# **ENGINEERING CHEMISTRY**

# **FOR DIPLOMA STUDENTS**

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# **CONTENTS**

### **UNIT-1: PHYSICAL CHEMISTRY**

<u>SI. No</u>	<u>Chapter</u>	Pages
01	Atomic structure	3-15
02	Chemical bonding	16-24
03	Acid-base theory	25-31
04	solutions	32-48
05	electrochemistry	49-55
06	corrosion	56-58

### **UNIT-2: INORGANIC CHEMISTRY**

07	Metallurgy	59-66
08	Alloy	67-68

## **UNIT-3: ORGANIC CHEMISTRY**

	09	Hydrocarbons	69-84
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### **UNIT-4: INDUSTRIAL CHEMISTRY**

10	Water treatments	85-93
11	Lubricants	94-95
12	Fuels	96-100
13	Polymers	101-108
14	Chemicals in Agriculture	109-110

# 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  $9.11 \times 10^{-31}$  kg and carrying a charge of -  $1.602 \times 10^{-19}$  Coulomb.

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

**Neutron:** Neutron is a fundamental sub-atomic particle having mass of  $1.675 \times 10^{-27}$  Kg and carrying no charge.

Fundamental Particle	Mass	Charge	Relative Charge
Electron	9.11 x 10 <sup>-31</sup> kg	- 1.602 x 10 <sup>-19</sup> coulomb	-1
Proton	1.672 x 10 <sup>-27</sup> kg	+ 1.602 x 10 <sup>-19</sup> Coulomb	+1
Neutron	1.675 X 10 <sup>-27</sup> kg	0	0

Rutherford's Gold-foil Experiment/Rutherford's  $\alpha$ -scattering Experiment: (Discovery of Nucleus)

In 1911, E. Rutherford gave the first information about the almost-correct-picture of an atom. He bombarded a number of  $\alpha$ -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  $\alpha$ -particles.



**Observation and conclusion:** 

From the  $\alpha$ - scattering experiment, Rutherford observed that:

- > Most of the  $\alpha$ -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.
- 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.
- > A very few (0.01%)  $\alpha$ -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<sup>-13</sup> cm.

#### RUTHERFORD'S ATOMIC MODEL:

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

- > An atom consists of two parts; they are (i) Nucleus and (ii) extra nuclear part.
- > Every atom consists of a very small but heavy positively charged body, called nucleus.
- > The whole mass of an atom is concentrated at the nucleus.
- Electrons revolve around the nucleus with tremendous speed, like planets revolve around the sun. Therefore, the electrons are also called as planetary electrons.
- 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:

- 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. 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
- The model is silent about the definite energy and velocity possessed by the revolving electrons.
- This theory fails to explain the atomic spectra.
- This theory fails to explain the cause of chemical combination



#### **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:

- 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'.
- 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 content of various shells are compared by the formula:

$E_n = 2\pi^2 m e^4 z^2 / n^2 h^2$	where, m=mass of electron
	e=charge of electron
E <sub>n</sub> = -1312/n <sup>2</sup> KJ mol <sup>-1</sup>	z=atomic number
	n=no. of shell/principal quantum number (1,2,3,)
	h=plank's constant=6.626 x 10 <sup>-31</sup> joule sec.

- 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.
- 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  $h/2\pi$ , that is



#### mvr = n $h/2\pi$

where, n = 1, 2, 3, ..... m=mass of e<sup>-</sup> v=tangential velocity of revolving e<sup>-</sup> r=radius of orbit h=plank'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



#### FAILURES OF BOHR'S ATOMIC MODEL:

- 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 <sup>2</sup>
к	1	2 x 1 <sup>2</sup> =2
L	2	2 x 2 <sup>2</sup> =8
м	3	2 x 3 <sup>2</sup> =18
N	4	2 x 4 <sup>2</sup> =32

- 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:

		Electrons in			1
Atomic	Element	K-	L-	M-	N-
no.		Shell	Shell	Shell	Shell
01	Н	1			
02	Не	2			
03	Li	2	1		

04	Ве	2	2		
05	В	2	3		
06	С	2	4		
07	N	2	5		
08	0	2	6		
09	F	2	7		
10	Ne	2	8		
11	Na	2	8	1	
12	Mg	2	8	2	
13	Al	2	8	3	
14	Si	2	8	4	
15	Р	2	8	5	
16	s	2	8	6	
17	сі	2	8	7	
18	Ar	2	8	8	
19	ĸ	2	8	8	1
20	Са	2	8	8	2

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

 N.B- For charged species: Atomic Number = No. of Protons (p), electron number never be same as atomic number.

**For positive ion**: no. of electrons=atomic number - magnitude of charged carried by ion **For negative ion**: no. of electrons=atomic number + magnitude of charged carried by ion

For Examples:

Element	Atomic number(z)	Proton(p)	Electron(e)
0	8	8	8
N <sup>3-</sup>	7	7	10
Ca <sup>2+</sup>	20	20	18

**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)

For example:

Element	No of Protons (p)	No. of Neutrons (n)	Mass No. (A)
N	7	7	14
К	19	20	39

**Note:** (1)  $A - ne^{-} \rightarrow A^{n-}$ 

Example:  $Mg - 2e^- \rightarrow Mg^{2+}$ 

(2)  $A + ne^- \rightarrow A^{n-}$ 



Example: N +  $3e^- \rightarrow N^{3-}$ 

### Test Yourself:

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

Atom/Molecule/Ion	Р	е	n
0 <sup>2-</sup>			
Р			
Ν			
Ca <sup>2+</sup>			
NH4 <sup>+</sup>			
CO2			
H <sub>2</sub> O			
CO3 <sup>2-</sup>			
02			

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

Examples: Hydrogen has three isotopes: Protonium ( $_1H^1$ ), Deuterium ( $_1H^2$ ) and Tritium ( $_1H^3$ ) Similarly,  $_{17}Cl^{35}$  and  $_{17}Cl^{37}$ 

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: 18Ar40 & 20Ca40

#### **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;  $11Na^{23}$  and  ${}_{12}Mg^{24}$   ${}_{13}Al^{27}$  and  ${}_{14}Si^{28}$ 

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 + I) rule.

#### The (n + / ) Rule:

- 1. The sub-shell having lower (n+ /) value possesses lower energy and is filled first.
- 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.

Subshell	1s	2s	2p	3s	3p	3d	4s	4p	4d	4f	5s	5p
n	1	2	2	3	3	3	4	4	4	4	5	5
1	0	0	1	0	1	2	0	1	2	3	0	1
n+l	1	2	3	3	4	5	4	5	6	7	5	6

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

$$1s < 2s < 2p < 3s < 3p < 4s < 3d < 4p < 5s < 4d < 5p < 4f$$



### **ELECTRONIC CONFIGURATIONS: -**

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

<u>Elements</u>	Electronic configurations	<u>Elements</u>	Electronic configurations
₁H	1s <sup>1</sup>	<sub>16</sub> S	1s² 2s²2p <sup>6</sup> 3s²3p <sup>4</sup>
<sub>2</sub> He	1s <sup>2</sup>	17Cl	1s² 2s²2p <sup>6</sup> 3s²3p <sup>5</sup>
зLi	1s <sup>2</sup> 2s <sup>1</sup>	<sub>18</sub> Ar	1s² 2s²2p <sup>6</sup> 3s²3p <sup>6</sup>
<sub>4</sub> Be	1s <sup>2</sup> 2s <sup>2</sup>	19K	1s² 2s²2p <sup>6</sup> 3s²3p <sup>6</sup> 4s¹
<sub>5</sub> B	$1s^2 2s^2 2p^1$	<sub>20</sub> Ca	1s² 2s²2p <sup>6</sup> 3s²3p <sup>6</sup> 4s²
<sub>б</sub> С	$1s^2 2s^2 2p^2$	21 <b>Sc</b>	1s² 2s²2p <sup>6</sup> 3s²3p <sup>6</sup> 4s²3d ¹
<sub>7</sub> N	$1s^2 2s^2 2p^3$	22Ti	1s² 2s²2p <sup>6</sup> 3s²3p <sup>6</sup> 4s²3d ²
8O	1s² 2s²2p4	<sub>23</sub> V	1s² 2s²2p <sup>6</sup> 3s²3p <sup>6</sup> 4s²3d ³
<sub>9</sub> F	1s² 2s²2p <sup>5</sup>	<sub>24</sub> Cr	1s² 2s² 2p <sup>6</sup> 3s² 3p <sup>6</sup> 4s¹ 3d <sup>5</sup>
10 <b>Ne</b>	1s² 2s²2p <sup>6</sup>	<sub>25</sub> Mn	1s² 2s²2p <sup>6</sup> 3s²3p <sup>6</sup> 4s²3d <sup>5</sup>
11 <b>Na</b>	1s <sup>2</sup> 2s <sup>2</sup> 2p <sup>6</sup> 3s <sup>1</sup>	<sub>26</sub> Fe	1s² 2s²2p <sup>6</sup> 3s²3p <sup>6</sup> 4s²3d <sup>6</sup>

<sub>12</sub> Mg	1s <sup>2</sup> 2s <sup>2</sup> 2p <sup>6</sup> 3s <sup>2</sup>	<sub>27</sub> Co	1s² 2s²2p <sup>6</sup> 3s²3p <sup>6</sup> 4s²3d <sup>7</sup>
13AI	1s <sup>2</sup> 2s <sup>2</sup> 2p <sup>6</sup> 3s <sup>2</sup> 3p <sup>1</sup>	<sub>28</sub> Ni	1s² 2s²2p <sup>6</sup> 3s²3p <sup>6</sup> 4s²3d <sup>8</sup>
14 <b>S</b> i	1s² 2s²2p <sup>6</sup> 3s²3p²	29 <b>Cu</b>	1s² 2s² 2p <sup>6</sup> 3s² 3p <sup>6</sup> 4s¹ 3d <sup>10</sup>
15 <b>P</b>	1s² 2s²2p <sup>6</sup> 3s²3p³	зоZn	1s² 2s²2p <sup>6</sup> 3s²3p <sup>6</sup> 4s²3d <sup>10</sup>

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

The electronic configurations of 'Cr' & 'Cu' should be  ${}_{24}Cr = [Ar] 4s^2 3d^4 \& {}_{29}Cu = [Ar] 4s^2 3d^9$  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: O<sup>2-</sup>, Ca<sup>2+</sup>, P<sup>3-</sup>, Ti<sup>2+</sup>, Cr<sup>3+</sup>, Cu<sup>2+</sup>.

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+l) rule? Which out of 4s and 3d sub-shells has lower energy?

Q 4. What do you mean by 3d<sup>2</sup>?

#### 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.

**NOTE:** - 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<sup>+</sup>?

# 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 electro valency.

Features of Ionic bond: The formation of ionic bond involves:

- 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.
- 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 Ionization 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 IA and Gr IIA** 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 VIA and Gr VIIA 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 NaCl.

The electronic configurations of Na and Cl are given below:

<sub>11</sub>Na – 1s<sup>2</sup> 2s<sup>2</sup> 2p<sup>6</sup> 3s<sup>1</sup>

#### 17C/-1s<sup>2</sup>2s<sup>2</sup>2p<sup>6</sup>3s<sup>2</sup>3p<sup>5</sup>

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. Na becomes Na+ with 8 electrons in valence shell and attains the nearest noble gas configuration of Ne; while C*I* atom becomes Cl<sup>-</sup> 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<sup>+</sup>** and **Cl<sup>-</sup>** results in the formation of **NaCl**.

Example: II: Formation of MgCl<sub>2</sub>

The electronic configurations of Mg and Cl are given below: 12Mg - 1s<sup>2</sup> 2s<sup>2</sup> 2p<sup>6</sup> 3s<sup>2</sup> 17Cl - 1s<sup>2</sup> 2s<sup>2</sup> 2p<sup>6</sup> 3s<sup>2</sup> 3p<sup>5</sup>

An atom magnesium and chlorine contain 2 and 7 valence electrons respectively. During the formation of MgCl<sub>2</sub>, 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. Now Mg becomes **Mg<sup>2+</sup>** with **8** valence electrons, with electronic configuration similar to that of Neon. On the other hand, each chlorine atom after accepting an electron becomes **Cl**<sup>-</sup> ion with 8 valence electronic configuration similar to that of Argon.



The electrostatic force of attraction between Calcium and chloride ions results in the formation of MgCl<sub>2</sub>. Other examples of ionic compounds:

KCl, KBr, KI, CaBr<sub>2</sub>,Cal<sub>2</sub>, Na<sub>2</sub>O, CaO, MgO, etc.



**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 H<sub>2</sub> 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.

*Example:* 2: Formation of Cl<sub>2</sub> molecule.

The electronic configuration of 'Cl' is

17Cl - 1s<sup>2</sup> 2s<sup>2</sup> 2p<sup>6</sup> 3s<sup>2</sup> 3p<sup>5</sup>

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 electron with each other to form a covalent bond.



$$: ::: + ::: \to (::: :::)$$

*Example :3:* Formation of O<sub>2</sub> molecule

The electronic configuration of 'O' is

### 8O- 1s<sup>2</sup> 2s<sup>2</sup> 2p<sup>4</sup>

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.



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



#### *Example: 5:* Formation of H<sub>2</sub>O molecule.

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

<sub>8</sub>O- 1s<sup>2</sup> 2s<sup>2</sup> 2p<sup>4</sup>

#### <sub>1</sub>H - 1s<sup>1</sup>

The electronic configuration indicates 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. The shape of water molecule is bent shape or 'V' shape with bond angle 104.5<sup>o</sup>.





