** These polymers contain linear chains having some branches, *e.g.*, low density polythene, glycogen, etc.
- **Cross-linked or Network Polymers :** These polymers are usually formed from bifunctional and trifunctional monomers and contain strong covalent bonds between various linear polymer chain, *e.g.*, Bakelite, melamine, etc.
- **Addition Polymers :** A polymer formed by direct addition of repeated monomers without the elimination of by product molecules are called addition polymer, *e.g.*, polythene, buna-S, buna-N.
- **Condensation Polymers :** A polymer formed by the condensation of two or more than two monomers with the elimination of simple molecules like water, ammonia, alcohol, etc., is called condensation polymer. *e.g.*, nylon 6, 6 and nylon, terylene, etc.
- **Elastomers :** In these polymers, the polymer chains are held together by the weakest intermolecular forces. These weak binding forces allow the polymer to be stretched. A few cross links, when introduced in between the chains, helps the polymer to retract to its original position after the stretching force is removed, *e.g.*, buna-S, buna-N, etc.
- **Fibers :** These are the polymers which have strongest intermolecular forces such as hydrogen bond or dipole-dipole interactions. *e.g.*, nylon 6, 6 and terylene.
- **Thermoplastics :** These polymers possess intermolecular force of attraction intermediate between elastomers and fibers. These are linear or slightly branched chain polymers capable of repeatedly softening on heating and hardening on cooling. *e.g.*, polythene, polypropylene, etc.
- **Thermosetting polymers :** These polymers are cross linked or heavily branched molecules, which on heating undergo extensive cross linking in moulds and again become infusible. These cannot be reshaped, *e.g.*, Bakelite, urea, formaldehyde, resins, etc.
- **Mechanism of Polymerisation :**

  (a) Chain growth polymerisation :

  It involves two basic mechanisms :

(i) Free radical polymerisation : It is initiated by molecules like tert. butyl peroxide.



$$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-O-O-\underset{CH_3}{\overset{CH_3}{C}}-CH_3 \xrightarrow{373\text{-}423\ K} 2CH_3-\underset{CH_3}{\overset{CH_3}{C}}-O^{\bullet} \text{ represented as In (initiator)}$$

(tert. butoxy free radical)

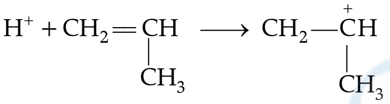
$$In + CH_2{=}CH_2 \longrightarrow In-CH_2-\dot{C}H_2 \xrightarrow{CH_2=CH_2} In-CH_2-CH_2-CH_2-\dot{C}H_2$$

$$\xrightarrow{nCH_2=CH_2} In-(CH_2-CH_2)_n$$

(ii) Ionic addition polymerisation :

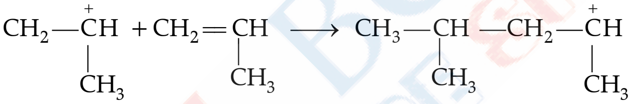
– **Cationic addition polymerisation :** When initiator is cationic in nature, on addition to the double bond, it would generate carbocation. If functional group attached to vinyl group which is electron releasing, it will undergo cationic polymerisation, *e.g.*, propene.

(a) Chain initiation step :



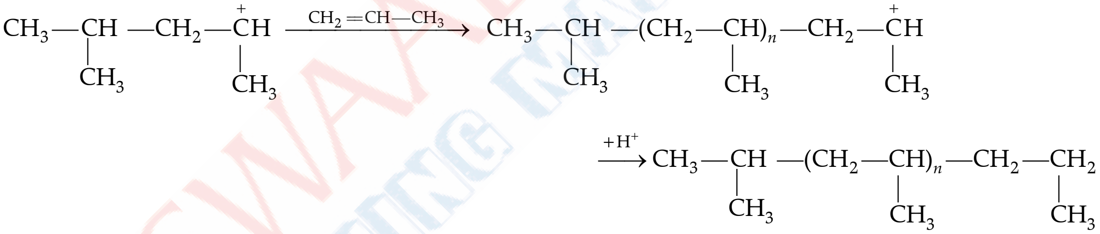
$$H^+ + CH_2=\underset{CH_3}{CH} \longrightarrow CH_2-\underset{CH_3}{\overset{+}{C}H}$$

