



LECTURE NOTE

DEPARTMENT OF HUMANITY

ENGINEERING CHEMISTRY

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SEMESTER-1ST

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Syllabus Th.2b. Engineering Chemistry (1st/ 2nd Semester Common)

Theory: 4 Periods per Week Total Periods: 60 Periods Examination: 3 Hours

I.A: 20 Marks Term End Exam: 80 Marks TOTAL MARKS: 100 Marks

Objective:

Engineering Chemistry is concerned with the changes of matters with its environment and an ever growing subject. So, the aim of teaching Engineering Chemistry in Diploma Courses is to acquaint the students with the basic Chemistry of different materials used in industry and to equip the students with the basic principles of chemical changes taking place in different aspects connected to engineering fields. They also develop the right attitude to cope up with the continuous flow of new technology.

SI. No	Topics/ Units	Periods
А	Physical Chemistry	22
В	Inorganic Chemistry	08
С	Organic Chemistry	10
D	Industrial Chemistry	20
	TOTAL	60

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A. PHYSICAL CHEMISTRY

Chapter 1: Atomic structure: Fundamental particles (electron, proton & neutron Definition, mass and charge). Rutherford's Atomic model (postulates and failure), Atomic mass and mass number, Definition, examples and properties of Isotopes, isobars and isotones. Bohr's Atomic model (Postulates only), Bohr-Bury scheme, Aufbau's principle, Hund's rule, Electronic configuration (up to atomic no 30).

Chapter 2: Chemical Bonding: Definition, types (Electrovalent, Covalent and Coordinate bond with examples (formation of NaCl, MgCl₂, H₂, Cl₂, O₂, N₂, H₂O, CH₄, NH₃, NH₄⁺, SO₂).

Chapter 3: Acid base theory: Concept of Arrhenius, Lowry Bronsted and Lewis theory for acid and base with examples (Postulates and limitations only). Neutralization of acid & base. Definition of Salt, Types of salts (Normal, acidic, basic, double, complex and mixed salts, definitions with 2 examples from each).

Chapter 4: Solutions: Definitions of atomic weight, molecular weight, Equivalent weight. Determination of equivalent weight of Acid, Base and Salt. Modes of expression of the concentrations (Molarity, Normality & Molality) with Simple Problems. pH of solution (definition with simple numerical) Importance of pH in industry (sugar, textile, paper industries only)

Chapter 5: Electrochemistry: Definition and types (Strong & weak) of Electrolytes with example. Electrolysis (Principle & process) with example of NaCl (fused and aqueous solution). Faraday's 1st and 2nd law of Electrolysis (Statement, mathematical expression and Simple numerical) Industrial application of Electrolysis- Electroplating (Zinc only).

Chapter 6: Corrosion: Definition of Corrosion, Types of Corrosion- Atmospheric Corrosion, Waterline corrosion. Mechanism of rusting of Iron only. Protection from Corrosion by (i) Alloying and (ii) Galvanization.

B. INORGANIC CHEMISTRY

Chapter 7: Metallurgy: Definition of Mineral, ores, gangue with example. Distinction between Ores and Minerals. General methods of extraction of metals,

i) Ore Dressing

ii) Concentration (Gravity separation, magnetic separation, Froth floatation & leaching)

iii) Oxidation (Calcinations, Roasting)

iv) Reduction (Smelting, Definition & examples of flux, slag)

v) Refining of the metal (Electro refining, & Distillation only)

Chapter 8: Alloys: Definition of alloy. Types of alloys (Ferro, Non-Ferro & Amalgam) with example. Composition and uses of Brass, Bronze, Alnico, Duralumin

C. ORGANIC CHEMISTRY

Chapter 9: Hydrocarbons: Saturated and Unsaturated Hydrocarbons (Definition with example) Aliphatic and Aromatic Hydrocarbons (Huckle's rule only). Difference between Aliphatic and aromatic hydrocarbons. IUPAC system of nomenclature of Alkane, Alkene, Alkyne, alkyl halide and alcohol (up to 6 carbons) with bond line notation. Uses of some common aromatic compounds (Benzene, Toluene, BHC, Phenol, Naphthalene, Anthracene and Benzoic acid) in daily life.

D. INDUSTRIAL CHEMISTRY

Chapter 10: Water Treatment: Sources of water, Soft water, Hard water, hardness, types of Hardness (temporary or carbonate and permanent or non-carbonate), Removal of hardness by lime soda method (hot lime & cold lime—Principle, process & advantages), Advantages of Hot lime over cold lime process. Organic Ion exchange method (principle, process, and regeneration of exhausted resins)

Chapter 11: Lubricants: Definition of lubricant, Types (solid, liquid and semisolid with examples only) and specific uses of lubricants (Graphite, Oils, Grease), Purpose of lubrication

Chapter 12: Fuel: Definition and classification of fuel, Definition of calorific value of fuel, Choice of good fuel. Liquid: Diesel, Petrol, and Kerosene --- Composition and uses. Gaseous: Producer gas and Water gas (Composition and uses). Elementary idea about LPG, CNG and coal gas (Composition and uses only).

Chapter 13: Polymers: Definition of Monomer, Polymer, Homo-polymer, Co-polymer and Degree of polymerization. Difference between Thermosetting and Thermoplastic, Composition and uses of Polythene, & Poly-Vinyl Chloride and Bakelite. Definition of Elastomer (Rubber). Natural Rubber (its drawbacks). Vulcanisation of Rubber. Advantages of Vulcanised rubber over raw rubber.

Chapter 14: Chemicals in Agriculture: Pesticides: Insecticides, herbicides, fungicides Examples and uses. Bio Fertilizers: Definition, examples and uses.

Syllabus Coverage up to I.A

Chapter 1,2,3,4,5,6

Books Recommended

1. Textbook of Intermediate Chemistry Part-1 and Part-2 by Nanda, Das, Sharma, Kalyani Publishers

- 2. Engg. Chemistry by B.K. Sharma, Krishna Prakashan Media Pvt. Ltd
- 3. Engineering Chemistry by Y.R. Sharma and P. Mitra, Kalyani Publishers
- 4. Engineering Chemistry for Diploma Dr. R K Mohapatra, PHI Publication, New Delhi.
- 5. Engineering Chemistry- Jain & Jain, Dhanpat Roy and Sons.

Engineering Chemistry Course Outcome

Sl. No.	Course Outcome
CO 1	Understand the constituent particles of different atoms, bond formation ability of elements and explain the structure of atoms and organic molecules.
C02	Express the concentrations of solutions in different modes and apply the knowledge of P^{H} in different manufacturing industries.
C03	Apply the knowledge of electrolysis in the field of industrial application like galvanization, electrolytic extraction of metals.
C04	Explain the process of metallurgical operation for the extraction of metals from ores and apply their knowledge for protection of different metals from corrosion.
C05	Develop innovative methods to produce soft water for industrial use and potable water at cheaper cost

CHAPTER - 1 ATOMIC STRUCTURE

Introduction:

According to *Dalton's Atomic theory* "Every matter is composed of very small particles called 'atoms' (Greek, a = cannot be; tom = cut) which cannot be further subdivided". But modern researches revealed that an atom is divisible and has a rather complex structure containing a large number of sub-atomic particles such as electrons, protons, neutrons, mesons, leptons, antiprotons, neutrinos, antineutrinos, positrons, quarks etc.

Fundamental Particles:

The sub-atomic particles 'electrons, protons and neutrons' are called fundamental particles of all matters.

Electron: Electron is a fundamental sub-atomic particle having negligible mass of 9.11 x 10 $^{-31}$ kg and carrying a charge of -1.602×10^{-19} Coulomb.

Proton: Proton is a fundamental sub-atomic particle having mass of 1.672×10^{-27} kg and carrying a charge of + 1.602×10^{-19} Coulomb.

Neutron: Neutron is a fundamental sub-atomic particle having mass of 1.675x10⁻²⁷ Kg and carrying no charge.

Fundamental Particle	Mass	Charge	Relative Charge		
Electron	9.11 x 10 ⁻³¹ Kg	- 1.602 x 10 ⁻¹⁹ Coulomb	- 1		
Proton	1.672 X 10 ⁻²⁷ Kg	+ 1.602 x 10 ⁻¹⁹ Coulomb	+1		
Neutron	1.675 X 10 ⁻²⁷ Kg	0	0		

<u>Rutherford's Gold-foil Experiment/Rutherford's α-scattering Experiment: (Discovery of Nucleus)</u>

In 1911, E. Rutherford gave the first information about the almost-correct-picture of an atom. He

bombarded a number of α particles (*He*²⁺ *ions*) emitting from a radioactive material like Uranium on a very thin gold foil. A circular zinc sulphide (**ZnS**) screen was provided at the back side of the gold foil in order to register the impressions made by the α -particles (Fig. 1.1).



Observations and Conclusions:

From the *a*- scattering experiment, Rutherford observed that:

- 1. Most of the α -particles went undeflected, i.e. they passed straight through the gold foil without any deviation. This clearly indicates that most of the parts of an atom are empty.
- **2.** A few α-particles were found to be deflected strongly from their normal paths. This indicates the presence of a heavy positively charged body inside the atom. This heavy positively charged body is called nucleus.
- **3.** A very few (0.01%) α -particles were found to be retracted their original paths (deflected through almost 180°). This indicates that the size of nucleus is very small. The size of atomic nuclei is of the order of 10⁻¹³ cm.

RUTHER FORD'S ATOMIC MODEL:

Based on the conclusions drawn from the α -scattering experiment, Rutherford proposed an atomic model, as follows:

- 1. An atom consists of two parts; they are (i) Nucleus and (ii) extra nuclear part.
- 2. Every atom consists of a very small but heavy positively charged body, called nucleus.
- 3. The whole mass of an atom is concentrated at the nucleus.
- 4. Electrons revolve around the nucleus with tremendous speed, like planets revolve around the sun. Therefore, the electrons are also called as planetary electrons.
- 5. The electrostatic force of attraction (acting inward) between the nucleus and electrons is balanced by the centrifugal force (acting outward) arising due to the motion of electrons. That is why electrons do not fall into the nucleus.

DRAWBACKS OR FAILURES OF RUTHERFORD'S ATOMIC MODEL:

1. Stability of Atom:

The theory fails to explain the stability of atoms. According to the law of electrodynamics (by Clark Maxwell), whenever a charged particle revolves around another charged particle, the revolving charged particle emits (loses) energy continuously (Fig. 1.2).

As the energy of the revolving electron decreases, it should be attracted towards the nucleus, and should follow a spiral path and ultimately fall into the nucleus. However, this never happens.

2. The model is silent about the definite energy and velocity possessed by the revolving electrons.

3. The theory fails to explain *atomic spectra*.



4. It fails to explain the cause of chemical combinations.

BOHR'S ATOMIC MODEL (THEORY)

An almost correct picture of atomic model was provided by a **Dutch physicist** *Niels Bohr* in 1913. The Bohr's Atomic model is based on 'Planck's Quantum Theory' and 'quantization of energy'.

Postulates of Bohr's atomic model:

- 1. Every atom consists of a heavy positively charged body at the centre called 'nucleus' and electrons revolve around the nucleus in certain permitted definite circular paths called 'shells', 'orbits' or 'stationary states'.
- 2. The stationary states or shells are designated as K, L, M, N, O.....etc. for 1st, 2nd, 3rd, 4th.....shells respectively.
- **3.** Each shell is associated with a certain definite quantity of energy. Hence the shells are also called as **'Energy levels'**.
- 4. The energy contents of various shells are compared by the formula:

$$\mathsf{E}_{\mathsf{n}} = - \frac{2\pi^2 m e^4 z^2}{n^2 h^2}$$

where, m = mass of an electron

e = charge of electron z = Atomic number n = No. of shell or principal quantum number (1,2,3.....)

 $h = Planck's constant = 6.625 \times 10^{-27} erg sec.$

$$E_n = -\frac{1312}{n^2} KJ / Mol,$$
 for Hydrogenatom

5. The energy content increases on moving from lower to higher shells and become zero for the shell which is present at an infinite distance from the nucleus.

6. The energy levels are not equally spaced (Fig. 1.3).

7. Through a large number of concentric circles are possible around the nucleus, only those circular paths are allowed for the electrons to revolve for which the **angular momentum** value (mvr) is a whole number

multiple of
$$\frac{h}{2\pi}$$
, that is
mvr = n $\frac{h}{2\pi}$, where n = 1, 2, 3,....

Here, m = mass of the electron,

v = tangential velocity of the revolving electron,

.

r = radius of the orbit.

h = Planck's constant,

8. When the electrons in an atom are in their normal energy state (ground state), they keep on revolving in their respective orbits without losing energy.

9. When external source of energy is supplied to an atom, the electrons jump from lower ground states to the higher excited





states by absorbing energy. Electrons in the excited states are unstable and jump back to the lower ground states by releasing energy. The energy thus released appears in the form of light which is the origin of spectral lines (Fig. 1.4).

Failures of Bohr's Atomic Model:

- 1. According to Bohr's atomic model, the path followed by electrons is two-dimensional circular. But modern researches (Heisenberg's Uncertainty Principle) revealed that electrons revolve in three-dimensional paths called orbitals.
- 2. It fails to explain the spectra of multi-electron species.
- 3. It fails to explain the relative intensities of spectral lines.
- 4. It fails to explain the splitting up of spectral lines when exposed to electric field (Stark Effect) and magnetic field (Zeeman Effect).
- 5. It fails to explain the cause of chemical combinations.

BOHR-BURY SCHEME:

Bohr-Burry scheme deals with the arrangement of electrons in various shells. Various postulates of the scheme are:

1. A shell can contain a maximum $2n^2$ number of electrons. Where n = number of the shell.

Shell	n	Maximum No. of Electrons = $2n^2$					
к	1	$2 \times 1^2 = 2$					
L	2	$2 \times 2^2 = 8$					
М	3	2 x 3 ³ = 18					
Ν	4	2 X 4^4 = 32, and so on.					

- 2. The outer most shell (valence shell) of an element cannot hold more than '8' electrons.
- **3.** The penultimate shell (the shell just before the outer most shell) cannot hold more than '18' electrons.
- 4. A higher orbit may start filling before the lower orbit is completely filled.

Arrangements of electrons in different orbits of some elements according to the Bohr-Bury scheme are given below:

Element	Electrons in							
	K- Shell	L-Shell	M-Shell	N-Shell				
₁H	1							
₂ He	2							
₃ Li	2	1						
₄ Be	2	2						
₅B	2	3						
10 Ne	2	8						
₁₁ Na	2	8	1					
₁₂ Mg	2	8	2					

₁₃ AI	2	8	3	
₁₈ Ar	2	8	8	
₁₉ K	2	8	8	1
₂₀ Ca	2	8	8	2
21 Sc	2	8	9	2

<u>Atomic Number(Z)</u>: The total number of protons present in one atom of an element is called its atomic number.

Atomic Number = No. of Protons (p)

For Examples:

Element	No of Protons (p)	Atomic No. (Z)
Carbon (C)	6	6
Nitrogen (N)	7	7
Oxygen (O)	8	8

Mass Number (A): The total number of protons and neutrons present in one atom of an element is called its mass number.

Mass Number (A) = No. of Protons (p) + No. of Neutrons (n)

Element	No of Protons (p)	No. of Neutrons (n)	Mass No. (A)
Carbon (C)	6	6	12
Nitrogen (N)	7	7	14
Sodium (Na)	11	12	23



Note: A – ne⁻ \rightarrow Aⁿ⁺ Example: Mg – 2e⁻ \rightarrow Mg²⁺

A + ne⁻ \rightarrow Aⁿ⁻ Example: N + 3e⁻ \rightarrow N³⁻

Assignment:

Q. Find the no. of protons, electrons and neutrons in the following.

Atom/Molecule/Ion	Р	е	n
0			
Р			
N ^{3 –}			

Ca ²⁺		
NH ₃		
H ₂ O		
NH₄ ⁺		
CO		
CO ₂		

Isotopes: Isotopes are the atoms of the same element having the same atomic number but different mass numbers.

Examples: Hydrogen has three isotopes: Protium (${}^{1}_{1}H$), Deuterium (${}^{2}_{1}H$) and Tritium (${}^{3}_{1}H$) Similarly, ${}^{35}_{17}Cl$ and ${}^{37}_{17}Cl$ Properties of Isotopes:

- > These are atoms of the same element.
- > These have the same atomic no. but different mass number.
- > These have the same no. of protons and electrons.
- > These differ in their no. of neutrons.
- > These have similar chemical properties.
- > These have different physical properties such as m.pt., b.pt, density, viscosity, etc.

Isobars: Isobars are the atoms of different elements having the same mass number but different atomic numbers.

Examples: ${}^{40}_{18}Ar$ and ${}^{40}_{20}Ca$

Properties of Isobars:

- > These are atoms of different elements.
- > These have the different atomic no. but same mass number.
- > These have the different no. of protons and electrons.
- > These have different chemical properties.
- > These have different physical properties such as m.pt., b.pt, density, viscosity, etc.

Isotones: Isotones are the atoms of the elements having the same no of neutron.

Examples: ${}^{23}_{11}Na$ and ${}^{24}_{12}Mg$ ${}^{27}_{13}Al$ and ${}^{28}_{14}Si$ ${}^{31}_{15}P$ and ${}^{32}_{16}S$

Note: The subatomic particles (protons and neutrons) present inside the nucleus are collectively called as nucleons.

Aufbau Principle:

The word "Aufbau" means "building up". This principle describes how the subs-hells are filled with electrons.

Aufbau principle may be stated as "electrons are filled in different sub-shells in order of their increasing energy content".

The sub-shell with lowest energy is filled with electron first and those with higher energies are filled with electrons later. The energy content of the various sub-shells can be compared by

(n+ /) rule.

<u>The (n + /) Rule:</u>

- i. The sub-shell having lower (n+ /) value possesses lower energy and is filled first.
- ii. If the (n + *l*) value for two given sub-shells are equal, then the one with lower value of 'n' possesses lower energy and is filled first.

Following the (n+*I*) rule, let us compare the energy possessed by various sub-shells.

Sub- shell→	1s	2s	2р	3s	3р	3d	4s	4р	4d	4f	5s	5р
(n+/)	1+0	2+0	2+1	3+0	3+1	3+2	4+0	4+1	4+2	4+3	5+0	5+1
	=1	=2	=3	=3	=4	=5	=4	=5	=6	=7	=5	=6

Hence the increasing order of energy content of sub-shells is

1s < 2s < 2p < 3s < 3p < 4s < 3d < 4p < ...



ELECTRONIC CONFIGURATIONS: -

Electronic configuration is the arrangement of electrons of an atom in different sub-shells/orbitals in the increasing order of their energy content. The electronic configurations of some elements are given below:

Elements	Electronic configurations	Elements	Electronic configurations
₁H	1s ¹	₁₆ S	1s² 2s²2p ⁶ 3s²3p ⁴
₂ He	1s ²	17 CI	1s² 2s²2p ⁶ 3s²3p ⁵
₃ Li	1s ² 2s ¹	₁₈ Ar	1s² 2s²2p ⁶ 3s²3p ⁶
4Be	1s ² 2s ²	19 K	1s ² 2s ² 2p ⁶ 3s ² 3p ⁶ 4s ¹
5B	1s ² 2s ² 2p ¹	₂₀ Ca	1s ² 2s ² 2p ⁶ 3s ² 3p ⁶ 4s ²
^{6}C	1s ² 2s ² 2p ²	₂₁ Sc	1s ² 2s ² 2p ⁶ 3s ² 3p ⁶ 4s ² 3d ¹
7 N	1s ² 2s ² 2p ³	₂₂ Ti	1s² 2s²2p ⁶ 3s²3p ⁶ 4s²3d ²
O ₈	$1s^2 2s^2 2p^4$	₂₃ V	1s ² 2s ² 2p ⁶ 3s ² 3p ⁶ 4s ² 3d ³
₉ F	1s ² 2s ² 2p ⁵	₂₄ Cr	1s² 2s²2p ⁶ 3s²3p ⁶ 4s¹3d ⁵
10 Ne	1s ² 2s ² 2p ⁶	₂₅ Mn	1s ² 2s ² 2p ⁶ 3s ² 3p ⁶ 4s ² 3d ⁵
11 Na	1s ² 2s ² 2p ⁶ 3s ¹	₂₆ Fe	1s² 2s²2p ⁶ 3s²3p ⁶ 4s²3d ⁶

12 Mg	1s ² 2s ² 2p ⁶ 3s ²	27 C 0	1s ² 2s ² 2p ⁶ 3s ² 3p ⁶ 4s ² 3d ⁷
₁₃ AI	1s ² 2s ² 2p ⁶ 3s ² 3p ¹	28 Ni	1s² 2s²2p ⁶ 3s²3p ⁶ 4s²3d ⁸
14Si	1s ² 2s ² 2p ⁶ 3s ² 3p ²	29 Cu	1s ² 2s ² 2p ⁶ 3s ² 3p ⁶ 4s ¹ 3d ¹⁰
15 P	1s ² 2s ² 2p ⁶ 3s ² 3p ³	₃₀ Zn	1s ² 2s ² 2p ⁶ 3s ² 3p ⁶ 4s ² 3d ¹⁰

Exceptional Electronic Configuration: Some elements like 'Cr' and 'Cu' show exceptional electronic configurations.

The electronic configurations of 'Cr' & 'Cu' should be:

 ${}_{24}Cr = [Ar]4s^23d^4 \& {}_{29}Cu = [Ar]4s^23d^9$ respectively.