**Example: 6:** Formation of methane (CH<sub>4</sub>) molecule. The electronic configuration of 'C' and 'H' are <sub>6</sub>C - 1s<sup>2</sup> 2s<sup>2</sup> 2p<sup>2</sup> <sub>1</sub>H - 1s<sup>1</sup>

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 1more 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  $109^0$  28'.

*Example: 7:* Formation of ammonia (NH<sub>3</sub>) molecule.

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

#### 7N - 1s<sup>2</sup> 2s<sup>2</sup> 2p<sup>3</sup>

#### $_{1}H - 1s^{1}$

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. The shape of NH3 is pyramidal with a bond angle of 107<sup>0</sup>.



Other examples of covalent compounds: F<sub>2</sub>, Br<sub>2</sub>, I<sub>2</sub>, BF<sub>3</sub>, AlCl<sub>3</sub>, HCl, HF, SiO<sub>2</sub>, 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 CCl<sub>4</sub>, 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 co-ionic bond.



#### Example:1: Formation of ammonium ion (NH<sub>4</sub><sup>+</sup>)

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

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

Ammonia (NH<sub>3</sub>) contains a lone pair of electrons over 'N' while 'H<sup>+</sup>' ion contains no electron and requires two electrons to become duplet. Thus, the unshared pair of electrons over nitrogen in NH<sub>3</sub> is partially shared with H<sup>+</sup> ion and a Coordinate bond is formed.



#### Example: 2: Formation of Sulphur dioxide (SO<sub>2</sub>) molecule.

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

#### 16S - 1s<sup>2</sup> 2s<sup>2</sup> 2p<sup>6</sup> 3s<sup>2</sup> 3p<sup>4</sup>

#### 80- 1s<sup>2</sup> 2s<sup>2</sup> 2p<sup>4</sup>

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.



#### **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.



#### Assígnment

Q. Draw the Lewis structures of the following: MgCl<sub>2</sub>, O<sub>2</sub>, N<sub>2</sub>, SO<sub>2</sub>, NH<sub>4</sub><sup>+</sup> and H<sub>3</sub>O<sup>+</sup>.

# Chapter - 3 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 pH 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. Lowry – Bronsted Theory

3. Lewis Theory.

#### **ARRHENIUS THEORY:**

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

Example of Acid: HCl  $\longrightarrow$  H<sup>+</sup> (ag) + Cl<sup>-</sup>(ag)

Other examples of acids are: HNO<sub>3</sub>, H<sub>2</sub>SO<sub>4</sub>, CH<sub>3</sub>COOH, etc.

Examples of Bases: NaOH(s)  $\xrightarrow{water}$  Na<sup>+</sup>(ag) + OH<sup>-</sup> (ag)

Other examples of bases are: LiOH, KOH, NH<sub>4</sub>OH, Ca(OH)<sub>2</sub>, Al(OH)<sub>3</sub>, etc

#### **Salient Features:**

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

HCl + NaOH  $\rightarrow$  NaCl + H<sub>2</sub>O (Acid) (Base) (Salt) (Water)

Neutralization reaction may be represented as:

 $H^+(aq) + OH^-(aq) \rightarrow H_2O(I)$ 

(from acid) (from base)

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

#### Limitations:

i. H<sup>+</sup> ion does not exist in aqueous solution. It combines with H<sub>2</sub>O, as soon as its formation to give hydronium ion (H<sub>3</sub>O<sup>+</sup>).

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

**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 SO<sub>2</sub>, CO<sub>2</sub>, SiO<sub>2</sub>, P<sub>2</sub>O<sub>5</sub>, BF<sub>3</sub>, AlCl<sub>3</sub>, etc. which cannot provide  $H^+$  ions.

**iv.** The theory fails to explain the basic nature of the substances like  $NH_3$ ,  $PH_3$ ,  $Na_2O$ ,  $K_2O$ , 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<sup>+</sup> ion) to any other substance, while bases are the substances (molecules/ions) which accept a proton (H<sup>+</sup> ion) from any other substance".

In other words, acids are proton donors where as a bases are proton acceptors.

For example:



Since, HCl has donated a proton (to  $NH_3$ ), it acts as an acid. On the other hand,  $NH_3$  has accepted a proton from HCl and thus it acts as a base. Other examples of Acids are:

i. All Arrhenius acids are Bronsted-Lowry acids; (HCl, HNO<sub>3</sub>, H<sub>2</sub>SO<sub>4</sub>, H<sub>3</sub>PO<sub>4</sub>, CH<sub>3</sub>COOH, H<sub>2</sub>CO<sub>3</sub>

etc.), however the reverse is not true.

ii. Ions having capacity to donate H<sup>+</sup> ion: (HS<sup>-</sup>, HCO<sub>3</sub><sup>-</sup>, HPO<sub>4</sub><sup>2-</sup>, HSO<sub>4</sub><sup>-</sup> etc.)

Examples of Bases:

i. Neutral molecules such as: H<sub>2</sub>O, NH<sub>3</sub>, RNH<sub>2</sub>, PH<sub>3</sub>, AsH<sub>3</sub>, 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<sup>+</sup> ion) is called a conjugate acid-base pair.

Acid –  $H^+ \rightarrow$  Conjugate base

Base +  $H^+ \rightarrow$  Conjugate acid

**ii.** The substances such as  $H_2O$ ,  $HS^-$ ,  $HCO_3^-$ ,  $HPO_4^{2^-}$ ,  $HSO_4^{--}$ , 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.

 $HCI + H_2O \rightarrow H_3O^+ + CI^-$ 

[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 Na<sub>2</sub>O, K<sub>2</sub>O, 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 + H<sub>2</sub>O.

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

Acid	Conjugate- Base	Base	Conjugate- Acid
HCI	CI -	Br –	HBr
H <sub>2</sub> SO <sub>4</sub>	hso <sub>4</sub> -	CN⁻	HCN
HS⁻	s <sup>2-</sup>	0 <sup>2</sup> -	OH -
$NH_4^+$	NH <sub>3</sub>	$NH_3$	$NH_4$ +
H <sub>2</sub> O	OH-	H <sub>2</sub> O	H <sub>3</sub> O <sup>+</sup>

#### **Test Yourself:**

- 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<sub>3</sub>NH<sub>2</sub>, (C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>NH, NO<sub>3</sub><sup>-</sup>, NH<sub>3</sub>

#### 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<sub>3</sub><sup>+</sup>, H<sup>+</sup>, Mg<sup>2+</sup>, Al<sup>3+</sup>, Fe<sup>3+</sup> etc.

ii. Neutral molecules containing electron deficient atoms are Lewis acids. For example: BF<sub>3</sub>, AlCl<sub>3</sub>, FeCl<sub>3</sub>, ZnCl<sub>2</sub>, 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<sub>4</sub>, SiCl<sub>4</sub>, etc.

iv. The molecules having multiple bonding (= or  $\equiv$ ) between the atoms of different elements are acidic in nature. For example: CO<sub>2</sub> (O = C = O), SO<sub>2</sub>, etc.

#### **Examples of Bases: -**

i. All anions are Lewis bases:  $F^-$ ,  $Cl^-$ ,  $CO_3^{2^-}$ , etc.

ii. Neutral molecules containing, at least one lone pair of electrons are Lewis bases:

#### **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  $NH_3$  (Lewis base) and  $H^+$  (Lewis acid) results in the formation of a dative bond.



#### All Bronsted- Lowry 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.** Catalytic activity of Lewis acids cannot be explained because catalytic activity of many acids is due to their tendency to furnish H<sup>+</sup> ion. Lewis acids are lacking this activity.

iii. The theory fails to explain the relative strengths of different acids and bases.

iv. It fails to explain acid-catalysed 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 pH of about 7 and is neutral.

Example: HCl + NaOH  $\rightarrow$  NaCl + H<sub>2</sub>O

2. Neutralization between a Strong Acid and a weak Base: A strong acid reacts with a weak base to form an acidic salt. Its aqueous solution has a pH < 7 and the solution is acidic.

Example: HCl + NH<sub>4</sub>OH → NH<sub>4</sub> Cl + H<sub>2</sub>O

3. 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 pH > 7 and is alkaline.

Example: CH<sub>3</sub>COOH + NaOH → CH<sub>3</sub>COONa + H<sub>2</sub>O

4. **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 pH > 7 and is alkaline.

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

#### SALTS:

Def<sup>n</sup> (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.

Def<sup>n</sup> (2): Salts are ionic compounds which produce cation other than H+ and anion other than OH- in aqueous solution.

Def<sup>n</sup> (3): Salts are the compounds formed by the neutralization reaction between acids and bases.

#### **TYPE OF SALTS:**

Salts may be classified in to 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 hydrolysed in aqueous solution.

Example:	<u>Acids</u>	Normal salts
	HCI	NaCl, KCl, CaCl <sub>2</sub> , MgCl <sub>2</sub> , etc
	HNO₃	NaNO3, KNO3, Ca(NO3)2 , Mg(NO3)2 , etc.
	$H_2SO_4$	Na <sub>2</sub> SO <sub>4</sub> , K <sub>2</sub> SO <sub>4</sub> , CaSO <sub>4</sub> , MgSO <sub>4</sub> , etc.
	$H_3PO_4$	Na <sub>3</sub> PO <sub>4</sub> , K <sub>3</sub> PO <sub>4</sub> , Ca <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> , Mg <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> , 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:	Acids	Acidic salts
	$H_2SO_4$	NaHSO <sub>4</sub> , KHSO <sub>4</sub> etc.
	$H_3PO_4$	NaH <sub>2</sub> PO <sub>4</sub> , KH <sub>2</sub> PO <sub>4</sub> ,

#### Na<sub>2</sub>HPO<sub>4</sub>, K<sub>2</sub>HPO<sub>4</sub> etc.

Also these are the salts obtained by the neutralization between strong acids and weak bases. For examples:  $NH_4Cl$ ,  $NH_4NO_3$ ,  $(NH_4)_2SO_4$ , 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)Cl, Mg(OH)Cl, Zn(OH)Cl, Al(OH)2Cl etc. Also these are the salts obtained by the neutralization reaction between weak acids and strong bases. For examples: CH<sub>3</sub>COONa, CH<sub>3</sub>COOK, Na<sub>2</sub>CO<sub>3</sub>, K<sub>2</sub>CO<sub>3</sub>, 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<sub>2</sub>SO<sub>2</sub>.Al<sub>2</sub>(SO4)<sub>3</sub>.24H<sub>2</sub>O water 2K<sup>+</sup> + 2Al<sup>3+</sup> + 3SO<sub>4</sub><sup>2-</sup>

(Potash Alum)

Other examples: Mohr's Salt [FeSO<sub>4</sub>.(NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>.6H<sub>2</sub>O], carnallite (KCl. MgCl<sub>2</sub>.6H<sub>2</sub>O), 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:  $K_4[Fe(CN)_6]$  water  $4K^+ + [Fe(CN)_6]^-$ 

Other examples: K<sub>3</sub>[Fe(CN)<sub>6</sub>], [Cu(NH<sub>3</sub>)<sub>4</sub>]SO<sub>4</sub>, 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)Cl; Sodium potassium sulphate NaKSO<sub>4</sub>, etc.

 $Ca(OCI)CI \rightarrow Ca^{2+} + OCI^{-} + CI^{-}$ 

 $NaKSO_4 \rightarrow Na^+ + K^+ + SO4^{2-}$ 

# Chapter - 4 SOLUTIONS

#### 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 are 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 (12C) 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

At. No	Element	Symbol	Atomic weight in a.m.u
01	Hydrogen	Н	1
02	Helium	Не	4
03	Lithium	Li	7
04	Beryllium	Ве	9
05	Boron	В	11

Atomic masses of some elements are given below:

06	Carbon	С	12
07	Nitrogen	N	14
08	Oxygen	0	16
09	Fluorine	F	19
10	Neon	Ne	20
11	Sodium	Na	23
12	Magnesium	Mg	24
13	Aluminium	AI	27
14	Silicon	Si	28
15	Phosphorus	Р	31
16	Sulphur	S	32
17	Chlorine	Cl	35.5
18	Argon	Ar	36
19	Potassium	К	39
20	Calcium	Са	40
21	Scandium	Sc	45
22	Titanium	Ti	48
23	Vanadium	V	51
24	Chromium	Cr	53
25	Manganese	Mn	55
26	Iron	Fe	56
27	Cobalt	Со	58.6
28	Nickel	Ni	59
29	Copper	Cu	63
30	Zinc	Zn	65

108	silver	Ag	108
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#### GRAM ATOMIC MASS:

The gram atomic mass of an element is simply its atomic mass expressed in gram.

For example:	<u>Element</u>	<u>Gm.atomic mass</u>
	Н	1.008 gm
	0	16 gm
	Mg	24 gm

**Note:** 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 (6.023x 1023 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<sub>2</sub>SO<sub>4</sub>) can be obtained as

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

= 2 × 1+32+4×16 = **98 amu** 

Other examples:

	Compound	Molecular weight
	NaCl	23+35.5 = 58.5 amu
	HNO <sub>3</sub>	1+14+48 = 63 amu
	CaCO <sub>3</sub>	40+12+48 = 100 amu
	Al <sub>2</sub> (SO4) <sub>3</sub>	2×27+3×32+12×16 = 342 amu

Assignment

Q 1. Find the molecular weights of the following: Na<sub>2</sub>SO<sub>4</sub>, (NH4) CO<sub>3</sub>, (NH<sub>4</sub>)<sub>3</sub>PO<sub>4</sub>, CuSO<sub>4</sub>.5H<sub>2</sub>O

#### Gram molecular weight: -

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

<u>Compound</u>	<u>Gm. mol. weight</u>	
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.