(b) Chain propagation step :



$$CH_2-\underset{CH_3}{\overset{+}{C}H} + CH_2=\underset{CH_3}{CH} \longrightarrow CH_3-\underset{CH_3}{CH}-CH_2-\underset{CH_3}{\overset{+}{C}H}$$

(c) Chain termination step :

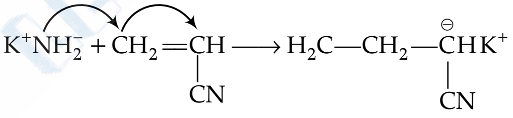


$$CH_3-\underset{CH_3}{CH}-CH_2-\underset{CH_3}{\overset{+}{C}H} \xrightarrow{CH_2=CH-CH_3} CH_3-\underset{CH_3}{CH}-(CH_2-\underset{CH_3}{CH})_n-CH_2-\underset{CH_3}{\overset{+}{C}H}$$

$$\xrightarrow{+H^+} CH_3-\underset{CH_3}{CH}-(CH_2-\underset{CH_3}{CH})_n-CH_2-\underset{CH_3}{CH_2}$$

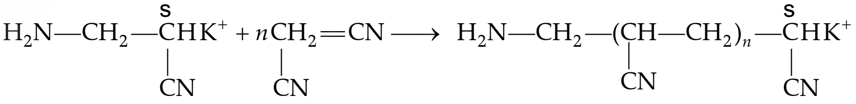
- **Anionic polymerisation :** When initiator is *n*-butyl lithium or KNH_2, on addition to double bond, it would generate carbanion. If functional group attached to vinyl group which is electron withdrawing such as —CN, —Cl, —$COOCH_3$, —C_6H_5, it will undergo anionic polymerisation.

(a) Chain initiation step :



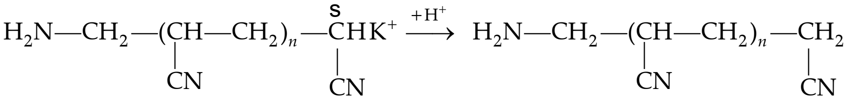
$$K^+NH_2^- + CH_2=\underset{CN}{CH} \longrightarrow H_2C-CH_2-\underset{CN}{\overset{\ominus}{C}H}K^+$$

(b) With propagation step :



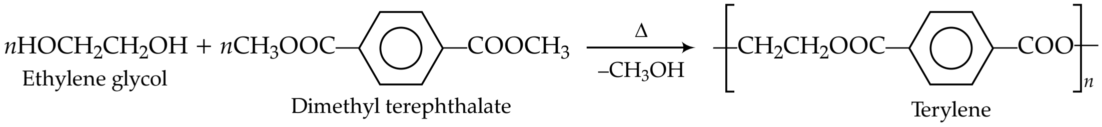
$$H_2N-CH_2-\underset{CN}{\overset{S}{C}H}K^+ + n\underset{CN}{CH_2}=CN \longrightarrow H_2N-CH_2-(\underset{CN}{CH}-CH_2)_n-\underset{CN}{\overset{S}{C}H}K^+$$

(c)



$$H_2N-CH_2-(\underset{CN}{CH}-CH_2)_n-\underset{CN}{\overset{S}{C}H}K^+ \xrightarrow{+H^+} H_2N-CH_2-(\underset{CN}{CH}-CH_2)_n-\underset{CN}{CH_2}$$

(d) Step growth polymerisation :



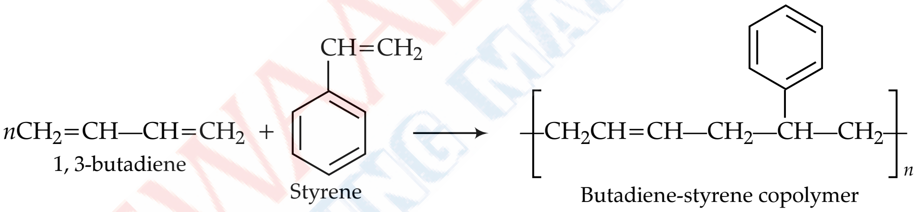
- **Differences between chain growth and step growth polymerisation :**