But the actual electronic configurations are

 $_{24}$ Cr = [Ar] $4s^{1}3d^{5}$ & $_{29}$ Cu = [Ar] $4s^{1}3d^{10}$

The exceptional electronic configuration is due to the fact that half-filled and ful-filled orbitals are more stable due to the orbital symmetry and exchange energy.

Assignment:

Q 1. Write down the electronic configurations of the following: O²⁻, Ca²⁺, P³⁻, Ti²⁺, Cr³⁺, Cu²⁺.

Q 2. Arrange the following sub-shells in the increasing order of their energy content: 3d, 5p, 4s, 4p, 6s, 4d.

Q 3. What is (n+I) rule? Which out of 4s and 3d sub-shells has lower energy?

Q 4. What do you mean by 3d²?

Hund's Rule: -

Hund's rule may be stated as "**Pairing of electrons do not take place in the degenerate orbitals of** *p*, *d*, and *f*-sub shells until each degenerate orbital in the given sub-shell contains one electron."

The above is due to the reason that electrons being identical in charge repel each other when present in the same orbital. This repulsion can, however, be minimized if two electrons move as far apart as possible by occupying different degenerate orbitals.

Let us consider the electronic configurations of the following elements.

In case of boron the 5th electron is occupied by the $2p_x$ orbital. In carbon the 6th electron will not be

paired with the electron of the $2p_x$ orbital, rather it will be occupied by the $2p_y$ orbital. Similarly, in case of nitrogen all the 2p – electrons will remain unpaired. The rule is also called 'maximum multiplicity rule' because the total spin value of all the electrons of degenerate orbitals of a given sub-shell becomes maximum if they are arranged as per Hund's rule.

<u>NOTE</u> :- Degenerate orbitals are the orbitals having same or nearly same energy content. For example $2p_x$, $2p_y$, $2p_z$ are degenerate orbitals.

Assignment

Q 1. How many vacant orbitals are there in C, O, P and Ti?

Q 2. How many unpaired electrons are there in N, F, Fe and Na⁺?



Exercise

(02 Marks Questions)

- 1. What are fundamental sub-atomic particle?
- 2. Write any two drawbacks of Rutherford's atomic model.
- 3. What are the results of Rutherford's gold foil experiment?
- 4. What do you mean by quantization of energy?
- 5. What do you mean by the stationary states of atoms?
- 6. How electronic transition occurs according to Bohr's atomic model?
- 7. What is the origin of spectral lines according to Bohr's atomic model?
- 8. Which circular orbits are allowed for the electrons to revolve?
- 9. Arrange the following in the increasing order of their energy content: 4f, 5p, 6s, 4p, 3d.
- 10. Write down the electronic configurations of Cr and Cu.
- 11. Write down the electronic configurations of Ca²⁺ and O $^{2-}$.
- 12. Write down the electronic configurations of Mg^{2+} and N^{3-} .
- 13. Write down the electronic configurations of Mn^{2+} and Cu .
- 14. Write down the electronic configurations of Cr^{3+} and Fe^{2+} ions.
- 15. Define mass number. How many protons, electrons and neutrons are present in an ion of N³⁻?
- 16. Define isotope with suitable example.
- 17. Define isotope. What are the isotopes of chlorine?
- 18. Define isobar with a suitable example.
- 19. Define isotone with a suitable example.

(05 Marks Questions)

- 1. Explain the Discovery of atomic nuclei.
- 2. Explain Rutherford's atomic model.
- 3. Explain the failures of Rutherford's atomic model.

Write down the postulates of Bohr-Bury Scheme.

- 4. Define and explain Aufbau principle. Write down the electronic configuration of manganese.
- 5. How did Bohr overcome Rutherford's atomic model?
- 6. Define and explain Hund's rule of maximum multiplicity.
- 7. Explain electronic transition according to Bohr's atomic theory.
- 8. Explain the origin of atomic spectral lines.



CHAPTER - 2 CHEMICAL BONDING

Definition of Chemical bonding: The force of attraction which holds together the constituent atoms in a molecule or ion is called chemical bond.

Types of Chemical Bonding:

Depending upon the mode of bond formation (transfer or sharing of electrons), chemical bonding may be classified into the following types:

- 1. Ionic Bonding or Electrovalent bonding
- 2. Covalent bonding
- 3. Co-ordinate bonding or Dative Bonding
- 4. Hydrogen bonding
- 5. Metallic bonding

IONIC OR ELECTROVALENT BONDING:

"The chemical bond which is formed by the complete transfer of one or more valance electrons from one atom to another is called ionic or electrovalent bond and the compound formed is called ionic compound or electrovalent compound".

The number of electrons lost or gained by an atom during ionic bond formation is called its electrovalency. **Features of Ionic bond:** The formation of ionic bond involves:

Termetien of a positive ion bulless of electron /s from one bind of

- Formation of a positive ion by loss of electron/s from one kind of atom.
 Formation of a negative ion by gain of electron/s from another kind of atom.
- Formation of a negative for by gain of electroni/s from another kind of at Electrostatic force of attraction between the appealitely abarged ions.

Electrostatic force of attraction between the oppositely charged ions.

Conditions for the formation of Ionic bond:

- **1.** *Nature of element:* Atoms of different elements form ionic bonds. Atoms of the same element never form *ionic bond*.
- 2. Low lonization potential: Ionization potential of an element is the quantity of energy required to remove one valence electron from an isolated, neutral, gaseous atom. One of the combining atoms should have low IP. The elements of Gr 1 and Gr 2 of the modern periodic table have low ionization potentials; and hence they can form *ionic bonds*.
- 3. High Electron Affinity: It is the amount of energy released when an extra electron is added to an isolated, neutral, gaseous atom. Another participating atom should have high electron affinity. The elements of Gr 16 and Gr 17 of the modern periodic table have high electron affinities; and hence they can form *ionic bonds*.
- **4. High Lattice Energy:** The quantity of energy involved during the formation of or breaking of one mole of an ionic bond is called lattice energy. Higher is the lattice energy more is the stability of the ionic compound. Thus, the lattice energy of ionic compounds should be high.

Example: I: Formation of NaCI.

The electronic configurations of Na and Cl are given below:

₁₁Na – 1s²2s²2p⁶3s¹ ₁₇C/ – 1s²2s²2p⁶3s²3p⁵ The electronic configurations indicate the presence of one and seven valence electrons in sodium and chlorine respectively. During the formation of NaC*I*, the sodium atom donates its valence electron completely to the chlorine atom (Fig. 2.1). Na becomes Na⁺ with 8 electrons in valence shell and attains the nearest noble gas configuration of Ne; while C*I* atom becomes CI^- ion with '8' electrons in valence shell and attains the nearest noble gas configuration of Ar.





Now the electrostatic force of attraction between the oppositely charged ions Na⁺ and Cl⁻⁻ results in the formation of **NaCl**.

Example :II : Formation of MgCl₂

The electronic configurations of Mg and Cl are given below:

12Mg - 1s²2s²2p⁶3s²

17C/-1s²2s²2p⁶3s²3p⁵

An atom magnesium and chlorine contain 2 and 7 valence electrons respectively. During the formation of $MgCl_2$, one of the valence electrons of Mg is completely transferred to one atom of chlorine

while the second valence electron is transferred to another atom (Fig. 2.2). Now Mg becomes Mg^{2+} with **8** valence electrons, with electronic configuration similar to that of Neon. On the other hand, each chlorine atom after accepting an electron becomes CI^- ion with 8 valence electrons, acquiring electronic configuration similar to that of Argon.



The electrostatic force of attraction between calcium and chloride ions results in the formation of MgC*I*₂.

Other examples of ionic compounds: KCl, KBr, KI, CaF₂, CaBr₂, CaI₂, Na₂O, K₂O, CaO, MgO, Na₂S, K₂S etc.



Figure: 2.2

Characteristics of ionic compounds: Ionic compounds possess the following characteristic properties.

- 1. These exist in solid states.
- 2. These are hard and rigid.
- 3. These are crystalline in nature.
- **4.** These have high melting and boiling point.
- 5. These have high densities.
- **6.** These are soluble in polar solvents like water, but are insoluble in non-polar solvents like CCl_4 , ethers, benzene, toluene [$C_6H_5 CH_3$], petrol, diesel, kerosene, etc.
- **7.** These are bad conductor of electricity in solid states, but are good conductor in molten, fused or solution state.
- 8. These do not show isomerism.
- 9. These are polar in nature.

COVALENT BOND:

The chemical bond formed by the mutual (equal) sharing of valence electrons between two atoms is called covalent bond and the compound formed is called covalent compound.

The number of electrons shared by an atom during covalent bond formation is called **covalency**. A covalent may be formed between the atoms similar or dissimilar elements. When two, four and six electrons are shared between two atoms, then a single, double and a triple bond are formed respectively.

Example : I : Formation of H₂ molecule. The electronic configuration of 'H' is **1^H - 1s**¹

The electronic configuration indicates the presence of 1



valence electron in 'H' and requires one more electron to become duplet. Thus, each hydrogen atom shares its electron with each other to form a covalent bond (Fig. 2.3).

Example : 2 : Formation of Cl₂ molecule.

The electronic configuration of 'Cl' is

17C/-1s²2s²2p⁶3s²3p⁵

The electronic configuration indicates the presence of 7 valence electrons in 'Cl' and requires one more electron to become octet. Thus, each chlorine atom shares one of its valence electrons with each other to form a covalent bond (Fig. 2.4).





Example :3 : Formation of O₂ molecule.

The electronic configuration of 'O' is

80-1s²2s²2p⁴

The electronic configuration indicates the presence of 6 valence electrons in 'O' and requires two more electrons to become octet. Thus, each oxygen atom shares two of its valence electrons with each other to form a double covalent bond (Fig. 2.5).



OR O = 0: Be Be Oxygen molecule

Example : 4 : Formation of N₂ molecule.

The electronic configuration of 'N' is

7N-1s²2s²2p³

The electronic configuration indicates the presence of 5 valence electrons in 'N' and requires three more electrons to become octet. Thus, each nitrogen atom shares three of its valence electrons with each other to form a triple covalent bond (Fig. 2.6).



Example : 5 : Formation of H_2O molecule.

The electronic configuration of 'O' and 'H' are:

80-1s²2s²2p⁴

1^H - 1s¹

The electronic configurations indicate the presence of 6 and 1 valence electrons in 'O' and 'H' respectively. The central 'O' atom requires two more electrons to become octet while each hydrogen atom needs one electron to become duplet. Thus, each hydrogen atom shares its valence electron with the valence electrons of oxygen to form covalent bonds (Fig. 2.7). The shape of water molecule is bent shape or 'V' shape with bond angle 104.5^o.



Example: 6: Formation of methane (CH₄) molecule.

The electronic configuration of 'C' and 'H' are

6^C - 1s²2s²2p² 1^H - 1s¹ The electronic configurations indicate the presence of 4 & 1 valence electrons in 'C' & 'H' respectively. Thus, the central carbon atom requires four more electrons to become octet and 'H' requires 1 more electron to become duplet.

Thus, each hydrogen atom shares its electron with one valence electron of carbon to form four single covalent bonds. By sharing an electron each hydrogen atom becomes duplet while carbon becomes octet. The shape of CH_4 is tetrahedral with a bond angle of 109^028 (Fig. 2.8)['].



Example: 7: Formation of ammonia (NH₃) molecule.

The electronic configuration of 'C' and 'H' are

₇N - 1s²2s²2p³ ₁H - 1s¹

The electronic configurations indicate the presence of 5 & 1 valence electrons in 'N' & 'H' respectively. Thus, the central nitrogen atom requires three more electrons to become octet and each 'H' atom requires 1 more electron to become duplet.





Thus, each hydrogen atom shares its valence electron with one valence electron of nitrogen to form three single covalent bonds (Fig. 2.9). The shape of NH_3 is pyramidal with a bond angle of 107^0 .

Other examples of covalent compounds: , F₂, Br₂, I₂, BF₃, AlCl₃, HCl, HF, SiO₂, etc.

Characteristics of Covalent Compounds:

- 1. These may exist in all the three states of matter i.e. solid, liquid and gaseous states.
- 2. These are generally soft.
- 3. These are non-crystalline in nature.
- **4.** These are generally insoluble in polar solvent like water, but are soluble in non-polar solvents such as CCl₄, ethers, benzene, toluene, petrol, diesel, kerosene, etc.
- 5. These have low melting and boiling points.
- 6. These have low densities.
- 7. These are bad conductor of heat and electricity.
- 8. These compounds may show isomerism.
- 9. These are generally non-polar.

CO-ORDINATE BOND:

The chemical bond formed by the partial donation and partial sharing of a lone pair of electrons between two atoms (or ions) is called a co-ordinate or dative bond.

Conditions for the formation of co-ordinate or Dative bond:

- i. One of the participating atoms should have at least one lone or unshared pair of electrons.
- ii. The other atom should be in short of a pair of electrons than the nearest inert gas element.

The lone pair of electrons present over one atom is partially shared by both the combining atoms. A co-ordinate bond is represented by an arrow (\rightarrow) sign, the head of which points towards the acceptor atom, while the tail points towards the donor atom.

Since co-ordinate bond has some polar character, it is also known as dative or semi-polar bond or coionic bond.



Example: 1: Formation of ammonium ion (NH₄⁺).

Ammonium ion (NH_4^+) is formed by the combination of NH_3 and H^+ ion.

 $NH_3 + H^+ \rightarrow NH_4^+$

Ammonia (NH₃) contains a lone pair of electrons over 'N' while 'H⁺' ion contains no electron and requires two electrons to become duplet.

Thus, the unshared pair of electrons over nitrogen in NH_3 is partially

shared with H⁺ ion and a Co-ordinate bond is formed (Fig. 2.11).



Example: 2: Formation of Sulphur dioxide (SO₂) molecule.

The electronic configurations of 'S' and 'O' are

80-1s²2s²2p⁴

The electronic configurations indicate the presence of 6 valence electrons in each of 'S' & 'O'. the central sulphur atom forms a double covalent by sharing two of its valence electrons with two valence electrons of one of the oxygen atoms. One of the lone pair of electrons of the central sulphur atom is partially shared with another oxygen atom to form a co-ordinate bond (Fig. 1.12).



Characteristics of Coordinate Compound:

- i. These bonds are rigid and directional.
- ii. Coordinate bonds do not ionise in a state of fusion of solution.
- iii. They are usually insoluble in water but dissolve in non-polar solvents.
- iv. Their melting and boiling points are higher than those of covalent compounds and lower than those of ionic compounds.
- v. These are semi-polar, that is more polar than covalent compounds and less polar than ionic compounds.
- vi. They show isomerism.

Lewis Structure:

A **Lewis Structure** is a simple representation of the valence shell electrons in a molecule. It is used to show how the electrons are arranged around individual atoms in a molecule. Electrons are shown as "dots" or for bonding electrons as a line between the two atoms. For examples:



Assignment

Q. Draw the Lewis structures of the following: MgCl₂, O₂, N₂, SO₂, NH₄⁺ and H₃O⁺.

Exercise

(02 Marks Questions)

- 1. Define chemical bonding.
- 2. Define electrovalent bonding.
- 3. Define covalent bonding.
- 4. Define co-ordinate bonding.
- 5. What is Lattice energy? How is it related with the strength of an ionic bond?
- 6. Mention the conditions for formation of electrovalent bonding.
- 7. Mention the conditions for formation of co-ordinate bonding.
- 8. Define ionization potential. What should be the value of it for the metals to form ionic bond?
- 9. Define electron affinity. What should be the value of it for the metals to form ionic bond?
- 10. Which types of chemical bondings exist in $MgCl_2$ and NH_3 ?
- 11. Which types of chemical bondings exist in MgCl₂ and H₂O?

(05 Marks Questions)

- 1. Define and explain electrovalent bonding with a suitable example.
- 2. Define and explain covalent bonding with a suitable example.
- 3. Define and explain co-ordinate bonding with a suitable example.
- 4. Explain the formation of NH_3 and NH_4^+ .
- 5. Explain the conditions of formation of electrovalent bond.
- 6. Explain the conditions of formation of co-ordinate bond.
- 7. Define covalent bond. Explain the formation of CH_4 molecule.
- 8. Define covalent bond. Explain the formation of H_2O molecule.
- 9. Define covalent bond. Explain the formation of O_2 molecule.
- 10. Define covalent bond. Explain the formation of $N_{\rm 2}$ molecule.
- 11. Define covalent bond. Explain the formation of $\ensuremath{\mathsf{NH}}_3$ molecule.
- 12. Define electrovalent bonding. Explain the formation of $MgCl_2$ molecule.
- 13. Define and explain co-ordinate bonding and explain the formation of NH_4^+ ion.
- 14. Define and explain co-ordinate bonding and explain the formation of SO₂ molecule.
- 15. Write down at least ten properties of ionic compounds.
- 16. Write down at least ten properties of covalent compounds.

<u>CHAPTER - 3</u> ACID – BASE THEORIES

Introduction:

There are many practical methods to identify a substance as an acid or a base. The practical methods include use of p^{H} meter, indicator, litmus paper, chemical reactions, etc. However, theoretically it is now possible to know whether a substance is acid or a base. Accordingly, three theories have been proposed by different chemists. They are:

- 1. Arrhenius Theory
- 2. Lowery Bronsted Theory
- 3. Lewis Theory.

ARRHENIUS THEORY:

According to Arrhenius theory, "Acids are the substances which produce H^+ ions (protons) in aqueous solution while bases are the substances which produce OH^- ions in aqueous solution."

Example of Acid: HCI \xrightarrow{water} H⁺(aq) + Cl⁻(aq)

Other examples of acids are: HNO₃, H₂SO₄, CH₃COOH, etc.

Examples of Bases: NaOH_(s) \xrightarrow{water} Na⁺(aq) + OH⁻(aq)

Other examples of bases are: LiOH, KOH, NH4OH, Ca(OH)2, AI(OH)3, etc

Salient Features:

i. According to Arrhenius theory an acid reacts with a base to form salt and water and the reaction is called **<u>neutralization reaction</u>**.

HC/	+	NaOH	\rightarrow	NaC/	+	H ₂ O
(Acic	1)	(Base)		(Salt)		(Water)

Neutralization reaction may be represented as:

H ⁺ (aq)	+	OH [_] _(aq) →	H ₂ O _(/)
(from acid)		(from base)	

ii. Higher is the degree of dissociation higher is the acidic or basic nature of the substance.

Limitations:

i. H^+ ion does not exist in aqueous solution. It combines with H_2O , as soon as its formation to give hydronium ion (H_3O^+).

 $H^+ + H_2O \rightarrow H_3O^+$

- ii. The theory fails to explain the acidic and basic nature of the substances in solvents other than water.
- iii. The theory fails to explain the acidic nature of the substances like SO₂, CO₂, SiO₂, P₂O₅, BF₃, AlCl₃, etc. which cannot provide H⁺ ions.

- **iv.** The theory fails to explain the basic nature of the substances like NH₃, PH₃, Na₂O, K₂O, CaO etc. which can't provide OH⁻ ions.
- v. The theory fails to explain neutralization reactions between some acidic and basic substances which do not produce water. $HCI + NH_3 \rightarrow NH_4CI$

2. BRONSTED - LOWRY THEORY:

According to Bronsted-Lowry theory "Acids are the substances (molecules/ions) which donate a proton (H^+ ion) to any other substance, while bases are the substances (molecules/ions) which accept a proton (H^+ ion) from any other substance".

In other words, acids are proton donors whereas a bases are proton acceptors. For example:



Since, HC/ has donated a proton (to NH_3), it acts as an acid. On the other hand, NH_3 has accepted a proton from HC/ and thus it acts as a base.

Other examples of Acids are:

- i. All Arrhenius acids are Bronsted-Lowry acids; (HCI, HNO₃, H₂SO₄, H₃PO₄, CH₃COOH, H₂CO₃ etc.), however the reverse is not true.
- ii. Ions having capacity to donate H^+ ion: (HS⁻, HCO₃⁻, HPO₄^{2⁻}, HSO₄⁻ etc.)

Examples of Bases:

- i. Natural molecules such as: H₂O, NH₃, RNH₂, PH₃, AsH₃, etc.
- ii. Ions having capacity to accept H^+ ion, like OH^- , CN^- , HCO_3^- , etc.

Salient Features:-

i. According to this theory an acid reacts with a base to form **another pair of acid and base**. For example:



The pair of acid and base which differ by a proton (H^+ ion) is called a conjugate acid-base pair.

Acid $-H^+ \rightarrow$ Conjugate base

Base + $H^+ \rightarrow Conjugate acid$

ii. The substances such as H₂O, HS⁻, HCO³⁻, HPO₄²⁻, HSO₄⁻, etc. which act as both acid (proton donor) as well as base (proton acceptor) are called amphoteric substances.

iii. Stronger is an acid weaker is its conjugate base and vice versa.

[Strong acid]

[Weak base]

Limitations of the theory:

- i. It fails to explain the acidic nature of the substances, such as SiO_2 , CO_2 , SO_2 , BF_3 , etc. which cannot donate H⁺ ion.
- **ii.** It fails to explain the basic nature of the substances, such as Na₂O, K₂O, CaO etc. which cannot accept H⁺ ion.
- iii. It fails to explain the reaction between some acids and bases which do not give another pair of acid and base. Example: HCl + NaOH \rightarrow NaCl + H₂O.

