

**E-Learning Material**  
on  
**Engineering Chemistry**  
of  
1<sup>st</sup>/2<sup>nd</sup> semester of all Engineering Branches



**State Council for Technical Education and  
Vocational Training, Odisha  
Bhubaneswar-751012**

**E-Learning Material**

**Engineering Chemistry**

of

1<sup>st</sup>/2<sup>nd</sup> semester of all Engineering Branches of Diploma courses of SCTE&VT,  
Odisha

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Published by  
SCTE&VT, Odisha, Bhubaneswar-12  
<https://sctevtodisha.nic.in/en/>  
secretarysctevt@gmail.com, [material.sctevt@gmail.com](mailto:material.sctevt@gmail.com)

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**Syllabus**  
**Th.2b. Engineering Chemistry**  
**(1<sup>st</sup> / 2<sup>nd</sup> Semester Common)**

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

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

**Objective:**

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

**Topic wise distribution of periods**

Sl. No	Topics/ Units	Periods
A	Physical Chemistry	22
B	Inorganic Chemistry	08
C	Organic Chemistry	10
D	Industrial Chemistry	20
	<b>TOTAL</b>	<b>60</b>

**A. PHYSICAL CHEMISTRY**

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

**Chapter 2: Chemical Bonding:** Definition, types (Electrovalent, Covalent and Coordinate bond with examples (formation of NaCl, MgCl<sub>2</sub>, H<sub>2</sub>, Cl<sub>2</sub>, O<sub>2</sub>, N<sub>2</sub>, H<sub>2</sub>O, CH<sub>4</sub>, NH<sub>3</sub>, NH<sub>4</sub><sup>+</sup>, SO<sub>4</sub><sup>2-</sup>).

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

**Chapter 4: Solutions:** Definitions of atomic weight, molecular weight, Equivalent weight. Determination of equivalent weight of Acid, Base and Salt. Modes of expression of the concentrations (Molarity, Normality &

Molality) with Simple Problems. pH of solution (definition with simple numerical) Importance of pH in industry (sugar, textile, paper industries only)

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

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

## **B. INORGANIC CHEMISTRY**

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

- i) Ore Dressing
- ii) Concentration (Gravity separation, magnetic separation, Froth floatation & leaching)
- iii) Oxidation (Calcinations, Roasting)
- iv) Reduction (Smelting, Definition & examples of flux, slag)
- v) Refining of the metal (Electro refining, & Distillation only)

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

## **C. ORGANIC CHEMISTRY**

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

## **D. INDUSTRIAL CHEMISTRY**

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

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

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

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

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

### **Syllabus Coverage up to I.A**

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

#### **Books Recommended**

1. Textbook of Intermediate Chemistry Part-1 and Part-2 by Nanda, Das, Sharma, Kalyani Publishers
2. Engg. Chemistry by B.K. Sharma, Krishna Prakashan Media Pvt. Ltd
3. Engineering Chemistry by Y.R. Sharma and P. Mitra, Kalyani Publishers
4. Engineering Chemistry for Diploma – Dr. R K Mohapatra, PHI Publication, New Delhi.
5. Engineering Chemistry- Jain & Jain, Dhanpat Roy and Sons.

## 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.

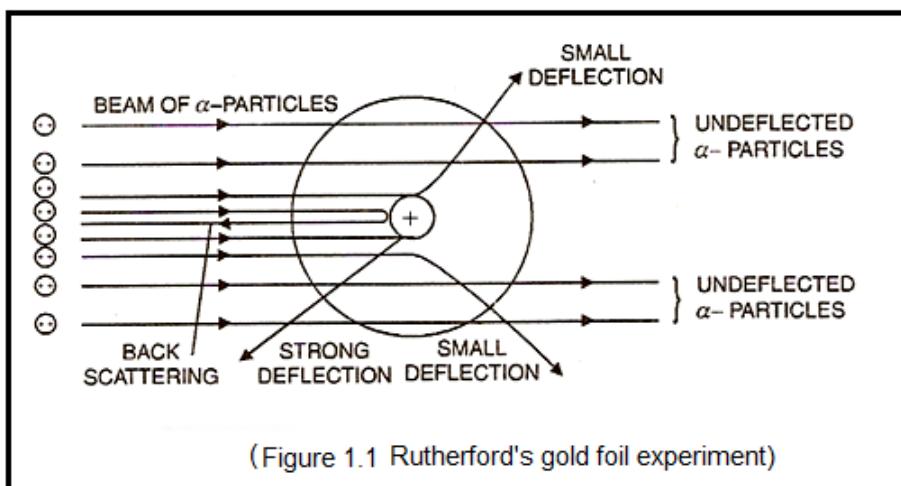
**Proton:** Proton is a fundamental sub-atomic particle having mass of  $1.672 \times 10^{-27}$  kg and carrying a charge of  $+1.602 \times 10^{-19}$  Coulomb.

**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	$9.11 \times 10^{-31}$ Kg	$-1.602 \times 10^{-19}$ Coulomb	- 1
Proton	$1.672 \times 10^{-27}$ Kg	$+1.602 \times 10^{-19}$ Coulomb	+1
Neutron	$1.675 \times 10^{-27}$ 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 (Fig. 1.1).



### **Observations and Conclusions:**

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

1. 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.
2. A few  $\alpha$ -particles were found to be deflected strongly from their normal paths. This indicates the presence of a heavy positively charged body inside the atom. This heavy positively charged body is called nucleus.
3. A very few (0.01%)  $\alpha$ -particles were found to be retracted their original paths (deflected through almost  $180^0$ ). This indicates that the size of nucleus is very small. The size of atomic nuclei is of the order of  $10^{-13}$  cm.

### **RUTHERFORD'S ATOMIC MODEL:**

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

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

### **DRAWBACKS OR FAILURES OF RUTHERFORD'S ATOMIC MODEL:**

#### **1. Stability of Atom:**

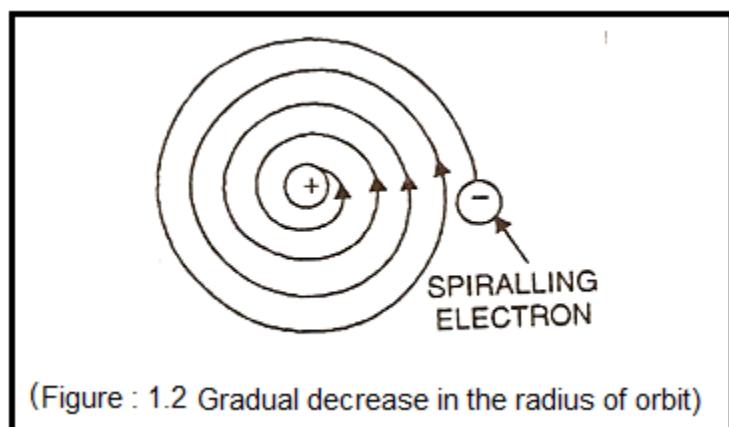
The theory fails to explain the stability of atoms. According to the law of electrodynamics (by Clark Maxwell), whenever a charged particle revolves around another charged particle, the revolving charged particle emits (loses) energy continuously (Fig. 1.2).

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

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

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

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



## **BOHR'S ATOMIC MODEL (THEORY)**

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

### **Postulates of Bohr's atomic model:**

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

$$E_n = - \frac{2\pi^2 me^4 z^2}{n^2 h^2}$$

where,  $m$  = mass of an electron

$e$  = charge of electron

$z$  = Atomic number

$n$  = No. of shell or principal quantum number (1,2,3.....)

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

$$E_n = - \frac{1312}{n^2} \text{ KJ / Mol,} \quad \text{for Hydrogen atom}$$

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

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

7. Through a large number of concentric circles are possible around the nucleus, only those circular paths are allowed for the electrons to revolve for which the **angular momentum** value ( $mvr$ ) is a whole number multiple of  $\frac{h}{2\pi}$ , that is

$$mvr = n \frac{h}{2\pi}, \text{ where } n = 1, 2, 3, \dots$$

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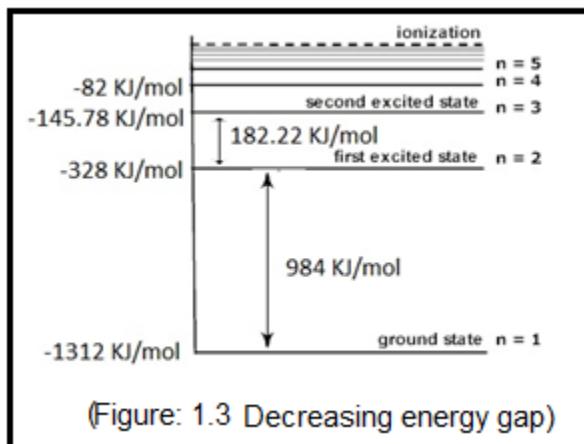
Here,  $m$  = mass of the electron,

$v$  = tangential velocity of the revolving electron,

$r$  = radius of the orbit.