S.No.	Chain Growth Polymerisation	Step Growth Polymerisation
1.	Concentration of monomers disappears early in the reaction.	Concentration of monomers decreases steadily throughout the reaction.
2.	Reaction is fast and polymer is formed at once.	The polymer is formed in gradual steps.
3.	There is very little change in the molecular mass throughout the reaction.	The molecular mass of polymer increases throughout the reaction.
4.	Increase in reaction time increases the yield but molecular weight is affected a little.	Long reaction time is required to get high molecular mass polymer.
5.	Only one repeating unit is added at a time.	Any two species present can react.
6.	Reaction mixture contains only monomer, polymer and growing chain.	All molecular species are present at any stage.

- **Differences between addition and condensation polymerisation :**

S.No.	Addition Polymerisation	Condensation Polymerisation
1.	They are formed by adding monomers to a growing polymer chain without loss of any molecule.	Monomers combine together with the loss of small molecules like H_2O, NH_3, CO_2, CH_3OH.
2.	They are formed from unsaturated compounds.	Monomers have di or poly functional groups.
3.	It involves chain reaction, *e.g.*, polythene, polypropene, PVC, teflon, etc.	It does not involve chain reaction, *e.g.*, nylon-6, 6, nylon-6, terylene, bakelite, etc.

- **Copolymerisation :** A polymerisation reaction in which a mixture of more than one monomeric species are allowed to polymerise to both chain growth and step growth polymerisation. *e.g.*, Butadiene-styrene copolymer.

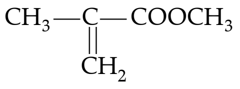
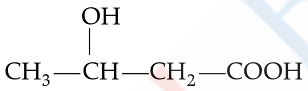
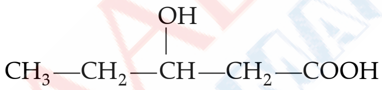


- **Natural Polymers :**

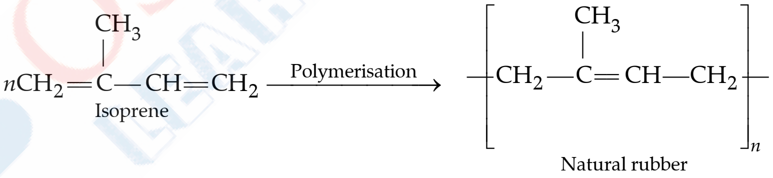
S.No.	Polymer	Monomer	Class	Uses
1.	Cellulose	β-glucose	Biopolymer	Occurs in cotton, cell wall
2.	Starch	α-glucose	Biopolymer	Food material storage in plants
3.	Proteins	Amino acids	Biopolymer	Essential for growth
4.	Nucleic acid	Nucleotides	Biopolymer	Essential for life perpetuation
5.	Rayon (artificial silk)	β-Glucose	Processed cellulose	Fabrics, surgical dressings
6.	Natural rubber	*cis*-Isoprene (*cis*-2-methyl-1, 3-butadiene)	Natural polymer Elastomer	Used for tyres after vulcanisation
7.	Gutta percha	*trans*-Isoprene	Elastomer	Rubber like material

- **Synthetic Polymers :**

S.No.	Polymer	Monomer	Class	Uses
1.	Polyethene	Ethene ($CH_2{=}CH_2$)	Addition and chain growth	Electrical insulator, packing material, films, bottles, etc.
2.	Polypropene	Propene ($CH_3{-}CH{=}CH_2$)	Addition and chain growth	Storage battery tanks
3.	Polystyrene	Styrene ($C_6H_5{-}CH{=}CH_2$)	Addition and chain growth	In combs, plastic handles, toys