Note: Some conjugate acid-base pairs are given below:

Acid	Conjugate- Base	Base	Conjugate- Acid
HCI	CI -	Br –	HBr
H_2SO_4	HSO ₄ -	CN ⁻	HCN
HS ⁻	S ²⁻	0 ² -	он -
NH_4^+	NH ₃	NH_3	NH4 ⁺
H ₂ O	OH-	H ₂ O	H ₃ O+

Assignment:

Q 1. What are the conjugate bases of the following acids?

HCN, H_2CO_3 , H_3PO_3 , CH_3COOH , H_2O

Q 2. What are the conjugate acids of the following bases?

 CH_3NH_2 , $(C_2H_5)_2NH$, NO_3^- , NH_3

3. LEWIS THEORY: -

According to Lewis theory "Acids are the substances (molecules/ions) which can accept a pair of *electrons* from any other substance, while bases are the substances (molecules/ions) which can donate a pair of electrons to any other substance."

In other words, acids are electron acceptors while bases are electron donors.

Examples of acids: -

- i. Cations like: CH_3^+ , H^+ , etc.
- Neutral molecules containing electron deficient atoms are Lewis acids. For example: BF₃, AlCl₃, FeCl₃, ZnCl₂, etc.
- iii. Neutral molecules containing vacant d-orbitals in the central atom for the accommodation of incoming electrons act as Lewis acids. For example: SiF_4 , $SiCl_4$, etc.
- iv. The molecules having multiple bonding (= or \equiv) between the atoms of different elements are acidic in nature. For example: CO₂ (O = C = O), SO₂, etc.

Examples of Bases: -

- i. All anions are Lewis bases: F^- , CI^- , CO_3^{2-} , etc.
- ii. Neutral molecules containing, at least one lone pair of electrons are Lewis bases: Examples: NH₃, PH₃, H₂O, etc.

Salient Features:

i. According to this theory, an acid reacts with a base to form a co-ordinate or dative bond. For example, the reaction between NH₃ (Lewis base) and H⁺ (Lewis acid) results in the formation of a dative bond.



All Bronsted- Lowery bases are Lewis bases while the reverse is not always true.

Limitations:

- i. According to this theory, the reaction between an acid and base results in the formation of a dative bond. Formation of a coordinate bond is a slow process. While the reactions between the acids and the bases are instantaneous or fast.
- ii. The theory fails to explain the relative strengths of different acids and bases.
- iii. It fails to explain reaction between some acids and bases where no coordinate bond is formed.
- iv. It fails to explain the acidic nature of well-known acids like HCl, HNO₃, H₂SO₄, etc. which cannot accept electrons.
- v. It fails to explain the basic nature of well-known bases like NaOH, KOH, etc. which cannot donate electrons.
- vi. It fails to explain acid-catalyzed reactions, where H⁺ ion plays important role.

Neutralization of Acids and Bases:

According to Arrhenius Theory, acid react with bases to form salt and water. This type of reaction is called *neutralization reaction*. Neutralization reaction may take place as follows:

1. Neutralization between a Strong Acid and a Strong Base: A strong acid reacts with a strong base to form a simple or normal salt. Its aqueous solution has a p^H of about 7 and is neutral.

Example: HCI + NaOH \rightarrow NaCl + H₂O

2. Neutralization between a Strong Acid and a weak Base: A strong acid reacts with a weak base to form a acidic salt. Its aqueous solution has a $p^{H} < 7$ and the solution is acidic.

Example: HCl + NH₄OH \rightarrow NH₄Cl + H₂·O

 Neutralization between a Weak Acid and a Strong Base: A weak acid reacts with a strong base to form a basic salt. Its aqueous solution has a p^H > 7 and is alkaline.

Example: $CH_3COOH + NaOH \rightarrow CH_3COONa + H_2O$

 Neutralization between a Weak Acid and a Weak Base: A weak acid reacts with a weak base to form a neutral salt. Its aqueous solution has a p^H > 7 and is alkaline.

Example: $CH_3COOH + NH_4OH \rightarrow CH_3COONH_4 + H_2O$

SALTS:

 $Def^{n}(1)$: Salts are regarded as ionic compounds made up of positive and negative ions. The positive part comes from a base while negative part from an acid.

Defⁿ (2) : Salts are ionic compounds which produce cation other than H^+ and anion other than OH^- in aqueous solution.

Defⁿ (3) : Salts are the compounds formed by the neutralization reaction between acids and bases.

TYPE OF SALTS:

Salts may be classified into the following types:

1. Normal salts: The salt obtained by the complete replacement of all the replaceable hydrogen atoms of an acid by metal atoms is called a normal salt. These salts are obtained by the reaction between strong acids and strong bases. These salts are not hydrolyzed in aqueous solution.

Example:	<u>Acids</u>	Normal salts
	HCI	NaCl, KCl, CaCl ₂ , MgCl ₂ , etc
	HNO₃	NaNO ₃ , KNO ₃ , Ca(NO ₃) ₂ , Mg(NO ₃) ₂ , etc.
	H_2SO_4	Na ₂ SO ₄ , K ₂ SO ₄ , CaSO ₄ , MgSO ₄ , etc.
	H_3PO_4	Na ₃ PO ₄ , K ₃ PO ₄ , Ca ₃ (PO ₄) ₂ , Mg ₃ (PO ₄) ₂ , etc.

2. Acidic salts: The salt obtained by the partial replacement of replaceable hydrogen atoms of an acid by metal atoms is called an acidic salt. These types of salts still contain one or more replaceable hydrogen atoms.

Example:	<u>Acids</u>	Acidic salts
	H_2SO_4	NaHSO ₄ , KHSO ₄ etc.
	H ₃ PO ₄	NaH ₂ PO ₄ , KH ₂ PO ₄ ,
		Na ₂ HPO ₄ , K ₂ HPO ₄ etc.

Also, these are the salts obtained by the neutralization between strong acids and weak bases. For examples: NH_4CI , NH_4NO_3 , $(NH_4)_2SO_4$, etc.

3. Basic salt: These are the salts obtained by the incomplete neutralization of poly acidic bases. Such salts contain one or more 'OH' groups. Example: Ca (OH)C/, Mg(OH)C/, Zn(OH)C/, Al(OH)₂Cl etc.

Also, these are the salts obtained by the neutralization reaction between weak acids and strong bases.

For examples: CH₃COONa, CH₃COOK, Na₂CO₃, K₂CO₃, etc.

4. Double salts: These are the molecular addition compounds obtained from two simple salts, the ions of which retain their identity in aqueous solution. Such salts give the test of all the constituent ions when dissolved in water.

Example: K_2SO_4 . $Al_2(SO_4)_3$. $24H_2O \xrightarrow{water} 2K^+ + 2Al^{3+} + 3SO_4^{2-}$

(Potash Alum)

Other examples: Mohr's Salt [FeSO₄.(NH₄)₂SO₄.6H₂O], carnalite (KCI. MgC*l*₂.6H₂O), etc.

5. Complex Salts: These are the molecular addition compounds obtained by the combination of simple salts, the ions of which lose their identity in aqueous solution. Such salts do not give tests of all the constituent ions in aqueous solution.

Example: $K_4[Fe(CN)_6] \xrightarrow{water} 4K^+ + [Fe(CN)_6]^{4-}$

Other examples: $K_3[Fe(CN)_6]$, $[Cu(NH_3)_4]SO_4$, etc.

6. Mixed Salts: These are the salts which give either more than one cation or more than one anion in aqueous solution.

Examples: Bleaching powder Ca (OCI)CI; Sodium potassium sulphate NaKSO₄, etc.

Exercise

(02 Marks Questions)

- 1. Define Arrhenius theory of acids and bases.
- 2. Define Bronsted-Lowery theory of acids and bases.
- 3. Define Lewis theory of acids and bases.
- 4. Justify that all Arrhenius acids are Bronsted-Lowery acids.
- 5. Explain how BF_3 is a Lewis acid.
- 6. Explain how $SiCl_4$ is a Lewis acid.
- 7. Explain how BF_3 is a Lewis acid.
- 8. Explain how $AICI_3$ is a Lewis acid.
- 9. Explain how SO_2 is a Lewis acid.
- 10. Explain how NH_3 is both a Bronsted-Lowery base and a Lewis base.
- 11. Write down the conjugate acids and conjugate bases of H_2O & NH_3 .
- 12. What do you mean by conjugate acid-base pair? Explain with a suitable example.
- 13. CH₃COOH is a weak acid while CH₃COO⁻ is a strong base. Explain.
- 14. What is neutralization reaction? Give an example of it.
- 15. Define salt. How does an acidic salt form?
- 16. Define salt. How does a basic salt form?
- 17. What is double salt? Give an example.
- 18. What is co-ordination salt? Give an example.
- 19. What is mixed salt? Give an example.
- 20. Explain how bleaching powder is a mixed salt.
- 21. Explain how potash alum is a double salt.

(05 Marks questions)

- 1. Define and explain Arrhenius theory of acids and bases.
- 2. Define and explain Bronsted-Lowery theory of acids and bases.
- 3. Define and explain Lewis theory of acids and bases.
- 4. Explain the limitations of Arrhenius theory.
- 5. Explain the limitations of Bronsted-Lowery theory.
- 6. Explain the limitations of Lewis theory.
- 7. Justify that all Arrhenius acids are Bronsted-Lowery acids, but all Arrhenius bases are not Bronsted Lowery bases.
- 8. Explain how SiCl₄ and BF_3 are acids.
- 9. Explain why SiCl₄ is an acid but CCl_4 is not.
- 10. Define and explain conjugate acid-base pair with a suitable example.
- 11. Justify your answer that H_2O is amphoteric.
- 12. How many grams of KOH are required to get 2 lit of its solution having P^H 10?
- 13. Explain how potash alum is a double salt while, K_3 [Fe(CN)₆] is a complex salt.
- 14. 14.7 grams of H_2SO_4 are present in 2 liters of its solution. Find morality and normality of the solution.
- 15. How many grams of calcium hydroxide are required to prepare 10⁻² M and 10⁻² N solutions?
- 16. How many grams of decahydrated sodium carbonate of 80% purity are required to prepare 2.5 lit. of its decinormal solution?

<u>CHAPTER – 4</u> <u>SOLUTIONS</u>

Introduction:

A solution is a special type of homogeneous mixture composed of two or more substances. In such a mixture, a solute is a substance dissolved in another substance, known as a solvent. The mixing process of a solution happens at a scale where the effects of chemical polarity are involved, resulting in interactions that are specific to solvation. The solution usually has the state of the solvent when the solvent is the larger fraction of the mixture, as is commonly the case. One important parameter of a solution is the concentration, which is a measure of the amount of solute in a given amount of solution or solvent. The term "aqueous solution" is used when one of the solvents is water. Solutions may be of three basic types: solid solutions, liquid solutions and gaseous solutions. A binary solution is composed of two components, one is solute and the other is solvent.

Atomic weight/mass:

The atomic mass of an element may be defined as "the average relative mass of one atom of the element as compared to the mass of an atom of carbon (^{12}C) taken as 12".

Unit: amu (atomic mass unit) or simply 'u'.

For example:	Element	Atomic mass in amu
	Н	1.008 ≈ 1
	Ν	14
	0	16

Atomic masses of some elements are given below:

	U	
<u>Element</u>	<u>Symbol</u>	Atomic Weight in a.m.u
Hydrogen	Н	1
Helium	He	4
Lithium	Li	7
Berylium	Be	9
Boron	В	11
Carbon	С	12
Nitrogen	Ν	14
Oxygen	0	16
Fluorine	F	19
Neon	Ne	20
Sodium	Na	23
Magnesium	Mg	24
Aluminium	AI	27
Silicon	Si	28
Phosphorous	Р	31
Sulphur	S	32

Chlorine	Cl	35.5
Argon	Ar	40
Potassium	K	39
Calcium	Ca	40
Chromium	Cr	52
Iron	Fe	56
Copper	Си	63.5
Bromine	Br	80
Silver	Ag	108
Lead	Pb	207

GRAM ATOMIC MASS:

The gram atomic mass of an element is simply its atomic mass expressed in gram. For example: Element Gm.atomic mass

ennatenne ma
1.008 gm
16 gm
24 gm

<u>Note:</u> When the mass is expressed in amu, it refers to the mass one atom of the element. But, when expressed in gm, it refers to the mass of 1 mole of atoms (6.023×10^{23} atoms) of the element.

MOLECULAR WEIGHT:

The molecular weight of a substance may be defined as "the relative average weight of one molecule of the substance as compared to the weight of an atom of carbon (^{12}C) taken as 12".

Molecular weight of a substance is calculated by adding the atomic weights of the constituent atoms present in one molecule.

Unit: amu (atomic mass unit)

For example: The molecular wt. of sulphuric acid (H_2SO_4) can be obtained as

H₂SO₄ = [2 × At.wt.of H] + At.wt. of sulphur +[4 × At.wt of oxygen]

= 2 × 1+32+4×16 = **98 amu**

Other examples:

<u>Compound</u>	Molecular weight
NaCl	23+35.5 = 58.5 amu
HNO3	1+14+48 = 63 amu
CaCO ₃	40+12+48 = 100 amu
Al ₂ (SO ₄) ₃	2x27+3x32+12x16 = 342 amu

Assignment

Q 1. Find the molecular weights of the following: Na₂SO₄, (NH₄)₂CO₃, (NH₄)₃PO₄, CuSO₄.5H₂O

Gram molecular weight: -

The gram molecular weight of a substance is simply its molecular weight expressed in gram. *For example*:

<u>Compound</u>	Gm. mol. weight
NaCl	58.5 gm
HNO3	63 gm

EQUIVALENT WEIGHT:

The equivalent weight of a substance may be defined as "the number of parts by mass of it, which combines with or displaces directly or indirectly 1.008 parts by mass of hydrogen, 8 parts by mass of oxygen or 35.5 parts by mass of chlorine."

Unit: Equivalent weight has no unit.

<u>Gram equivalent weight</u>: The gram equivalent weight of a substance is its equivalent weight expressed in gram.

Example :1 The equivalent wt. of 'Ca' in CaCl₂ can be calculated as follows:

Ca C*l*₂ 40 parts 2×35.5 parts

2×35.5 parts by mass of chlorine combines with 'Ca' = 40 parts

or 35.5 parts by mass of chlorine combines with calcium = $\frac{40}{2x35.5}x35.5 = 20$ parts

Thus, equivalent weight of 'Ca' in CaCl₂ is 20.

Assignment

Q 2. Find out the equivalent weights of the underlined elements in the followings.

<u>Mg</u>Cl₂, <u>Ca</u>H₂, <u>Fe</u>O, <u>Fe₂O₃</u>

Q 3. Find out the equivalent weight of 'Mg' from the following chemical equation.

 $Mg + H_2SO_4 \rightarrow MgSO_4 + H_2$

Relationship between atomic weight, equivalent weight and valency :

Consider a metal M with atomic weight 'A' and valency 'V'. The metal combines with hydrogen to forms the compound " MH_v ".

In MH_{v,}

V X 1.008 parts by mass of hydrogen combines with metal 'M' = 'A' parts

Or, 1.008 parts by mass of hydrogen combines with M =
$$\frac{A}{(V \ X \ 1.008)} X \ 1.008$$
 parts = $\frac{A}{V}$

Hence, equivalent weight (E) = $\frac{A}{V}$

Or, Equivalent weight (E) = $\frac{Atomic \ weight}{Valency}$

Variable equivalent weights:

Since equivalent weight is related with valency, the elements like *Cu, Fe, Sn, Pb,* Hg etc. having variable valencies have variable equivalent weights.

For example, the equivalent weight of iron in $FeCl_2$ and $FeCl_3$ are:

Eq. Wt. of 'Fe' in FeC/₂ =
$$\frac{Atomic weight}{Valency} = \frac{56}{2} = 28$$

Eq. Wt. of 'Fe' in FeC/₃ = $\frac{Atomic weight}{Valency} = \frac{56}{3} = 18.66$

EQUIVALENT WEIGHTS OF ACIDS, BASES AND SALTS:

Equivalent weights of acids:

The equivalent weight of an acid is numerically equal to the molecular weight of the acid divided by the basicity.

$$\mathsf{E}_{\mathsf{Acid}} = \frac{Molecular weight}{Basicity}$$

Where 'basicity' is the number of replaceable hydrogen atoms present one molecule of the acid.

ACID	FORMULA	MOL.Wt	<u>BASCIT</u>	<u>Y</u> <u>EQ.Wt.</u>
Nitric Acid	HNO ₃	63	1	63/1 = 63
Sulphuric Acid	H ₂ SO ₄	98	2	98/2 = 49
Phosphoric Acid	H ₃ PO ₄	98	3	98/3 = 32.66
Formic Acid	HCOOH	46	1	46/1=46
Acetic Acid	CH3COOH	60	1	60/1 = 60
Oxalic Acid	роон			
	соон	90	2	90/2=45
Phosphorous Acid	H ₃ PO ₃	82	2	82/2 = 41
Boric Acid	H ₃ BO ₃	62	1	62/1 = 62
Note: HCOOH \rightarrow HC	COO ⁻ + H ⁺	I	$H_3PO_3 \rightarrow 2H^+$	+ HPO3 ^{2 -}
$CH_3COOH \rightarrow$	CH ₃ COO ⁻ + H ⁺	I	$H_3BO_3 \rightarrow H^+ +$	H ₂ BO ₃ -

Equivalent weights of bases:

The equivalent weight of a base is numerically equal to the molecular weight of the base divided by the acidity.

 $E_{Base} = \frac{Molecular weight}{Acidity}$, Where acidity is the number of replaceable OH groups present in one

molecule of the base.

Exaamples:-

Base	Mol.formula	Mol. wt.	acidity	Equivalent Wt.
Potassium hydroxide	KOH	56	1	56/1 = 56
Calcium hydroxide	Ca(OH) ₂	74	2	74/2 = 37
Aluminium hydroxide	AI(OH) ₃	78	3	78/3 = 26

Equivalent Weights of Salts:

The equivalent weight of a salt is numerically equal to the molecular weight of the salt divided by the total number of positive or negative charges.

 $\mathsf{E}_{\mathsf{Salt}} = \frac{Molecular\,weight}{Total\,no.\,of + ve\,or - ve\,ch\,\mathrm{arg}\,e}$

Note: Total no of positive charge = No. of metal X valency.

Salt	Molecular formula	Mol. weight	Total +ve or – ve Charge	Eq. weight
Sodium chloride	NaCl	58.5	1x1 = 1	58.5
Potassium carbonate	K ₂ CO ₃	138	1x2 = 2	69
Calcium Sulphate	CaSO ₄	136	1x2 = 2	68
Aluminium Suplhate	$AI_2(SO_4)_3$	342	2x3 = 6	57

<u>Assignment</u>

Q 4: Determine the equivalent weights of the following acids, bases and salts.

Acids: H_2CO_3 , HNO_3 , C_2H_5COOH Bases: $Mg(OH)_2$, LiOH Salts: KCI, Na_2CO_3

EQUIVALENT WEIGHTS OF METALS

i. Oxidation method:

In this method metals like Na, K, Mg, Ca etc. are heated strongly to get the respective metal oxides. However, metals like Cu, Sn etc. are first treated with HNO₃ to get the respective metal nitrates. The metal nitrates so obtained are ignited strongly to get metal oxides. From the weights of metals and metal oxides, the equivalent weights of the metals are calculated as follows:

 $\begin{array}{rrrr} M & + & O_2 & \rightarrow & MO_2 \\ x \mbox{ gm} & (y-x) \mbox{ gm} & y \mbox{ gm} \end{array}$
Let the weight of metal = x gm

The weight of metal oxide = y gm

Hence, the weight of oxygen = (y - x) gm

(y - x) gm of oxygen is combined with metal = x gm

:. 8 gm of oxygen is combined with metal =
$$\frac{x}{(y-x)}X$$
 8

Hence, the equivalent weight of metal = $\frac{x}{(y-x)}X = \frac{weight of metal}{weight of oxygen}X = \frac{x}{weight of oxygen}X$

Numerical Problems:

EXAMPLE I: Find out the equivalent weights of the underlined elements in the following compounds.

(a) $\underline{Fe_2O_3}$ (b) $\underline{CuCl_2}$ (c) $\underline{Al_2O_3}$

SOLUTION:

In Fe₂O₃

3x16 parts by mass of 'O' combines with 'Fe' = 2x56 parts

 \Rightarrow 8 parts by mass of 'O' combines with 'Fe' = $\frac{2 \times 56}{3 \times 16} \times 8 = 18.66$

In CuCl₂

2x35.5 parts by mass of 'Cl' combines with 'Cu' = 63.5 parts

$$\Rightarrow$$
 35.5 parts by mass of Cl' combines with 'Cu' = $\frac{63.5}{2 \times 35.5} \times 35.5 = 31.75$

EXAMPLE II: 1.201 g. of a metal dissolved in nitric acid. The nitrate was ignited when 1.497g. of the oxide was obtained. Calculate the equivalent weight of the metal.

SOLUTION:

Given Data: Weight of metal = 1.201 gm. Weight of metal oxide = 1.497 gm. \therefore Weight of oxygen = 1.497 - 1.201 = 0.296 gm Hence, equivalent weight of metal = $\frac{weight of metal}{weight of oxygen} \times 8 = \frac{1.201}{0.296} \times 8 = 32.45$

EXAMPLE III: 0.723g. of copper displaced 2.455g. of silver from a solution of silver nitrate. Calculate equivalent weight of copper that of sliver being 107.88.