**Gram equivalent weight:** The gram equivalent weight of a substance is its equivalent weight expressed in gram.

**Example :1** The equivalent wt. of 'Ca' in CaCl<sub>2</sub> can be calculated as follows:

	Са	Cl <sub>2</sub>
	40 parts	2×35.5 parts
	2×35.5 parts by mass o	f chlorine combines with 'Ca' = 40 parts
		40
Or	or 35.5 parts by mass of chlorine combines with calcium = x 35.5 2 x 35.5	
	Thus, equivalent weigh	t of 'Ca' in CaCl <sub>2</sub> is 20.

Assignment:

Q 2. Find out the equivalent weights of the underlined elements in the followings MgCl<sub>2</sub>, CaH<sub>2</sub>,

<u>Fe</u>O, <u>Fe</u><sub>2</sub>O<sub>3</sub>

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 MHv,

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

 $M = \frac{A}{V \times 1.008} \quad X \quad 1.008 \text{ parts} = \frac{A}{V}$ 

Hence, equivalent weight (E) = A/V

Or, Equivalent weight (E) = 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<sub>2</sub> and FeCl<sub>3</sub> are:

Eq. Wt. of 'Fe' in FeCl<sub>2</sub> =atomic weight /valency =56/2=28

Eq. Wt. of 'Fe' in FeCl<sub>3</sub> =atomic weight/valency=56/3=18.6

#### 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.

$$E_{Acid} = \frac{Molecular \ weight}{Basicity}$$

Where 'basicity' is the number of replaceable hydrogen atoms present one molecule of the acid.
ACID	FORMULA	MOL.Wt.	BASCITY	EQ.Wt.
Nitric Acid	HNO <sub>3</sub>	63	1	63/1 = 63
Sulphuric Acid	H <sub>2</sub> SO <sub>4</sub>	98	2	98/2 = 49
Phosphoric Acid	H <sub>3</sub> PO <sub>4</sub>	98	3	98/3 = 32.66
Formic Acid	НСООН	46	1	46/1=46
Acetic Acid	CH3COOH	60	1	60/1 = 60
Oxalic Acid	соон			
	соон	90	2	90/2=45
Phosphorous Acid	H <sub>3</sub> PO <sub>3</sub>	82	2	82/2 = 41
Boric Acid	H <sub>3</sub> BO <sub>3</sub>	62	1	62/1 = 62
Note: HCOOH → H	COO <sup>-</sup> + H <sup>+</sup>	Ha	$PO_3 \rightarrow 2H^+$	+ HPO3 <sup>2-</sup>

 $\mathrm{CH_3COOH} \rightarrow \mathrm{CH_3COO}^- + \mathrm{H^+}$ 

 $H_3PO_3 \rightarrow 2H^+ + HPO_3^2$ 

 $H_3BO_3 \rightarrow H^+ + H_2BO_3^-$ 

### 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 <sub>Base</sub> = 
$$\frac{Molecular weight}{Acidity}$$

Where acidity is the number of replaceable OH groups present in one molecule of the base. Examples: -

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

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

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

Salt	Mol.formula	Mol.wt.	Total +ve Charges	Eq. wt.
Sodium chloride	NaCl	58.5	1x1 =1	58.5
Potassium carbonate	K <sub>2</sub> CO <sub>3</sub>	138	1x2 = 2	69
Calcium Sulphate	CaSO <sub>4</sub>	136	1x2 = 2	68
Aluminium Suplhate	Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	342	2x3 = 6	57

### Assignment

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

Acids: H<sub>2</sub>CO<sub>3</sub>, HNO<sub>3</sub>, C<sub>2</sub>H<sub>5</sub>COOH Bases: Mg(OH)<sub>2</sub>, LiOH

Salts: KCl, Na<sub>2</sub>CO<sub>3</sub>

### **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 HNO<sub>3</sub> 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:

 $M + O2 \rightarrow MO2$  x gm (y-x) gm y gmLet 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 =  $\frac{x}{(y-x)}X 8 = \frac{\text{weight of metal}}{\text{weight of oxygen}}X 8$ 

### **Numerical Problems:**

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

(a)  $\underline{Fe}_2O_3$  (b)  $\underline{Cu}Cl_2$  (c)  $\underline{Al}_2O_3$ 

### SOLUTION:

<u>In Fe2O3;</u>

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

 $\Rightarrow$  8 parts by mass of 'O' combines with 'Fe' = = 18.66

In CuCl<sub>2</sub>;

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.

∴ Weight of oxygen = 1.497 – 1.201 = 0.296 gm

Hence, equivalent weight of metal =  $\frac{\text{weight of metal}}{\text{weight of oxygen}} \times 8 = \frac{1.201}{0.296} \times 8 = 32.45$ 

**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<sub>cu</sub> = 0.723 gm

Weight of Silver W<sub>Ag</sub> = 2.455 gm

Equivalent weight of Silver E<sub>Ag</sub> = 107.88

Equivalent weight of Copper Ecu = ?

Applying Faraday's 2nd law of electrolysis:

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

### EQUIVALENT WEIGHT OF IONS:

Equivalent weight of Ion (E<sub>100</sub>) =  $\frac{Ionic Mass}{Total Ch \arg e}$ 

For example,

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

### Assignment:

Q 5. Find out the equivalent masses of the underlined atoms in the following. CaCl<sub>2</sub>, FeO, NaHCO<sub>3</sub>, FeCl<sub>3</sub>.

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 litre of solution".

Unit = gram mole/litre or M.

Mathematically,

$$M = \frac{w \ x \ 1000}{Ms \ x \ Vml}$$

Where, w = weight of the solute in gram Ms = Molecular weight of the solute.

Vml = Volume of solution in ml.

### Molar solution:

The solution containing 1 gm mole of the solute per litre 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<sub>2</sub>SO<sub>4</sub> per litre of solution is called molar solution.

NOTE: 1. Deci molar solution means (1/10) M solution, Semi-molar solution means (1/2) 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  $(V_{ml}) = 200 \text{ ml}.$ 

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

Thus, Molarity (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

Deci molar 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 = 
$$\frac{w \ x \ 1000}{Ms \ x \ Vml} \Rightarrow w = \frac{M \ x \ Ms \ x \ Vml}{1000} = \frac{0.1 \ x \ 56 \ x \ 1500}{1000} = 8.4 \text{ gram.}$$

Thus, 8.4 gm of caustic potash is required to prepare 1.5 lit. of decimolar 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/litre or 'N'.

Mathematically,

$$\mathsf{N} = \frac{w \, x \, 1000}{Es \, x \, Vml}$$

Where, w = weight of solute in gm. V<sub>ml</sub> = volume of solution in ml. Es = 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 H2SO4 or 40 gm of NaOH per litre 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,  $V_{ml} = 800 \text{ ml}.$ Equivalent weight of solute, KOH (Es) =  $\frac{Molecular \text{ weight}}{Acidity} = \frac{56}{1} = 56$ 

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

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.

Solution: Given Data,

Wt. of solute, w = density  $\times$  volume = 1.2  $\times$ 10 = 12 gm.

Volume of solution,  $V_{ml} = 400$  ml.

Equivalent weight of H<sub>2</sub>SO<sub>4</sub> =  $\frac{Molecular \ weight}{Basicity}$  = 98/2 = 49

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

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,

$$\mathsf{m} = \frac{w \ x \ 1000}{Ms \ x \ W}$$

Where, w = weight of solute in gm W = weight of solvent in gm Ms = 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 H<sub>2</sub>SO<sub>4</sub> 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, Ms (NaCl) = 23+35.5 = 58.5 amu.

Thus, molality(m) = 
$$\frac{w \times 1000}{Ms \times W} = \frac{5.85 \times 1000}{58.5 \times 200} = 0.5 \text{m}$$

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

Thus, molality (m) =  $\frac{w \ x \ 1000}{Ms \ x \ W} = N = -\frac{5.6 \ x \ 1000}{56 \ x \ 294.4} = 0.339 \text{ m.}$ 

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 semimolar solution?

**Q 10.** 9.8 gm of H<sub>2</sub>SO<sub>4</sub> is present in 400ml of its solution. Calculate its molarity and normality.

**Q 11.** 0.49 gm of  $H_2SO_4$  is present in 600ml of its solution having density 1.2 gm/ml. Find molarity, normality and molality of the solution.

### <u>pH of Solutions</u>

The  $p_{\rm H}$  of a solution may be defined as "the negative logarithm of H+ ion concentration in moles/litre or molarity."

### *Thus, pH* = - log[H<sup>+</sup>]

**pH** is normally used to know whether a solution acidic, alkaline or neutral in nature.

0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 greater in acidity Neutral pH greater in alkalinity

The pH scale

- I. If *pH* < 7; the solution is Acidic,
- II. If *pH* > 7; the solution is Alkaline,
- III. If *pH* = 7; the solution is Neutral.

**Note:** Pure water has a  $P_H$  value of '7' at 25<sub>0</sub>C and is neutral. The  $P_H$  value of water decreases with the increase in temperature.

### Some important Formulae:

- I. pH = -log [H<sup>+</sup>]
- II.  $pOH = -log [OH^-]$
- III. pH + pOH = 14
- IV.  $[H^+][OH^-] = 10^{-14}$
- V. [H<sup>+</sup>] = 10<sup>-pH</sup>
- VI. [OH<sup>-</sup>] = 10<sup>-pOH</sup>

### **QUESTIONS FOR DISCUSSION:**

- **1.** Find out the *p*<sub>H</sub> values of the following solutions.
- i. 0.01M HCl solution
- ii. 0.001 M HNO<sub>3</sub> solution
- iii. 0.01M NaOH solution
- iv. 0.01M H<sub>2</sub>SO<sub>4</sub> solution

### Solutions: -

i. HCl  $\rightarrow$  H<sup>+</sup> + Cl<sup>-</sup>

- 0.01M 0.01M
- $[HCI] = [H^+] = 0.01M = 10^{-2}M$
- Hence  $pH = -\log[H^+] = -\log(10^{-2}) = -(-2)\log 10 = 2$
- ii. HNO3  $\rightarrow$  H<sup>+</sup> + NO<sup>-</sup><sub>3</sub>
- 0.001M 0.001M
- $[HNO3] = [H^+] = 0.001M = 10^{-3} M$
- Hence,  $pH = -\log[H+] = -\log_{10-3} = -(-3)\log_{10} = 3$ .
- **iii.** NaOH  $\rightarrow$  Na<sup>+</sup> + OH<sup>-</sup>

0.01M 0.01M

 $[NaOH] = [OH-] = 0.01M = 10^{-2} M$ 

We know [H<sup>+</sup>] [OH<sup>-</sup>] = 10<sup>-14</sup>

$$\implies [H^+] = \frac{10^{-14}}{[OH^-]} = \frac{10^{-14}}{10^{-2}} = 10^{-12}$$

Hence,  $pH = -\log [H^+] = -\log (10^{-12}) = 12$ 

iv.  $H_2SO_4 \rightarrow 2H^+ + SO_4^{2-}$ 

0.01M (2 x 0.01) M

 $[H_{+}] = 2 \times 0.01 = 2 \times 10^{-2} \text{ M}$ 

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

### Assignment

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

(i) 1 M HNO<sub>3</sub> solution (ii) 0.1 M Mg (OH)<sub>2</sub> solution. [Ans: (i) 0, (ii) 12.301]

Q 13. One litre of a solution contains 5.85 gm of HCl. Find the PH value of the solution. [Ans: 1]

**Q 14.** 500 ml of an aqueous solution contains 1.6 gm of NaOH. Find PH of the solution.

### Importance of pH in Industries:

**1.** In sugar Industry: - The *PH* value of the sugar cane juice should be nearly '7' i.e. it should be neural. If the *PH* value of sugar cane juice becomes less than '7', the sucrose in the juice is hydrolysed in to 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 pH. Cobb control is done by addition of Alum (which is in the range of 2-3 pH) 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 pH 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 pH 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 pH dependent. The amount of chemicals required for a given process is directly related to the pH. The solubility of substances, such as dyes and impurities, vary with pH. The corrosive and scaling potential of processing solutions is also heavily influenced by pH. All of 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 pH of 10 is considered optimum for the removal of wool wax.

In the instance of vat dyeing, pH 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 pH 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 pH 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

47

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 pH 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,  $HO_2^{-1}$ , is used to perform the actual bleaching. To ensure an adequate concentration of  $HO_2^{-1}$ , the solution pH must be tightly controlled. Sodium hydroxide is used to maintain the pH at a very alkaline level of 12-12.5.

**4.** In chemical Industry: - Certain chemical reactions occur at definite *P*<sub>H</sub> values. Thus, the *pH* values of such type of reactions are carefully maintained to have a better control over the chemical reactions.

**5.** In Electroplating: - For smooth and shining deposits the *P*<sub>H</sub> values of the electrolytic baths are carefully maintained during the process of electrolysis.

**6.** In water Treatment: - In city water supplies the *P*<sub>H</sub> value of the water should be carefully maintained. For the effective action of coagulant, the *P*<sub>H</sub> value of water should be maintained between 4.2 to 7.6.

**7. Effluents from chemical Industries:** - The waste materials from chemical industries should be properly treated to make them neutral before they are discharged in to the water bodies. Otherwise highly acidic or alkaline substances may corrode the bridges, structures etc

## CHAPTER - 5 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 is called electrolytes. Example: All acids, all alkalis and all salts.