4.	Polyvinyl chloride (PVC)	$CH_2{=}CHCl$	Addition and chain growth	Pipes, raincoats, vinyl floorings
5.	Polytetrafluoroethene PTFE (Teflon)	$CF_2{=}CF_2$	Addition and chain growth	Non-stick kitchenwares, electrical insulator
6.	Polymethyl methacrylate (PMMA) (perspex, Lucite or Acrylite)	 $CH_3-\underset{CH_2}{\underset{\Vert}{C}}-COOCH_3$ Methyl methacrylate	Addition and chain growth	substitute of glass and decorative material
7.	Polyethyl acrylate	$CH_2{=}CH-COOC_2H_5$ Ethyl-2-propenoate	Addition and chain growth	Lacquers, films, house piping
8.	Polyvinyl acetate	$CH_2{=}CH-O-COCH_3$ Vinyl acetate	Addition and chain growth	Floor coverings and fibres
9.	Polyacrylonitrile or Acrylane (Orlon)	$CH_2{=}CH-C{\equiv}N$ Vinyl cyanide (Acrylonitrile)	Addition and chain growth	It closely resembles wool.
10.	Buna-S	1, 3-butadiene and Styrene	Addition and chain growth	Automobile tyres
11.	Buna-N	1, 3-Butadiene and Acrylonitrile	Addition and chain growth	Uses for strong oil and solvents
12.	Poly-β-hydroxy-butyrate-co-β-hydroxy valerate (PHBV)	 $CH_3-\overset{OH}{\overset{\vert}{C}H}-CH_2-COOH$  $CH_3-CH_2-\overset{OH}{\overset{\vert}{C}H}-CH_2-COOH$	Condensation polymer	In packaging, orthopaedic and in controlled drug release.
13.	Nylon-2-Nylon-6	Glycine (H_2NCH_2COOH) and aminocaproic acid $H_2N(CH_2)_5COOH$	Condensation polymer	Biodegradable polymer

- **Rubber :** Rubber is an example of elastomer. Natural rubber is considered as a linear 1, 4-polymer of isoprene (2, methyl-1, 3-butadene). In this polymer, the residual double bonds are located between C_2 and C_3 is isoprene units in the polymer. All these double bonds have cis-configuration.

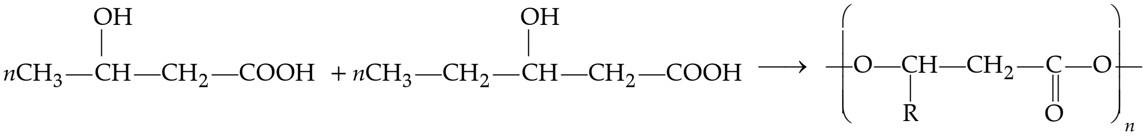


$$nCH_2=\overset{CH_3}{\overset{|}{C}}-CH=CH_2 \xrightarrow{\text{Polymerisation}} \left[-CH_2-\overset{CH_3}{\overset{|}{C}}=CH-CH_2-\right]_n$$

Isoprene

Natural rubber

- **Bakelite :** The monomer with the Bakelite are phenol and formaldehyde. They are both linear chain and cross-linked in nature. As a result of cross-linking, bakelites become hard and brittle, soft bakelites are used for making glues, for binding laminated sheets, wooden planks and in lacquers. Hard bakelites are used in the manufacture of combs, fountain pens, electric goods, etc.
- **Biodegradable Polymers :** A polymer that can be decomposed by microorganisms within a definite period of time so that the polymer or its degraded product does not cause any harm to the environment, is called biodegradable polymers. For example, polyhydroxybutyrate-co-β-hydroxy valerate (PHBV), polyglycolic acid (PGA), polylactic acid (PLA).
- **PHBV :** It is a copolymer of 3-hydroxybutanoic acid and 3-hydroxypentanoic acid in which the monomers are connected by ester linkages.



$$nCH_3-\overset{OH}{\overset{|}{C}H}-CH_2-COOH + nCH_3-CH_2-\overset{OH}{\overset{|}{C}H}-CH_2-COOH \longrightarrow \left(-O-\underset{R}{\underset{|}{C}H}-CH_2-\underset{O}{\underset{\|}{C}}-O-\right)_n$$

PHBV

The properties of PHBV vary according to ratio of both the acids, 3-hydroxybutyric acid provides stiffness and 3-hydroxypentanoic acid provides flexibility to copolymer. It is used in speciality packaging, orthopaedic devices and even in controlled drug release.