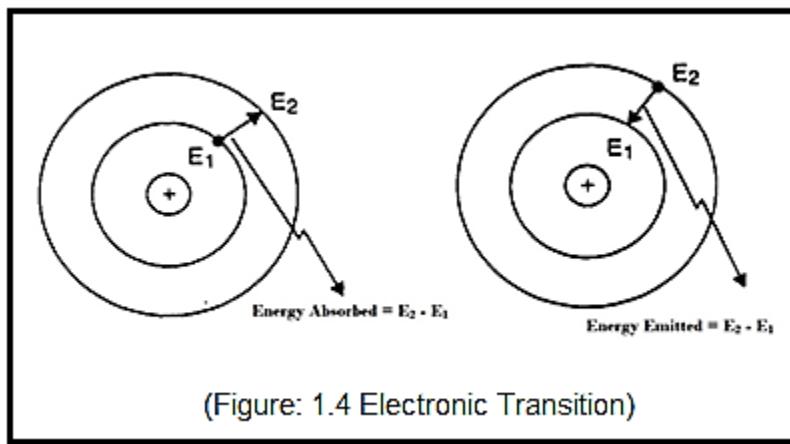
$h$  = Planck's constant,

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



(Figure: 1.3 Decreasing energy gap)

9. When external source of energy is supplied to an atom, the electrons jump from lower ground states to the higher excited states by absorbing energy. Electrons in the excited states are unstable and jump back to the lower ground states by releasing energy. The energy thus released appears in the form of light which is the origin of spectral lines (Fig. 1.4).



#### **Failures of Bohr's Atomic Model:**

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

#### **BOHR-BURY SCHEME:**

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

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

Shell	$n$	Maximum No. of Electrons = $2n^2$
K	1	$2 \times 1^2 = 2$
L	2	$2 \times 2^2 = 8$
M	3	$2 \times 3^2 = 18$
N	4	$2 \times 4^2 = 32$ , and so on.

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

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

Element	Electrons in			
	K- Shell	L-Shell	M-Shell	N-Shell
<sub>1</sub> H	1			
<sub>2</sub> He	2			

${}_3\text{Li}$	2	1		
${}_4\text{Be}$	2	2		
${}_5\text{B}$	2	3		
${}_{10}\text{Ne}$	2	8		
${}_{11}\text{Na}$	2	8	1	
${}_{12}\text{Mg}$	2	8	2	
${}_{13}\text{Al}$	2	8	3	
${}_{18}\text{Ar}$	2	8	8	
${}_{19}\text{K}$	2	8	8	1
${}_{20}\text{Ca}$	2	8	8	2
${}_{21}\text{Sc}$	2	8	9	2

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

Atomic Number = No. of Protons (p)

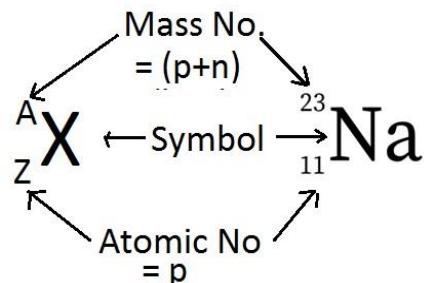
For Examples:

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

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

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

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



Note:  $A - ne^- \rightarrow A^{n+}$       Example:  $Mg - 2e^- \rightarrow Mg^{2+}$

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

### Assignment:

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

Atom/Molecule/Ion	P	e	n
O			
P			
N <sup>3-</sup>			
Ca <sup>2+</sup>			
NH <sub>3</sub>			
H <sub>2</sub> O			
NH <sub>4</sub> <sup>+</sup>			
CO			
CO <sub>2</sub>			

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

Examples: Hydrogen has three isotopes: Protium (<sup>1</sup>H), Deuterium (<sup>2</sup>H) and Tritium (<sup>3</sup>H)

Similarly, <sup>35</sup>Cl and <sup>37</sup>Cl

#### Properties of Isotopes:

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

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

Examples: <sup>40</sup><sub>18</sub>Ar and <sup>40</sup><sub>20</sub>Ca

#### Properties of Isobars:

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

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

Examples: <sup>23</sup><sub>11</sub>Na and <sup>24</sup><sub>12</sub>Mg      <sup>27</sup><sub>13</sub>Al and <sup>28</sup><sub>14</sub>Si      <sup>31</sup><sub>15</sub>P and <sup>32</sup><sub>16</sub>S

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

### **Aufbau Principle:**

The word “*Aufbau*” means “building up”. This principle describes how the sub-shells 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+l) rule.

### **The (n + l) Rule:**

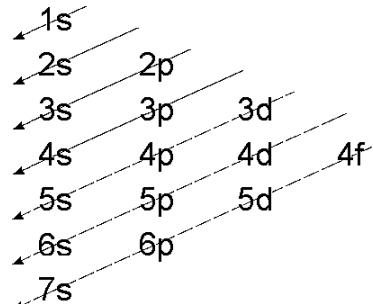
- i. The sub-shell having lower (n+l) value possesses lower energy and is filled first.
- ii. If the (n+l) value for two given sub-shells are equal, then the one with lower value of ‘n’ possesses lower energy and is filled first.

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

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

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

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



### **ELECTRONIC CONFIGURATIONS:**

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

<u>Elements</u>	<u>Electronic configurations</u>	<u>Elements</u>	<u>Electronic configurations</u>
<sub>1</sub> H	1s <sup>1</sup>	<sub>16</sub> S	1s <sup>2</sup> 2s <sup>2</sup> 2p <sup>6</sup> 3s <sup>2</sup> 3p <sup>4</sup>
<sub>2</sub> He	1s <sup>2</sup>	<sub>17</sub> Cl	1s <sup>2</sup> 2s <sup>2</sup> 2p <sup>6</sup> 3s <sup>2</sup> 3p <sup>5</sup>
<sub>3</sub> Li	1s <sup>2</sup> 2s <sup>1</sup>	<sub>18</sub> Ar	1s <sup>2</sup> 2s <sup>2</sup> 2p <sup>6</sup> 3s <sup>2</sup> 3p <sup>6</sup>
<sub>4</sub> Be	1s <sup>2</sup> 2s <sup>2</sup>	<sub>19</sub> K	1s <sup>2</sup> 2s <sup>2</sup> 2p <sup>6</sup> 3s <sup>2</sup> 3p <sup>6</sup> 4s <sup>1</sup>

<sub>5</sub> B	$1s^2 2s^2 2p^1$	<sub>20</sub> Ca	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2$
<sub>6</sub> C	$1s^2 2s^2 2p^2$	<sub>21</sub> Sc	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^1$
<sub>7</sub> N	$1s^2 2s^2 2p^3$	<sub>22</sub> Ti	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^2$
<sub>8</sub> O	$1s^2 2s^2 2p^4$	<sub>23</sub> V	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^3$
<sub>9</sub> F	$1s^2 2s^2 2p^5$	<sub>24</sub> Cr	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^1 3d^5$
<sub>10</sub> Ne	$1s^2 2s^2 2p^6$	<sub>25</sub> Mn	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^5$
<sub>11</sub> Na	$1s^2 2s^2 2p^6 3s^1$	<sub>26</sub> Fe	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^6$
<sub>12</sub> Mg	$1s^2 2s^2 2p^6 3s^2$	<sub>27</sub> Co	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^7$
<sub>13</sub> Al	$1s^2 2s^2 2p^6 3s^2 3p^1$	<sub>28</sub> Ni	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^8$
<sub>14</sub> Si	$1s^2 2s^2 2p^6 3s^2 3p^2$	<sub>29</sub> Cu	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^1 3d^{10}$
<sub>15</sub> P	$1s^2 2s^2 2p^6 3s^2 3p^3$	<sub>30</sub> Zn	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10}$

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

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

$${}_{24}\text{Cr} = [\text{Ar}]4s^2 3d^4 \text{ & } {}_{29}\text{Cu} = [\text{Ar}]4s^2 3d^9 \text{ respectively.}$$

But the actual electronic configurations are

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

The exceptional electronic configuration is due to the fact that half-filled and full-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>?

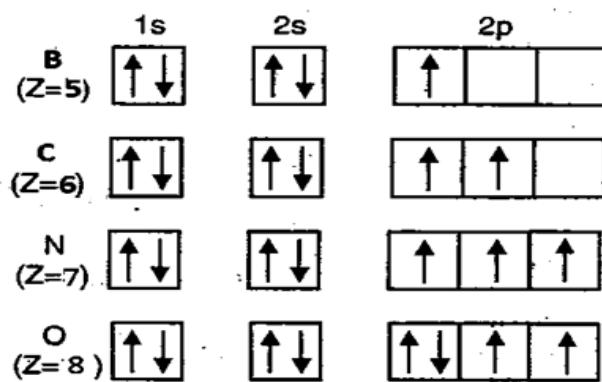
### Hund's Rule: -

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 5<sup>th</sup> electron is occupied by the 2p<sub>x</sub> orbital. In carbon the 6<sup>th</sup> electron will not be paired with the electron of the 2p<sub>x</sub> orbital, rather it will be occupied by the 2p<sub>y</sub> 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  $\text{Na}^+$ ?

## **Exercise**

### **(02 Marks Questions)**

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

### **(05 Marks Questions)**

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

## CHAPTER - 2 CHEMICAL BONDING

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

### **Types of Chemical Bonding:**

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

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

### **IONIC OR ELECTROVALENT BONDING:**

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

The number of electrons lost or gained by an atom during ionic bond formation is called its electrovalency.

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

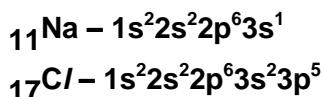
- ☞ Formation of a positive ion by loss of electron/s from one kind of atom.
- ☞ Formation of a negative ion by gain of electron/s from another kind of atom.
- ☞ Electrostatic force of attraction between the oppositely charged ions.