### Non-electrolyte:

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

### **Classification of Electrolytes:**

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

- i. Strong electrolytes
- ii. Weak electrolytes

**i. Strong electrolytes:** These are the electrolytes which undergo almost complete ionization in aqueous solution. Example: a) acids like HCl, HNO<sub>3</sub>, H<sub>2</sub>SO<sub>4</sub>, etc. b) alkalis like NaOH, KOH, Ca(OH)<sub>2</sub>, Mg(OH)<sub>2</sub>, etc. c) salts like NaCl, KCl, CaCl<sub>2</sub>, MgCl<sub>2</sub>, etc.

**ii. Weak electrolytes:** These are the electrolytes which undergo partial ionization in aqueous solution.

Example:

- a) Organic acids like CH<sub>3</sub>COOH, HCOOH, (COOH)<sub>2</sub>, etc.
- b) Inorganic acids like H<sub>2</sub>CO<sub>3</sub>, 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**.

### 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 NaCl.

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

### At Anode:

 $Cl^{-} - e - \rightarrow Cl$  (Primary change)

 $CI + CI \rightarrow CI2$  (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 NaCl solution.

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

$$NaCl \rightarrow Na^{+}(aq) + Cl^{-}(aq)$$

$$H2O \rightarrow H^+ + OH^-$$

Out of Cl<sup>-</sup> and OH<sup>-</sup> ions, the former has lower discharge potential and hence preferably gets discharged at the anode.

$$2Cl^{-} - 2e - \rightarrow Cl^{2}$$

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

$$2H^+ + 2e - \rightarrow H2$$

Thus, electrolysis of aqueous NaCl 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,

WαQ	Where, W = Amount of substance in gram
$\Rightarrow$ W $\alpha$ I t	Q = Quantity of electricity or Charge in coulomb
$\Rightarrow$ W = Z I t	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

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.

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

 $\Rightarrow$  1 coulomb of charge deposits =  $\frac{1 gram \ equivalent}{96500 C}$ 

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

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 AgNO<sub>3</sub> for 1 hour?

Solution:

Given Data: I = 10 Ampere

t = 1 hr = 3600 Sec.

$$Z = \frac{1 gram equivalent}{96500 C} = \frac{A tomic mass / Valency}{96500} = \frac{108 / 1}{96500} = -\frac{108}{96500} = 0.0011$$

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<sup>2+</sup> into Ca.

ii. Two moles of Al<sup>3+</sup> into A*l*.

Solution:

i. Ca<sup>2+</sup> + 2e -  $\rightarrow$  Ca

1 mole of electrons carries 96500 coulombs.

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

### ii. 2Al₃++ 6e - → 2Al

1 mole of electrons carries 96500 coulombs.

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

**Question 3:** How many coulombs of charge are required to get 10 grams of calcium from molten CaCl<sub>2</sub>?

Solution:

W = 10 gm, Q =?

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

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

### 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 of substances deposited at various electrodes are directly proportional to their equivalent masses".

Mathematically,

W α 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<sub>Ag</sub> α E<sub>Ag</sub> ------(1)

Wcu α Ecu -----(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 genera

al 
$$\frac{W_1}{W_2} = \frac{E_1}{E_2} = \frac{Z_1}{Z_2}$$
 or  $W \alpha E \alpha Z$ 

**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 WH2 = 0.0132 gm Weight of copper WCu = 0.4164 gm Equivalent weight of hydrogen EH2 = 1.008 Equivalent weight of hydrogen EH2 =? 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 **Galvanisation**.

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. 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 (Zn2+) which get discharged ad deposited over the cathode. In this way a coating of zinc is applied over the surface of the iron article.



## CHAPTER - 6 CORROSION

### 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<sub>2</sub>, SO<sub>2</sub>, etc. The following changes stake place on the surface o iron during the process of corrosion.



### 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.

 $H2O + O + 2e \rightarrow 2OH^{-1}$ 

The Fe2+ ions and  $OH^-$  ions then diffuse under the influence of dissolved oxygen and  $Fe^{2+}$  ions are oxidized into  $Fe^{3+}$  ions. These ferric ions then combine with  $OH^-$  ions to form hydrated ferric oxide which is nothing but rust.

 $2Fe^{2+} + H2O + O \rightarrow 2Fe^{3+} + 2OH^{-}$ 

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

Note: Rust is nothing but hydrated ferric oxide (Fe<sub>2</sub>O<sub>3</sub>.nH<sub>2</sub>O)

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.

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. Durian is a silica-iron alloy. It is resistant to acids as a layer of silicon oxide is formed at the surface of iron.

**2. Galvanization:** 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 **Galvanisation**. During the process of galvanisation 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.

## Chapter - 7

### Metallurgy

### Introduction:

**Metallurgy** is a domain of materials science and engineering that studies the physical and chemical behavior of metallic elements, their inter-metallic compounds, and their mixtures, which are called alloys. Metallurgy encompasses both the science and the technology of metals. That is, the way in which science is applied to the production of metals, and the engineering of metal components used in products for both consumers and manufacturers. The science of metallurgy is subdivided into two broad categories: chemical metallurgy and physical metallurgy. Chemical metallurgy is chiefly concerned with the reduction and oxidation of metals, and the chemical performance of metals. Basically, in this chapter the general principles and processes of extraction of metals will be discussed.

### **MINERALS:** -

"The natural material in which the metal or their compounds occur in the earth crust is known as mineral". In other words, the combined state occurrences of metals are called minerals. For example: NaCl, NaNO<sub>3</sub>, Na<sub>2</sub>SO<sub>4</sub>, etc. are the minerals of 'Na'. Similarly, Al<sub>2</sub>O<sub>3</sub>.2H<sub>2</sub>O (bauxite), Al<sub>2</sub>O<sub>3</sub>.2SiO<sub>2</sub>. 2 H<sub>2</sub>O (kaolin) are the minerals of 'Al'.

### ORE: -

# "Ores are the minerals from which the concerned metals can be extracted conveniently and economically."

For example: Both bauxite ( $AI_2O_3.2H_2O$ ) and Kaolin ( $AI_2O_3.2SiO_2.2H_2O$ ) 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, hence kaolin is simply a mineral of aluminium. All ores are minerals however all minerals are not ores.

### **Distinction between Minerals and Ores:**

MINERALS	ORES		
i. The combined state occurrence of	i. Ores are the minerals from which the		
metals is called minerals.	concerned metals can be extracted		
	conveniently and economically.		
ii. Extraction of metals from minerals is	ii. Extraction of metals from ores is		
difficult and non-profitable.	convenient and profitable.		
iii. Minerals contain low percentage of	iii. Ores contain high percentage of		
metals but high percentage of impurities.	metals but low percentage of impurities.		
iv. All minerals are not ores.	iv. All ores are minerals.		
v. Example: Kaoline ((A/ <sub>2</sub> O <sub>3</sub> .2SiO <sub>2</sub> .2H <sub>2</sub> O) is	v. Example: Bauxite (A/ <sub>2</sub> O <sub>3</sub> .2H <sub>2</sub> O) is an		
a mineral of aluminium.	ore of aluminium.		

### SOME IMPORTANT METALS AND THEIR MINERALS

METALS	MINERALS	FORMULA
Na	Rock Salt	NaCl
	Borax	Na <sub>2</sub> B <sub>4</sub> O <sub>7</sub>
К	Carnalite	KCI.MgCl <sub>2</sub> .6H <sub>2</sub> O
	Niter	KNO <sub>3</sub>
Mg	Magnesite	MgCO <sub>3</sub>
	Dolomite	MgCO <sub>3</sub> .CaCO <sub>3</sub>
	Epsom salt	MgSO <sub>4</sub> .7H <sub>2</sub> O
	Carnalite	KCI.MgCl <sub>2</sub> .6H <sub>2</sub> O
Ca	Lime stone	CaCO <sub>3</sub>
	Dolomite	MgCO <sub>3</sub> .CaCO <sub>3</sub>
	Gypsum	CaSO <sub>4</sub> .2H <sub>2</sub> O
Cu	Copper pyrite	CuFeS <sub>2</sub>
	Copper glance	Cu <sub>2</sub> S
	Cuprite	Cu <sub>2</sub> O
Ag	Silver glance	Ag <sub>2</sub> S
	Horn silver	AgCl
Zn	Zinc blend	ZnS
	Zincite	ZnO
	Calamine	ZnCO <sub>3</sub>
Hg	Cinnabar	HgS
AI	Bauxite	Al <sub>2</sub> O <sub>3</sub> .2H <sub>2</sub> O
	Cryolite	Na <sub>3</sub> AIF <sub>6</sub>
Sn	Tin stone	SnO <sub>2</sub>
Pb	Galena	PbS
Cr	Chromite	FeO.Cr <sub>2</sub> O <sub>3</sub>
Fe	Haematite	Fe <sub>2</sub> O <sub>3</sub>
	Magnetite	Fe <sub>3</sub> O <sub>4</sub>
	Limonite	Fe <sub>2</sub> O <sub>3</sub> .3H <sub>2</sub> O

**METALLURGICAL OPERATION:** - 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.

Step-I: Crushing and Grinding,

Step-II: Concentration or Ore Dressing,

Step-III: Oxidation,

Step-IV: Reduction,

Step-V: Refining.

### **STEP-I: CRUSHING AND GRINDING**

The ores obtained from mines are in the form of huge lumps. These are first crushed into small pieces with the help of jaw crusher and then grinded in to their powder form with the help of stamp mill.

### **STEP-II: CONCENTRATION**

The process of removal maximum impurities (gangue or matrix) from ores is called concentration or ore dressing. The method of concentration to be followed depends upon the nature of impurities present.

### METHODS OF CONCENTRATION

### **1. 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 or pulverized ores are kept in some containers over a specially designed table called wilfly table. The table contains a number of transverse grooves. The table is kept slightly in inclined 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 in the grooves, which are finally carried out in to the main canal. 2. FROTH FLOATATION METHOD: This method is suitable for the concentration of sulphide

### ores

only. In this method of concentration two interconnected tanks are used. In one of the tanks, a mixture of ore, oil (preferably pine oil), water and a little quantity of 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 is covered over the surface of sulphide ores. These sulphide ores become lighter and float over the surface of the mixture, which are carried out in to the second container along with the foam formed due to agitation.

**3. MAGNETIC SEPARATION METHOD**: This method of concentration is suitable only when there is a magnetic behaviour difference between the ores and the impurities. Normally 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 up of magnet. Pulverized ore is added over the belt through a hopper. The pulverized ore move towards the magnetic pulley along with the rotating belt.





The non-magnetic impurities fall directly below the magnetic pulley while the magnetic ore form a separate heap due to the influence of the magnetic field.

### 3. 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 discarded 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.

$$AI_2O_3.2H_2O + 2NaOH \rightarrow 2NaAIO_2 + 3H_2O$$

(soluble sod. Meta aluminate)

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

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

The precipitate obtained is dried and ignited (heated) strongly to get pure alumina.

$$2AI(OH)_3$$
 heat  $AI_2O_3 + 3H_2O_3$ 

**STEP-III OXIDATION** (Conversion of ores into metal oxides)

In the third step of metallurgical operation the concentrated ores are converted into the respective metal oxides. This is achieved by the following two methods:

#### 1.CALCINATION: -

The process of heating an ore strongly below its melting point in absence of or in a limited supply of air is called **calcination**. Various functions of calcination are: -

i. It removes moisture.

 $Al_2O_3.2H_2O \rightarrow Al_2O_3 + 2H_2O \uparrow$ 

ii. It removes volatile impurities like S, P, As, Sb, etc.

$$S + O_2 \rightarrow SO_2 \uparrow$$

 $2P + 5O_2 \rightarrow 2P_2O_5 \uparrow$ 

iii. It oxidizes oxidizable substances ('ous' to 'ic')

 $4FeO + O_2 \rightarrow 2Fe_2O_3$ 

iv. It decomposes carbonates of alkali and alkaline earth metals into oxides.

 $CaCO_3 \rightarrow CaO + CO_2 \uparrow$ 

#### 2. ROASTING: -

The process of heating an ore strongly below its melting point in a free but controlled supply of air is called **roasting.** Various functions of roasting are: -

i) It removes moisture.

 $AI_2O_3.2H_2O \rightarrow AI_2O_3 + 2H_2O \uparrow$ 

ii) It removes volatile impurities like S, P, As, Sb, etc.

 $S + O_2 \rightarrow SO_2 \uparrow$ 

iii) It oxidizes oxidizable substances ('ous' to 'ic')

 $4FeO + O_2 \rightarrow Fe_2O_3$ 

iv) It decomposes carbonates into oxides.

 $CaCO_3 \rightarrow CaO + CO_2 \uparrow$ 

v) It makes the ore porous.

The process of roasting is carried out in reverberatory furnace.

STEP- IV REDUCTION (Conversion of metal oxides into metals)

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: -

### **1. 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 electro positive metals such as Zn, Fe, Cu, Cr, W etc. the reducing agents like H2O, CO, Na, K etc are used.

 $PbO + C \rightarrow Pb + CO$ 

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

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

Impurity + flux  $\rightarrow$  slag

Thus, "a substance added during the process of smelting to convert the gangue or matrix into fusible mass (slag) is called flux. "Slag is the fusible mass obtained during the process of smelting when flux combines with impurities".



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

### $SiO_2$ + CaO $\rightarrow$ CaSiO<sub>3</sub> Impurity Flux Fusible Slag (Acidic) (Basic)

Smelting is carried out in a blast furnace which is a tall cylindrical furnace made up 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.