SOLUTION:

Weight of Copper $W_{Cu} = 0.723$ gm Weight of Silver $W_{Ag} = 2.455$ gm Equivalent weight of Silver $E_{Ag} = 107.88$ Equivalent weight of Cu $E_{Cu} = ?$

Applying Faraday's 2nd law of electrolysis:

 $\frac{W_{Cu}}{W_{Ag}} = \frac{E_{Cu}}{E_{Ag}} \implies E_{Cu} = \frac{W_{Cu}}{W_{Ag}} \times E_{Ag} \implies E_{Cu} = \frac{0.723}{2.455} \times 107.88 = 31.77$

EQUIVALENT WEIGHT OF IONS:

Equivalent weight of Ion (E_{Ion}) = $\frac{IonicMass}{TotalCharge}$

For example,

$$E_{Ca^{2+}} = \frac{40}{2} = 20; \ E_{CO_3^{2-}} = \frac{12+48}{2} = 30$$

<u>Assignment</u>

Q 5. Find out the equivalent masses of the underlined atoms in the following. <u>Ca</u>C l_2 , <u>Fe</u>O, <u>Na</u>HCO₃, <u>Fe</u>C l_3 .

Q 6. 1 gm. of a metal on heating produces 1.5 gm of its oxide. Find the equivalent mass of the metal.

Q 7. 4 gm of a divalent metal 'M' reacts with chlorine to form 11.1 gm of its chloride. Find the equivalent and atomic mass of the metal. Also write the formulae of metal chloride and metal sulphate.

Q 8. Certain mass of a metal is heated in oxygen. The mass is found to be increased by 10%. Find the equivalent mass of the metal.

MODES OF EXPRESSIONS OF CONCENTRATION

Concentration of a solution is the measure of the amount of solute in a given amount of solution or solvent. The concentration of a solution can be expressed in the following ways:

- Molarity
- > Normality
- > Molality
- > Strength
- > Percentage
- Parts per million (ppm)
- Mole fraction, etc.

MOLARITY (M):

Molarity of a solution may be defined as "the number of gram mole of the solute present per liter of solution".

Unit = gram mole/liter or M.

Mathematically,

$$M = \frac{w \ x \ 1000}{Ms \ x \ Vml} \quad ; \qquad Where \ w = weight of the solute in gram$$

Ms = Molecular weight of the solute. $V_{ml} = Volume of solution in ml.$

Molar solution:

The solution containing 1 gm mole of the solute per liter of solution is called a 'molar' solution.

For example: The solution containing 36.5 gm of HCl, 40 gm of NaOH, 58.5 gm of NaCl or 98 grams of H_2SO_4 per liter of solution is called molar solution.

- **NOTE: 1.** Deci molar solution means (1/10) M solution, Semi-molar solution means (½) M solution, centi-molar solution means (1/100) M solution.
- 2. The solution whose strength is known is called *standard solution*.

PROBLEMS FOR DISCUSSION:

QUESTION: 1. 0.4 gm of caustic soda (NaOH) is present in 200 ml of its solution. Find out the molarity of the solution.

Solution : Given Data

weight of solute (w) = 0.4 gm

Volume of solution (V_{ml}) = 200 ml.

Mol.wt. of solute (NaOH), $M_s = 23.+16+1 = 40$ amu.

Thus, Molarity (M) = M =
$$\frac{w \times 1000}{Ms \times Vml} = \frac{0.4 \times 1000}{40 \times 200} = 0.05 \text{ M}$$

Hence, the molarity of the solution is 0.05M.

QUESTION:2. How many grams of caustic potash (KOH) are required to prepare 1.5 lit. of a decimolar solution?

Solution : Given Data

Weight of solute (w) = ? Volume of the solution (V_{ml}) = 1.5 lit = 1500 ml. Molecular weight of solute, Ms for KOH =39+16+1 =56 amu Molarity of the solution = 1/10 M = 0.1M

Thus, $M = \frac{w \ x \ 1000}{Ms \ x \ Vml} \implies w = \frac{M \ x \ Ms \ x \ Vml}{1000} = \frac{0.1 \ x \ 56 \ x \ 1500}{1000} = 8.4 \text{ gram.}$

Thus, 8.4 gm of caustic potash is required to prepare 1.5 lit. of deci-molar solution.

NORMALITY (N):

Normality of a solution may be defined as "the number of gram equivalent of the solute present per litre of solution." It is represented by 'N'. Unit: - gram equivalent/liter or 'N'.

Mathematically,

 $N = \frac{w \ x \ 1000}{Es \ x \ Vml};$ Where, $w = weight \ of \ solute \ in \ gm.$ $V_{ml} = volume \ of \ solution \ in \ ml.$ $E_{S} = Equivalent \ weight \ of \ solute$

Normal Solution: The solution containing 1 gm. equivalent of the solute per litre of solution or the solution having normality '1' is called a normal solution or 1N solution.

For example: The solution containing 36.5 gm of HCl, 49 gm of H_2SO_4 or 40 gm of NaOH per liter of solution is called a **normal solution**.

PROBELMS FOR DISCUSSION:

QUESTION:1. 5.6 gm of caustic potash (KOH) is present in 800 ml of its solution. What is the normality of the solution?

Solution: Given Data

Weight of solute, w = 5.6 gm

Volume of solution, $V_{ml} = 800$ ml.

Equivalent weight of solute, KOH (E_s) = $\frac{Molecular weight}{Acidity} = \frac{56}{1} = 56$

Normality 'N' =
$$\frac{w \times 1000}{Es \times Vml} = \frac{5.6 \times 1000}{56 \times 800} = 0.125 \text{ N}$$

Hence, the normality of the solution is 0.125N.

QUESTION:2. 10 ml of sulphuric acid (H_2SO_4) having density 1.2 gm/ml is present in 400 ml of its solution. Calculate the normality of the solution.

Soution : Given Data,

Wt. of solute, w = density × volume = $1.2 \times 10 = 12$ gm Volume of solution, V_{ml} = 400 ml Equivalent weight of H₂SO₄ = $\frac{Molecularweight}{Basicity} = 98/2 = 49$

Normality N =
$$\frac{w x 1000}{Es x Vml} = \frac{12 x 1000}{49 x 400} = 0.612N$$

Hence, normality of the solution is 0.612N.

MOLALITY (m):

Molality of a solution may be defined as "the number of gram mole of solute present per 1000gm (1kg) of solvent" and it is represented by the symbol 'm'. Unit: - gram mole/kg.

Mathematically,

$$m = \frac{w \times 1000}{M_S \times W}$$

Where, w = weight of solute in gm

W = weight of solvent in gm $M_{\rm S}$ = Molecular weight of solute

Molal solution:

The solution containing 1 gm mole of solute per 1000gm of solvent is called molal solution. For example: 58.5 gm of NaCl, 40 gm of NaOH, 56 gm of KOH or 98gm of H₂SO₄ per 1000 gm of water (solvent) is called molal solution.

PROBLEMS FOR DISCUSSION:

QUESTION:1. 5.85 gm of common salt (NaCl or table salt) is present in 200 gm of water. Calculate the molality of the solution.

Solution : Given Data

wt. of solute, w = 5.85 gm wt. of solvent, W = 200 gm, Mol. wt. of Solute, M_{S} (NaCl) = 23+35.5 = 58.5 amu. $m = \frac{w \times 1000}{M_{\rm S} \times W}$ $=\frac{5.85 \times 1000}{585 \times 200} = 0.5 \text{m}$

Hence, molality of the solution is 0.5m.

QUESTION:2. 5.6 gm of potassium hydroxide is present in 300 gm of its solution in water. Calculate the molality of the solution.

Solution : **Given Data**

wt. of solute, w = 5.6 gm wt. of solution = 300 gm wt. of solvent, W = wt. of solution - wt. of solute = 300 - 5.6 = 294.4 gm $m = \frac{W \times 1000}{M_S \times W} = \frac{5.6 \times 1000}{56 \times 294.4} = 0.339 \text{ m}.$

Thus, molality

Hence, molality of the solution is 0.339 m.

Assignment

Q 9. How many gm of Common salt is required to prepare 2 litres of a semi molar solution?

- Q 10.9.8 gm of H₂SO₄ is present in 400ml of its solution. Calculate its molarity and normality.
- Q 11.0.49 gm of H₂SO₄ is present in 600ml of its solution having density 1.2 gm/ml. Find molarity, normality and molality of the solution.

P^H of Solutions

The p^{H} of a solution may be defined as "the negative logarithm of H⁺ ion concentration in moles/liter or molarity."

Thus, $P^{H} = -\log[H^{+}]$

p^H is normally used to know whether a solution acidic, alkaline or neutral in nature.



- If $P^{H} < 7$; the solution is Acidic, i.
- If $P^{H} > 7$; the solution is Alkaline, ii.
- iii. If $P^{H} = 7$; the solution is Neutral.

Note: Pure water has a P^{H} value of '7' at 25°C and is neutral. The P^H value of water decreases with the increase in temperature.

Some important Formulae:

- i. $P^{H} = -\log [H^{+}]$
- ii. $P^{OH} = -\log [OH]$
- $P^{H} + P^{OH} = 14$ iii.
- $[H^+][OH^-] = 10^{-14}$ iv.
- $[H^+] = 10^{-P^H}$
- v. vi. $[OH^{-}] = 10^{-P^{OH}}$

QUESTIONS FOR DISCUSSION:

- **1.** Find out the p^{H} values of the following solutions.
 - 0.01M HCl solution i.
 - ii. 0.001 M HNO₃ solution
 - 0.01M NaOH solution iii.
 - iv. 0.01M H₂SO₄ solution

Solutions:-

i. HCI H⁺ + Cl⁻ 0.01M 0.01M

 $[HCI] = [H^+] = 0.01M = 10^{-2}M$ Hence $p^{H} = -\log[H^{+}] = -\log(10^{-2}) = -(-2)\log 10 = 2$ $HNO_3 \rightarrow H^+ + NO_3^$ ii. 0.001M 0.001M $[HNO_3] = [H^+] = 0.001M = 10^{-3}M$ Hence, $p^{H} = -\log[H^{+}] = -\log_{10^{-3}} = -(-3)\log_{10} = 3$. iii. NaOH \rightarrow Na⁺ + OH. 0.01M 0.01M $[NaOH] = [OH^{-}] = 0.01M = 10^{-2}M$ We know $[H^+][OH^-] = 10^{-14}$ $\Rightarrow [H^+] = \frac{10^{-14}}{[OH^-]} = \frac{10^{-14}}{10^{-2}} = 10^{-12}$ Hence, $P^{H} = -\log[H^{+}] = -\log(10^{-12}) = 12$ 2H⁺ + SO4²⁻ iv. H_2SO_4 \rightarrow 0.01M (2 x 0.01)M $[H^+] = 2 \times 0.01 = 2 \times 10^{-2} M$

Hence, $p^{H} = -\log[H^{+}] = -\log(2 \times 10^{-2}) = 1.699$.

Assignment

Q 12. Find out the pH values of the following solutions.

(i) 1 M HNO3 solution (ii) 0.1 M Mg $(OH)_2$ solution.[Ans: (i) 0, (ii) 12.301]Q13. One liter of a solution contains 5.85 gm of HCl. Find the P^H value of the solution.[Ans: 1]

Q 14. 500 ml of an aqueous solution contains 1.6 gm of NaOH. Find P^H of the solution.

Importance of P^H in Industries:

- **1.** In sugar Industry: The P^{H} value of the sugar cane juice should be nearly '7' i.e., it should be neural. If the P^{H} value of sugar cane juice becomes less than '7', the sucrose in the juice is hydrolyzed into glucose and fructose. On the other hand, if it exceeds '7', undesirable acids and coloured substances are produced.
- 2. In Paper Industries: Paper is used in a broad array of products essential for everyday life, from newspapers, books, magazines, printing, writing papers to cardboard boxes and bags, paper napkins, sanitary tissues etc. We are daily surrounded by paper products.

The most important use of paper is writing. The quality of paper used for printing or writing should be good and it depends on many parameters. One of the parameters is Cobb, which needs to be controlled. Cobb control is nothing but the control of quality and binding of pulp in such a fashion that whatever is written by any source such as ink, etc on paper it should not spread as well as leave its impression on back side of the paper. Cobb variation is minimized by maintaining pH of the pulp in the range of 5-6 pH. Before processing, the raw pulp has pH in the range of 7-8. This should be controlled and brought down to acidic range i.e., 5 to 6 p^H.

Cobb control is done by addition of Alum (which is in the range of 2-3 p^H) and rosin to pulp. When alum and rosin are mixed with pulp after a certain distance pH of the mixture is measured and if it is not in the desired range the transmitter will control the Alum dosing via controller so that p^H of the pulp is maintained. Rosin on the other side has no such controlled action. It will be getting dosed to the pulp continuously in a specific quantity. It is the Alum whose dosing is controlled depending upon p^H variations.

3. In Textile Industries: In all textile processes in which aqueous solutions are used, balancing the pH of the solution is primary. pH control is critical for a number of reasons. The effectiveness of oxidizing and reducing agents is p^H dependent. The amount of chemicals required for a given process is directly related to the p^H. The solubility of substances, such as dyes and impurities, vary with p^H. The corrosive and scaling potential of processing solutions is also heavily influenced by p^H. All these issues affect quality and costs.

Along with surface tension, pH plays an important role in the wetting and saturating processes. For example, caustic solutions cause interfibrillar swelling in cotton cellulose and cannot be squeezed out as easily as water, which can reduce quality in subsequent processing.

The scouring of wool is a good example of a process where maintaining the pH value permits a better solubilization of certain impurities. For example, a p^{H} of 10 is considered optimum for the removal of wool wax.

In the instance of vat dyeing, p^{H} controls the solubilization of the dyes. Initially, the quantity of caustic soda present must be adequate to ensure the solubility of the leuco form. Once the dye has been exhausted, the p^{H} is adjusted such that the dye returns to its insoluble form and is mechanically trapped in the fibre.

Between the colour kitchen and processing, controlling the p^H improves the lab-to-bulk reproducibility of colour. Monitoring and controlling pH ensures consistency of colour from batch to batch, as well.

To effectively bleach cellulose (e.g., cotton) with a minimum amount of damage, the bleaching solution must be alkaline. This keeps the hypochlorite stable and also prevents the presence of

reducing groups that cause an apparently well-bleached cloth to yellow with age. Additionally, an acidic solution will form toxic and corrosive chlorine gas. Bleaching liquor is therefore usually maintained at a p^{H} of 9. The permanence of the white obtained is thereby increased, and the bleaching is safe. Due to environmental concerns in recent times, hydrogen peroxide bleaching has become more prevalent. Its reaction products, oxygen and water, are relatively harmless. However, hydrogen peroxide is a weak acid. Thus, its conjugate base, HO_2^{-} , is used to perform the actual bleaching. To ensure an adequate concentration of HO_2^{-} , the solution p^{H} must be tightly controlled. Sodium hydroxide is used to maintain the p^{H} at a very alkaline level of 12-12.5.

Exercise

(02 Marks Questions)

- 1. Define atomic weight.
- 2. Define molecular weight. What is the molecular weight of sulphuric acid?
- 3. Define equivalent weight. What is the equivalent weight of H_3PO_4 ?
- 4. Find the molecular weights of $AI_2(SO_4)_3$ and $CuCO_3$.
- 5. Find the equivalent weights of H_3PO_4 and H_3PO_3 .
- 6. Find the equivalent weights of $Ca(HCO_3)_2$ and H_3BO_3 .
- 7. Find the equivalent weights of acetic acid and calcium hydroxide.
- 8. Derive a relationship between atomic weight, equivalent weight and valency.
- 9. Define variable equivalent weights. Give suitable examples.
- 10. Why do the equivalent weights of FeO and Fe_2O_3 vary?
- 11. 1 gm of a metal on heating with air produces 1.5 g of its oxide. Calculate the equivalent weight of the metal.
- 12. An oxide of metal contains 60% oxygen. Find the equivalent weight of the metal.
- 13. Find the equivalent weights of Ca(OH)₂ and CH₃COOH.
- 14. Define molarity. Mention its unit.
- 15. How many grams of NaCl are required to prepare 2 liters of its solution having molarity 1M?

16. Define normality.

17. 4 grams of NaOH are present 2 lit of its solution. Find its normality.

18. Define molality.

- 19. 5.6 gram of KOH are present in 200 grams of water. Find molality of the solution.
- 20. Find the equivalent weights of calcium chloride and nitric acid.
- 21.8 grams of NaOH are present in 108 gram of its solution. Find molality of the solution.
- 22. Define normality. Mention its unit.
- 23. What do you mean by decimolar solution?
- 24. How many gms of Na₂CO₃ are required to prepare one litre of its decimolar solution?
- 25. Obtain a relationship between molarity and normality.
- 26. Convert 0.01 M H_2SO_4 in to normality.
- 27. Convert 10^{-2} N H₂SO₄ in to molarity.

28. Define P^{H} and P^{OH} .

- 29. The P^H of a basic solution is 12. What is its hydroxyl ion concentration in moles/lit?
- 30. Define ionic product of water. What is its value at 25°C?
- 31. What is the importance of P^H in sugar industry?
- 32. Write down the importance of P^{H} in textile industries.
- 33. Find the P^H value of 0.001 M HCl solution.
- 34. Find the P^H value of 0.01 M NaOH solution.
- 35. Find the P^H value of 0.01 M H₂SO₄ solution.

<u>CHAPTER – 5</u> ELECTROCHEMISTRY

Introduction:

Electrochemistry is the branch of chemistry which deals with the study of electricity relating to redox reactions. A redox reaction is that in which both oxidation as well as reduction reactions take place.

Depending upon electrical conductivity, substances can be classified into the following types:



Electrolyte:

The chemical substances which allow electricity to pass through their molten, fused or solution state are called electrolytes. Example: All acids, all alkalies and all salts.

Non-electrolyte:

The chemical substances which do not allow electricity to pass through their molten, fused or solution state are called non-electrolytes. Example: urea, sugar, glucose, fructose, maltose, lactose, etc.

Classification of Electrolytes:

Depending upon the strength, electrolytes may be classified into the following types:

- i. Strong electrolytes
- ii. Weak electrolytes

i. <u>Strong electrolytes</u>: These are the electrolytes which undergo almost complete ionization in aqueous solution.

Example: a) acids like HC/, HNO₃, H₂SO₄, etc.

- b) alkalies like NaOH, KOH, Ca (OH)₂, Mg (OH)₂, etc.
- c) salts like NaCl, KCl, CaCl₂, MgCl₂, etc.
- **ii.** <u>Weak electrolytes</u>: These are the electrolytes which undergo partial ionization in aqueous solution. Example: a) Organic acids like CH₃COOH, HCOOH, (COOH)₂, etc.

b) Inorganic acids like H₂CO₃, HCN, etc.

c) Base like NH₄OH

ELECTROLYSIS:

The process of chemical decomposition of an electrolyte by the passage of electricity through its molten fused or solution state is called *electrolysis*.

Apparatus: The apparatus used in the process of electrolysis is called electrolytic cell, which is made up of an insulating material like glass. An electrolytic solution is taken in the electrolytic cell. Two metallic electrodes are partially dipped in the solution. The electrodes are connected to the terminals of a battery. The electrode which is connected to the positive terminal of the battery is called **anode** and the electrode which is connected to the negative terminal of the battery is called **cathode** (Fig. 5.1).

Working Process:

Electrolytes exist in the ionic form in their molten, fused or solution state. When electricity is allowed to pass through the electrolytic solution, the ions migrate towards the oppositely charged electrodes. Cations migrate towards the cathode while anions migrate towards the anode. While reaching at the electrodes the ions get discharged at their respective electrodes to give neutral species (primary change). The neutral species may further undergo secondary change to give stable substances.



Example 1: Electrolysis of molten NaCI.

Molten NaC/ exists in the ionic form Na⁺ and C/⁻ During the process of electrolysis, Na⁺ ions migrate towards the cathode while C/⁻ ions migrate towards the anode. During electrolysis the following changes take place at different electrodes.

At Anode:

 $CI^- - e^- \rightarrow CI$ (Primary change)

 $CI + CI \rightarrow CI_2$ (Secondary change)

At Cathode:

Na⁺ + $e^- \rightarrow$ Na (Primary change)

Thus, electrolysis of molten NaC/ liberates chlorine gas at the anode while metallic sodium at the cathode.

Example 2: Electrolysis of aqueous NaC/ solution.

In aqueous solution NaCl exists in ionic form. Also, water undergoes partial ionization to produce H^+ and OH^- ions.

NaCl \rightarrow Na⁺_(aq) + Cl⁻_(aq) H₂O \rightarrow H⁺ + OH⁻

Out of Cl⁻ and OH⁻ ions, the former has lower discharge potential and hence preferably gets discharged at the anode.

 $2CI^-$ - $2e^- \rightarrow CI_2$

On the other hand, out of H⁺ and Na⁺ ions, the former has lower discharge potential and hence preferably gets discharged at the cathode.

 $2H^+$ + $2e^- \rightarrow H_2$

Thus electrolysis of aqueous NaC*I* solution liberates chlorine gas at the anode and hydrogen gas at the cathode.

Faraday's 1st Law of Electrolysis:

The law may be stated as "during the process of electrolysis, the amount of substance (W) deposited or liberated at the electrode is directly proportional to the quantity of electricity (Q) passed through the electrolyte".

Mathematically,

$$W \propto Q$$

 $\Rightarrow W \propto I \times T$

$$\Rightarrow W = Z \times I \times T$$

Where, W = Amount of substance in gram

Q = Quantity of electricity or Charge in coulomb

I = Current in ampere

t = time of flow of current in second.