### **Conditions for the formation of Ionic bond:**

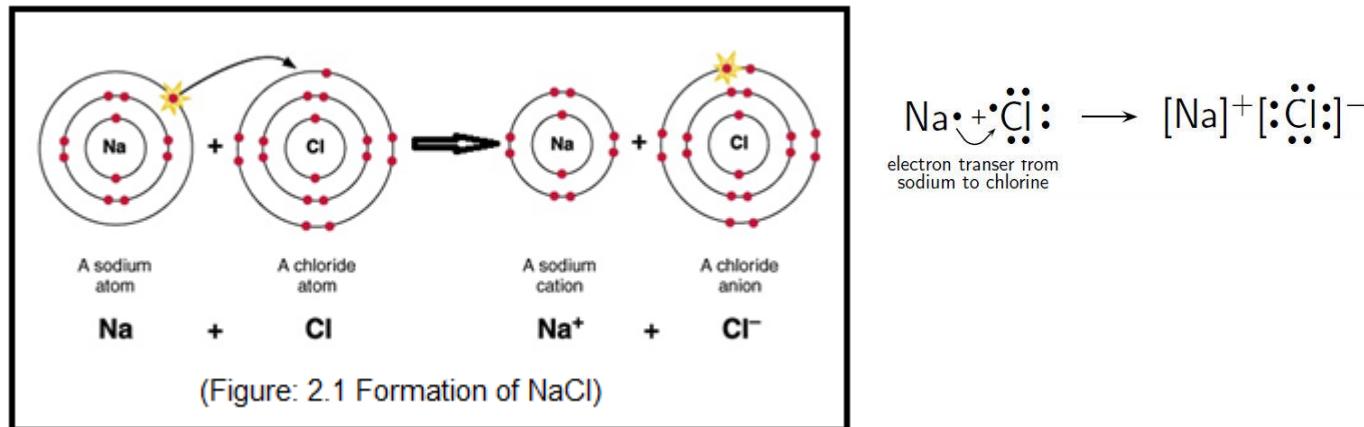
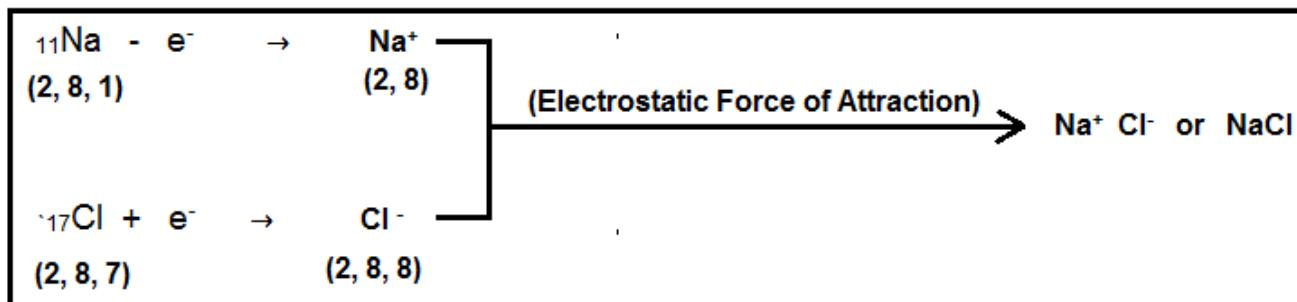
1. **Nature of element:** Atoms of different elements form ionic bonds. Atoms of the same element never form *ionic bond*.
2. **Low Ionization potential:** Ionization potential of an element is the quantity of energy required to remove one valence electron from an isolated, neutral, gaseous atom. One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

**Example: I:** Formation of NaCl.

*The electronic configurations of Na and Cl are given below:*



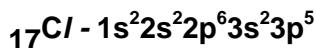
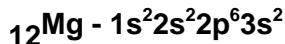
The electronic configurations indicate the presence of one and seven valence electrons in sodium and chlorine respectively. During the formation of NaCl, the sodium atom donates its valence electron completely to the chlorine atom (Fig. 2.1). Na becomes  $\text{Na}^+$  with 8 electrons in valence shell and attains the nearest noble gas configuration of Ne; while Cl atom becomes  $\text{Cl}^-$  ion with '8' electrons in valence shell and attains the nearest noble gas configuration of Ar.



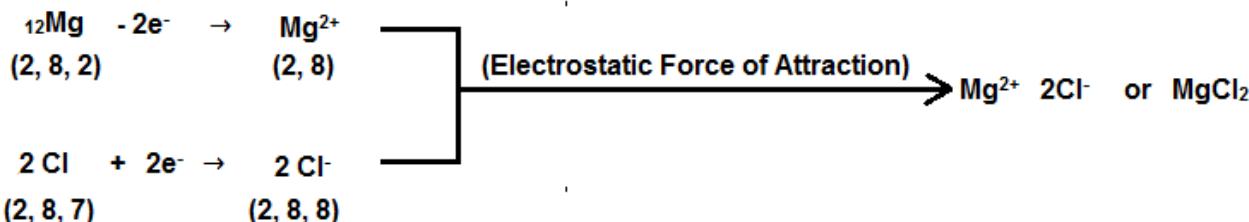
Now the electrostatic force of attraction between the oppositely charged ions  $\text{Na}^+$  and  $\text{Cl}^-$  results in the formation of  $\text{NaCl}$ .

#### *Example :II : Formation of $\text{MgCl}_2$*

*The electronic configurations of Mg and Cl are given below:*



An atom magnesium and chlorine contain 2 and 7 valence electrons respectively. During the formation of  $\text{MgCl}_2$ , one of the valence electrons of Mg is completely transferred to one atom of chlorine while the second valence electron is transferred to another atom (Fig. 2.2). Now Mg becomes  $\text{Mg}^{2+}$  with 8 valence electrons, with electronic configuration similar to that of Neon. On the other hand, each chlorine atom after accepting an electron becomes  $\text{Cl}^-$  ion with 8 valence electrons, acquiring electronic configuration similar to that of Argon.



The electrostatic force of attraction between calcium and chloride ions results in the formation of  $\text{MgCl}_2$ .

**Other examples of ionic compounds:**  $\text{KCl}$ ,  $\text{KBr}$ ,  $\text{KI}$ ,  $\text{CaF}_2$ ,  $\text{CaBr}_2$ ,  $\text{CaI}_2$ ,  $\text{Na}_2\text{O}$ ,  $\text{K}_2\text{O}$ ,  $\text{CaO}$ ,  $\text{MgO}$ ,  $\text{Na}_2\text{S}$ ,  $\text{K}_2\text{S}$  etc.

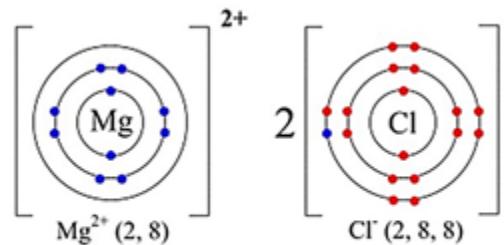


Figure: 2.2

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

1. These exist in solid states.
2. These are hard and rigid.
3. These are crystalline in nature.
4. These have high melting and boiling point.
5. These have high densities.
6. These are soluble in polar solvents like water, but are insoluble in non-polar solvents like  $\text{CCl}_4$ , ethers, benzene, toluene [ $\text{C}_6\text{H}_5 - \text{CH}_3$ ], 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.

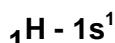
### COVALENT BOND:

**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  $\text{H}_2$  molecule.

The electronic configuration of 'H' is



The electronic configuration indicates the presence of 1

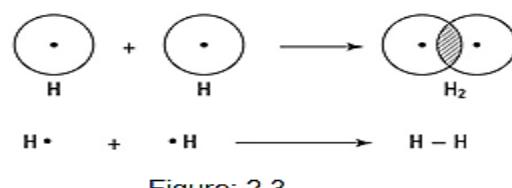
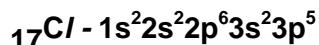


Figure: 2.3

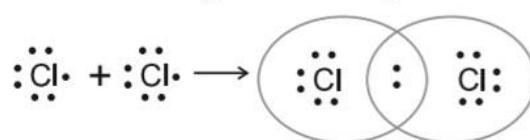
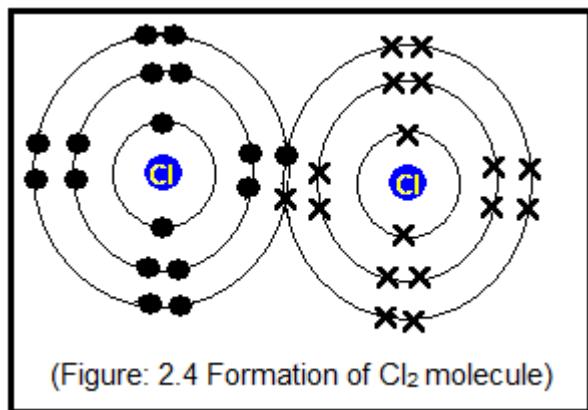
valence electron in 'H' and requires one more electron to become duplet. Thus, each hydrogen atom shares its electron with each other to form a covalent bond (Fig. 2.3).