### **STEP-V 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.

### **1. DISTILLATION METHOD:**

This method of refining is suitable for volatile metals like Hg, Zn, Pb etc. 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 left at the bottom of the distillation flask.

### 2. ELECTRO REFINING

This method is employed to refine the less electro positive metals such as Zn, Pb, Al, Cu etc. The impure metal bar is used as anode while a pure metal (same metal) bar is taken as cathode. 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 over the cathode.

### Assignment:

- Q 1. What are flux and slag?
- Q 2. What is acidic flux? Give a suitable example.
- Q 3. What is acidic flux? Give a suitable example.
- Q 4. Which method of concentration is employed for sulphide ores and why?

## Chapter - 8

### ALLOYS

**Introduction:** An alloy is a homogeneous solid material obtained by melting together a metal with other metals or with non-metals or metalloids. Basically, it is a homogeneous mixture of elements of which at least one is having metallic property.

The resulting mixture forms a substance with properties that often differ from those of the pure metals, such as increased strength or hardness. Alloys are used in a wide variety of applications, from the steel alloys, used in everything from buildings to automobiles to surgical tools, to exotic titanium-alloys used in the aerospace industry, to beryllium-copper alloys for nonsparking tools. In some cases, a combination of metals may reduce the overall cost of the material while preserving important properties. In other cases, the combination of metals imparts synergistic properties to the constituent metal elements such as corrosion resistance or mechanical strength.

**Alloy:** An alloy is a homogeneous solid material obtained by melting together a metal with other metals or with non-metals or metalloids.

### **Classification of Alloys:**

Alloys may be classified in to the following types:

- **1.** Ferro Alloys
- 2. Non-ferro Alloys
- **3.** Amalgam.
- **1. Ferro Alloys:** The alloy containing iron as the main constituent is called a ferro alloy.

For example: Stainless steel, Manganese steel etc.

**2. Non-ferro Alloys:** The alloy which does not contain iron as the main constituent is called non ferro alloys. For example: Brass, Bronze, Solder, Gun metal, Bell metal etc.

**3. Amalgam:** The alloys containing mercury as one of its components is called as an amalgam.

Example: Silver amalgam, sodium amalgam, potassium amalgam, etc. Amalgams are good reducing agents.

### COMPOSITIONS AND USES OF SOME ALLOYS:

SI No.	Alloys	Composition	Uses
01	Brass	Cu: 60 – 90% Zn: 10 – 40%	It is used in making: i. Utensils ii. Jewellery iii. Musical instrument, iv. Battery caps v. Condenser Tubes, vi. Name plates, etc.
02	bronze	Cu: 80 – 95% Sn: 5 – 20%	It is used in making: i. Making imitation jewellery ii. Water fittings, iii. Statues, iv. Medals, coins v. Turbine blades, vi. Pump Valves,
03	alnico	Steel: 50% Al: 20% Ni: 21% Co: 9%	It is used in making: Permanent Magnet.
04	duralumin	Al: 95% Cu: 4% i. Air ships Cu: 4% Mn: 0.5% Mg: 0.5%	It is used in making: i. Air ships ii. Light weight vehicular parts, etc.

### Assignment:

Q 1. What are the advantages of alloys over single metal?

Q 2. What is amalgam? Mention any one use of it.

Q 3. What is ferro alloy? Give a suitable example.

Q 4. What is non-ferro alloy? Give an example of it.

## Chapter - 9 HYDROCARBONS

**Introduction:** The branch of chemistry which deals with the study of covalently bonded compounds of carbon except, oxides of carbon (CO, CO<sub>2</sub>), carbonates, bicarbonates, nitriles and carbides (Na<sub>2</sub>CO<sub>3</sub>, NaHCO<sub>3</sub>, NaCN, KCN, CaC<sub>2</sub>, 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, lime stone, bauxite, etc.

Lavoisier could 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 can't 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 could able to prepare an organic compound in laboratory. He heated ammonium cyanate, an inorganic compound and got the rearranged product 'urea' which is purely an organic compound.

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

Later on, Berthelot synthesized methane (CH4) starting from the carbon and hydrogen. Again, 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: alkanes, alkenes, alkynes etc.

### **IUPAC SYSTEM OF NOMENCLATURE:**

In early days organic compounds were named as per their sources of origin and their

characteristics. Such system of nomenclature is called 'Trivial System'.

Compound	Source	Trivial Name
CH <sub>4</sub>	Marshy Area/ Damp Area	Marsh Gas
НСООН	Formica (Latin – Formica = Red Ant)	Formic Acid
CH₃COOH	Acetum (Vinegar)	Acetic Acid
NH <sub>2</sub> CONH <sub>2</sub>	Urine	Urea

Later on a systematic way of nomenclature was started at 'Geneva' called 'Geneva system' which is finally modified by IUPAC (International Union of Pure and Applied Chemistry) System. According to IUPAC System of nomenclature an organic compound may contain the following four parts:

### 1. Word Root 2. Prefix 3. Primary Suffix 4. Secondary Suffix

### 1. WORD ROOT:

It refers to the number of carbon atoms present in the parent chain of the organic compound.

No. of 'C'	Word Root	No. of 'C'	Word Root
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 the organic compound. Some groups always act as substituent or side chain.

They are:

Group	Prefix
-F	- fluoro
-Cl	- chloro
-Br	- bromo
-1	- iodo
-NO <sub>2</sub>	- nitro
-R	- alkyl
-OR	- alkoxy

### 3. PRIMARY SUFFIX:

It refers to the presence of carbon-carbon single (C – C), double (C = C) or triple (C = C) bond in the compound.

Nature of Bond	Primary Suffix
All C – C bond	-ane
One C = C bond	-ene
Two C = C bonds	-adiene
Three C = C bonds	-atriene
One C $\equiv$ C bond	-yne
$Two\;C\;{\equiv}\;C\;bonds$	-adiyne

### 4. SECONDARY SUFFIX:

It refers to the presence of functional groups in the compound. Functional groups are the atoms or group of atoms which are responsible for the physical and chemical properties of the organic compounds.

Class of Compound	Functional Group	Secondary Suffix
-OH	Alccohol	-ol
-CHO	Aldehyde	-al
-CO-	Ketone	-one
-СООН	Carboxylic Acid	-oic acid
-NH <sub>2</sub>	Amine	-amine
-CONH <sub>2</sub>	Acid amide	-amide
-COCI	Acid Chloride	-oylchloride

### CLASS OF COMPOUNDS:

 ALKANES: General formula: CnH2n+2, Representation: C – C , PS: - ane, IUPAC Name: WR + ane.

Formula	Common name	IUPAC Name
CH <sub>4</sub>	Methane	Methane
$C_2H_6$	Ethane	Ethane
C <sub>3</sub> H <sub>8</sub>	Propane	Propane

ALKENES: General formula: CnH2n, Representation: C = C , PS: - ene, IUPAC Name: WR + ene

Formula	Common name	IUPAC Name
$C_2H_4$	Ethylene	Ethane
$C_3H_6$	Propylene	Propene
C <sub>4</sub> H <sub>8</sub>	Butylene	Butene
ALKYNES: General formula: CnH2n – 2 , Representation: C ≡ C , PS: - yne, IUPAC Name: WR + yne.

Formula	Common name	IUPAC Name
$C_2H_2$	Acetylene	Ethyne
$C_3H_4$	Propyne	Propyne
$C_4H_6$	Butyne	Butyne

4. ALKYL: General formula: CnH2n+1 –, Representation: R – , Common name: Alkyl, IUPAC Name: WR + yl.

Formula	Common name	IUPAC Name	
CH <sub>3</sub> –	Methyl	Methyl	
C <sub>2</sub> H <sub>5</sub> –	Ethyl	Ethyl	
C <sub>3</sub> H <sub>7</sub> –	Propyl	Propyl	

 ALKYL HALIDES OR HALOALKANES: General formula: CnH2n+1 – X or R – X, where R= Alkyl, X= halogen (F, Cl, Br, I) Representation: R – X, Common name: Alkyl halide, IUPAC Name: Halo +WR + ane.

Formula	Common name	IUPAC Name
CH <sub>3</sub> – Cl	Methyl chloride	Chloromethane
$C_2H_5 - Br$	Ethyl bromide	Bromoethane
C <sub>3</sub> H <sub>7</sub> – I	Propyl Iodide	Iodopropane

 ALKANOL OR ALCOHOL: General formula: CnH2n+1 – OH or R – OH , where R= Alkyl, Common name: Alkyl alcohol, IUPAC Name: WR+an+ol.

Formula	rmula Common name IUP	
CH₃ – OH	Methyl alcohol	Methanol
$C_2H_5 - OH$	Ethyl alcohol	Ethanol
C <sub>3</sub> H <sub>7</sub> – OH	Propyl alcohol	Propanol

#### 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.



**2. Selection of Parent Chain:** The longest continuous carbon chain is called parent chain. The parent chain is selected. The groups which are outside the parent chain are called substituents or side chains.



**3. Numbering of Carbon:** After selecting the parent chain, the carbon atoms of the parent chain are numbered.

**a. Presence of one Substituent or one Side Chain:** If a compound contains a substituent or a side chain then **minimum numbe**r is given to the carbon containing substituent or side chain. Examples:

Cl  

$$CH_{3} = CH_{2} = CH_{2} = CH_{2} = CH_{2} = CH_{3} = CH_{2} = CH_{2} = CH_{3} = CH_{3}$$

#### b. Presence of two substituents at the same

**position from either end:** In this case minimum number is given to the carbon containing the substituent which comes 1st in dictionary i.e. alphabetical order is considered.

$$\begin{array}{c} \stackrel{1}{\mathsf{C}}\mathsf{H}_3 - \stackrel{2}{\mathsf{C}}\mathsf{H} - \stackrel{3}{\mathsf{C}}\mathsf{H} - \stackrel{4}{\mathsf{C}}\mathsf{H} - \stackrel{5}{\mathsf{C}}\mathsf{H}_3 \\ \stackrel{1}{\mathsf{I}}_{\mathsf{Br}} \quad \stackrel{1}{\mathsf{CI}} \\ \stackrel{1}{\mathsf{CI}} \\ \end{array} \right) \qquad \begin{array}{c} \stackrel{5}{\mathsf{C}}\mathsf{H}_3 - \stackrel{4}{\mathsf{C}}\mathsf{H} - \stackrel{3}{\mathsf{C}}\mathsf{H} - \stackrel{2}{\mathsf{C}}\mathsf{H} - \stackrel{1}{\mathsf{C}}\mathsf{H}_3 \\ \stackrel{1}{\mathsf{I}}_{\mathsf{NO}_2} \\ \stackrel{1}{\mathsf{I}} \\ \end{array} \right) \\ \begin{array}{c} \stackrel{1}{\mathsf{NO}_2} \\ \stackrel{1}{\mathsf{I}} \\ \end{array} \right)$$

c. Presence of more than one substituent or side chains at any positions: In this case *Lowest locants rule* is followed.

$$\begin{array}{c} 1\\ H_{3} - \frac{2}{CH} - \frac{3}{CH} - \frac{4}{CH} - \frac{5}{CH} - \frac{5}{CH} - \frac{6}{CH} - \frac{7}{CH} - \frac{8}{CH} - \frac{9}{CH} - \frac{10}{CH} + \frac{10}{14} + \frac{10}{14}$$

**d.** Presence of multiple bond: If a compound contains a multiple bond (C = C or  $C \equiv C$ ) then, minimum number is given to the carbon containing the multiple bond irrespective of the position of the substituents or side chains.

Example:

$$CH_3 - CH_2 - CH - CH_2 - CH_2 - CH_2 - CH = CH - CH_3$$
  
CH<sub>3</sub>

**Note: 1.** If a compound contains more than one = and/or  $\equiv$  bond then lowest locants rule is first followed. If they are at the same positions from either end then the carbon atom containing double bond (C = C) is given the minimum number. If a compound contains both = and  $\equiv$  bonds then the compound is named as –en-yne.

$${}^{1}_{CH_{2}} = {}^{2}_{CH} \cdot {}^{3}_{CH_{2}} \cdot {}^{4}_{CH_{2}} \cdot {}^{5}_{C} \equiv {}^{6}_{C} \cdot {}^{7}_{CH_{3}} \qquad {}^{6}_{CH_{3}} \cdot {}^{5}_{CH} = {}^{4}_{CH} \cdot {}^{3}_{CH_{2}} \cdot {}^{2}_{C} \equiv {}^{1}_{CH}$$

$${}^{1}_{CH_{2}} = {}^{2}_{CH} - {}^{3}_{CH_{2}} - {}^{4}_{C} \equiv {}^{5}_{CH}$$

**e. Presence of Functional group:** 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.

$$\overset{5}{\mathbf{CH}}_{2} = \overset{4}{\mathbf{CH}} - \overset{3}{\mathbf{CH}}_{2} - \overset{2}{\mathbf{CH}} - \overset{1}{\mathbf{CH}}_{3}$$

$$\begin{matrix} \mathbf{I} \\ \mathbf{OH} \end{matrix}$$

3. Arrangement of Word Root, Prefix, Primary Suffix and Secondary Suffix:

In an organic compound the WR, Prefix, PS and SS are arranged in the following way.