Z = Electrochemical equivalent (ECE)

When, I = 1 ampere; t = 1 second,

W = Z

 \Rightarrow

Thus, electrochemical equivalent is numerically equal to the amount of substance deposited or liberated at the electrode when 1 ampere of current is passed through an electrolyte for 1 second. Or it is the amount of substance deposited or liberated at the electrode when 1 coulomb of charge is made to flow through an electrolyte.

A bigger unit of charge is Faraday.

1 Faraday = 96500 coulomb

Experimentally it is observed that when 1 Faraday (96500 C) of charged is passed through an electrolyte 1gram equivalent of the substance is deposited at the electrode.

96500 Coulomb of charge deposits 1 gram equivalent

1 coulomb of charge deposits
$$\frac{1 gramequivalent}{96500C}$$

Hence, Electrochemical Equivalent (Z) = $\frac{1 gramequivalent}{96500C} = \frac{Atomic mass/Valency}{96500}$

Unit of 'Z' is gram equivalent/coulomb.

Note: 1 mole of electrons carries 1 Faraday or 96500 Coulomb of charge.

Question 1: How many grams of silver will be deposited at the cathode by the passage of 10 ampere of current through an aqueous solution of AgNO₃ for 1 hour?

Solution:

t = 1 hr = 3600 Sec.

$$Z = \frac{1 \, gramequivalent}{96500C} = \frac{Atomic mass/Valency}{96500} = \frac{108/1}{96500} = \frac{108}{96500} = 0.0011$$

Applying Faraday's 1st Law of electrolysis

W = ZIt = 0.0011 X 10 X 3600 = 39.6 gram.

Question 2: How many coulombs are required for the following changes?

- i. One mole Ca^{2+} into Ca.
- ii. Two moles of AI³⁺ into AI.

Solution:

i. $Ca^{2+} + 2e^- \rightarrow Ca$

1 mole of electrons carries 96500 coulombs.

 \Rightarrow 2 moles of electrons carry (2 x 96500) coulomb = 193000 Coulombs.

ii. $2AI^{3+} + 6e^- \rightarrow 2AI$

1 mole of electrons carries 96500 coulombs.

 \Rightarrow 6 moles of electrons carry (6 x 96500) coulomb = 579000 Coulombs.

Question 3: How many coulombs of charge are required to get 10 grams of calcium from molten CaC*l*₂? **Solution:**

W = 10 gm, Q =?
W = Z Q

$$= \frac{Eq.mass/Valency}{96500} \times Q$$

$$\Rightarrow 10 = \frac{40/2}{96500} \times Q \Rightarrow Q = 10 \times \frac{96500}{20} = 48250Coulomb$$

Assignment

Q 1. Find the ECE of Ca and Al.

- Q 2. How many coulombs of charges are required to reduce 10 gm of calcium ions into calcium?
- Q 3. How many coulombs of charge are required to get 3.6 grams of aluminium from molten alumina?
- Q 4. How many grams of copper will be deposited at the cathode by the passage of 20 ampere of current through an aqueous solution of CuSO₄ for half an hour?

Faraday's 2nd Law of Electrolysis:

The law may be stated as "when the same quantity of electricity is passed through different electrolytes connected in series, the amounts (W) of substances deposited at various electrodes are directly proportional to their equivalent masses (E)".

Mathematically,

 $W \propto E$

Let us consider two electrolytic solutions AgNO₃ and CuSO₄ taken in two different electrolytic cells. Both the cells are connected in series and the same quantity of electricity is passed through the electrolytes.

Applying Faraday's 2nd law of electrolysis,

$$W_{Ag} \propto E_{Ag}$$
 -----(1)

 $W_{Cu} \propto E_{Cu}$ -----(2)



From equation (1) and (2), we have

$$\Rightarrow \frac{W_{Ag}}{W_{Cu}} = \frac{E_{Ag}}{E_{Cu}} \Rightarrow \frac{W_{Ag}}{W_{Cu}} = \frac{\frac{E_{Ag}}{96500}}{\frac{E_{Cu}}{96500}} = \frac{Z_{Ag}}{Z_{Cu}}$$

In general,
$$\boxed{\frac{W_1}{W_2} = \frac{E_1}{E_2} = \frac{Z_1}{Z_2}}$$
 or $W \propto E \propto Z$

Question: 1. The same quantity of electricity is passed simultaneously through acidulated water and copper sulphate solution. Weights of hydrogen and copper liberated are 0.0132 and 0.4164 gram respectively. Find out the equivalent weight of copper.

Solution: Weight of hydrogen $W_{H_2} = 0.0132$ gm

Weight of copper $W_{Cu} = 0.4164 \text{ gm}$

Equivalent weight of hydrogen E_{H_2} = 1.008

Equivalent weight of copper $E_{Cu} = ?$

Applying Faraday's 2nd law of electrolysis,

$$\frac{W_{H_2}}{W_{Cu}} = \frac{E_{H_2}}{E_{Cu}} \implies E_{Cu} = E_{H_2} \times \frac{W_{Cu}}{W_{H_2}} = 1.008 \times \frac{0.4164}{0.0132} = 31.79$$

Industrial Application of Electrolysis:

1. Electroplating: The process of applying a coating of one metal over another by the process of electrolysis is called electroplating. Electroplating is used for three main purposes: a) Decoration, b) repairing and c) protection.



Zinc Platting: Normally iron gets rusted when exposed to moist air. Rusting of iron can be prevented by

applying a coating of zinc or chromium over it. The process of applying a coating of zinc over iron with a view to protect it from rusting is called **Galvanization.**

During the process of galvanization, zinc plate is used as anode and iron article is used as cathode. Both the electrodes are connected to the terminals of a battery (Fig: 5.2). The electrodes are dipped in an aqueous solution of zinc sulphate. When electricity is passed, the anode, i.e., zinc plate dissolves in its aqueous salt solution to liberate zinc ion (Zn^{2+}) which get discharged ad deposited over the cathode. In this way a coating of zinc is applied over the surface of the iron article.

Exercise

(02 Marks Questions)

- 1. Define electrolyte. Give an example of it.
- 2. Define strong and weak electrolytes with examples.
- 3. What are non-electrolytes? Give examples.
- 4. Define electrolysis. Which gas is evolved at the cathode during electrolysis of acidulated water?
- 5. Define Faraday's 1st law of electrolysis.
- 6. Define Faraday's 2nd law of electrolysis.
- 7. Define electrochemical equivalent. Mention its unit.
- 8. Find the electrochemical equivalent of calcium.
- 9. Find the electrochemical equivalent of aluminium.
- 10. How many coulombs of charge are required to get 10 grams of calcium from molten calcium chloride?
- 11. Define electroplating.
- 12. What is Galvanisation?
- 13. What is the relationship between the masses of the substances and their equivalent weights, when the same quantity of electricity is passed through different electrolytes?
- 14. What is the difference between electrolytes and non-electrolytes?

(05 Marks Questions)

- 1. Define electrolyte and electrolysis. What are strong and weak electrolytes? Give examples.
- 2. Define electrolysis. Explain the process of electrolysis of molten NaCl.
- 3. Define Faraday's 1st law of electrolysis. How many grams of calcium will be deposited at the cathode by passing 15 ampere of currents through molten CaCl₂ for 30 minutes?
- 4. Define electrochemical equivalent. Find the ECE of Ca and Al.
- 5. Define and explain Faraday's 2nd law of electrolysis.
- 6. Explain the process of applying a coating of zinc over an iron article by the process of electrolysis.
- 7. Explain the electro refining process of a crude copper bar.
- 8. Define and explain electrometallurgy.
- 9. Explain the electrolysis of acidulated water.
- 10. Define and explain Galvanisation.
- 11. Define Faraday's 1st law of electrolysis. How many coulombs of charges are required to get 36 grams of magnesium from molten magnesium chloride?



Introduction:

Corrosion is a natural process that converts a refined metal into a more chemically-stable form such as oxide, hydroxide, or sulphide. It is the gradual destruction of materials (usually a metal) by chemical and/or electrochemical reaction with their environment. Corrosion engineering is the field dedicated to controlling and preventing corrosion.

In the most common use of the word, this means electrochemical oxidation of metal in reaction with an oxidant such as oxygen or sulphates. Rusting, the formation of iron oxides is a well-known example of electrochemical corrosion. This type of damage typically produces oxide(s) or salt(s) of the original metal and results in a distinctive orange colouration. Corrosion can also occur in materials other than metals, such as ceramics or polymers, although in this context, the term "degradation" is more common. Corrosion degrades the useful properties of materials and structures including strength, appearance and permeability to liquids and gases.

Many structural alloys corrode merely from exposure to moisture in air, but the process can be strongly affected by exposure to certain substances. Corrosion can be concentrated locally to form a pit or crack, or it can extend across a wide area more or less uniformly corroding the surface. Because corrosion is a diffusion-controlled process, it occurs on exposed surfaces. As a result, methods to reduce the activity of the exposed surface, such as passivation and chromate conversion, can increase a material's corrosion resistance. However, some corrosion mechanisms are less visible and less predictable.

Corrosion:

The process of conversion of a metal into an undesirable compound on exposure to atmospheric conditions i.e., moisture (water) and air is called *corrosion*. It is also called weeping of metals.

Types of Corrosion: - Corrosion is of the following types:

- i. Atmospheric corrosion
- ii. Water line corrosion
- iii. Pitting corrosion
- iv. Stress corrosion
- i. **Atmospheric corrosion:** The process of development of undesirable substances usually oxide over the surface of a metal when exposed to atmosphere is called *atmospheric corrosion*. Example: (a) rusting of iron, (b) tarnishing of silver, (c) developing of green coating over copper and bronze.

Mechanism of Rusting of Iron:

Pure iron does not rust. However commercial form of iron behaves like a tiny electric cell in presence of water containing dissolved oxygen and acidic substances like CO_2 , SO_2 , etc. The following changes stake place on the surface of iron during the process of corrosion (Fig. 6.1).

At Anode:

At anode iron gets oxidized in to ferrous ion.

$$2Fe \rightarrow 2Fe^{2+} + 4e^{-}$$

The electrons thus formed migrate towards the cathodic part of the piece of iron.

At Cathode:

At the cathodic part, the electrons combine with moisture and dissolved oxygen to form hydroxyl ions.

 H_2O + O + $2e^- \rightarrow 2OH^-$



The Fe²⁺ ions and OH ⁻ ions then diffuse under the influence of dissolved oxygen and Fe²⁺ ions are oxidized into Fe³⁺ ions. These ferric ions then combine with OH ⁻ ions to form hydrated ferric oxide which is nothing but rust.

 $2Fe^{2+} + H_2O + O \rightarrow 2Fe^{3+} + 2OH^{-}$

 $2Fe^{3+} \ + \ 6OH^- \rightarrow \ Fe_2O_3.3H_2O \ (Rust)$

Note:

- Rust is nothing but hydrated ferric oxide (Fe₂O₃.nH₂O)
- Presence of CO₂ in water or trace of Cu or Zn in iron accelerates the process of corrosion. Also, corrosion process is accelerated in saline water.
- Presence of alkalis in water or Cr, Ni in iron slows down the process of corrosion.
- ii. Water line Corrosion: This type of corrosion occurs due to differential oxygen concentration above and below the level of water. When water is stored in a steel tank, it is noticed that corrosion occurs along the line just below the level of water (Fig. 6.2).

The concentration of oxygen in the area above the water line is high and hence the area is called cathodic part. The area just below the water line is called anodic part as this part is deficient in oxygen. This type of corrosion is mostly seen in ships, water tanks, etc.



Protection of Corrosion:

- 1. Alloying: Corrosion can be prevented by alloying a metal. Alloying prevent corrosion in two ways.
 - **i. Homogeneity:** Alloying increases the homogeneity of the metal for which the rate of corrosion is reduced. Rusting of iron can be prevented by alloying it with chromium. It is important to note that only uniform alloy can prevent corrosion to a maximum extent.
 - **ii. Oxide film:** In some cases, the oxide film formed at the surface of the metal prevents corrosion. Duriron is a silica-iron alloy. It is resistant to acids as a layer of silicon oxide is formed at the surface of iron.
- 2. <u>Galvanization</u>: Normally iron gets rusted when exposed to moist air. Rusting of iron can be prevented by applying a coating of zinc or chromium over it. The process of applying a coating of zinc over iron with a view to protect it from rusting is called **Galvanization**.

During the process of galvanization of iron, zinc is used as anode and iron bar is used as cathode. Both the electrodes are connected to the terminals of a battery. The electrodes are dipped in an aqueous solution of zinc sulphate. When electricity is passed, the anode, i.e., zinc bar dissolves in its aqueous salt solution to liberate zinc ion (Zn^{2+}) which get discharged ad deposited over the cathode. In this way a coating of zinc is applied over the surface of iron.

Exercise

(02 Marks Questions)

- 1. What do you mean by corrosion?
- 2. What is atmospheric corrosion?
- 3. What is water-line corrosion?
- 4. How is corrosion prevented by the alloy durriron?
- 5. How the rate of rusting of iron is accelerated in presence of CO₂ in moisture?

(05 Marks Questions)

- 1. Define and explain atmospheric corrosion.
- 2. Define corrosion. Explain waterline corrosion.
- 3. Explain the alloying process of protection of corrosion.

<u>CHAPTER – 7</u> <u>METALLURGY</u>

Mineral: - The natural material in which the metal or their compounds occur in the earth's crust is known as mineral.

Example: Bauxite $(Al_2O_3, 2H_2O)$ and Kaolin $(Al_2O_3, 2SiO_2, 2H_2O)$ are the minerals of Aluminium.

Ores: - Ores are the minerals from which the concerned metals can be extracted conveniently and profitably.

Example: Both Bauxite and Kaolin are the minerals of 'Al'. However, 'Al' can be extracted easily and profitably from Bauxite. Thus, Bauxite is an ore of 'Al'. On the other hand, it is difficult and non-profitable to extract 'Al' from Kaolin, thus Kaolin is only a mineral of 'Al'.

All ores are minerals, but all minerals are not ores.

Difference between Minerals and Ores

	Minerals	Ores		
1.	The combined state occurrences of metals	These are the minerals from which the		
	are called Minerals and extraction of metals	concerned metals can be extracted easily		
	from minerals is difficult and non-profitable.	and economically.		
2.	Minerals contain low percentage of metals	Ores contain high percentage of metals but		
	and high percentage of impurities.	low percentage of impurities.		
3.	All minerals are not ores.	All ores are minerals.		
	Example: Kaolin and Bauxite are the	Example: Bauxite is an ore of aluminium.		
	minerals of aluminium.			

SOME IMPORTANT METALS AND THEIR MINERALS:

Metals	Minerals	Formula
Na	Rock Salt	NaCl
	Borax	Na ₂ B ₄ O ₇
К	Carnallite	KCI.MgCl ₂ .6H ₂ O
	Niter	KNO ₃
Mg	Magnesite	MgCO ₃
	Dolomite	MgCO ₃ .CaCO ₃
	Epsom salt	MgSO ₄ .7H ₂ O
	Carnallite	KCI.MgCl ₂ .6H ₂ O
Са	Limestone	CaCO ₃
	Dolomite	MgCO ₃ .CaCO ₃
	Gypsum	CaSO ₄ .2H ₂ O
Cu	Copper pyrite	CuFeS ₂
	Copper glance	Cu ₂ S
	Cuprite	Cu ₂ O
Ag	Silver glance	Ag ₂ S
	Horn silver	AgCl
Zn	Zinc blend	ZnS
	Zincite	ZnO
	Calamine	ZnCO ₃
Hg	Cinnabar	HgS
AI	Bauxite	Al ₂ O ₃ .2H ₂ O
	Cryolite	Na ₃ AIF ₆
Sn	Tin stone	SnO ₂

Pb	Galena	PbS	
Cr	Chromite	FeO.Cr ₂ O ₃	
Fe	Haematite	Fe ₂ O ₃	
	Magnetite	Fe ₃ O ₄	
	Limonite	Fe ₂ O ₃ .3H ₂ O	

METALLURGY: - The art of extraction of metals from ores conveniently and economically is called metallurgy or metallurgical operation.

The following steps are followed during the process of metallurgical operation.

- 1. Crushing and Grinding.
- 2. Concentration or Ore dressing.
- 3. Oxidation.
- 4. Reduction.
- 5. Refining.
- 1. CRUSHING AND GRINDING: The ores obtained from mines are in the form of solid rocks. These are first crushed into small pieces with the help of jaw crusher and then grinded into their powder form with the help of stamp mill or ball mill. The powdered form of ore is called pulverized ore.
- 2. CONCENTRATION OR ORE DRESSING: The process of removal of maximum impurities (gangue or matrix) from the powdered ore is called ore concentration. The method of concentration to be followed depends upon the nature of the impurities present. Following are the different methods of concentration:

(i) Gravity Separation Method: - This method of concentration is adopted only when there is a gravity difference between the ore and impurities. Normally, Carbonate and oxide ores are heavier

than the impurities associated with them and hence they are concentrated by this method. In this method the powdered ores are kept in some containers over a specially designed table called Wilfley table (Fig. 7.1).

The table contains a number of horizontal grooves. The table is kept slightly inclined in position and is provided with a rocking motion. When water is spread over the ore, lighter impurities are washed away while heavier ore particles get deposited

(Figure: 7.2 Froth floatation method)

ROTATING

ORE FROTH

PULP OF

PADDLE DRAWS

IN AIR AND STIRS

ORE + OIL

PADDLE

FOAM OF

TANK (2) JLPHIDE ORE

ORE





(ii) Froth Floatation Method: -

This method is suitable for the concentration of Sulphide Ores only. In this method, two

interconnected tanks are used (Fig. 7.2). In one of the tanks, a mixture of ore, oil (pine oil), water and a little quantity of mineral acid is agitated strongly by blowing air through it. Due to the preferential wetting of the sulphide ores by oil than by water, a layer of oil gets covered over the surface of sulphide ores. These sulphide ores become lighter and float over the surface of the mixture, which are carried out into the second container along with the foam formed due to agitation.

(iii) Magnetic Separation method: -

This method of concentration is suitable only when there is a difference in the magnetic behavior

between the ores and the impurities. Normally, the magnetic ores containing non-magnetic impurities are concentrated by this method. In this method, a belt is tied over two rollers of which one is made of a magnet (Fig. 7.3). Powdered ore is added over the belt through a hopper. The magnetic part of the ore is attracted by the magnetic roller and forms a heap near it. Whereas the non-magnetic part of the ore forms a separate heap a little away from magnetic part.



(iv) Leaching: -

This is a chemical method in which the impure ore is treated with a suitable solvent which dissolves the ore leaving behind the impurities. The solution is filtered, impurities are removed, and the mother liquor is treated with another suitable chemical reagent to get the pure ore.

For example: Impure bauxite ore is treated with dil NaOH solution which dissolves Bauxite to form soluble sodium meta-aluminate.

$$Al_2O_3.2H_2O + 2NaOH \rightarrow 2NaAlO_2 + 3H_2O$$

The solution is filtered to remove the impurities. The solution obtained is diluted with plenty of distilled water when a precipitate of $Al(OH)_3$ is formed.

$$NaAlO_2 + 2H_2O \rightarrow Al(OH)_3 + NaOH$$

The precipitate obtained is dried and heated strongly to get pure alumina from which aluminium is extracted.

$$2Al(OH)_3 \xrightarrow{\Delta} Al_2O_3 + 3H_2O_3$$

3. OXIDATION: - In this step of metallurgical operation, the concentrated ores are converted into their respective metal oxides. This is achieved by the following two methods:

(i) Calcination:

- The process of heating an ore strongly below its melting point in the absence of air or in the limited supply of air is called Calcination.
- > This method is employed for carbonate ores and hydrated ores.
- Carbon dioxide gas is produced along with metal oxides. Examples:

$$ZnCO_3 \rightarrow ZnO + CO_2$$

$$CuCO_3 \rightarrow CuO + CO_2$$

During calcination following changes takes place:

Moisture is removed: $Fe_2O_3 \cdot 2H_2O \xrightarrow{\Delta} Fe_2O_3 + 2H_2O$ Volatile impurities are removed: S, P etc. are removed as vapours. Carbonate ores get converted into oxides: $FeCO_3 \rightarrow FeO + CO_2$

(ii) Roasting:

- The process of heating an ore strongly below its melting point in a free but controlled supply of air is called Roasting.
- > This method is employed for Sulphide ores.
- > Sulphur dioxide gas is produced along with metal oxides.

Examples:
$$2PbS + 3O_2 \rightarrow 2PbO + 2SO_2$$

 $2Cu_2S + 3O_2 \rightarrow 2Cu_2O + 2SO_2$
 $2ZnS + 3O_2 \rightarrow 2ZnO + 2SO_2$

> The changes taking place during roasting are:

Moisture is removed.

Volatile impurities are removed.

Impurities like sulphur, Arsenic, Phosphorous, etc. are removed in the form of their gaseous oxides: $S + O_2 \rightarrow SO_2$

 $P_4 + 5O_2 \rightarrow 2P_2O_5 \quad , \quad 4As + 3O_2 \rightarrow 2As_2O_3$

It makes the ore porous.

The process of roasting is carried out in a reverberatory furnace.

4. REDUCTION: - In this step of metallurgical operation, the roasted ores are reduced to convert the metal oxides into the respective metals. The various methods of reduction are:

(i) Smelting: - The process of heating a roasted ore strongly above its melting point with a suitable quantity of coke or charcoal is called smelting. During the process of smelting, metal oxides are reduced into their respective metals. For the reduction of the oxides of less electropositive metals such as Zn, Fe, Cu, Cr etc., the reducing agents like Co, Na, K, H₂O etc. are used.