**Example : 2 :** Formation of  $\text{Cl}_2$  molecule.

The electronic configuration of 'Cl' is

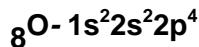


The electronic configuration indicates the presence of 7 valence electrons in 'Cl' and requires one more electron to become octet. Thus, each chlorine atom shares one of its valence electrons with each other to form a covalent bond (Fig. 2.4).

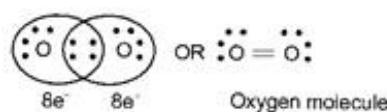
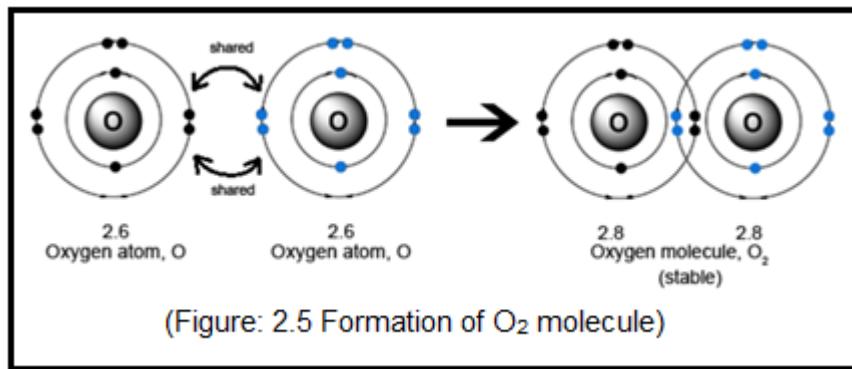


**Example : 3 :** Formation of  $\text{O}_2$  molecule.

The electronic configuration of 'O' is



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

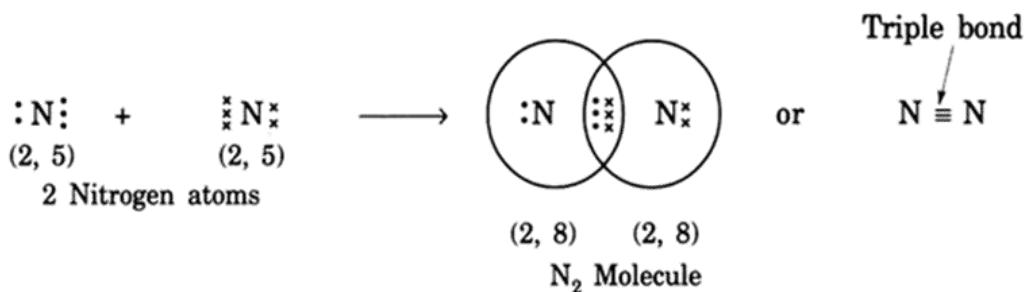
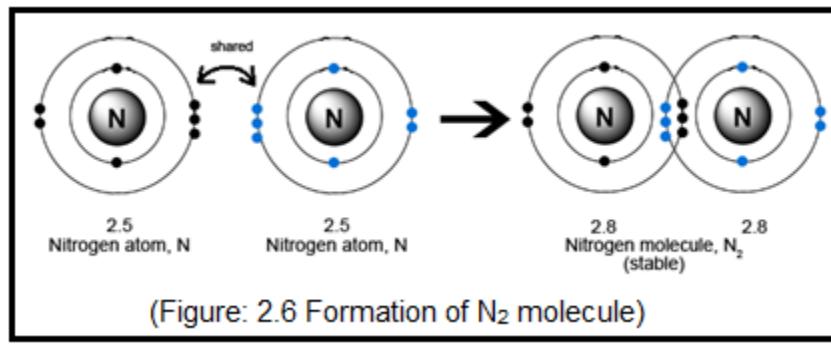


**Example : 4 :** Formation of  $\text{N}_2$  molecule.

The electronic configuration of 'N' is

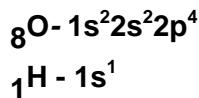


The electronic configuration indicates the presence of 5 valence electrons in 'N' and requires three more electrons to become octet. Thus, each nitrogen atom shares three of its valence electrons with each other to form a triple covalent bond (Fig. 2.6).

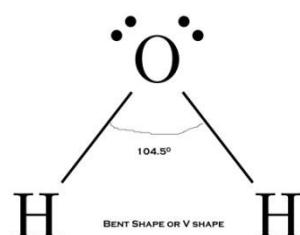
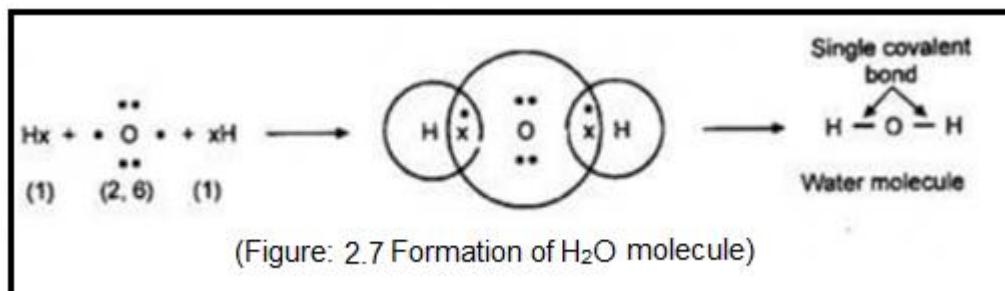


**Example : 5 :** Formation of H<sub>2</sub>O molecule.

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

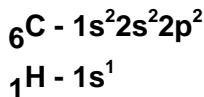


The electronic configurations indicate the presence of 6 and 1 valence electrons in 'O' and 'H' respectively. The central 'O' atom requires two more electrons to become octet while each hydrogen atom needs one electron to become duplet. Thus, each hydrogen atom shares its valence electron with the valence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



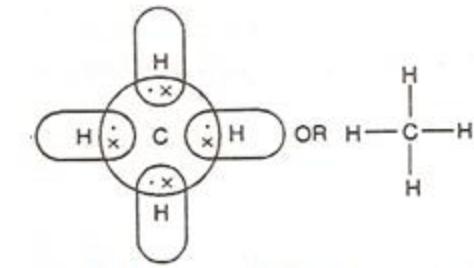
**Example: 6:** Formation of methane (CH<sub>4</sub>) molecule.

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



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

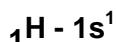
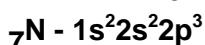
Thus, each hydrogen atom shares its electron with one valence electron of carbon to form four single covalent bonds. By sharing an electron each hydrogen atom becomes duplet while carbon becomes octet. The shape of  $\text{CH}_4$  is tetrahedral with a bond angle of  $109^{\circ}28$  (Fig. 2.8).



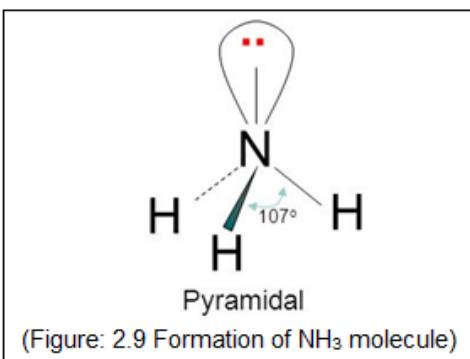
(Figure: 2.8 Formation of  $\text{CH}_4$  molecule)

**Example: 7:** Formation of ammonia ( $\text{NH}_3$ ) molecule.

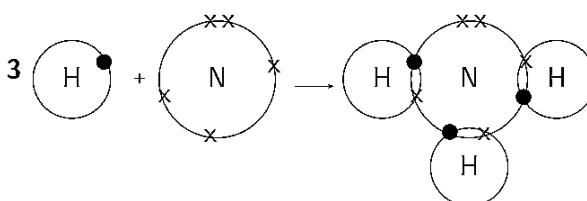
The electronic configuration of 'C' and 'H' are



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.



(Figure: 2.9 Formation of  $\text{NH}_3$  molecule)



Thus, each hydrogen atom shares its valence electron with one valence electron of nitrogen to form three single covalent bonds (Fig. 2.9). The shape of  $\text{NH}_3$  is pyramidal with a bond angle of  $107^{\circ}$ .

**Other examples of covalent compounds:** ,  $\text{F}_2$ ,  $\text{Br}_2$ ,  $\text{I}_2$ ,  $\text{BF}_3$ ,  $\text{AlCl}_3$ ,  $\text{HCl}$ ,  $\text{HF}$ ,  $\text{SiO}_2$ , 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  $\text{CCl}_4$ , 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:

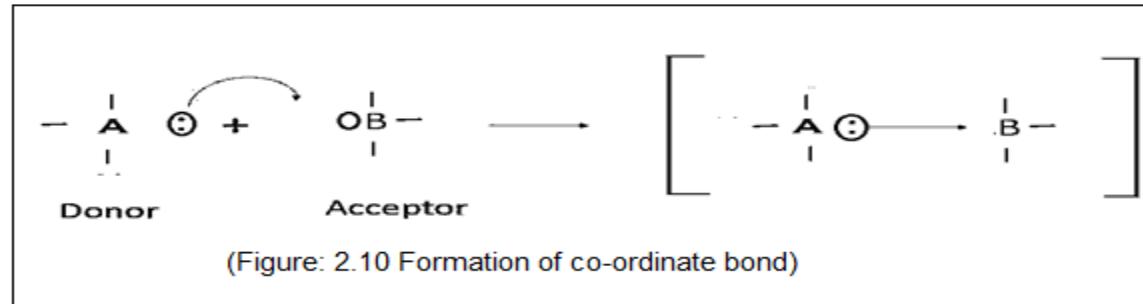
The chemical bond formed by the partial donation and partial sharing of a lone pair of electrons between two atoms (or ions) is called a co-ordinate or dative bond.