**4. Rules for alphabetical order:** If a compound contains more than one substituent or side chain then, while naming the substituents/side chains are arranged alphabetically. While following the rules for alphabetical order the prefixes like di, tri, tetra, etc. are ignored.

$$\begin{array}{cccc} C_2H_5 & CH_3 \\ 1 & 4 & 5 \\ CH_3 - CH - C - CH_2 - CH - CH_3 \\ 1 & 1 \\ Cl & CH_3 \end{array}$$

2-Chloro-3-ethyl-3, 5-dimethylhexane

#### SOME IMPORTANNT EXAMPLES:

CH3  ${}^{1}_{CH_{3}} - {}^{2}_{CH} = {}^{3}_{CH} - {}^{4}_{CH_{3}}$ But-2-ene  ${}^{1}_{CH_{2}} = {}^{2}_{CH} - {}^{3}_{CH} = {}^{4}_{CH} - {}^{5}_{CH} = {}^{6}_{CH_{2}}$ Hexa-1, 3, 5-triene  ${}_{CH_{2}}^{5} = {}_{CH_{2}}^{4} - {}_{CH_{1}}^{3} - {}_{C}^{\dagger} = {}_{CH_{2}}^{1}$  ${}^{1}_{C}H_{2} = {}^{2}_{C} - {}^{3}_{C} = {}^{4}_{C}H_{2}$  ${}^{1}_{C}H_{3} - {}^{3}_{C}H_{3}$  ${}^{1}_{C}H_{2} = {}^{2}_{C}H - {}^{3}_{C} = {}^{4}_{C}H - {}^{5}_{C}H_{3}$ CH2CH3 3-Ethyl-2-methylpenta-1, 4-diene 2, 3-Dimethyl buta-1, 3-diene 3-Ethylpenta-1, 3-diene  $\begin{array}{c} {}^{1}_{CH_{3}} - {}^{2}_{C} - {}^{3}_{CH_{2}} - {}^{4}_{CH_{3}} \\ {}^{1}_{CH_{3}} - {}^{2}_{C} - {}^{3}_{CH_{2}} - {}^{4}_{CH_{3}} \\ {}^{1}_{CH_{3}} - {}^{2}_{CH_{2}} - {}^{3}_{CH_{2}} - {}^{4}_{CH_{3}} \\ {}^{1}_{CH_{3}} - {}^{2}_{CH_{2}} - {}^{2}_{CH_{3}} \\ {}^{1}_{CH_{3}} - {}^{2}_{CH_{3}} - {}^{4}_{CH_{3}} - {}^{4}_{CH_{3}$ CH,CH(C,H,)CH,CH(C,H,)CH, 2. 2-Dimethylbutane 3-Methylpent-1-ene  $CH_{3} \rightarrow CH = C \rightarrow CH^{-3}CH^{-2}CH^{-1}CH_{3}$ 7CH (2,3-Dimethylheptane) (3-Bromo-4-chlorohex-4-en-2-ol)  $\overset{1}{\overset{1}{\operatorname{CH}}}_{3} - \overset{2}{\overset{C}{\operatorname{CH}}}_{1} - \overset{3}{\overset{C}{\operatorname{CH}}}_{1} - \overset{4}{\overset{C}{\operatorname{CH}}}_{3}$  $\overset{4}{CH}_{3}-\overset{3}{CH}-\overset{2}{CH}_{2}\overset{1}{CH}_{2}CH_{2}CH$  $\begin{array}{c} \mathsf{CH}_3 - \mathsf{CH}_2 - \mathsf{CH} - \mathsf{CH}_2 - \mathsf{CH}_3 \\ | \end{array}$ CI CH<sub>3</sub> CI CH3 3-Chloropentane 2-Chloro-3-methylbutane 1-Chloro-3-methylbutane

## Assignment:

- Q1. To which class the organic compound C<sub>8</sub>H<sub>16</sub> belong and how?
- Q2. To which class the organic compound C7H16 belong and how?
- Q3. To which class the organic compound C9H16 belong and how?
- Q4. What is vital force theory and who proposed it?
- Q5. What is the covalency of carbon atom?

Q6. What is catenation? Which element has highest catenation property?

Q7. Give the IUPAC names of the following compounds.



## Writing Structural formula from IUPAC Names:

**Step – I:** Arrange carbon atoms corresponding to the word root in a straight line separated by single bonds.

Step – 2: Number the carbon atoms from left to right.

**Step – 3:** Attach the substituents, side chains, multiple bonds and functional group whichever is required at their respective positions.

Step – 4: Attach hydrogen atoms to satisfy the tetra-covalency of each carbon atom.

#### **Examples:**

Give the structural formula of the compound

4,5 - Dichloro - 5 - methyl - 3 - nitrohex - 2 - en - 1 ol.

**Step – 1:** C - C - C - C - C - C

**Step - 2:**  $\stackrel{1}{C} \stackrel{2}{-} \stackrel{3}{C} \stackrel{4}{-} \stackrel{5}{C} \stackrel{6}{-} \stackrel{6}{C} \stackrel{-}{-} \stackrel{6}{C} \stackrel{-}{-} \stackrel{6}{C} \stackrel{-}{-} \stackrel{6}{C} \stackrel{-}{-} \stackrel{6}{C} \stackrel{-}{-} \stackrel{6}{-} \stackrel{-}{-} \stackrel{-}{-}$ 

Step – 3: 1 - 2 = 3 + 5 = 6 C - C = C - C - C - C | - C = C - C - C - C $OH - NO_2 C - C$ 

#### Assignment:

- Q 8. Give the structural formulae of the following compounds.
- i. 3,4 Dichlorohex-2-en-2-ol
- ii. 4,4,6 Tribromo 5 methyl hept -1 en -1-ol
- iii. Neo-hexane
- iv. Iso-pentane
- v. Iso-propyl alcohol
- vi. Tertiary butyl chloride.
- vii. 4,5 Dimethoxyhex-2-ene
- viii. 3-Bromomethyl 4- chloromethyl hexane

**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.

Write the IUPAC name of the following organic compounds.

(1) (ii)

Answer: 3 CH5  $H \gg_{CH_2}^5$ ĊH. (i) Penta-1,4-diene

(ii) 
$$\begin{array}{c} CH_{3} & CH_{3} \\ \downarrow & CH_{3} \\ \Gamma CH_{3} & \downarrow \\ CH_{3} \\ CH_{3} \end{array} \begin{array}{c} CH_{3} \\ \downarrow \\ CH_{3} \end{array} \begin{array}{c} CH_{3} \\ CH_{3} \end{array}$$

2,3,3-Trimethylpentane

## **Assignment:**

Q 9. Give the IUPAC names of the following organic compounds.



**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, pentene, etc.) and alkynes (ethyne, propyne, butyne, pentyne, etc.).

#### Distinction between Saturated and Unsaturated Hydrocarbons

	Saturated HC	Unsaturated HC
1	These are the hydrocarbons containing C – C single bonds and C – H bonds.	These are the hydrocarbons containing carbon carbon multiple bonds
2	These are less reactive.	These are more reactive.
3	These contain only sigma bonds.	These contain both sigma and pi bonds.

4	These do not decolorize the pink colour of alkaline KMnO4 solution.	These decolorize the pink colour of alkaline KMnO4 solution.
5	These do not decolorize the brown colour of bromine water.	These decolorize the brown colour of bromine water.
6	These show substitution reaction.	These show addition reaction.
7	These burn with blue flame.	These burn with sooty flame.
8	Examples: Alkanes Examples:	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:

$$CH_3 - CH_2 - CH_2 - CH_3 \qquad CH_3 - CH - CH_2 - CH_3$$
(n-butane)
$$CH_3$$
(2-methylbutane)

Aromatic hydrocarbons: These are the hydrocarbons which obey Huckel's rule of aromaticity.

Huckel's Rule of Aromaticity: The cyclic hydrocarbon containing (4n+2) 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:





Naphthalene



Anthracene

All benzene homologue are aromatics.



	Aliphatic Hydrocarbons	Aromatic Hydrocarbons
1	The open-chained hydrocarbons are called aliphatic hydrocarbons or acyclic hydrocarbons.	The cyclic hydrocarbon containing $(4n+2)\pi$ electrons in which single and double bonds are present in alternate positions is called an aromatic hydrocarbon.
2	These do not obey Huckel's rule.	These obey Huckel's rule.
3	These may be saturated or unsaturated hydrocarbons.	These are unsaturated hydrocarbons.
4	Unsaturated aliphatic hydrocarbons decolorize the pink colour of alkaline KMnO4 solution.	These do not decolorize the pink colour of alkaline KMnO4 solution.
5	Unsaturated aliphatic hydrocarbons decolorize the brown colour of bromine water.	These do not decolorize the brown colour of bromine water.
6	Unsaturated aliphatic hydrocarbons show addition reaction.	These mostly show substitution reaction.
7	These have high carbon to hydrogen ratio.	These have low carbon to hydrogen ratio.
8	Examples: Alkanes, Alkenes, Alkynes.	Benzene, toluene, xylene, phenol, etc.

## Distinction between Aliphatic & Aromatic Hydrocarbons.

## Use of some important aromatic compounds:

#### Benzene, Toluene, and BHC. Uses of Phenol, Naphthalene, Anthracene and benzoic Acid.

#### Benzene

Benzene is used:

- 1. In manufacturing rubber, tires.
- 2. in the printing industry for cleaning and maintaining printing equipment.
- 3. as an ingredient of a variety of painting products.
- 4. in manufacturing plastic products like resins, adhesives and synthetic products such as nylon,

styrene and Styrofoam.

- 5. In manufacturing chemicals like detergents, insecticides, herbicides, pesticides and dyes.
- 6. to clean parts such as hydraulic systems, fuel system components and brakes.

## <u>Toluene</u>

It is used:

- 1. in making Paint and acetones
- 2. as Avionics fuel
- 3. in the manufacture of Drug
- 4. in making Cleansers
- 5. as spot removers
- 6. in making elastic
- 7. as a radiator fluid
- 8. in manufacturing printing ink

## <u>BHC</u>

BHC stands for Benzene Hexachloride. The gamma isomer of BHC is called gammaxene. Gammaxene is an important insecticide and is available in market under the trade name of Lindane.

It is used:

- 1. as an important insecticide.
- 2. As medication to remove head lice.

## <u>Phenol</u>

1. Phenol is used as a disinfectant in household cleaners and in mouthwash when used in small quantity.

- 2. It was used as surgical antiseptic.
- 3. It is used in manufacturing cough drops and other antiseptics
- 4. In industry as a starting material to make plastics like Bakelite, explosives such as picric acid, and drugs such as aspirin.
- 5. As a component of photographic developer.
- 6. in making intensely coloured azo dyes.

- 7. as components in wood preservatives.
- 8. Phenol is also used in the study and extraction of bio-molecules
- 9. Phenol is also used in cosmetic industry in the manufacturing of sunscreens, skin lightening creams and hair colouring solutions.

#### **Naphthalene**

- 1. It is used in mothballs.
- 2. It's also used to manufacture something called **phthalic anhydride**. This chemical is used to make, artificial resins, like glyptal, and pharmaceuticals.
- 3. Naphthalene also helps manufacture a very famous kind of plastic, that of polyvinyl chloride (PVC), as well.
- 4. It is used in making insecticides, artificial tanning agents, and dyes.
- 5. It is used as an abrasive
- 6. It is used as fuel.
- 7. It is used in manufacturing agricultural chemicals, other than pesticides
- 8. It is also used in making Paint additives, etc.

#### **Anthracene**

- 1. It is used as a preservative in wood and lumber and use as an insecticide for crops.
- 2. It is used in making anthraquinone which is used as a building block for a lot of dyes that the

fabrics and textile.

#### **Benzoic acid**

- 1. Benzoic acid is used as a preservative in food industry.
- 2. It is used in care industry as an ingredient in cosmetic products.
- 3. In personal care products, it's found in mouthwash, toothpaste, powder, lipstick and facial cleanser.
- 5. It is used in making dyes and insect repellents.

## Chapter – 10

## Water Treatment

#### Introduction:

**Water** is an inorganic, transparent, tasteless, odourless, and nearly colourless chemical substance, which is the main constituent of Earth's hydrosphere and the fluids of most living organisms. It is vital for all known forms of life, even though it provides no calories or organic nutrients. Its chemical formula is H<sub>2</sub>O, meaning that each of its molecules contains one oxygen and two hydrogen atoms, connected by covalent bonds. Water is the name of the liquid state of H<sub>2</sub>O at standard ambient temperature and pressure. About 3/4th of the surface of earth is covered with water. In this chapter we will deal with various sources of water, hard water, soft water and the methods of softening of hard water.





#### A. Surface water:

The surface water can further be classified in to the following categories

#### 1. Rain water:

- i. Rain is formed by the continuous evaporation and condensation of surface water due to the global phenomenon called 'water cycle'.
- ii. Rain water is considered to be the purest form of natural water.
- iii. It does not contain any dissolved minerals.
- *iv.* However during its downward movement, it comes across a number of industrial gases like *CO*<sub>2</sub>, *SO*<sub>2</sub>, *SO*<sub>3</sub>, *NOx* etc. which dissolves them to form acid rain.

 $CO_2 + H_2O \rightarrow H_2CO_3$ 

 $SO_2 + H_2O \rightarrow H_2SO_3$ 

 $SO_3 + H_2O \rightarrow H_2SO_4$ 

v. All the water obtained as a result of rain fall is not available for further use, because some it is lost in evaporation, percolation and transpiration.

#### 2. River water:

- vi. The over flown surface water (surface run off), which seen in the form of various streams join together to form river.
- vii. It is also formed due to the melting of glaciers.
- viii. It contains a high percentage of dissolved minerals like NaCl, KCl, NaNO<sub>3</sub>, CaCO<sub>3</sub>, NaHCO<sub>3</sub> etc.
- ix. More is the contact of the water with the soil more is the amount of mineral deposit in the river.