Examples:
$$PbO + C \rightarrow Pb + CO$$

$$CuO + CO \rightarrow Cu + CO_2$$

During the process of smelting, an additional chemical substance called 'flux' is added which combines with the solid impurities to form fusible 'slag'.

Impurity + Flux \rightarrow Slag

Flux: A substance added during the process of smelting to convert the solid gangue into fusible mass (slag) is called flux.

The nature of the flux to be added depends upon the nature of the impurity present. For acidic impurities basic flux are used and for basic impurities acidic flux are used.

Acidic Flux: It is used to remove basic impurities such as metallic oxides.

Example: $FeO + SiO_2 \rightarrow FeSiO_3$ (Slag) Impurity flux (Basic) (Acidic) Basic flux: It is used to remove acidic impurity such as sand. $SiO_2 + CaO \rightarrow Ca SiO_3$ (Slag)



Impurity Flux (Acidic) (Basic)

Slag: It is the fusible mass obtained during the process of smelting when flux combines with the solid impurities.

Example: $SiO_2 + CaO \rightarrow CaSiO_3$ Smelting is carried out in a blast furnace (fig. 7.4) which is a tall cylindrical furnace made of steel plates lined inside with fire bricks. Since the density of slag is lower, it floats over the molten metal. The molten metal is tapped out at the bottom of the furnace.

- **5. REFINING:** The metals obtained after reduction still contain some impurities. The process of removal of impurities from crude metal is called refining. The method of refining to be followed depends upon the nature of the metal and the impurity contaminated with it. The following are the methods of refining:
 - (i) **Distillation Method**: This method of refining is suitable for volatile metals like Hg, Zn, Pb contaminated with non-volatile impurities. The impure metal is heated in a distillation flask attached with a water condenser. During heating the volatile metal gets evaporated and condensed which is collected in a separate container while the non-volatile impurities are left at the bottom of the distillation flask.



(ii) Electro refining: - This method is employed to refine the less electropositive metals such as Zn, Pb, Cu, Al. The impure metal bar is used as anode while a pure metal (same metal) bar is taken as cathode (Fig. 7.5). Both the electrodes are dipped in a suitable aqueous salt solution of the concerned metal. During the process of electrolysis, the impure metal dissolves in its aqueous salt solution providing metal ions which get discharged and deposited at the cathode.

ASSIGNMENT

- 1. Define Minerals and Ores. Give examples.
- 2. Differentiate between Minerals and Ores.
- 3. Which method is employed for the concentration of Sulphide Ores and why? Explain the process.
- 4. Explain leaching.
- 5. Explain gravity separation method.
- 6. Explain magnetic separation method of concentration of ores.
- 7. Differentiate between Calcination and Roasting.
- 8. What is smelting?
- 9. Explain Electrolytic Refining.
- 10. Define Flux and Slag with examples.

11. Define gangue.

Exercise

(02 Marks Questions)

- 1. What do you mean by gangue?
- 2. Mention the basic steps involved in the metallurgical operation.
- 3. What do you mean by concentration of ore?
- 4. What happens during oxidation step of metallurgical operation?
- 5. What happens during reduction step of metallurgical operation?
- 6. Why only sulphide ores are concentrated by froth floatation method?
- 7. Which types of ores are concentrated by magnetic separation?
- 8. Which types of ores are concentrated by gravity separation method?

- 9. What is leaching?
- 10. What is the purpose of adding charcoal or coke during smelting?
- 11. What do you mean by smelting?
- 12. Define calcinations and roasting.
- 13. What is slag?
- 14. What is the principle of distillation method of refining of crude metals?
- 15. What is electrometallurgy?
- 16. What is the purpose of addition of flux during smelting?

(05 Marks questions)

- 1. Explain the gravity separation method of concentration of ores.
- 2. Explain the froth floatation method of concentration of ores.
- 3. Explain the magnetic separation method of concentration of ores.
- 4. Explain the gravity leaching process of concentration of ores.
- 5. Define calcinations. Write down its functions.
- 6. Define roasting. Write down its function.
- 7. Define and explain smelting.
- 8. Explain the electrolytic method of purification of impure copper.

<u>CHAPTER – 8</u> <u>ALLOYS</u>

Alloy: The homogeneous material obtained by melting together metals or metals with non-metals or metals with metalloids is called an alloy.

Types of alloys:

- 1. **Ferro Alloys:** The alloy containing iron as the main constituent is called a ferro alloy. Example: Stainless Steel, Manganese Steel etc.
- 2. **Non-Ferro Alloy:** The alloy which does not contain iron as the main constituent is called as non-ferro alloy.

Example: Brass, Bronze, Gun metal etc.

3. **Amalgam:** Alloys containing mercury as one of the constituents is called amalgam. Example: Silver Amalgam, Sodium amalgam, Copper amalgam is used for filling dental cavities; Tin amalgam is used for silvering cheap mirrors.

SI. No. Composition Uses Alloys Cu: 60 – 90% 1. Brass It is used in making: Zn: 10 – 40% Utensils, Jewellery, Musical instrument, Battery caps, Condenser Tubes, Name plates, etc. 2. Bronze Cu: 80 – 95% It is used in making: Sn: 5 – 20% Making imitation jewellery, Water fittings, Statues, Medals, Turbine blades, Pump Valves, Coins, etc. 3. Alnico Steel: 50% It is used in making: AI: 20% Permanent Magnet. Ni: 21% Co: 9% 4. Duralumin AI: 95% It is used in making: Cu: 4% Air ships, Light weight vehicular Mn: 0.5% parts, etc. Mg: 0.5%

COMPOSITION AND USES OF BRASS, BRONZE, ALNICO AND DURALUMIN

ASSIGNMENT

- 1. Define Alloy. Classify them as ferro and non-ferro alloys with examples.
- 2. What is amalgam? Give examples.
- 3. Give the composition and uses of Brass, Bronze, Alnico and Duralumin.

Exercise

(02 Marks Questions)

- 1. What is alloy? Give an example of non-ferrous alloy.
- 2. What is amalgam? How is it formed?
- 3. What is the composition and uses of Brass?
- 4. What is the composition and uses of Bronze?

(05 Marks Questions)

- 1. Define alloy. Write down the composition and uses of Brass and Bronze.
- 2. Define alloy. Classify alloys into different types with examples.
- 3. Define alloy. What do you mean by amalgam? Write the important uses of amalgams.

<u>CHAPTER – 9</u> <u>HYDROCARBONS</u>

Introduction:

The branch of chemistry which deals with the study of covalently bonded compounds of carbon except, oxides of carbon (CO, CO₂), carbonates, bicarbonates, nitriles, and carbides (Na₂CO₃, NaHCO₃, NaCN, KCN, CaC₂, etc.) of certain metals is called organic chemistry.

Lemery classified all the substances in to three categories.

- 1. Compounds of Plant Origin: Vanaspati ghee, vegetable oil, honey, etc.
- 2. Compounds of animal origin: fats, etc.
- 3. Compounds of mineral origin: Rock salt, gypsum, limestone, bauxite, etc.

Lavoisier could be able to show that the first two categories of compounds essentially contain carbon, while the third category may or may not contain carbon. Hence, he reclassified the compounds into two categories. The first two categories are called organic compounds, while the third category referred as inorganic.

Till 18th century it was believed that organic compounds cannot be prepared in laboratories. The scientist Berzelius, put forth a theory called '*vital force theory*' according to which "There is an unseen supernatural force called 'vital force', which guides the formation of organic compounds." Since plants and animals (from which organic compounds are derived) are the creation of the almighty God and as human being we do not have any power over God, we can't prepare organic compounds in laboratories.

In 1828, a German Chemist named Wohler for the first time prepared an organic compound in laboratory. He heated ammonium cyanate, an inorganic compound and got the rearranged product 'urea' which is purely an organic compound.

 $\begin{array}{ccc} NH_4CNO & \stackrel{\Delta}{\leftrightarrow} & NH_2CONH_2 \\ (\text{Ammonium cyanate}) & (Urea) \end{array}$

Later, Berthelot synthesized methane (CH₄) starting from the carbon and hydrogen. Again, Lavoisier synthesized acetic acid (CH₃COOH) starting from the constituent elements C, H & O. soon after these syntheses, the whole idea about organic chemistry has changed and the 'vital force theory' got a strong blow.

Hydrocarbons:

The compounds containing carbon and hydrogen are called hydrocarbons. For example: CH_4 , C_2H_6 , C_2H_4 , C_2H_2 , C_6H_6 , etc.

Classification of hydrocarbons: -

HYDROCARBONS

Saturated hydrocarbons or alkanes

Alkenes

Alkynes

SATURATED HYDROCARBONS: These are the hydrocarbons containing C – C single bonds only. Example: Alkanes (Methane, ethane, propane, butane, pentane, etc.).

UNSATURATED HYDROCARBONS: These are the hydrocarbons containing carbon-carbon multiple bonds ($C = C, C \equiv C$).

Example: Alkenes (ethene, propene, butene, etc.) and alkynes (ethyne, propyne, butyne, etc.).

IUPAC SYSTEM OF NOMENCLATURE: -

IUPAC stands for "International **U**nion of **P**ure and **A**pplied **C**hemistry". According to this system an organic compound may contain the following four parts.

- 1. Root Word
- 2. Prefix
- 3. Primary Suffix
- 4. Secondary Suffix
- 1. **ROOT WORD:** It refers to the number of carbon atoms present in the parent chain of an organic compound.

No. of C	Root word	No. of	Root word
atom		C atom	
1	Meth	6	Hex
2	Eth	7	Hept
3	Prop	8	Oct
4	But	9	Non
5	Pent	10	Dec

2. PREFIX: It refers to the presence of substituent or side chain in the parent chain of an organic compound. Some groups that act as a substituent or side chain are:

Group	Prefix
—F	Fluoro
-CI	Chloro
—Br	Bromo
—I	lodo
-NO ₂	Nitro
–R	Alkyl
–OR	Alkoxy

3. PRIMARY SUFFIX: It refers to the presence of (C–C), (C=C), (C=C) in the compound.

Nature of Bond	Primary Suffix
All C–C bond	-ane
One C=C	—ene
Two C=C bond	-adiene
Three C=C bond	-atriene
One C≡C bond	—yne
Two C≡C bond	—adiyne

4. SECONDARY SUFFIX: It refers to the presence of functional groups in the compounds.

Functional Group	Secondary Suffix	
Alcohol(–OH)	—ol	
Aldehyde(-CHO)	—al	
Ketone(–CO–)	-one	
Carboxylic acid(–COOH)	–oic acid	
Amine(–NH ₂)	-amine	
Acid amide(–CONH ₂)	-amide	
Acid chloride(-COCI)	-oylchloride	

CLASS OF COMPOUNDS:

- (i) Alkanes
- (ii) Alkenes
- (iii) Alkynes
- (iv) Alkyl halides
- (v) Alcohol
- 1. Alkanes: These are the saturated hydrocarbons in which the carbon atoms are linked by single bonds (C–C). These are also called Paraffins.

General Formula: $C_n H_{2n+2}$ where 'n' is the no. of carbon atoms.

Primary Suffix: ane

n (No. of carbon atoms)	Molecular Formula	Structural formula	Common name	IUPAC name

1	CH4	H + - C - IH 	Methane	Methane
2	<i>C</i> ₂ <i>H</i> ₆	нн н-с-с-н н	Ethane	Ethane
3	<i>C</i> ₃ <i>H</i> ₈	ннн н-С-С-С-н ннн	Propane	Propane

2. Alkenes: These are the unsaturated hydrocarbons which have a carbon- carbon double bond (C=C) in their molecules. They are also called Olefins.

Primary Suffix: ene					
n (No. of carbon atoms)	Molecular Formula	Structural formula	Common name	IUPAC name	
2	C_2H_4	H-C=C-H H H	Ethylene	Ethene	
3	C ₃ H ₆	H-C=C-C-H H H H	Propylene	Propene	

3. Alkynes: These are the unsaturated hydrocarbons which have a carbon-carbon triple bond (C≡C) in

their molecules. These are also called Acetylenes.

General Formula: $C_n H_{2n-2}$ where 'n' is the no. of carbon atoms. **Primary Suffix:** yne

n (No. of carbon atoms)	Molecular Formula	Structural formula	Common name	IUPAC name
2	C_2H_2	H - C≡C - H	Acetylene	Ethyne
3	<i>C</i> ₃ <i>H</i> ₄	H H - C≡C - C - H I H	Methyl acetylene	Propyne

4. Alkyl halides or Haloalkanes: These are derived by replacing one H-atom of an alkane by a halogen atom.

General Formula: $C_nH_{2n+1}-X$ where 'n' is the no. of carbon atoms and 'X' refers to halogen atoms (F, Cl, Br, I).

n (No. of carbon atoms)	Molecular Formula	Structural formula	Common name	IUPAC name
1	CH3—Cl	н 	Methyl Chloride	Chloromethane
2	C₂H₅—Br	H H H - C - C - Br H H	Ethyl Bromide	Bromoethane

5. Alcohol: These are obtained by replacing one H-atom of an alkane by a hydroxyl group (–OH). The IUPAC name of an alcohol is obtained by replacing 'e' of the corresponding alkane by '**ol**'.

General Formula: $C_n H_{2n+1} - OH$ where 'n' is the no. of carbon atoms.

Suffi	x: o

n (No. of carbon atoms)	Molecular Formula	Structural formula	Common name	IUPAC name
1	СН ₃ —ОН	н н-С-Он н	Methyl alcohol	Methanol
2	С ₂ Н5—ОН	H H H-C-C-OH H H	Ethyl alcohol	Ethanol

RULES FOR IUPAC SYSTEM OF NOMENCLATURE:

1. **Expansion of chain:** Sometimes condensed groups are present in organic compounds. These condensed groups are to be separated.

Examples:



Selection of Parent Chain: The longest continuous carbon chain is called parent chain. The
parent chain is selected and the groups which are outside the parent chain are called substituent
or side chains.
Example:



- 3. Numbering of Carbon atoms: (Lowest number rule or lowest sum rule).
- a. Presence of one substituent or one side chain: The numbering of carbon atoms in the continuous carbon chain is done from one end to the other end, so that the carbon atom carrying the substituent get the lowest number. Examples:

b. Presence of 2 Substituents at the same position from either end: In this case minimum number is given to the carbon containing the substituent which comes first in alphabetical order. Example:

c. Presence of more than one substituents or side chains at any positions: In this case, number the parent chain from such an end so as to give lowest set of numbers possible to the substituents (Lowest Sum Rule).

Example:

CH₃
1 2 3 4 5
CH₃ - CH₂ - CH - CH - CH₃
5 4 3 2 1
CH₃
L → R: Sum = 3 + 4 = 7 X
R → L : Sum = 2 + 3 = 5
$$\sqrt{$$

- 4. Presence of Multiple bonds (double and triple bonds):
- (i) Select the longest continuous carbon chain as the principal chain which contains the maximum number of multiple bonds.

Example:





(ii) If a compound contains a multiple bond, then minimum number is given to the carbon containing the multiple bonds, irrespective of the position of the substituent or the side chain. Example:
- (iii) If the principal chain (parent chain) contains 2 or more multiple bonds, then number the principal chain from one end so that the multiple bonds get the lowest set of numbers. Example:
 - 1 2 3 4 5 χ C-C=C-C≡C 5 4 3 2 1 \checkmark L→R: Sum = 2 + 4 = 6 R→L: Sum = 1 + 3 = 4
- (iv) If the numbering of principal chain from both the ends gives the same set of numbers to multiple bonds, then select the set which gives lower number to the double bond. Example:

5. Presence of Functional groups: If a compound contains a functional group then, minimum number is given to the carbon containing the functional group irrespective of the position of the substituents, side chains or even multiple bonds. Example:

6. Arrangement of Prefixes: In an organic compound the WR, Prefix, PS and SS are arranged in the following way.

() - Prefix---- Root Word -----() - Primary Suffix ----- () - Secondary Suffix

Separate the number from the name of the substituent by a hyphen (-) and the numbers are separated by comma (,). If a particular substituent appears 2 or more times, then attach the prefix di, tri, tetra respectively to the name of the substituent and if there are 2 different substituents then they are written in alphabetical order. While following the rules for alphabetical order, the prefixes like di, tri, tetra etc. are ignored.

Example:

IUPAC Name: 4-Bromo-3-chloro-3-methylhex-4-en-2-ol

Note: The primary suffix for double bond is ene and for triple bond is yne. 'e' of ene is omitted if it is followed by a suffix starting with a, i, o, u, y. If the principal chain contains 2 double or two triple bonds, then suffix is diene or diyne respectively. In such cases 'a' is added to root word.

Examples:

Hex-1-en-5-yne

Hexa-1,4-diene

EXAMPLES:

Write the I.U.P.A.C names of the following organic compounds:

(i)
$$CH_3 - C - CH_2 - C - CH_3$$

 $I_{C_2H_5} C_2H_5$
(ii) $(CH_3)_2CH - C = CH$
(iii) $CH_3 - CH_2 - C = CH$
(iii) $CH_3 - CH_2 - C = CH - CH_2 - CI$
 $I_{H_1} Br$
 Br Br
(iv) $CH_3 - CH - CH - CH - CH_2 - CH_3$
 $I_{H_2} OH$
(v) $CH_3 - CH - CH - CH - CH_3$
 $I_{H_2} C_2H_5$
(v) $CH_3 - CH - CH - CH_3$
 $I_{H_2} C_2H_5$

Solution:

$$\begin{array}{cccc} F & CI \\ I & I \\ (i) CH_3 - C - CH_2 - C - CH_3 \\ I & I \\ C_2H_5 & C_2H_5 \end{array}$$

On expanding the condensed groups, we have F \$CI\$

$$\begin{array}{c} & & & \\ 5 & 4 & 3 \\ CH_3 - C - CH_2 - C - CH_3 \\ & & 6 \\ CH_2 & 2 \\ CH_2 \\ & 7 \\ CH_3 \\ & 1 \\ CH_3 \end{array}$$

3-Chloro-5-fluoro-3,5-dimethylheptane

(ii) $(CH_3)_2CH - C \equiv CH$

On expanding the condensed groups, we have

4 3 2 1

$$CH_3 - CH - C = CH$$

 I_{CH_3}
3-Methylbut-1-yne
(iii) $5 4 3^{I} 2 1$
 $CH_3 - CH_2 - C - CH - CH_2 - CI$
 $I I_{Br} Br$
1-Chloro-2,3-dibromo-3-methylpentane
(iv) $1 2 3 4^{I} 5 6$
 $(iv) CH_3 - CH - CH - CH - CH_2 - CH_3$
 I_{OH}
4-Methyl-2-nitrohexan-3-ol

(v) $CH_3 - CH - CH - CH_3$ | | $C_2H_5 C_2H_5$

On expanding the condensed groups, we have

$$\begin{array}{c} CH_{3} \stackrel{5}{-} CH \stackrel{4}{-} CH_{2} \stackrel{3}{-} CH - CH_{3} \\ \stackrel{6}{-} CH_{2} \qquad 2 \stackrel{1}{-} CH_{2} \\ \stackrel{7}{-} \stackrel{1}{C} H_{3} \qquad 1 \stackrel{1}{-} CH_{3} \\ \hline 3,5-Dimethylheptane \\ (vi) CH_{3} - CH_{2} \stackrel{2}{-} \stackrel{3}{-} CH \stackrel{4}{-} CH_{3} \\ \stackrel{1}{-} \begin{array}{c} H_{3} \\ CH_{3} \\ CH_{3} \end{array}$$

2-Ethyl-3-methylbut-1-ene

5-Bromo-4-chloro-4-methylhex-2-en-2ol

ASSIGNMENT:

Write the IUPAC names of the following:

WRITING STRUCTURAL FORMULA FROM IUPAC NAMES:

Steps to be followed:

- **1.** Arrange the carbon atoms corresponding to the root word in a single line separated by single bonds.
- 2. Number the carbon atoms from any end.
- **3.** Attach the side chains, substituents, multiple bonds and functional groups whichever is required at their respective positions.
- 4. Attach hydrogen atoms to satisfy the tetravalency of each carbon atom.

TYPES OF CARBON ATOMS IN ALKANES:

- 1. Primary (1°) carbon atom: It is the carbon atom attached to one carbon atom or all hydrogen atoms.
- 2. Secondary (2°) carbon atom: It is the carbon atom bonded to other carbon atoms on 2 different sides.
- 3. Tertiary (3°) carbon atom: It is the carbon atom bonded to other carbon atoms on 3 different sides.
- 4. Quaternary (4°) carbon atom: It is the carbon atom bonded to other carbon atoms on 4 different sides.

RULES FOR WRITING THE COMMON NAMES OF SOME SIMPLE ALKANES:

The simple branched chain alkanes can be assigned common names. According to common system of nomenclature, all the isomeric alkanes (having same molecular formula but different structural

formula) have the same parent name but are distinguished by prefixes. The prefix indicates the type of branching in the molecule.

(i) The prefix **n** (normal) is used for all those alkanes in which all the carbon atoms form a continuous chain with no branching.

CH₃ - CH₂ - CH₂ - CH₃ CH₃ - CH₂ - CH₂ - CH₂ - CH₂ - CH₃ n - butane n - pentane

(ii) Prefix iso is used for those alkanes in which one methyl group (formed by removal of one Hatom from methane) is attached to the second last carbon atom of the continuous chain. Examples:

iso-butane

iso-pentane

(iii) Prefix neo is used for those alkanes which have 2 methyl groups attached to the second last carbon atom of the continuous chain. Examples:

neo-pentane

neo-hexane

(If the branching occurs at any other position then these prefixes are not used.)