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

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

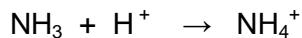
The lone pair of electrons present over one atom is partially shared by both the combining atoms. A co-ordinate bond is represented by an arrow ( $\rightarrow$ ) sign, the head of which points towards the acceptor atom, while the tail points towards the donor atom.

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



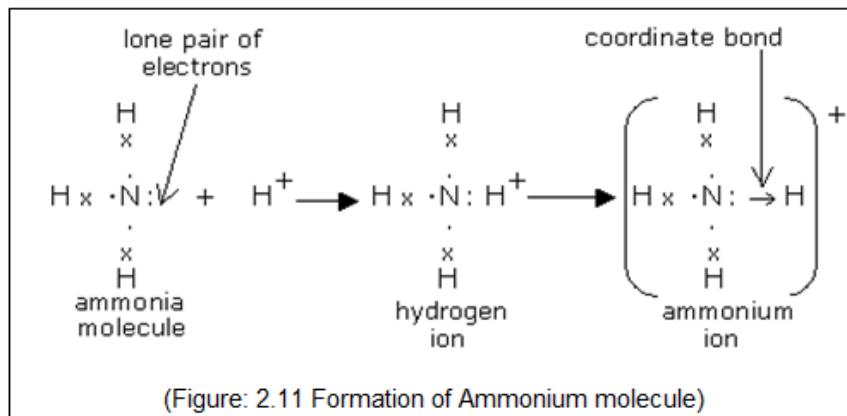
### Example: 1: Formation of ammonium ion ( $\text{NH}_4^+$ ).

Ammonium ion ( $\text{NH}_4^+$ ) is formed by the combination of  $\text{NH}_3$  and  $\text{H}^+$  ion.



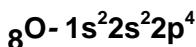
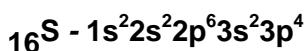
Ammonia ( $\text{NH}_3$ ) contains a lone pair of electrons over 'N' while ' $\text{H}^+$ ' ion contains no electron and requires two electrons to become duplet.

Thus, the unshared pair of electrons over nitrogen in  $\text{NH}_3$  is partially shared with  $\text{H}^+$  ion and a Co-ordinate bond is formed (Fig. 2.11).

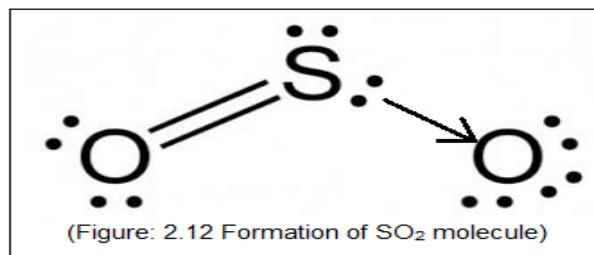


### Example: 2: Formation of Sulphur dioxide ( $\text{SO}_2$ ) molecule.

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



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

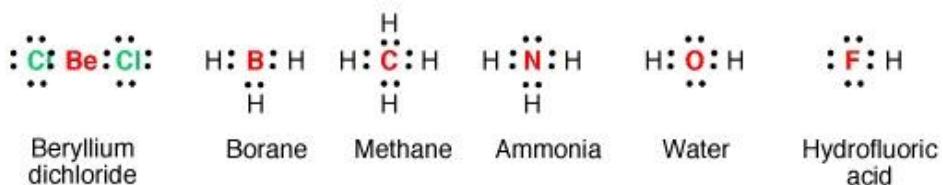


### Characteristics of Coordinate Compound:

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

### Lewis Structure:

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



### Assignment

Q. Draw the Lewis structures of the following:  $\text{MgCl}_2$ ,  $\text{O}_2$ ,  $\text{N}_2$ ,  $\text{SO}_2$ ,  $\text{NH}_4^+$  and  $\text{H}_3\text{O}^+$ .

## **Exercise**

### **(02 Marks Questions)**

1. Define chemical bonding.
2. Define electrovalent bonding.
3. Define covalent bonding.
4. Define co-ordinate bonding.
5. What is Lattice energy? How is it related with the strength of an ionic bond?
6. Mention the conditions for formation of electrovalent bonding.
7. Mention the conditions for formation of co-ordinate bonding.
8. Define ionization potential. What should be the value of it for the metals to form ionic bond?
9. Define electron affinity. What should be the value of it for the metals to form ionic bond?
10. Which types of chemical bondings exist in  $MgCl_2$  and  $NH_3$ ?
11. Which types of chemical bondings exist in  $MgCl_2$  and  $H_2O$ ?

### **(05 Marks Questions)**

1. Define and explain electrovalent bonding with a suitable example.
2. Define and explain covalent bonding with a suitable example.
3. Define and explain co-ordinate bonding with a suitable example.
4. Explain the formation of  $NH_3$  and  $NH_4^+$ .
5. Explain the conditions of formation of electrovalent bond.
6. Explain the conditions of formation of co-ordinate bond.
7. Define covalent bond. Explain the formation of  $CH_4$  molecule.
8. Define covalent bond. Explain the formation of  $H_2O$  molecule.
9. Define covalent bond. Explain the formation of  $O_2$  molecule.
10. Define covalent bond. Explain the formation of  $N_2$  molecule.
11. Define covalent bond. Explain the formation of  $NH_3$  molecule.
12. Define electrovalent bonding. Explain the formation of  $MgCl_2$  molecule.
13. Define and explain co-ordinate bonding and explain the formation of  $NH_4^+$  ion.
14. Define and explain co-ordinate bonding and explain the formation of  $SO_2$  molecule.
15. Write down at least ten properties of ionic compounds.
16. Write down at least ten properties of covalent compounds.

## **CHAPTER - 3** **ACID – BASE THEORIES**

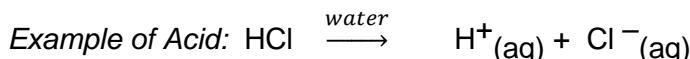
### **Introduction:**

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

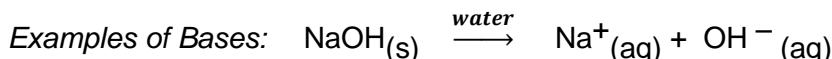
- 1. Arrhenius Theory**
- 2. Lowery – Bronsted Theory**
- 3. Lewis Theory.**

### **ARRHENIUS THEORY:**

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



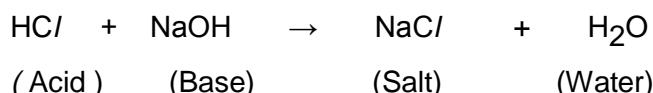
Other examples of acids are:  $HNO_3$ ,  $H_2SO_4$ ,  $CH_3COOH$ , etc.



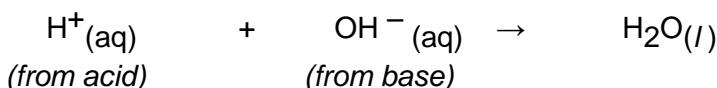
Other examples of bases are:  $LiOH$ ,  $KOH$ ,  $NH_4OH$ ,  $Ca(OH)_2$ ,  $Al(OH)_3$ , etc

### **Salient Features:**

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



Neutralization reaction may be represented as:



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

### **Limitations:**

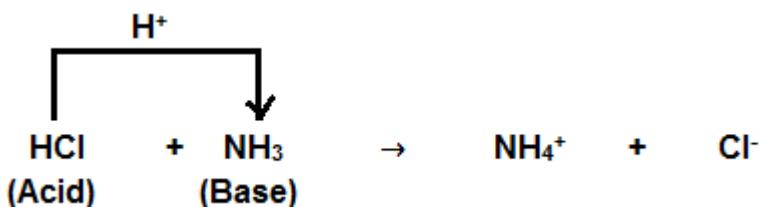
- $H^+$  ion does not exist in aqueous solution. It combines with  $H_2O$ , as soon as its formation to give hydronium ion ( $H_3O^+$ ).  
$$H^+ + H_2O \rightarrow H_3O^+$$
- The theory fails to explain the acidic and basic nature of the substances in solvents other than water.
- The theory fails to explain the acidic nature of the substances like  $SO_2$ ,  $CO_2$ ,  $SiO_2$ ,  $P_2O_5$ ,  $BF_3$ ,  $AlCl_3$ , etc. which cannot provide  $H^+$  ions.

- iv. The theory fails to explain the basic nature of the substances like  $\text{NH}_3$ ,  $\text{PH}_3$ ,  $\text{Na}_2\text{O}$ ,  $\text{K}_2\text{O}$ ,  $\text{CaO}$  etc. which can't provide  $\text{OH}^-$  ions.
- v. The theory fails to explain neutralization reactions between some acidic and basic substances which do not produce water.  $\text{HCl} + \text{NH}_3 \rightarrow \text{NH}_4\text{Cl}$

## 2. BRONSTED - LOWRY THEORY:

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

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



Since,  $\text{HCl}$  has donated a proton (to  $\text{NH}_3$ ), it acts as an acid. On the other hand,  $\text{NH}_3$  has accepted a proton from  $\text{HCl}$  and thus it acts as a base.