PGA and PLA are used in sutures. Dextron was the first bioabsorbable suture made from biodegradable polyesters for post operation.

KNOW THE TERMS

- **Homopolymers :** The polymers formed by the polymerisation of single monomeric species are known as homopolymers.
- **Plasticizers :** These are the substances which are added in the formation of polymers in order to alter their physical properties.
- **PMMA :** It represents polymethylmethacrylate.
- **PAN :** It represents polyacrylonitrile.
- **PTFE :** It represents polytetrafluoroethene.
- **PCTFE :** It represents polymonochlorotrifluoroethene.

❒❒❒

Chapter 30

Chemistry in Everyday Life

» Revision Notes

- **Drugs or medicines :** Chemical substances used for treatment of diseases and for reducing pain are called drugs or medicines.
- **Analgesics :** These are the medicines which gives relief from pain. They are of two types :
  - **(a) Non-Narcotic (non-addictive) analgesics :** Aspirin, paracetamol, phenylbutazone or butazolidine are the common examples of this group. They are effective in relieving skeletal pain such as arthritis. Aspirin is the most common analgesic with antipyretic properties. It has also anti blood clotting action. It also reduces body temperature in fever.
  - **(b) Narcotic analgesics :** These are the drug which produce sleep and unconsciousness *e.g.*, opium, alkaloids like morphine, codeine, heroine, etc. In poisonous doses, they cause convulsions and ultimately death. These are mainly used for the relief of post opetitive pain, cardiac pains and pains of terminal cancer.
- **Tranquilizers :** These are neurologically active drugs also known as psychotherapeutic drugs, *e.g.*, vetonal, seconal, amytal, chlordiazepoxide, etc. These are used for the treatment of stress, mild and severe mental diseases.
- **Antiseptics :** These are the chemicals which prevent the growth of microorganisms or kill them but are not harmful to human beings. These are applied externally to the living, tissues such as wounds, cuts and diseased skin surfaces. *e.g.*, Dettol (chloroxylenol + α-terpineol), bithionol, furacin, tincture of iodine.
- **Disinfectants :** These are chemicals which kill microorganisms or prevent their growth but are not safe for human beings. These are applied on inanimate objects such as floors, drainage systems. Some substances can act as an antiseptic as well as disinfectant, by varying the concentration. *e.g.*, 0.2% solution of phenol is an antiseptic while its 1% solution is disinfectant.
- **Antimicrobials :** These are drugs which are used to cure diseases caused by a variety of microbes such as bacteria, fungi, virus etc. *e.g.*, antibiotic, antiseptic, disinfectants, etc.
- **Antibiotics :** These are chemical substances (prepared wholly or partially by chemical synthesis) which in low concentration, either kill or inhibit the growth of microorganisms. The antibiotics may be either bactericidal (kill the organisms in the body) *e.g.*, penicillin, ofloxacin, etc. or bacteriostatic (inhibit the growth of organisms), *e.g.*, erythromycin, chloramphenicol, etc.
- Penicillin is a narrow spectrum antibiotic whereas ampicillin and amoxicillin are wide spectrum antibiotics which exerts antimicrobial activity on more than one type of microorganisms.
- **Antifertility Drugs :** These are the chemical substances used to control the pregnancy in woman, *e.g.*, norethindrone and ethynylestradiol. These are essentially a mixture of estrogen and progesterone derivatives which are more potent than the natural hormones.
- **Antihistamines :** These drugs are also called anti allergic drugs. They prevent reactions by diminishing or abolishing the main actions of histamine released in the body. *e.g.*, diphenhydramine, ethinlyestradiol, etc.
- **Antacids :** An antacid is a substance that removes the excess of acid and the pH of stomach to appropriate level and give relief from acid indigestion, acidity, heat burns and gastric ulcers. *e.g.*, magnesium hydroxide, magnesium carbonate, sodium bicarbonate, etc.

Chemicals in Foods

- Chemicals are added to food for various purposes like, for preservation, for enhancing their appeal and for adding nutritive value, etc.
- **Preservatives :** Food preservatives are the substances which are capable of inhibiting or arresting the process of fermentation, acidification of the food. These are added to food materials in order to prevent their spoilage and to preserve them for a longer period. *e.g.*, sodium benzoate, sodium metabisulphite.