(iv) The prefixes sec and tert before the name of the alkyl group indicates the removal of H-atom from 2° and 3° carbon atoms respectively. Examples:

Sec-butyl alcohol

Tert-butyl alcohol

ASSIGNMENT:

Write the structural formulae of the following organic compounds:

(i) Tert-butyl alcohol

(ii) But-1-en-3-yne

- (iii) 3,4-dimethyl pentan-2-ol
- (iv) 1,1,2,2-tetrafloro ethene
- (v) 2,3-dibromo-1,4-dichloro but-2-ene
- (vi) Iso-hexane
- (vii) n-propyl iodide
- (viii) n-butyl bromide
- (ix) iso-pentyl alcohol
- (x) 4,5-dimethoxy hex-2-ene
- (xi) Propylene
- (xii) 3-Ethyl penta-1,3-diene

BOND-LINE REPRESENTATION: In bond line representation, each corner and terminal is considered as a carbon atom and the rest are considered as hydrogen atoms to satisfy the tetra-covalency of each carbon atom.

Examples: I.U.P.A.C names of the following bond line notation:



Substituting the carbon hydrogen atoms, we have,



2-Bromo-3-chloro-4-methylpent-2-ene

ASSIGNMENT:

Write the I.U.P.A.C names of the following:





DISTINCTION BETWEEN SATURATED AND UNSATURATED HYDROCARBONS:

SI. No.	Saturated hydrocarbons	Unsaturated hydrocarbons
1	Contain C–C single bonds and C–H	Contain carbon-carbon multiple bonds
	bonds.	(C = C and C≡C).
2	Less reactive.	More reactive.
3	Burn with blue flame.	Burn with sooty flame.
4	Show substitution reaction.	Show addition reaction.
5	Contain only sigma bonds.	Contain both sigma and pi bonds.
6	Examples: Alkanes.	Examples: Alkenes and Alkynes.

Aliphatic hydrocarbons: The open-chained hydrocarbons are called aliphatic hydrocarbons or acyclic hydrocarbons. These may be straight chain or branched chain. Example:

$$\begin{array}{c} CH_3-CH_2-CH_2-CH_3\\ n\ \text{ - pentane} \end{array} \qquad \begin{array}{c} CH_3-CH\ -CH_2-CH_3\\ |\\ CH_3\\ 2-Methylbutane \end{array}$$

Aromatic hydrocarbons: These are the closed chain or cyclic hydrocarbons. They obey Huckel's rule of aromaticity.

Huckel's Rule of Aromaticity: The cyclic hydrocarbon containing $(4n+2) \pi$ electrons in which single and double bonds are present in alternate positions is called an aromatic hydrocarbon. Where n = 0, 1, 2, 3, etc.

For example:



DISTINCTION BETWEEN ALIPHATIC & AROMATIC HYDROCARBONS.

SI. No.	Aliphatic hydrocarbons	Aromatic hydrocarbons
1	Open chain or Acyclic hydrocarbons.	Cyclic hydrocarbons containing (4n+2) π electrons in which single and double bonds are present in alternate positions.
2	Do not obey Huckel's rule.	Obey Huckel's rule.
3	No pleasant odour.	Pleasant odour.
4	Alkanes burn with non-sooty flame.	Burn with sooty flame.
5	Examples: Alkanes, Alkenes, Alkynes.	Examples: Benzene, Napthalene, Toluene.

USE OF SOME IMPORTANT AROMATIC COMPOUNDS:

- 1. Benzene: It is used:
 - (a) in manufacturing rubber, tyres.
 - (b) in the printing industry for cleaning and maintaining printing equipment.
 - (c) as an ingredient of a variety of painting products.
 - (d) in manufacturing chemical and plastic products.
 - (e) to clean parts such as hydraulic system, fuel system components and brakes.

2. Toluene: It is used:

- (a) as a solvent for paint, paint thinner, printer ink etc.
- (b) used in the synthesis of Trinitrotoluene (TNT) explosives.
- (c) in making elastic.
- (d) as a radiator fluid.
- (e) in breaking of RBC in order to extract the hemoglobin in biochemistry experiments.
- 3. BHC (Benzene Hexachloride): Also called gammaxene. It is used:
 - (a) as an important insecticide.
 - (b) as medication to remove head lice.

4. Phenol: It is used:

- (a) as disinfectant in household cleaners and in mouthwash when used in small quantity.
- (b) as surgical antiseptic.
- (c) in the manufacturing of cough syrups and other antiseptics.
- (d) as a starting material to make plastics and drugs such as aspirin.
- (e) in the study and extraction of biomolecules.
- 5. Naphthalene: It is used:

(a) in the form of mothballs and toilet deodorant blocks.

- (b) in making dyes, resins, insecticides.
- (c) in manufacturing of PVC (polyvinyl chloride).
- 6. Anthracene: It is used:
 - (a) in wood preservatives, insecticides.
 - (b) as a scintillator for detectors of high energy photons, electrons and alpha particles.
- 7. Benzoic acid: It is used:
 - (a) as a food preservative.
 - (b) in mouthwash, toothpaste, facial cleanser.
 - (c) in making dyes and insect repellents.
 - (d) a constituent of Whitfield's ointment which is used for the treatment of fungal skin disease.

ASSIGNMENT:

- 1. Define Saturated and Unsaturated hydrocarbons with examples.
- 2. Differentiate between Aromatic and Aliphatic hydrocarbons.
- 3. State Huckel's rule.
- 4. To which class the organic compound C_8 H₁₆ belong and how?
- 5. C₄H₈ belongs to which homologous series?
- 6. Distinguish between Saturated and Unsaturated hydrocarbons.

Exercise

(02 Marks Questions)

- 1. To which class of compound C_4H_{10} belongs and how?
- 2. To which class of compound C_5H_{10} belongs and how?
- 3. To which class of compound C_6H_{10} belongs and how?

- 4. What are saturated hydrocarbons?
- 5. What are unsaturated hydrocarbons?
- 6. How C_4H_8 is unsaturated?
- 7. What are aliphatic hydrocarbons? Give any two examples of it.
- 8. What is the IUPAC name of isopropyl alcohol?
- 9. What is the IUPAC name of tertiary butyl alcohol?
- 10. What is the IUPAC name of isobutyl chloride?
- 11. Give the structural formula of 4-Chloro-5-methylpent-2-en-2-ol.
- 12. Define Huckel's rule for aromativity.
- 13. How benzene is aromatic?
- 14. What is tertiary alkyl halide? Give an example of it.
- 15. What is the general formula of monohydric alcohols? Five a suitable example of it.

(05 Marks Questions)

- 1. What are saturated and unsaturated hydrocarbons? Is benzene saturated? Justify your answer.
- 2. Define and explain Huckel's rule of aromaticity with suitable examples.
- 3. What are aliphatic hydrocarbons? How can you classify them?
- 4. Define with example: Prefix, word root, primary suffix and secondary suffix.
- 5. What are the conditions of aromaticity?
- 6. Mention any two uses of benzene and toluene.
- 7. Mention any two uses of toluene and phenol
- 8. Mention any two uses of toluene naphthalene.
- 9. Mention any two uses of benzene and Anthracene
- 10. Mention any two uses of benzene and BHC.

<u>CHAPTER – 10</u> WATER TREATMENT

Water: -Water is one of the most plentiful and readily available of all chemicals. Next to air, water is the important constituent of life-support systems. It is called Universal Solvent because it can dissolve more substances than any other liquid. Although it is most often perceived as a liquid at normal atmospheric pressure, water exists as a solid below 0°C and as a gas above 100°C.

Sources of water: - The sources of water can be classified as follows.



A. Surface water- Surface water is just what the name implies; it is water found in a river, lake or other surface cavity.

- 1. Rainwater:
 - Rainwater is considered to be the purest form of natural water as impurities and salts present in water on earth are left behind during vaporization by the sun.
 - But when the rain droplets fall, they dissolve gases like carbon dioxide, oxides of sulphur and nitrogen which make the rain slightly acidic.

 $CO_2 + H_2O \rightarrow H_2CO_3$

 $SO_2 + H_2O \rightarrow H_2SO_3$

2. River water:

- A river is a naturally flowing watercourse, usually freshwater, flowing towards a sea lake or another river.
- Rivers are nourished by precipitation, by surface runoff, through springs or from melting of glaciers.
- > It contains high percentage of dissolved minerals like NaCl, KCl, NaNO₃, CaCO₃, NaHCO₃ etc.

3. Lake water:

- Lake is a relatively large body of slowly moving or standing water that occupies an inland basin of appreciable size.
- Lake water contains lesser amounts of dissolved minerals but considerable amount of suspended and organic matters.

4. Sea water:

- Sea water is the water from sea or ocean and is the most impure form of natural water.
- It contains about 3.5% of dissolved minerals out of which about 2.5% is only NaCl. Sea water also contains a number of dissolved gases like nitrogen, oxygen, carbon dioxide and noble gases and biomaterials like carbohydrates, proteins, amino acids etc.

B. Underground Water:

- Groundwater is the water that occurs below the surface of Earth, where it occupies all or part of the void spaces in soils or geologic strata.
- It is naturally replenished by rain and snow melt that seeps down into the cracks and crevices beneath the land's surface.

Underground water is of two types.

1.Spring water:

- > A spring is a natural outflow of water from an underground supply to the ground surface.
- It is a clearer form of natural water.
- It contains high percentage of minerals like magnesium, calcium, sodium and potassium & thus its hardness is very high.

2.Well water:

- > A well is a hole drilled, dug, or driven into the earth to obtain groundwater.
- It is a clearer form of natural water.
- > It contains many dissolved minerals and some organic matter.

Types of water

Water is of 02 types:

- (1) Soft water & (2) Hard water.
- 1. Soft water: Water which forms lather with soap solution is called soft water.

Ex: - Rainwater, demineralized water, distilled water etc.

2. Hard water: - Water which does not form lather with soap solution is called hard water. Instead, it forms a curdy white precipitate.

Ex: - Sea water, river water, Pond water etc.

Hardness of water:

It is the characteristic of water which prevents the lathering of soap due to the presence of bicarbonate, sulphate and chloride of calcium and magnesium in it.

Soap reacts with hard water as

 $\begin{array}{rcl} 2C_{17}H_{35}COONa + & MgSO_4 & \rightarrow & (C_{17}H_{35}COO)_2Mg + Na_2SO_4 \\ \mbox{(Sodium stearate)} & (Impurity in hard water) & (Magnesium stearate) \\ & soap \end{array}$

Types of hardness:

Hardness of water is of two types:

- A. Temporary or Carbonate hardness
- B. Permanent or Non-carbonate hardness
- A. Temporary hardness: The temporary hardness of water arises due to the presence of bicarbonates of Ca and Mg, [Ca (HCO3)2, Mg (HCO3)2].

It is named temporary hardness because the soluble bicarbonates decompose into insoluble carbonates simply on heating. Thus, water becomes soft. It is also called carbonate hardness.

B. Permanent hardness: The permanent hardness of water arises due to the presence of chlorides of Ca, Mg (CaCl₂, MgCl₂).It is named permanent hardness because such a hardness cannot be removed by simply boiling the water.

Unit of hardness

(1) PPM – Parts per million.

(2) mg/L – Milligrams per Litre.

Softening of water or removal of hardness:

Water softening is the process of removing the dissolved calcium and magnesium salts that cause hardness in water.

Removal of temporary hardness:

When temporary hard water is boiled, the soluble bicarbonates present in water decompose to give insoluble carbonates which settle down easily. Then the soft water is filtered off.

$Ca(HCO_3)_2 \xrightarrow{Boil} CaCO_3 + H_2O + CO_2 \uparrow$

Hard Water (insoluble)

(soluble)

$Mg(HCO_3)_2 \xrightarrow{Boil} MgCO_3 + H_2O + CO_2 \uparrow$

Hard Water (insoluble)

(Soluble)

Removal of permanent hardness:

A. Lime Soda Process: In this process hard water is treated with a calculated quantity of lime and soda. Lime and soda convert the soluble hardness

causing chemicals present in hard water into insoluble substances called sludges.The precipitate or sludge formed is then removed by filtration to get soft water.

 $\begin{array}{rcl} CaCl_2 + & Na_2CO_3 & \rightarrow & CaCO_3 \downarrow & + & 2NaCl \\ (soluble) & soda & (insoluble) \\ MgCl_2 + & Ca(OH)_2 & \rightarrow & Mg(OH)_2 \downarrow & + & CaCl_2 \\ (soluble) & soda & (Insoluble) \end{array}$

Lime-Soda process is of two types. (a) Cold Lime soda process (b) Hot lime soda process

(a) Cold Lime Soda Process:

Principle: When hard water is treated with calculated amount of lime $[Ca(OH)_2]$ and soda (Na_2CO_3) at room temperature 25°C, the soluble Ca and Mg salt present in hard water are chemically converted into ppt. of calcium carbonate $(CaCO_3)$ and magnesium hydroxide $[Mg(OH)_2]$. These ppts are removed by filtration. Thus, soft water is obtained.

CaCl ₂ +	$Na_2CO_3 \rightarrow$	CaCO ₃ ↓ +	2NaCl
hard water	soda	ppt	
MgCl ₂ +	Ca(OH) ₂ \rightarrow	Mg(OH)2↓ +	CaCl ₂
hard water	lime	ppt	

Process:

The apparatus consists of a conical shaped steel tank (Fig. 10.1) Raw water, lime, soda and coagulants are added from the top inner vertical circular chamber which is fitted with rotating shaft carrying many paddles. The dissolved salts of Ca and Mg combine with lime soda and coagulants and form an insoluble precipitate as sludge. Softened water rises upwards and the heavy sludge settles down. Then the softened water passes through wood fibre filter and the filtered soft water is collected through the outlet. The sludge setting down at the bottom is removed. The residual hardness left in this process is about 50 - 60 ppm.



Dis-advantages:

- It is a slow process because reactions during water softening take place in very dilute solutions and room temp.
- > It requires coagulant for setting particles of ppt. formed during reaction of water softening.
- Softening capacity of this process is less.
- > Soft water obtained by this process consists of dissolved gases.

(b) Hot Lime Soda process:

Principle: This process involves treatment of hard water with lime and soda at a temp. of 80-150°C. **Process:** In the hot lime soda process, the reactions take place at higher temperature near about boiling point of water. The chemical mixing process is same as the cold lime soda process, but steam is applied in mixture tank. As a result, precipitation becomes almost complete very quickly.



Apparatus:

The apparatus consists of 3 main parts (Fig. 10.2).

- (a) Reaction tank in which hard water, lime & soda are mixed thoroughly.
- (b)Conical sedimentation vessel in which sludges settle down.
- (c)Sand filter where sludge is completely removed.

Advantages:

- **1.** It is much economical.
- **2.** The reaction is completed within a short period.
- **3.** The reaction proceeds faster. Hence the softening capacity in increased.
- 4. No coagulant is required, as the sludge settles down easily.
- 5. Dissolved gasses like CO₂, air etc. are removed.
- 6. Under hot condition viscosity of water is lowered. Thus, filtration becomes easier.
- 7. Pathogenic bacterias are destroyed.
- **8.** The residual hardness left in this process is much lower (15-30 ppm) as compared to that in the cold L-S process (50-60 ppm).

Dis-advantages:

- > For efficient and economical softening careful operation and skilled supervision is required.
- > Disposal of large amounts of sludge creates problem.
- > This can remove hardness only up to 15ppm, which is not suitable for high pressure boilers.

	Cold Lime soda process	Hot lime soda process
1.	This process is conducted at room temp. (25°C)	This process is conducted at 80° to 150° C.
2.	It is costlier.	It is much economical.
3.	The process takes longer time to complete.	It takes comparatively less time for completion.
4.	The reaction is slower.	The reaction proceeds faster. Hence the softening capacity in increased.
5.	Coagulant like alum is required.	No coagulant is required, as the sludge settles down easily.
6.	Dissolved gases are not escaped.	Dissolved gasses like CO ₂ , air etc. are removed.
7.	Filtration is comparatively slower.	Under hot condition viscosity of water is lowered. Thus, filtration becomes easier.
8.	Pathogenic bacterias are not destroyed.	Pathogenic bacterias if any are destroyed.
9.	The residual hardness left is more, i.e., 50 – 60 ppm.	The residual hardness left in this process is much lower (15-30 ppm) as compared to that in the cold L-S process (50-60 ppm).

Difference between cold lime soda process & hot lime soda process

Advantages of Hot soda lime process over cold soda lime process: -

(i) The precipitation reaction becomes almost complete.

(ii) The reaction takes place faster.

(iii) The sludge settles rapidly.

(iv) No coagulant is needed.

(v) Dissolved gases are removed.

(vi) Residual hardness is low as compared to the cold lime-soda process.

Ion – Exchange Process [Deionization or De-mineralization process]:

In this method, the ions responsible for hardness are exchanged with other ions which don't make water hard.

Organic ion-exchangers (Ion-exchange resins): -

These are organic polymers having:

(i) high molecular weight.

(ii) Open and permeable molecular structure.

(iii) acidic (-COOH, -SO₃H) or basic groups (-OH⁻, -NH₂) attached with them.

Ion-exchange resins are of two types:

(a) Cation-exchange resin(R-H⁺): If the active ion in ion-exchanger is a cation, generally acidic functional groups, the resin is called cation-exchange resin, $Ex - (Resin-H^+)$

(b) Anion-exchange resin (R-H⁻): If the active ion in ion-exchanger is an anion, generally basic functional groups, the resin is called anion-exchange resin Ex – (Resin-OH⁻)

Process: The hard water is passed through a column of cation exchange resin called zero-carb. All the cations present in hard water get exchanged with H⁺ ions of the resin (Fig. 10.3).

2RH	+	Ca ²⁺ –	→ R ₂ Ca	+	2H ⁺
(Cation-I	Exchange R	esin) hard water	Exhausted	l Resin	
2RH	+	${ m Mg^{2+}} \longrightarrow$	R ₂ Mg	+	$2H^+$
(Cation-I	Exchange R	esin) hard water	Exhausted	l Resin	

Then the hard water is passed through the column of anion exchange resin. All the anions present in water get exchanged with OH- ions of the resin.

ROH	+	$Cl^- \rightarrow$	RCl +	OH-

(Anion-Exchange Resin) hard water

Exhausted Resin

H⁺ and OH⁻ ions released from the cation and anion exchange columns respectively get combined to produce water molecules.

 $H^{\scriptscriptstyle +} \textbf{+} O H^{\scriptscriptstyle -} {\rightarrow} H_2 O$

Thus, the water coming out from the exchanger is free from cations as well as anion. Such water is known as deionized or demineralized water.



Regeneration of resins:

When all the H^+ and OH^- ions of the resins are

exchanged by the cations and anions present in hard water, then the resins are said to be exhausted and regeneration can be done.

The cation-exchange resin can be regenerated by the treatment with dilute acids like dil. HCl or dil.H₂SO₄.

R ₂ Ca	+	2HCl	\rightarrow	2RH	+	CaCl ₂
(T-1)to	d			(D	(mineral has	

(Exhausted resin)

(Regenerated resin)

Similarly, the anion-exchange resin can be regenerated by the treatment with dilute alkali like, dil NaOH solution.

(Exhausted resin)

(Regenerated resin)

The regenerated resins may be used again. Advantages of Ion – Exchange Process –

- i. This process can be used to soften highly acidic or alkaline water.
- ii. It produces water of very low hardness (up to 2 ppm). So, it is good for treating water for use in high pressure boilers.

Dis-advantages of Ion – Exchange Process:

- The equipment is costly and more expensive chemicals are needed.
- *The second area of the second area of the second area of the second area.*

Exercise

(02 Marks Questions)

- 1.Define soft water and hard water.
- 2.What is hardness of water?
- 3. Why hard water does not produce lather with soap solution?
- 4. What do you mean by temporary and permanent hardness?
- 5. How temporary hardness can be removed?
- 6.What is the principle of Lime soda process?
- 7. What are the advantages of Hot Lime-Soda process?
- 8. What are the advantages of Ion-exchange process?

(05 Marks Questions)

- 1.Explain the softening of water by Lime-Soda process.
- 2. How hard water can be softened by lon-exchange process?
- 3. Write the difference between cold lime-soda process and hot lime-soda process.

CHAPTER – 11 LUBRICANTS

Introduction:

Lubricant is a substance, usually organic, introduced to reduce frictional resistance between surfaces in mutual contact, which ultimately reduces the heat generated when the surfaces move. It may also have the function of transmitting forces, transporting foreign particles, or heating or cooling the surfaces. The property of reducing friction is known as lubricity.

In addition to industrial applications, lubricants are used for many other purposes. Other uses include cooking (oils and fats in use in frying pans, in baking to prevent food sticking), bio-applications on humans (e.g., lubricants for artificial joints), ultrasound examination, medical examination. It is mainly used to reduce friction and to contribute to a better and efficient functioning of a mechanism.

Definition of Lubricants: Lubricants are the chemical substances applied in between two moving or sliding surfaces with a view to reduce the frictional resistance between them.

Types of lubricants: Basing upon the physical states, lubricants can be classified into three categories.

1.Solid lubricants: The lubricants that exist in solid form are called solid lubricants. Solid lubricants are preferred where the working temperature is very high and where there is a chance of contamination of the products with the lubricant.