Other examples of Acids are:

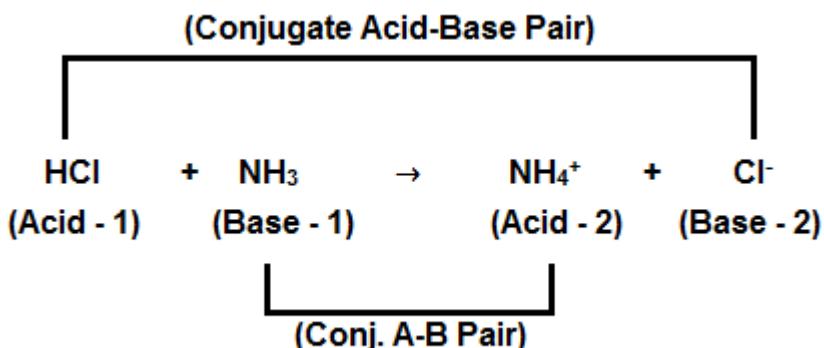
- i. All Arrhenius acids are Bronsted-Lowry acids; ( $\text{HCl}$ ,  $\text{HNO}_3$ ,  $\text{H}_2\text{SO}_4$ ,  $\text{H}_3\text{PO}_4$ ,  $\text{CH}_3\text{COOH}$ ,  $\text{H}_2\text{CO}_3$  etc.), however the reverse is not true.
- ii. Ions having capacity to donate  $\text{H}^+$  ion: ( $\text{HS}^-$ ,  $\text{HCO}_3^-$ ,  $\text{HPO}_4^{2-}$ ,  $\text{HSO}_4^-$  etc.)

Examples of Bases:

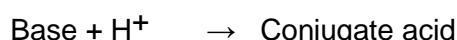
- i. Natural molecules such as:  $\text{H}_2\text{O}$ ,  $\text{NH}_3$ ,  $\text{RNH}_2$ ,  $\text{PH}_3$ ,  $\text{AsH}_3$ , etc.
- ii. Ions having capacity to accept  $\text{H}^+$  ion, like  $\text{OH}^-$ ,  $\text{CN}^-$ ,  $\text{HCO}_3^-$ , etc.

### Salient Features:-

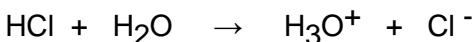
- i. According to this theory an acid reacts with a base to form another pair of acid and base. For example:



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



- ii. The substances such as  $\text{H}_2\text{O}$ ,  $\text{HS}^-$ ,  $\text{HCO}_3^-$ ,  $\text{HPO}_4^{2-}$ ,  $\text{HSO}_4^-$ , 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.



[Strong acid]

[Weak base]

#### Limitations of the theory:

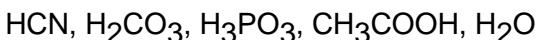
- It fails to explain the acidic nature of the substances, such as  $\text{SiO}_2$ ,  $\text{CO}_2$ ,  $\text{SO}_2$ ,  $\text{BF}_3$ , etc. which cannot donate  $\text{H}^+$  ion.
- It fails to explain the basic nature of the substances, such as  $\text{Na}_2\text{O}$ ,  $\text{K}_2\text{O}$ ,  $\text{CaO}$  etc. which cannot accept  $\text{H}^+$  ion.
- It fails to explain the reaction between some acids and bases which do not give another pair of acid and base. Example:  $\text{HCl} + \text{NaOH} \rightarrow \text{NaCl} + \text{H}_2\text{O}$ .

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

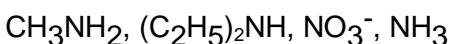
Acid	Conjugate- Base	Base	Conjugate- Acid
$\text{HCl}$	$\text{Cl}^-$	$\text{Br}^-$	$\text{HBr}$
$\text{H}_2\text{SO}_4$	$\text{HSO}_4^-$	$\text{CN}^-$	$\text{HCN}$
$\text{HS}^-$	$\text{S}^{2-}$	$\text{O}^{2-}$	$\text{OH}^-$
$\text{NH}_4^+$	$\text{NH}_3$	$\text{NH}_3$	$\text{NH}_4^+$
$\text{H}_2\text{O}$	$\text{OH}^-$	$\text{H}_2\text{O}$	$\text{H}_3\text{O}^+$

#### Assignment:

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



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



#### 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: -

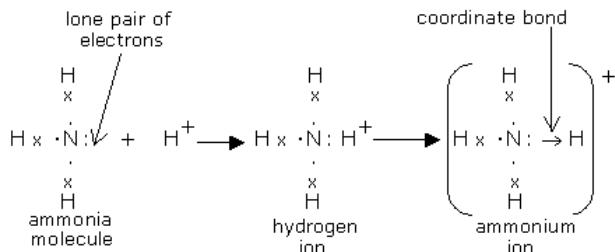
- Cations like:  $\text{CH}_3^+$ ,  $\text{H}^+$ , etc.
- Neutral molecules containing electron deficient atoms are Lewis acids. For example:  
 $\text{BF}_3$ ,  $\text{AlCl}_3$ ,  $\text{FeCl}_3$ ,  $\text{ZnCl}_2$ , etc.
- Neutral molecules containing vacant d-orbitals in the central atom for the accommodation of incoming electrons act as Lewis acids. For example:  $\text{SiF}_4$ ,  $\text{SiCl}_4$ , etc.
- The molecules having multiple bonding ( $=$  or  $\equiv$ ) between the atoms of different elements are acidic in nature. For example:  $\text{CO}_2$  ( $\text{O} = \text{C} = \text{O}$ ),  $\text{SO}_2$ , etc.

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

- i. All anions are Lewis bases:  $\text{F}^-$ ,  $\text{Cl}^-$ ,  $\text{CO}_3^{2-}$ , etc.
- ii. Neutral molecules containing, at least one lone pair of electrons are Lewis bases: Examples:  $\text{NH}_3$ ,  $\text{PH}_3$ ,  $\text{H}_2\text{O}$ , etc.

### **Salient Features:**

- i. According to this theory, an acid reacts with a base to form a co-ordinate or dative bond. For example, the reaction between  $\text{NH}_3$  (Lewis base) and  $\text{H}^+$  (Lewis acid) results in the formation of a dative bond.



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

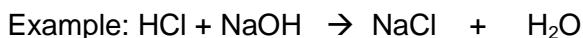
### **Limitations:**

- 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. The theory fails to explain the relative strengths of different acids and bases.
- iii. It fails to explain reaction between some acids and bases where no coordinate bond is formed.
- iv. It fails to explain the acidic nature of well-known acids like  $\text{HCl}$ ,  $\text{HNO}_3$ ,  $\text{H}_2\text{SO}_4$ , etc. which cannot accept electrons.
- v. It fails to explain the basic nature of well-known bases like  $\text{NaOH}$ ,  $\text{KOH}$ , etc. which cannot donate electrons.
- vi. It fails to explain acid-catalyzed reactions, where  $\text{H}^+$  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  $\text{pH}$  of about 7 and is neutral.



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



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  $p^H > 7$  and is alkaline.



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  $p^H > 7$  and is alkaline.



## **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  $\text{H}^+$  and anion other than  $\text{OH}^-$  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 into the following types:

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

Example:	<b>Acids</b>	<b>Normal salts</b>
	HCl	NaCl, KCl, CaCl <sub>2</sub> , MgCl <sub>2</sub> , etc
	HNO <sub>3</sub>	NaNO <sub>3</sub> , KNO <sub>3</sub> , Ca(NO <sub>3</sub> ) <sub>2</sub> , Mg(NO <sub>3</sub> ) <sub>2</sub> , etc.
	H <sub>2</sub> SO <sub>4</sub>	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 <sub>3</sub> PO <sub>4</sub>	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:	<b>Acids</b>	<b>Acidic salts</b>
	H <sub>2</sub> SO <sub>4</sub>	NaHSO <sub>4</sub> , KHSO <sub>4</sub> etc.
	H <sub>3</sub> PO <sub>4</sub>	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<sub>4</sub>Cl, NH<sub>4</sub>NO<sub>3</sub>, (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>, 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)<sub>2</sub>Cl 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.

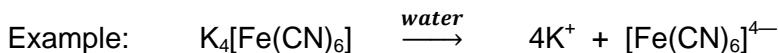
4. **Double salts:** These are the molecular addition compounds obtained from two simple salts, the ions of which retain their identity in aqueous solution. Such salts give the test of all the constituent ions when dissolved in water.



(Potash Alum)

Other examples: Mohr's Salt  $[\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}]$ , carnalite ( $\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ ), 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.



Other examples:  $\text{K}_3[\text{Fe}(\text{CN})_6]$ ,  $[\text{Cu}(\text{NH}_3)_4]\text{SO}_4$ , etc.

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

Examples: Bleaching powder  $\text{Ca}(\text{OCl})\text{Cl}$ ; Sodium potassium sulphate  $\text{NaKSO}_4$ , etc.