- Salting is also done to preserve food by adding sufficient amount of salt as it prevents the water from being available for microbial growth.
- **Antioxidants :** These are the chemical substances which prevent oxidation. These acts as a sacrificial materials as they are more reactive towards oxygen than the materials they are protesting.
- **Artificial sweetening agents :** These are the chemical compounds which are non-nutritive in nature and used as substituents for sugar in foods and beverages especially soft drinks. Some common artificial sweeteners are :
  - **(a) Saccharin :** It is useful as a sugar substitute for diabetic persons and those who need to control their caloric intake.
  - **(b) Aspartame :** It is methyl ester of dipeptide formed from aspartic acid and phenylamine. Aspartame is used only in cold foods and soft drinks as it is unstable at cooking temperature.
  - **(c) Alitame :** It is a high sweetener. The control of sweetness of food is difficult while using alitame.
  - **(d) Sucralose :** It is trichloro derivative of sucrose. It is stable at cooking temperature.

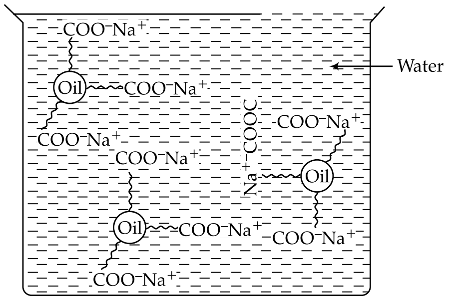
Cleansing Agent

- **Soaps :** Soaps are sodium or potassium salts of long chain fatty acids. It is prepared by a process called saponification in which fat reacts with alkali.
- **Action of soap on hard water :**
- Soaps give insoluble precipitate of magnesium and calcium soap in water.

$$\underset{\text{Soap}}{2C_{17}H_{35}COONa} + \underset{\substack{\text{Calcium Chloride}\\ \text{(in hard water)}}}{CaCl_2} \longrightarrow 2NaCl + \underset{\text{Insoluble Calcium Stearate}}{(C_{17}H_{35}COO)_2Cl}$$

- These insoluble soaps are useless as cleansing agent. Infect, there is a hindrance to good washing, because this precipitate adhered onto the fibers of the cloth as gummy mass hair washed with hard water looks dull because of this sticky precipitate. Dye does not absorb evenly on cloth washed with soap using hard water, because of this gummy mass.
- **Detergents :** These are soapless soaps and are used for cleaning purposes. It is of three types :
  - **(a) Anionic detergents :** These are sodium salts of sulphonated long chain alcohols or hydrocarbons. *e.g.*, sodium dodecylbenzene sulphonate. These are used in toothpaste and household works.
  - **(b) Cationic detergents :** There are quaternary ammonium salts of amines with acetates, chlorides or bromides e.g., cetyltrimethyl ammonium bromide. They have germicidal property.
  - **(c) Non-ionic detergents :** They do not contain any ion in their constitution. *e.g.*, liquid dishwash detergents.
- **Biodegradable detergents :** Detergents which contain straight chain hydrocarbons are biodegradable.
- **Non-Biodegradable detergents :** Detergents which have branched chain hydrocarbons are non-biodegradable and this leads to environmental pollution.
- **Cleansing action of soap and detergents :** Washing action of soap is due to the emulsification of grease and taking it away in the water along with dirt or dust present on grease.

  The cleansing action of soap can be explained keeping in mind that a soap molecule contains a non-polar hydrophobic group and a polar hydrophilic group. The dirt is held on the surface of clothes by oil or grease which is present. Since, oil, or dirt are not soluble in water, therefore, the dirt particles cannot be removed by simply washing the cloth with water. When soap is applied, the non-polar alkyl group dissolves in oil droplets while the polar —COO—Na$^+$ groups remain dissolved in water. In this way, each oil droplet is surrounded by negative charge. These negatively charged oil droplets cannot coalesce and a stable emulsion is formed. These oil droplets (containing dirt particles) can be washed away with water along with dirt particles.



❑❑❑