Examples: Layered Compounds like graphite, boron trinitride, molybdenum disulphide, mica etc. are used as solid lubricants.

Uses of graphite:

- It is used to lubricate air compressors, railway track joints, food stuff industries, IC engines, open gears etc.
- Graphite mixed with oil called oil dag is used in IC engines.
- Graphite mixed with water called aqua dag is used in food industries.

2.Liquid lubricants: These are also known as lubricating oils.

Examples: Petroleum oil, Animal and Vegetable oil, Blended oil etc.

Uses of liquid lubricants: Liquid lubricants are used when,

- The operating temperature is high.
- Speed of the roller is high.
- The sealing arrangement is perfect to prevent the loss of oil.

3.Semisolid lubricants: Semi-solid lubricants are gel-like substances which reduce friction between two moving surfaces.

Example-greases, Vaseline, waxes, etc.

Uses of Grease:

- Tused where oil cannot remain in place due to high load, low speed, sudden jerks like rail axle.
- In bearings and gears which work at high temperature.
- There dropping of oil affects the machine or products like production of paper, textile etc.

Purpose of lubrication or Functions of lubricants:

1. It reduces friction and minimizes were and tear.

- 2. It reduces loss of energy.
- 3. It reduces noise pollution.
- 4. It increases the efficiency of engines.
- 5. It enhances the durability of machinery parts.
- 6. It reduces expansion of metals.
- 7. It acts as a coolant by removing heat of friction.

Exercise

(02 Marks Questions)

1.Define lubricant. Give an example of a semi-solid lubricant.

2. Give example of solid lubricants. Write the uses of graphite.

3.What are liquid lubricants?

(05 Marks Questions)

1. What is a lubricant? Write the major functions of lubricants.

2.Define lubricant. Write the classification of lubricants with examples.

CHAPTER – 12 FUEL

Introduction:

Fuel is any material that can be made to react with other substances so that it releases energy as heat energy or to be used for work. The concept was originally applied solely to those materials capable of releasing chemical energy but has since also been applied to other sources of heat energy such as nuclear energy (via nuclear fission and nuclear fusion).

The heat energy released by reactions of fuels is converted into mechanical energy via a heat engine. Other times the heat itself is valued for warmth, cooking, or industrial processes, as well as the illumination that comes with combustion. Fuels are also used in the cells of organisms in a process known as cellular respiration, where organic molecules are oxidized to release usable energy. Hydrocarbons and related oxygen-containing molecules are by far the most common source of fuel used by humans, but other substances, including radioactive metals, are also utilized.

Fuels are contrasted with other substances or devices storing potential energy, such as those that directly release electrical energy (such as batteries and capacitors) or mechanical energy (such as flywheels, springs, compressed air, or water in a reservoir).

Definition: Fuel is defined as a combustible substance which on combustion produces a large amount of heat energy without producing excess by-products.

 $\mathsf{Fuel} + \mathsf{O}_2 \to \mathsf{Products} + \mathsf{Heat}$

Classification of Fuels:



- A. On the basis of their occurrence, fuels may be classified into two categories: -
 - 1. Natural Fuels: Such fuels are found in nature.

Ex-Wood, coal, petroleum, natural gas etc.

2. Artificial Fuels: Such fuels are prepared from natural fuels.

Ex-Coke, kerosene, petrol, water gas, producer gas etc.

- B. Based on their physical state, fuels may be classified into three categories:
 - 1. **Solid Fuels**: Fuels which are found in their solid state at room temperature are generally referred to as Solid Fuels.

Ex-Wood, coal, charcoal, straw etc.

2. Liquid Fuels: Most liquid fuels are derived from the fossilized remains of dead plants and animals by exposure to heat and pressure in the Earth's crust.

Ex-Petroleum, Kerosene, Petrol, Diesel, alcohol etc.

3. Gaseous Fuels: Most gaseous fuels are composed of hydrocarbons, carbon monoxide, hydrogen, or a mixture of them all.

Ex- Natural gas, Coal gas, Producer Gas, Water Gas, Hydrogen etc.

Calorific value of fuel:

Calorific value may be defined as "the amount of heat energy produced by the complete combustion of a unit mass or unit volume of fuel in air."

Units of Calorific value are: Cal/gm, Kcal/Kg, KJ/Kg, B.Th./lb (British Thermal Unit/pound) etc.

Characteristics of good fuel:

- 1. It should have high calorific value.
- 2. It should be cheap and readily available.
- 3. It should leave only small amount of residue or ash when burnt.
- 4. It should have a controllable combustion rate.
- 5. It should not produce harmful combustion products.
- 6. It should not produce much smoke.
- 7. It should have moderate ignition temperature.
- 8. It should not be explosive in nature.
- 9. It should have low moisture content.
- 10.It should require low storage volume.
- 11.It should be easy to transport.

Composition and uses of some liquid fuels:

Diesel

- > It contains a mixture of hydrocarbons between pentadecane to octadecane ($C_{15}H_{32}$ to $C_{18}H_{38}$).
- > Average composition: C = 85%, H = 12%, Rest = 3%
- Calorific Value = 11,000 Kcal/kg

Uses: It is used as a fuel in diesel engine.

Petrol or Gasoline

- > It contains a mixture of hydrocarbons between pentane to octane (C_5H_{12} to C_8H_{18}).
- It is volatile and inflammable.
- > Average Composition C = 84%, H=15%, O+S+N = 1%
- \succ Calorific Value = 11,250 Kcal / Kg.

Uses:

- It is used as a fuel for internal combustion engines of automobiles.
- It is used as a dry-cleaning agent.

Kerosene

- > It consists of hydrocarbons between decane to hexadecane ($C_{10}H_{22}$ to $C_{16}H_{34}$).
- Average Composition, C = 84 %, H = 16%, S < 0.1%</p>
- Calorific value = 11,100 Kcal/ Kg

Uses:

- It is used as a domestic fuel in stoves.
- It is used as jet engine fuel for making oil gas.

Composition and uses of some gaseous fuels:

1. Water Gas

- (i) It is a mixture of combustible gases CO and H_2 with a little quantity of non-combustible gases like CO_2 and N_2 .
- (ii) The average composition of water gas is H_2 = 51 %, CO = 41 %, CO₂ = 4% & N₂ = 4%,
- (iii) Its calorific value is 2800 Kcal / m³.

Uses: It is used:

- as a source of H₂ Gas.
- 🕿 as a fuel.
- as an illuminating gas.
- for welding purposes.

2. Producer Gas:

- (i) It is a mixture of combustible gases, CO and H_2 with large quantities of non-combustible gases CO_2 and N_2 .
- (ii) The avg. composition of producer gas is CO = 22-30%, H_2 = 8-12 %, N_2 = 52-55 % & CO₂ = 3%
- (iii) Its calorific value is 1,300 Kcal /m³.

Uses: It is used:

- For heating open-hearth furnaces in steel & glass manufacture, muffle furnace in coke & coal gas manufacture.
- As a reducing agent in metallurgical operations.

3. Coal gas:

(i) It is a mixture of a number of hydrocarbons along with N_2 , H_2 , CO & CO₂.

(ii) It is a colourless gas and burns with a sooty flame.

(iii) The average composition of coal gas is

 $H_2=40\%$, $CH_4=32\%$, CO=7%, $C_2H_2=2\%$, $C_2H_4=3\%$, $N_2=4\%$, $CO_2=1\%$ & rest=11% (iv) Its calorific value is 4900 Kcal /m³.

Uses: It is used:

- ൙ as a fuel.
- as a reducing agent in metallurgical operations.
- 🕿 as an illuminant.
- 4. LPG (Liquified petroleum gas):
 - (i) It is mainly C3, C4 hydrocarbons of alkane & alkene.
 - (ii) It is highly inflammable.
 - (iii) It is colourless and odourless but a smelling agent called ethyl mercaptan(C_2H_5SH) is added to it to detect the leakage.

(iv) The average composition of LPG is

n-butane=27%, iso-butane=25%, butene=43%, propene=2.5% & propane=2.5%.

(v) Its calorific value is 27,800 Kcal /m³.

Uses: It is used:

- As a domestic fuel.
- As an industrial fuel.
- As a vehicular fuel.

5. CNG (Compressed Natural Gas):

(i) It is a colourless, odourless gas and burns with a pale blue flame.

(ii) The average composition of CNG is:

CH₄=70-90%, C₂H₆=4-9% & traces of propane and butane.

(iii) Its calorific value is 12500 Kcal $/m^3$.

Uses: It is used:

- as a fuel in low emissive vehicles like ULEV (ultra-low emission vehicles).
- as a domestic and industrial fuel.
- ☞ as a source of carbon in tyre industry.
- $\ensuremath{\mathscr{P}}$ for the production of H2 gas needed in fertilizer industry.

Exercise

(02 Marks Questions)

1. Define fuel. Write the characteristics of a good fuel in terms of calorific value and moisture.

2. What is calorific value of fuel? Write its unit.

3.What is CNG?

4.Write the composition of coal gas.

5. Write the composition of producer gas.

6. What are derived fuels? Give two examples.

(05 Marks Questions)

- 1. Define fuel. What are the characteristics of a good fuel?
- 2.Write the composition and uses of water gas and producer gas.
- 3.Write short notes on LPG and CNG.

CHAPTER – 13 POLYMERS

Introduction:

Polymers are materials that are used in almost every material we encounter on a day-to-day basis. They have particular importance in today's increasingly industrial world. They are often found in the fields of science, technology and industry.

Product made from polymers are all around us: clothing made from synthetic fibers, polyethylene cups, fiberglass, nylon bearings, plastic bags, polymer-based paints, epoxy glue, polyurethane foam cushion, silicone heart valves, and Teflon-coated cookware. The list is almost endless.

Polymerization: The process of joining together a large number of simple small molecules to make large molecules of high molecular weight is called polymerization.

Polymers: Polymers are high molecular mass compounds whose structures are composed of a large number of simple molecules. For example: Polythene, PVC (polyvinyl chloride), Bakelite, Buna-S-rubber, Teflon, etc. are the examples of polymer.

The word "polymer" is derived from Greek word 'poly' meaning "many" and ' meres 'meaning "parts"

Monomer: Monomer is the single repeating unit which on polymerization gives a polymer. For example: Ethene is the monomer unit of polyethene.



(A)Depending upon the sources, polymers may basically be classified in to two types, they are:

- (i) Natural Polymers: These are the polymers which occur in the nature. Ex. Natural rubber, silk, polysaccharides, starch, cellulose, etc.
- (ii) Synthetic Polymers: These are the polymers which are manufactured in industries. Ex. Polythene, PVC, Bakelite, Teflon, Nylon, Buna-S, Buna-N, etc.
- (B) Depending upon the nature of monomers present, polymers may be classified into the following types.

i. Homo-polymer:

The polymer containing monomer units of identical chemical composition is called a homopolymer. In other words, the polymer formed from one type of monomer is called a homo-polymer. Example: polythene, PVC, Polystyrene etc.

-----M – M – M – M – M – ----- where, "A" is the monomer unit.

(homopolymer)

ii. Copolymer:

The polymer containing monomer units of different chemical composition is called co-polymer or mixed polymer. For example: Terylene is a polymer of two monomers ethylene glycol and terephthalic acid. Other examples of co-polymer are Bakelite, Nylon-6,6, Nylon-6,10, Buna-S, Buna-N etc.

----- $M_1 - M_2 - M_1 - M_2 - M_1 - M_2$ ------(Copolymer)

(C) Depending upon the nature of the polymeric chain/structure polymers may be classified as:

(i) **Linear polymers:** These are the polymers in which the monomer units are linked to one another to form long linear chains. These linear chains are closely packed in space. The close packing results in high densities, tensile strength and high melting and boiling points. e.g., high density polyethene, nylon and polyesters are linear polymers.

(ii) **Branched chain polymers** In such polymers, the monomer units are linked to form long chains with some branched chains of different lengths with source. As a result of branching, these polymers are not closely packed in space. Thus, they have low densities, low tensile strength as well as low melting and boiling points. Some common Examples of such polymers are low density polyethene, starch, glycogen etc.

(iii) **Cross-linked polymers or network polymers:** In such polymers, the monomer units are linked together to form three-dimensional network like structure. These are expected to be quite hard, rigid and brittle. Examples of cross-linked polymers are Bakelite, glyptal, melamine-formaldehyde polymer etc.

Classification of Polymers Based on Mode of Polymerization

(i) Addition polymers: The polymers formed by the polymerization of monomers containing double or triple bonds (unsaturated compounds) without elimination of simple molecules are called addition polymers. Addition polymers have the same empirical formula as their monomers. Examples: Polythene, PVC, Polystyrene, etc.

(ii) Condensation Polymers: The polymers which are formed by the combination of monomers with the elimination of small molecules such as water, alcohol, hydrogen chloride etc., are known as condensation polymers. Examples: Nylon-6,6 is formed by the condensation of hexamethylene diamine with adipic acid. Similarly, Bakelite is a condensation co-polymer of phenol and formaldehyde.

	Thermoplastics	Thermosetting
1	These are formed by addition	These are formed by condensation polymerization.
	polymerization.	
2	These are generally linear polymers.	These are three dimensional cross-linked

Distinction between Thermoplastics & Thermosetting.

Linear chain polymer



Branched chain polymer



Cross linked polymer

		polymers.
3	These are soft.	These are hard and rigid.
4	These are soluble in some solvents.	These are insoluble in any solvent.
5	These become soft on heating and become hard on cooling.	These burn to char on prolong heating.
6	These can be remoulded, reshaped and recycled.	These cannot be remoulded, reshaped and cannot recycled.
7	Examples: Polythene, PVC, Nylon, etc.	Examples: Bakelite, Urea-formaldehyde resin, Terylene, etc.

Polythene:

(i) Low density polythene (LDP)

$$n(CH_2 = CH_2) \xrightarrow[(Traces of oxygen]{1000 to 2000 atm} -[CH_2 - CH_2]_{\overline{n}}$$

$$(Traces of oxygen or a peroxide initiator)$$

It is tough, flexible, transparent, chemically inert as well as poor conductor of electricity. It has moderate tensile strength but good tearing strength.

Uses: It is used

- in the insulation of electrical wires, cables.
- manufacture of bottles, toys and flexible pipes.

(ii) High density polyethylene (HDP)

$$n(CH_2 = CH_2) \xrightarrow[6-7]{333-343 \text{ K}} (CH_2 = CH_2)_n$$

$$(Ziegler Natta catalyst)$$

It has high density due to close packing. It is also chemically inert, tougher, and harder.

Uses: It is used

- ☞ in making containers,
- house wares,
- bottles,
- ൙ toys,
- @ electric insulation etc.

PVC (Poly Vinyl Chloride):

When vinyl-Chloride undergo polymerization in presence of a small quantity of benzyl peroxide, Poly Vinyl Chloride is formed



Uses: It is used for making:

- Sheets for tank lining
- Safely helmets.
- Refrigerator components
- Tyres, cycle and motorcycle mudguards
- Raincoat packing
- Tablecloths
- Electrical insulators
- Chemical containers, etc.

Bakelite (Phenol-Formaldehyde Resin):

It is a co-polymer of **phenol and formaldehyde**. When phenol and formaldehyde are reacted together two isomeric compounds *O-hydroxy methylphenol and P-hydroxy methylphenol are obtained*.



The orthohydroxy methylphenol thus formed undergoes polymerization with phenol to form a linear polymer compound called **"NOVOLAC**".

During the process of polymerization, a little quantity of hexamethylene tetraamine $[(CH_2)_6N_4]$ is added which converts 'novolac' into a hard resinous mass *called Bakelite*.



Uses: It is used in the manufacture of:

- i. Electrical insulators like plug, switch etc.
- ii. Cabinets for Radio and TV
- iii. Telephone parts
- iv. Paints, varnishes
- v. Hydrogen exchange resin for softening of hard water.

RUBBER:

Rubber is a naturally occurring polymer. It is obtained as *latex* from rubber trees. It is highly elastic. It can be easily deformed but regains its original shape after the stress is relieved.

Rubber is obtained from rubber plants like '*Hevea brasiliensis*' generally found in the tropical regions of *Brazil, Indonesia, Malaysia* etc. Certain saps are cut on the rubber plants and the thick milky liquid *called* **Latex** is collected. It is then diluted with water and filtered to remove any impurities present in it. Then, the latex is treated with acetic acid (CH₃COOH) which coagulates the latex. The coagulated latex is then passed through a creeping machine to obtain sheets of rubber. These sheets of rubber are then put into moulding machine to get moulded articles.

Natural rubber consists of "*isoprene*" as the monomer units, which is in the form of the polymer polycis-isoprene. Thus, natural rubber is nothing but the polymer *polycis-isoprene*.



Draw backs of natural rubber:

Natural rubber or raw rubber has the following drawbacks:

- i. It has very low thermal stability
- ii. It has very low tensile strength
- iii. It has high water absorption capacity.
- iv. It is attacked by atmospheric oxygen and ozone.

v. It is attacked by acids and alkalis.

vi. It has the property of tackiness.

Vulcanization of rubber:

Natural rubber is a thermoplastic. There are no cross links between the polymer chains. It becomes soft and sticky when heated. It is not hard and tough. The properties of natural rubber can be modified and improved by the process of vulcanization. To improve the properties of natural rubber, it is heated with sulphur or sulphur containing compounds at a temperature of $100^{\circ} - 140^{\circ}$ C.

The chemical process in which natural rubber is heated with 4 to 6% sulphur or sulphur containing compounds with a view to overcome the drawbacks of natural rubber are called vulcanization.



During vulcanization sulphur cross-links are formed in between the layers of polyisoprene at the carbon atoms containing double bond.

The formation of cross links makes *rubber hard, tough with greater tensile strength*. Although natural rubber is thermoplastic substance, yet on vulcanization, it is set into a given shape which is retained.



Advantages of Vulcanization:

After vulcanization, almost all the drawbacks of raw rubber are eliminated. Vulcanized rubber:

- i. has higher thermal stability
- ii. has comparatively lower tensile strength
- iii. has low water absorption capacity.
- iv. is not attacked by atmospheric oxygen and ozone.
- v. is resistant to acids and alkalis.

Exercise

(02 Marks Questions)

1.Define monomer and polymer with example.

2.Define homopolymer and copolymer.

3. What is degree of polymerization?

4.Name the monomer of PVC. Write its two important applications.

5.Name the monomers of Bakelite. Write its two uses.

6.What is natural rubber?

7.Write two advantages of vulcanization.

(05 Marks Questions)

1.Explain the terms monomer, polymer, homopolymer, co-polymer & degree of polymerization with examples.

2. What is a polymer? Write the composition and uses of Bakelite.

3.Define polymer? Write the composition and uses of PVC.

4. What is vulcanization of rubber. Write the advantages of vulcanization.

5. What are the differences between thermoplastic and thermosetting polymers?

CHAPTER – 14 CHEMICALS IN AGRICULTURE

Pesticides: Pesticides are chemical compounds that are used to kill pests, including insects, rodents, fungi, and unwanted plants (weeds).

The term pesticide includes all the following:

- i. Insecticides
- ii. Herbicides
- iii. Fungicides.

Insecticides: Insecticides are substances used to kill insects.

Examples: - Chlorinated hydrocarbons like DDT, BHC (gammaxene), Aldrin, Dieldrin etc.

Uses- Insecticides are used in agriculture, medicine, industry and by consumers.

Herbicides: A herbicide is a chemical substance used to kill unwanted plants. These are commonly known as weedkillers.

Examples: Acetochlor, Amitrole, Arsenic acid, dinitrophenol, dipyridyl, carbamate, Propanil, Paraquat, etc.

Uses- Herbicides can be used to clear waste ground, industrial and construction sites, railways, and railway embankments as they kill all plant material with which they come into contact.

Also, these are applied in ponds and lakes to control algae & plants such as water grasses that can interfere with activities like swimming and fishing.

Fungicides: Fungicides are pesticides that prevent, kill, mitigate, or inhibit the growth of fungi on plants.

Ex- Bleaching powder, CuSO₄ solution, aluminium phosphide, Copper oxychloride, Carbendazim, Carboxin, Mancozeb, etc.

Uses-These are used to control fungi that damage plants.

Bio-fertilizers: Biofertilizers are the substance that contains living microorganism. Biofertilizers increase the nutrients of host plants when applied to their seeds, plant surface or soil by colonizing the rhizosphere of the plant. These are environment friendly substitute for harmful chemical fertilizers.

The microorganism in Biofertilizers restore the soil's natural nutrient cycle and build soil organic matter. These are extremely advantageous in enriching soil fertility & fulfilling plant nutrient requirements.

Ex-Rhizobium, Azotobacter, Azospirillum, Blue green algae etc.

Uses-

- i. Rhizobium inoculant is used for leguminous crops.
- ii. Azotobacter can be used with crops like wheat, maize. mustard etc.
- iii. Blue green algae is used for paddy crops.

iv. Azospirillum is used for maize, sugarcane, millets etc.

Exercise

(02 Marks Questions)

- 1. What are insecticides? Give two examples.
- 2. What are fungicides? Write its uses.
- 3.What are herbicides? Write its uses.

(05 Marks Questions)

- 1. Define pesticide. Classify pesticides into different types with examples.
- 2. Define insecticide, herbicide and fungicide with suitable examples.
- 3. What are bio-fertilizers? Mention its different types with examples.

References:

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- 6. Fundamentals of Chemistry (Part-1 & 2) by Dr. A K Sahu and others, Laxmi Publications (P) Ltd.
- 7. Elements of Industrial Chemistry by G Mohapatra, Kalyani Publishers.