## **Exercise**

### **(02 Marks Questions)**

1. Define Arrhenius theory of acids and bases.
2. Define Bronsted-Lowery theory of acids and bases.
3. Define Lewis theory of acids and bases.
4. Justify that all Arrhenius acids are Bronsted-Lowery acids.
5. Explain how  $\text{BF}_3$  is a Lewis acid.
6. Explain how  $\text{SiCl}_4$  is a Lewis acid.
7. Explain how  $\text{BF}_3$  is a Lewis acid.
8. Explain how  $\text{AlCl}_3$  is a Lewis acid.
9. Explain how  $\text{SO}_2$  is a Lewis acid.
10. Explain how  $\text{NH}_3$  is both a Bronsted-Lowery base and a Lewis base.
11. Write down the conjugate acids and conjugate bases of  $\text{H}_2\text{O}$  &  $\text{NH}_3$ .
12. What do you mean by conjugate acid-base pair? Explain with a suitable example.
13.  $\text{CH}_3\text{COOH}$  is a weak acid while  $\text{CH}_3\text{COO}^-$  is a strong base. Explain.
14. What is neutralization reaction? Give an example of it.
15. Define salt. How does an acidic salt form?
16. Define salt. How does a basic salt form?
17. What is double salt? Give an example.
18. What is co-ordination salt? Give an example.
19. What is mixed salt? Give an example.
20. Explain how bleaching powder is a mixed salt.
21. Explain how potash alum is a double salt.

### **(05 Marks questions)**

1. Define and explain Arrhenius theory of acids and bases.
2. Define and explain Bronsted-Lowery theory of acids and bases.
3. Define and explain Lewis theory of acids and bases.
4. Explain the limitations of Arrhenius theory.
5. Explain the limitations of Bronsted-Lowery theory.
6. Explain the limitations of Lewis theory.
7. Justify that all Arrhenius acids are Bronsted-Lowery acids, but all Arrhenius bases are not Bronsted – Lowery bases.
8. Explain how  $\text{SiCl}_4$  and  $\text{BF}_3$  are acids.
9. Explain why  $\text{SiCl}_4$  is an acid but  $\text{CCl}_4$  is not.
10. Define and explain conjugate acid-base pair with a suitable example.
11. Justify your answer that  $\text{H}_2\text{O}$  is amphoteric.
12. How many grams of KOH are required to get 2 lit of its solution having  $\text{P}^{\text{H}} 10$ ?
13. Explain how potash alum is a double salt while,  $\text{K}_3[\text{Fe}(\text{CN})_6]$  is a complex salt.
14. 14.7 grams of  $\text{H}_2\text{SO}_4$  are present in 2 liters of its solution. Find morality and normality of the solution.
15. How many grams of calcium hydroxide are required to prepare  $10^{-2}$  M and  $10^{-2}$  N solutions?
16. How many grams of decahydrated sodium carbonate of 80% purity are required to prepare 2.5 lit. of its decinormal solution?

## **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 may be of three basic types: solid solutions, liquid solutions and gaseous solutions. A binary solution is composed of two components, one is solute and the other is solvent.

### **Atomic weight/mass:**

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

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

For example:

<b><i>Element</i></b>	<b><i>Atomic mass in amu</i></b>
H	1.008 $\approx$ 1
N	14
O	16

***Atomic masses of some elements are given below:***

<b><u>Element</u></b>	<b><u>Symbol</u></b>	<b><u>Atomic Weight in a.m.u</u></b>
Hydrogen	H	1
Helium	He	4
Lithium	Li	7
Beryllium	Be	9
Boron	B	11
Carbon	C	12
Nitrogen	N	14
Oxygen	O	16
Fluorine	F	19
Neon	Ne	20
Sodium	Na	23
Magnesium	Mg	24
Aluminium	Al	27
Silicon	Si	28
Phosphorous	P	31
Sulphur	S	32

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

### **GRAM ATOMIC MASS:**

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

<u>Element</u>	<u>Gm.atomic mass</u>
H	1.008 gm
O	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 ( $6.023 \times 10^{23}$  atoms) of the element.

### **MOLECULAR WEIGHT:**

The molecular weight of a substance may be defined as “the relative average weight of one molecule of the substance as compared to the weight of an atom of carbon ( $^{12}\text{C}$ ) 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 ( $\text{H}_2\text{SO}_4$ ) can be obtained as

$$\begin{aligned} \text{H}_2\text{SO}_4 &= [2 \times \text{At.wt.of H}] + \text{At.wt. of sulphur} + [4 \times \text{At.wt of oxygen}] \\ &= 2 \times 1 + 32 + 4 \times 16 = 98 \text{ amu} \end{aligned}$$

Other examples:

<u>Compound</u>	<u>Molecular weight</u>
NaCl	$23 + 35.5 = 58.5 \text{ amu}$
$\text{HNO}_3$	$1 + 14 + 48 = 63 \text{ amu}$
$\text{CaCO}_3$	$40 + 12 + 48 = 100 \text{ amu}$
$\text{Al}_2(\text{SO}_4)_3$	$2 \times 27 + 3 \times 32 + 12 \times 16 = 342 \text{ amu}$

### **Assignment**

Q 1. Find the molecular weights of the following:  $\text{Na}_2\text{SO}_4$ ,  $(\text{NH}_4)_2\text{CO}_3$ ,  $(\text{NH}_4)_3\text{PO}_4$ ,  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$

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



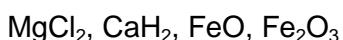
2×35.5 parts by mass of chlorine combines with 'Ca' = 40 parts

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

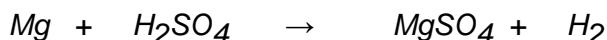
Thus, equivalent weight of 'Ca' in CaCl<sub>2</sub> is 20.

### Assignment

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



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



### 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<sub>V</sub>**".

In **MH<sub>V</sub>**,

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 =  $\frac{A}{(V \times 1.008)} \times V = \frac{A}{V}$

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

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

### 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  $\text{FeCl}_2$  and  $\text{FeCl}_3$  are:

$$\text{Eq. Wt. of 'Fe' in } \text{FeCl}_2 = \frac{\text{Atomic weight}}{\text{Valency}} = \frac{56}{2} = 28$$

$$\text{Eq. Wt. of 'Fe' in } \text{FeCl}_3 = \frac{\text{Atomic weight}}{\text{Valency}} = \frac{56}{3} = 18.66$$

## EQUIVALENT WEIGHTS OF ACIDS, BASES AND SALTS:

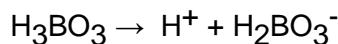
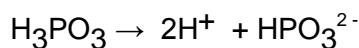
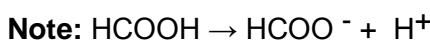
### Equivalent weights of acids:

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

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

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

<u>ACID</u>	<u>FORMULA</u>	<u>MOL.WT.</u>	<u>BASICITY</u>	<u>EQ.WT.</u>
Nitric Acid	$\text{HNO}_3$	63	1	$63/1 = 63$
Sulphuric Acid	$\text{H}_2\text{SO}_4$	98	2	$98/2 = 49$
Phosphoric Acid	$\text{H}_3\text{PO}_4$	98	3	$98/3 = 32.66$
Formic Acid	$\text{HCOOH}$	46	1	$46/1=46$
Acetic Acid	$\text{CH}_3\text{COOH}$	60	1	$60/1 = 60$
Oxalic Acid	$\begin{matrix} \text{COOH} \\   \\ \text{COOH} \end{matrix}$	90	2	$90/2=45$
Phosphorous Acid	$\text{H}_3\text{PO}_3$	82	2	$82/2 = 41$
Boric Acid	$\text{H}_3\text{BO}_3$	62	1	$62/1 = 62$



### Equivalent weights of bases:

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

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

Exaamples:-

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

$$E_{\text{Salt}} = \frac{\text{Molecular weight}}{\text{Total no. of +ve or -ve charge}}$$

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

Salt	Molecular formula	Mol. weight	Total +ve or - ve Charge	Eq. weight
Sodium chloride	NaCl	58.5	1x1 = 1	58.5
Potassium carbonate	K <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

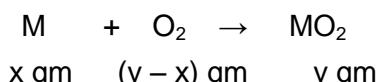
Bases: Mg(OH)<sub>2</sub>, LiOH

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:



Let the weight of metal = x gm

The weight of metal oxide = y gm

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

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

$$\therefore 8 \text{ gm of oxygen is combined with metal} = \frac{x}{(y-x)} \times 8$$

$$\text{Hence, the equivalent weight of metal} = \frac{x}{(y-x)} \times 8 = \frac{\text{weight of metal}}{\text{weight of oxygen}} \times 8$$

### Numerical Problems:

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



### SOLUTION:

In Fe<sub>2</sub>O<sub>3</sub>

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

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

In CuCl<sub>2</sub>

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

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

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

### SOLUTION:

Given Data: Weight of metal = 1.201 gm.

Weight of metal oxide = 1.497 gm.

$$\therefore \text{Weight of oxygen} = 1.497 - 1.201 = 0.296 \text{ gm}$$

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

**EXAMPLE III:** 0.723g. of copper displaced 2.455g. of silver from a solution of silver nitrate. Calculate equivalent weight of copper that of silver 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  $E_{Ag} = 107.88$

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

Applying Faraday's 2<sup>nd</sup> law of electrolysis:

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

### **EQUIVALENT WEIGHT OF IONS:**

$$\text{Equivalent weight of Ion (}E_{\text{ion}}\text{)} = \frac{\text{Ionic Mass}}{\text{Total Charge}}$$

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 liter of solution".*

*Unit = gram mole/liter or M.*

*Mathematically,*

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

$Ms$  = Molecular weight of the solute.