#### 3. Lake water:

- i. A lake is formed due to the collection of water in a natural basin or depression in a mountainous area or in planes, whereas natural lake is a large body of water within land with impervious bed.
- ii. Lake water contains a less percentage of dissolved minerals but a very high percentage of organic matters. Presence of high percentage of organic matters is due to the decomposition of vegetable matters and dead bodies of animals during natural calamities like flood, tsunami etc.

#### 4. Sea water:

- i. Sea is formed when a number of rivers meet together.
- ii. Sea water is considered to be the most impure form of natural water.
- iii. Sea water contains about 3.5% dissolved minerals of which about 2.6% is only NaCl.
- iv. The percentage of minerals is gradually increasing day by day due to the continuous evaporation of sea water.
- v. Besides NaCl, it also contains other minerals such as Na<sub>2</sub>SO<sub>4</sub>, KHCO<sub>3</sub>, Mg(HCO<sub>3</sub>)<sub>2</sub>, Ca(HCO<sub>3</sub>)<sub>2</sub>, KBr, MgBr<sub>2</sub> etc.

#### **B.** Underground water:

The sources of water which supply water from below the earth's surface are known **as underground water**. In this type of source, the water that has percolated into the ground is brought on the surface. Underground water is of two types:

#### a. Spring water b. Well water

#### a. Spring water:

- i. Spring is formed due to the melting of glaciers. It is also formed in the mountainous area. During rainy season a part of rain water percolates into the surface of earth. It dissolves many minerals which are in the way of this water. During its downward journey when it meets hard rock, it retards back and emerges out as spring in some weak areas.
- ii. It is a clearer form of natural water.
- iii. It contains high percentage of dissolved minerals and thus its hardness is very high.

#### b. Well water:

- i. it is man-made.
- ii. It is a clearer from of natural water.
- iii. It is obtained by digging the surface of earth to a high depth.
- iv. It contains many dissolved minerals
- v. It also contains some organic matters.

## CLASSIFICATION OF WATER:

- i. Soft water: Water which produces enough foam or lathers with soap solution is called soft water.
- **ii. Hard water:** Water which does not produce much foam or which does not lather with soap solution is called **hard water.**

## Hardness of water:

The property of water by virtue of which it prevents the formation of foam with soap solution is called **hardness**. The hardness of water is due to the presence of certain dissolved minerals like **Ca(HCO<sub>3</sub>)<sub>2</sub>, Mg(HCO<sub>3</sub>)<sub>2</sub>, CaCl<sub>2</sub>, MgCl<sub>2</sub>, FeSO<sub>4</sub>**, etc in water.

The unit of Hardness: Parts per million (PPM).

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(HCO<sub>3</sub>)<sub>2</sub>, Mg(HCO<sub>3</sub>)<sub>2</sub>].
- **ii.** Temporary hardness is also called carbonate hardness.

## **B.** Permanent of hardness:

The permanent hardness of water arises due to the presence of chlorides of Ca, Mg (CaCl<sub>2</sub>, MgCl<sub>2</sub>) and sulphates of certain heavy metals like Fe (FeSO<sub>4</sub>).

## **REMOVAL OF HARDNESS OR SOFTENING OF WATER:**

The process of decreasing the hardness of water is called **softening**. It involves decreasing the concentration of calcium and magnesium salts in Water.

#### Removal of Temporary hardness of Water:

#### 1.By boiling:

i. The temporary hardness of water can easily be removed just by boiling the water.

When hard water is boiled, the soluble Ca(HCO<sub>3</sub>)<sub>2</sub> and Mg(HCO<sub>3</sub>)<sub>2</sub> are decomposed in to insoluble carbonates, which are removed by filtration.

Ca(HCO\_3)2BoilCaCO\_3 + H\_2O + CO\_2^Hard Water<br/>(Soluble)(insoluble)Mg(HCO\_3)2BoilMgCO\_3 + H\_2O + CO\_2^Hard Water<br/>(Soluble)(insoluble)

## 2. By adding Slaked lime (Clark's Method)

- i. Water containing temporary hardness is treated with a calculated quantity of lime.
- ii. The soluble bicarbonates present in water are converted into insoluble carbonates called sludge.

$$\begin{array}{rcl} \mathsf{Ca}(\mathsf{HCO}_3)_2 &+ & \mathsf{Ca}(\mathsf{OH})_2 & \rightarrow & 2\mathsf{Ca}\mathsf{CO}_{3\downarrow} &+ & 2\mathsf{H}_2\mathsf{O} \\ \mathsf{Mg}(\mathsf{HCO}_3)_2 &+ & \mathsf{Ca}(\mathsf{OH})_2 & \rightarrow & \mathsf{Ca}\mathsf{CO}_{3\downarrow} &+ & \mathsf{Mg}\mathsf{CO}_{3\downarrow} &+ & 2\mathsf{H}_2\mathsf{O} \end{array}$$

The insoluble sludge thus formed is removed by filtration to get soft water.

#### Note: Effect of use of excess of lime:

When excess of lime is used during softening process, then soft water is converted into hard water by absorbing CO2 from atmosphere.

$$Ca(OH)_2 + CO_2 \rightarrow Ca(HCO_3)_2$$

**Removal of Permanent hardness of Water:** 

1. Lime – Soda Process:

#### **Principle:**

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 in to insoluble substances.

The precipitate or sludge formed is then removed by filtration to get soft water. Lime-Soda process is of two types.

## A. Cold LS Process:

#### **Principle:**

A calculated quantity of lime and soda is treated with hard water at room temperature. Lime and soda react with the hardness causing chemicals present in hard water and the precipitates or sludge formed are removed by filtration.

#### **Construction of Apparatus:**

The apparatus consists of a conical shaped steel tank, containing a rotating shaft at the middle. Also, it contains a wood fibre filter.

#### Working Process:

Hard water and a calculated quantity of lime, soda along with a little quantity of coagulant is introduced into the apparatus. When the shaft



rotates water is properly mixed with lime and soda.

The soluble hardness causing chemicals present in hard water react with lime and soda to form insoluble sludge.

CaCl <sub>2</sub>	+	Na <sub>2</sub> CO <sub>3</sub>	$\rightarrow$	CaCO <sub>3</sub> ↓ +	2NaCl
hard water		Soda		ppt	
MgCl <sub>2</sub>	+	Ca (OH) <sub>2</sub>	→	Mg (OH) <sub>2</sub> ↓ +	CaCl <sub>2</sub>
hard water		lime		ppt	

Coagulant aggregates the finely divided sludge particles which settle down in the conical sedimentation tank. The sludge is then removed from time to time through its outlet. Water is

now allowed to pass through the wood-fibre filter to get soft water. The residual hardness left in this process is about 50 – 60 ppm.

#### **B. Hot lime Soda Process:**

**Principle:** This process involves treatment of hard water with a calculated quantity of lime and soda in presence of super-heated steam (at 80<sup>°</sup> to 150<sup>°</sup> C).

Apparatus: The apparatus consists of three main parts:

- 1. Reaction tank: Here the reaction of lime and soda with the hard water takes places.
- 2. Conical sedimentation tank: Here the precipitates (sludge) are formed and deposited.
- 3. Filtering unit: It consists of a number of layers of gravels which is used to filter water.

#### Working Process:

Hard water along with a calculated quantity of lime and soda are introduced in to the reaction tank. Also, super-heated steam at 800 – 1500 C is passed in to it. The soluble hardness causing chemicals present in the hard water react with lime and soda to form insoluble sludge which settles down in the conical sedimentation tank. The sludge formed is removed periodically through its outlet. Water is



then allowed to pass thorough the filtering unit to get soft water. The residual hardness left in this process is only about 15 – 30 ppm.

#### Advantages of hot L-S process over Cold L-S Process:

- i. It is much economical.
- **ii.** The reaction is completed within a short period.
- iii. The reaction proceeds faster. Hence the softening capacity in increased.
- iv. No coagulant is required, as the sludge settles down easily.
- v. Dissolved gasses like CO2, air etc. are removed.
- vi. Under hot condition viscosity of water is lowered. Thus, filtration becomes easier.

- vii. Pathogenic bacteria are destroyed.
- viii. 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).

## 2. ION EXCHANGE PROCESS:

#### [Deionization process or De-mineralization process]

In this method ion-exchange resins are used. These are insoluble long chained organic copolymers having micro-porous structure. These resins contain either acidic or basic functional groups capable of exchanging their H<sup>+</sup> or OH<sup>-</sup> ion with the ions present in hard water. Ion-exchange resins are of two types.

## Cation-exchange resigns (RH):

These resins contain acidic functional groups like – COOH, - SO<sub>3</sub>H etc. which can exchange their  $H^+$  ions with the cations of the hardness causing chemicals present in hard water.

## Anion-exchange resigns (ROH):

These resins contain basic functional groups like  $- N^+Me_3OH -$  which can exchange their **OH**<sup>-</sup> ions with the anions of hardness causing chemicals.

Apparatus: The apparatus consists of two tall towers, one containing cation exchange resin and

the other containing anion exchange resin.

## Process:

Hard water is first passed through the cation Exchange resin. The resin exchanges its  $H^+$ ions with the cations (Ca<sup>2+</sup>, Mg<sup>2+</sup> etc.) of hard water.



Removal of hardness by the organic ion - exchanges

 $2H^+$ 

 $2H^+$ 

Then it is passed through the anion-exchange resin which exchange its OH - ions with the anions ( $CI^{-}$ ,  $SO_4^{2^{-}}$ , etc) present in the hard water.

 $\begin{array}{cccc} \mathbf{ROH} & + & \mathbf{Cl}^{-} & \rightarrow & \mathbf{RCl} & + & \mathbf{OH}^{-} \\ Anion-Excahange Resin & hard water & Exhausted Resin \end{array}$ 

#### **Regeneration of resins:**

When all the  $H^+$  and  $OH^-$  ions of the resins are exchanged by the ions of hard water, then the resins are said to be exhausted. The cation-exchange resin can be regenerated by the treatment of dil. HC/ with the exhausted cation-exchange resin.

 $\begin{array}{rcl} R_2Ca & + & 2HCl & \rightarrow & 2RH & + & CaCl_2 \\ (exhausted resin) & & & & & & & & & \\ \end{array}$ 

Similarly, the anion-exchange resin can be regenerated by the treatment of dil NaOH solution with the exhausted anion-exchange resin

<b>R</b> C <i>l</i> +	NaOH $\rightarrow$	ROH	+	NaCl
(•	exhausted resin)		(Rege	nerated resin)

Note: The residual hardness left in this process in only about 2 ppm

## CHAPTER – 11 LUBRICANTS

#### Introduction:

**Lubricant** is a substance, usually organic, introduced to reduce friction 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 orsliding surfaces with a view to reduce the frictional resistance between them.

#### Type of lubricants:

Depending upon the physical state, lubricants can be classified into three categories. They are:

**1. Solid lubricants**: For example: Graphite, mica, molybdenum disulphide, boron tri-nitride, etc.

- i. It is used where the working temperature is very high
- ii. It is used where there is a chance of contamination of the products with the lubricants.

**2. Liquid lubricants**: For example: Oils, Mobiles, petroleum oil, blended oil, animal oil, vegetable oil etc. Functions of Liquid Lubricants:

- i. It acts as a cooling medium
- ii. It reduces the chance of rusting of metals.
- iii. It prevents corrosion of machinery parts.

Liquid lubricants are used when:

- i. The operating temperature is very high
- ii. The speed of the roller is very high
- iii. The sealing arrangement is perfect to prevent the loss of oil.
- 3. Semi solid lubricants: For example: Grease

Some major components of greases are:

- i. Oil component: mineral oil, waxes, petroleum oils.
- **ii.** Thickening component: Na, K, Ca, Al soaps.
- iii. Modifiers: antioxidant, antirust agent, anti-wear agents, etc.

Semi solid lubricants are used where there is a chance of heavy jerk. Semi-solid lubricants stick to the rolling surfaces in spite of heavy jerk.

#### Purpose of Lubrication or functions of Lubrication:

Lubrication is highly important in industrial fields. The purposes of lubrications are:

- i. Lubrication helps to reduce frictional resistance between the moving, rolling or sliding surfaces.
- ii. It reduces wearing and tearing of machinery parts.
- iii. It reduces noise pollution
- iv. It reduces lose in energy
- v. It increases the efficiency of engines.
- vi. It enhances the durability of machinery parts.
- vii. It reduces expansion of metals
- viii. It acts as a cooling medium.

## CHAPTER – 12 FUELS

#### 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 of Fuel:** 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.

#### **Characteristics of good fuel:**

- 1. Its calorific value should be high.
- 2. It should be cheap and readily available.
- 3. It should be stored for a longer period i.e. it should be non -volatile and stable.
- 4. It should not produce much ash.
- 5. Transportation should be easy.
- 6. It should not produce any poisonous gas.
- 7. It should not produce much smoke.
- 8. It should have low ignition temperature.
- 9. It should not be explosive in nature.

- 10. It should not contain high percentage of moisture.
- 11. It should contain low percentage of volatile matter.
- 12. It should require low storage volume.
- 13. It should provide uniform fuel bed.

#### Calorific value:

Calorific value may be defined as "the net 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, British Thermal Unit (BTU), etc.

**Classification of Fuel:** Depending upon the physical state fuels may be classified in to three categories.

- 1. Solid fuel: (Coal, wood, saw dust, rice barn, straw)
- 2. Liquid fuel: (Kerosene, Petrol, Diesel, Spirit, alcohol, LPG, CNG, etc.)
- 3. Gaseous fuel: (Methane, butane, water gas, producer gas, bio-gas, coal gas, acetylene, hydrogen etc.)

#### **PETROLEUM:**

The word petroleum is coined from two Greek words, 'Petra' - means 'rock' and 'Oleum' - means 'Oil'. It is also known as rock oil and mineral oil. Origin of petroleum: *It is obtained deep in the earth crust and at the bottom of sea*. Petroleum is formed by the partial decomposition of aquatic creatures deep in the sea. The decomposition occurs as a result of high pressure and in the absence of air. Petroleum oil contains various constituents such as petrol, diesel, kerosene, fuel oil, paraffin, petroleum gas, etc.

#### Separation of different constituents from petroleum (Fractional Distillation Method)

Different constituents of crude petroleum oil are separated by fractional distillation method. The crude petroleum oil is passed through a furnace where it is heated to about 4000 C, so that all the fractions are converted into their gaseous form. The vapours are then passed through a fractional distillation unit. When the vapours move in upward direction, the temperature gradually falls and fractional condensation occurs at different heights of the distillation unit. Different fractions are collected from their respective outlets. The fraction with highest boiling point is collected at the bottom, while that with lowest boiling point is collected at the top.

#### Petrol or Gasoline:

- i. The fraction obtained between 400<sup>o</sup> -1200<sup>o</sup> C, chiefly contains petrol.
- ii. It consist of hydrocarbons between pentane to octane ( $C_5H_{12}$  to  $C_8H_{18}$ )
- iii. It is volatile and inflammable.
- iv. Average Composition C = 84%, H=15%, O+S+N =1%
- v. Calorific Value = 11,250 Kcal / Kg.

#### Uses:

- i. It is used as a fuel in the petrol engine.
- ii. It is used as a dry-cleaning agent.

#### Kerosene:

- i. It is obtained between  $180^{\circ} 250^{\circ}$  C
- ii. It consists of hydro carbons between decane to hexadecane ( $C_{10}H_{22}$  to  $C_{16}H_{34}$ ).
- iii. Average Composition, C = 84 %, H = 16%, S < 0.1%
- iv. Calorific value = 11, 100 Kcal/ Kg

#### Uses:

- i. It is used as a fuel in Kitchen for domestic.
- ii. It is used as a fuel in jet planes.
- iii. It is used in making oil gas.

#### Diesel:

- i. It is obtained between  $250^{\circ} 320^{\circ}$  C
- ii. It contains a mixture of hydrocarbons between pentadecane to octadecane ( $C_{15}H_{32}$  to  $C_{18}H_{38}$ ).
- iii. Average composition: C = 85%, H = 12%, Rest = 3%
- iv. Calorific Value = 11000Kcal/kg

#### Uses:

i. It is used as a fuel in diesel engine.

## Water Gas:

- i. It is a mixture of combustible gases CO and H2 with a little quantity of non-combustible gases  $CO_2$  and  $N_2$ .
- ii. The average composition of water gas is  $H_2$ = 51 %, CO = 14 %, CO<sub>2</sub> = 4%, N = 4%,
- iii. Its calorific value is 2800 Kcal / m3

## Uses:

It is used as:

- i. an illuminating gas.
- ii. a fuel
- iii. a source of H<sub>2</sub> Gas

## Producer Gas:

- i. It is a mixture of combustible gases, CO and H<sub>2</sub> with large quantities of non-combustible gases CO<sub>2</sub> and N<sub>2</sub>.
- ii. The average composition of producer gas is CO = 22- 30%, H2 = 8 12 %, CO2 = 3%, N2 =

52 - 55%

iii. Its calorific value is 1300 Kcal /m3.

## Uses:

It is used:

- i. in heating furnace in metallurgical operations.
- ii. As a reducing agent.

## Liquefied Petroleum Gas (LPG)

Liquefied petroleum gas (LPG) is a flammable mixture of hydrocarbon gases used as fuel in heating appliances, cooking equipment, and vehicles. It is extracted from crude oil and natural

gas.

## Composition of LPG:

The normal composition of LPG is propane (C<sub>3</sub>H<sub>8</sub>) and butane (C<sub>4</sub>H<sub>10</sub>). Small

concentrations of other hydrocarbons may also be present.

## **Properties of LPG:**

It is a colourless, odourless gas. However, a little quantity of ethyl mercaptan is added to

- i. detect leakage of the cylinder.
- ii. It is highly inflammable and burns with a pale blue flame.

iii. Its calorific value is 11840 Kcal/Kg.

## Uses of LPG:

- i. It is used as a domestic fuel.
- ii. It is used as an industrial fuel.

## **Compressed Natural Gas (CNG)**

CNG is made by compressing natural gas. Natural gas is formed by the decomposition of plant and animal species.

## **Composition of CNG:**

The main composition of CNG is methane (CH<sub>4</sub>).

## **Properties of CNG:**

- i. It is a colourless, odourless gas.
- ii. It is highly inflammable.

## Uses of CNG:

- i. It is used as a domestic fuel.
- ii. It is used as an industrial fuel.
- iii. It is used as a fuel in vehicles and locomotives.

## Coal Gas:

Coal gas is a flammable gaseous fuel made from coal. It is produced when coal is heated strongly in the absence of air.

## **Composition of Coal gas:**

Coal gas contains a variety of calorific gases including hydrogen ( $H_2$ ), carbon monoxide (CO), methane (CH<sub>4</sub>), ethylene ( $C_2H_4$ ) and volatile hydrocarbons together with small quantities of non-calorific gases such as carbon dioxide and nitrogen.

## Uses of Coal Gas:

- i. Coal gas is used in lightning.
- ii. This gas is also used for heating.
- iii. It is used as fuel.
- iv. Coal gas is also used as an illuminant.
- v. It is also used as fuel in industries.

# CHAPTER – 13 POLYMERS

**Introduction:** *Polymers* are one of the important products of chemical industry which have a great impact on our modern life. *Plastics, synthetic fibres, synthetic rubber, etc.* are common *examples of polymers*. These polymers have multifarious uses ranging from household articles, automobiles, clothes, furniture, etc. to space aircraft, biomedical and surgical operations.

**Polymerization:** The chemical process in which a large number of smaller molecular units are unite or joint together to form a bigger molecule of high molecular weight is **called polymerization.** 

**Polymers:** Compounds of very high molecular masses formed by the combination of a large number of simple molecules are called polymers. For example: *Polythene, PVC (polyvinyl chloride), Bakelite, Buna-S, Buna –N, Teflon, etc. are the examples of polymer.* In Greek, *poly means* many and meros *means* units or parts. The simple molecules which combine to give polymers are called monomers.



## Monomer:

Monomer is the single repeating unit which on polymerization gives a polymer.

For example: Ethene is the monomer unit of polyethene.

## **Classification of Polymers:**

(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.

## Homo-polymer:

The polymer containing monomer units of identical chemical composition is called a **homo polymer.** 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.

#### -----M1 – M2 – M1 – M2 – M1 –M2 ------

#### (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.

Linear chain polymer

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

Branched chain polymer

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.



**Cross linked polymer** 

## **Classification of Polymers Based on Mode of Polymerisation**

(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	1. These are formed by condensation		
polymerization.	polymerization.		
2. These are generally linear polymers.	2. These are three dimensional cross-linked		
3. These are soft.	polymers.		
4. These are soluble in some solvents.	3.These are hard and rigid		
5. These become soft on heating and	4. These are insoluble in any solvent.		
become hard on cooling.	5. These burn to char on prolong heating.		
6. These can be remoulded, reshaped and	6.These cannot be remoulded, reshaped and		
recycled.	cannot recycled.		
7. Examples: Polythene, PVC, Nylon, etc.	7.Examples: Bakelite, Urea-formaldehyde		
	resin, Terylene, etc.		

#### Distinction between Thermoplastics & Thermosetting.

## Polythene:

Polythene is formed when ethene gas is pumped into a vessel maintained at **1500** atm pressure and **150<sup>o</sup> to 250<sup>o</sup> C** in presence of a trace of oxygen.

 $\begin{array}{ccc} n(CH_2 = CH_2) & \longrightarrow & [--CH_2 - -CH_2 - -]_n \\ & & & & & \\ ethylene & & & & \\ polyethylene & & & \\ \end{array}$ 

Uses: It is used for making:

- i. Kitchen and domestic appliances
- ii. Toys, bottle caps
- iii. Flexible bottles
- iv. Tubes, pipes
- v. Coated wires, cables
- vi. High frequency insulation parts
- vii. Bags for packing

## 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:

- i. Sheets for tank lining
- ii. Safely helmets
- iii. Refrigerator components
- iv. Tyres, cycle and motor cycle mudguards
- v. Rain coat packing

vi. Table cloths

vii. Electrical insulators

viii. Chemical containers

#### 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 methyl phenol and P-hydroxy methyl phenol are obtained.



The Orth hydroxy methyl phenol thus, formed undergoes polymerisation 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.  $\rho_H$   $\rho_H$ 



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 **Heavia brasilians** 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 cis-polyisoprene. Thus, natural rubber is nothing but the polymer *Cis-polyisoprene*.



#### 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 *1000 - 1400 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.

CH <sub>3</sub> CH <sub>3</sub>		CH <sub>3</sub>	CH <sub>3</sub>
$-CH_2 - C = CH - CH_2 - CH_2 - C = CH - CH_2 - CH$	4 % - 6 % Sulphur	$\stackrel{-CH_2-C-CH_2-CH_2-}{\overset{\downarrow}{\overset{\downarrow}{\overset{\scriptstyle}{\overset{\scriptstyle}{\overset{\scriptstyle}{\overset{\scriptstyle}{\overset{\scriptstyle}{\scriptstyle$	$-CH_2 - C - CH - CH_2 - $ $\begin{cases} \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\$
(Raw Rubber)	(Vulcanisation of Rubber)	$-CH_2 - C - CH - CH_2 - CH_3$	-CH <sub>2</sub> - CH <sub>3</sub>
	(raidalidation of Rabbol)	(Vulcanised	Rubber)

During vulcanisation 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.

## I. What is the function of vulcanization of rubber?

**Ans:** Sulphur makes the rubber more elastic, more ductile, less plastic and non-sticky. Almost all the drawbacks of raw rubber are eliminated after vulcanization.

#### IV. What are the monomers of Bakelite?

**Ans:** The monomers of Bakelite are phenol and formaldehyde.

#### V. What do you mean by Addition polymer?

**Ans:** A polymer formed by direct addition of repeated monomers without the elimination of by product molecules is called addition polymer. In this case the monomers are unsaturated compounds and are generally derivatives of ethene. The addition polymers have the same empirical formula as their monomers. Example: polyethene, PVC, polystyrene, etc.

## VI. What do you mean by Condensation polymer?

**Ans:** A polymer formed by the condensation of two or more monomers with the elimination of simple molecules like water, ammonia, hydrogen chloride, etc. In this case each monomer generally, contains two functional groups. For example: nylon-66 is obtained by the condensation of two monomers; hexamethylenediamine and adipic acid with the loss of water molecules.
## CHAPTER – 14 CHEMICALS IN AGRICULTURE

**Pesticides**: Pesticides are the chemical substances used to kill or prevent pests including weeds. These are classified into the following types.

- 1. Insecticides
- 2. Fungicides
- 3. Herbicides
- 4. Bactericides
- <u>Insecticides:</u> These are the chemical substances used to kill or prevent growth of *insects.*

**Examples:** DDT, Gammaxene, Aldrin, Dieldrin, Chlordane, Chlordecone., Endozoan, Heptachlor, etc.

 <u>Fungicides:</u> These are biocidal chemical compounds or biological organisms used to kill parasitic fungi or their spores.

**Examples:** Copper oxychloride, Carbendazim, Carboxin, Mancozeb, etc.

3. <u>Herbicides</u>: These are the chemical substances used to destroy unwanted vegetation (like weeds).

Examples: Acetochlor, Amitrole, Arsenic acid, dinitrophenol, dipyridyl,

carbamate, Propanil, Paraquat, etc.

**<u>Bio-fertilizers</u>**: A bio- fertilizer is a substance which contains living microorganisms which, when applied to seeds, plant surfaces, or soil, colonize the interior of the plant and promotes growth by increasing the supply or availability of primary nutrients to the host plant.

## Benefits of bio-fertilizers:

- i. Bio-fertilizers fix atmospheric nitrogen in the soil and root nodules of legume crops and make it available to the plant.
- **ii.** They solubilize the insoluble forms of phosphates like tricalcium, iron and aluminium phosphates into available forms.
- iii. They scavenge phosphate from soil layers.

- iv. They produce hormones and anti-metabolites which promote root growth.
- v. They decompose organic matter and help in mineralization in soil.
- **vi.** When applied to seed or soil, bio-fertilizers increase the availability of nutrients and improve the yield by 10 to 25% without adversely affecting the soil and environment.

## Types of Bio-fertilizers:

Based on type of microorganism, the bio-fertilizer can also be classified as follows:

- i. Bacterial Bio-fertilizers: e.g. Rhizobium, Azospirilium, Azotobacter, Phosphobacteria.
- ii. Fungal Bio-fertilizers: e.g. Mycorrhiza
- iii. Algal Bio-fertilizers: e.g. Blue Green Algae (BGA) and Azolla.
- iv. Actinomycetes Bio-fertilizer: e.g. Frankia.

Bio-fertilizer are mostly cultured and multiplied it the laboratory. However, blue green algae and azolla can be mass-multiplied in the field.

THANK YOU