$V_{ml}$  = Volume of solution in ml.

### **Molar solution:**

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

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

- NOTE:** 1. Deci molar solution means  $(1/10)$  M solution, Semi-molar solution means  $(1/2)$  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 ml.

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

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

Hence, the molarity of the solution is 0.05M.

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

#### **Solution : Given Data**

Weight of solute ( $w$ ) = ?

Volume of the solution ( $V_{ml}$ ) = 1.5 lit = 1500 ml.

Molecular weight of solute,  $M_s$  for KOH =  $39+16+1 = 56$  amu

Molarity of the solution =  $1/10$  M = 0.1M

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

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

## **NORMALITY (N):**

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

Mathematically,

$$N = \frac{w \times 1000}{E_s \times Vml}; \quad \text{Where, } w = \text{weight of solute in gm.}$$

$V_{ml}$  = volume of solution in ml.

$E_s$  = Equivalent weight of solute

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

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

## **PROBLEMS FOR DISCUSSION:**

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

**Solution:** Given Data

Weight of solute, w = 5.6 gm

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

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

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

Hence, the normality of the solution is 0.125N.

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

**Solution :** Given Data,

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

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

$$\text{Equivalent weight of } H_2SO_4 = \frac{\text{Molecular weight}}{\text{Basicity}} = \frac{98}{2} = 49$$

$$\text{Normality N} = \frac{w \times 1000}{E_s \times Vml} = \frac{12 \times 1000}{49 \times 400} = 0.612 \text{ N}$$

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,**

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

Where,  $w$  = weight of solute in gm

$W$  = weight of solvent in gm

$M_S$  = Molecular weight of solute

### **Molal solution:**

The solution containing 1 gm mole of solute per 1000gm of solvent is called molal solution. For example: 58.5 gm of NaCl, 40 gm of NaOH, 56 gm of KOH or 98gm of 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,  $M_S$  (NaCl) = 23+35.5 = 58.5 amu.

$$\begin{aligned} m &= \frac{w \times 1000}{M_S \times W} \\ &= \frac{5.85 \times 1000}{58.5 \times 200} = 0.5\text{m} \end{aligned}$$

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

$$\text{Thus, molality } m = \frac{w \times 1000}{M_S \times W} = \frac{5.6 \times 1000}{56 \times 294.4} = 0.339 \text{ m.}$$

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 semi molar 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.

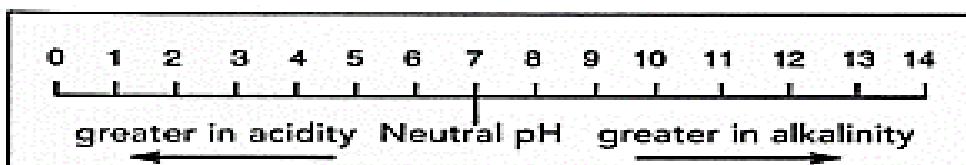
Q 11.0.49 gm of  $H_2SO_4$  is present in 600ml of its solution having density 1.2 gm/ml. Find molarity, normality and molality of the solution.

### $P^H$ of Solutions

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

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

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



*The pH scale*

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

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

### Some important Formulae:

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

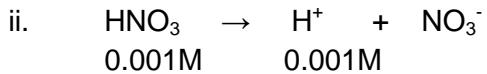
### **QUESTIONS FOR DISCUSSION:**

1. Find out the  $p^H$  values of the following solutions.
  - i. 0.01M HCl solution
  - ii. 0.001 M  $HNO_3$  solution
  - iii. 0.01M NaOH solution
  - iv. 0.01M  $H_2SO_4$  solution

**Solutions:-**

$$[\text{HCl}] = [\text{H}^+] = 0.01\text{M} = 10^{-2}\text{M}$$

$$\text{Hence } p^{\text{H}} = -\log[\text{H}^+] = -\log(10^{-2}) = -(-2) \log 10 = 2$$



$$[\text{HNO}_3] = [\text{H}^+] = 0.001\text{M} = 10^{-3}\text{M}$$

$$\text{Hence, } p^{\text{H}} = -\log[\text{H}^+] = -\log 10^{-3} = -(-3) \log 10 = 3.$$

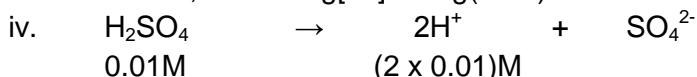


$$[\text{NaOH}] = [\text{OH}^-] = 0.01\text{M} = 10^{-2}\text{M}$$

$$\text{We know } [\text{H}^+] [\text{OH}^-] = 10^{-14}$$

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

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



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

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

**Assignment**

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

(i) 1 M  $\text{HNO}_3$  solution (ii) 0.1 M  $\text{Mg}(\text{OH})_2$  solution. [Ans: (i) 0, (ii) 12.301]

Q 13. One liter of a solution contains 5.85 gm of HCl. Find the  $P^{\text{H}}$  value of the solution. [Ans: 1]

Q 14. 500 ml of an aqueous solution contains 1.6 gm of NaOH. Find  $P^{\text{H}}$  of the solution.

## **Importance of $P^H$ in Industries:**

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

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

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

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

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

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

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

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

To effectively bleach cellulose (e.g., cotton) with a minimum amount of damage, the bleaching solution must be alkaline. This keeps the hypochlorite stable and also prevents the presence of reducing groups that cause an apparently well-bleached cloth to yellow with age. Additionally, an acidic solution will form toxic and corrosive chlorine gas. Bleaching liquor is therefore usually maintained at a  $p^H$  of 9. The permanence of the white obtained is thereby increased, and the bleaching is safe. Due to environmental concerns in recent times, hydrogen peroxide bleaching has become more prevalent. Its reaction products, oxygen and water, are relatively harmless. However, hydrogen peroxide is a weak acid. Thus, its conjugate base,  $\text{HO}_2^-$ , is used to perform the actual bleaching. To ensure an adequate concentration of  $\text{HO}_2^-$ , the solution  $p^H$  must be tightly controlled. Sodium hydroxide is used to maintain the  $p^H$  at a very alkaline level of 12-12.5.

## Exercise

### **(02 Marks Questions)**

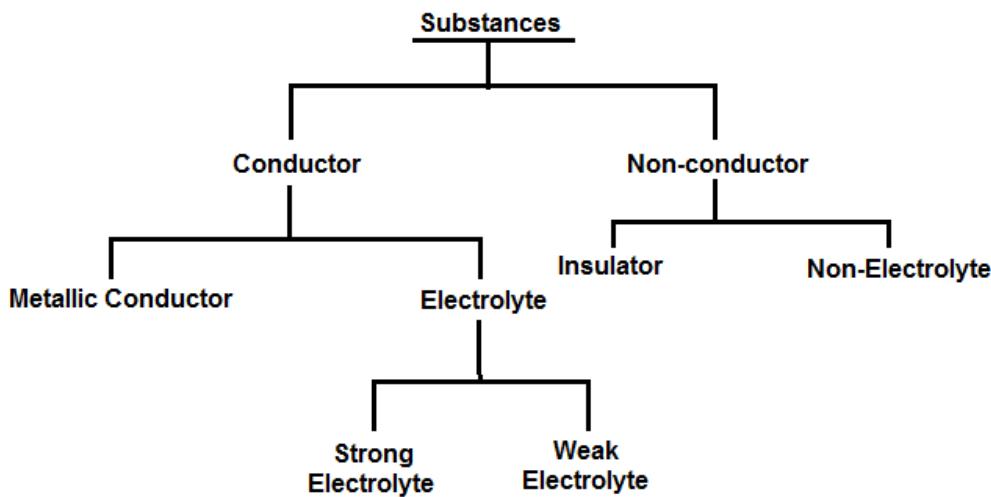
1. Define atomic weight.
2. Define molecular weight. What is the molecular weight of sulphuric acid?
3. Define equivalent weight. What is the equivalent weight of  $H_3PO_4$ ?
4. Find the molecular weights of  $Al_2(SO_4)_3$  and  $CuCO_3$ .
5. Find the equivalent weights of  $H_3PO_4$  and  $H_3PO_3$ .
6. Find the equivalent weights of  $Ca(HCO_3)_2$  and  $H_3BO_3$ .
7. Find the equivalent weights of acetic acid and calcium hydroxide.
8. Derive a relationship between atomic weight, equivalent weight and valency.
9. Define variable equivalent weights. Give suitable examples.
10. Why do the equivalent weights of  $FeO$  and  $Fe_2O_3$  vary?
11. 1 gm of a metal on heating with air produces 1.5 g of its oxide. Calculate the equivalent weight of the metal.
12. An oxide of metal contains 60% oxygen. Find the equivalent weight of the metal.
13. Find the equivalent weights of  $Ca(OH)_2$  and  $CH_3COOH$ .
14. Define molarity. Mention its unit.
15. How many grams of  $NaCl$  are required to prepare 2 liters of its solution having molarity 1M?
16. Define normality.
17. 4 grams of  $NaOH$  are present 2 lit of its solution. Find its normality.
18. Define molality.
19. 5.6 gram of  $KOH$  are present in 200 grams of water. Find molality of the solution.
20. Find the equivalent weights of calcium chloride and nitric acid.
21. 8 grams of  $NaOH$  are present in 108 gram of its solution. Find molality of the solution.
22. Define normality. Mention its unit.
23. What do you mean by decimolar solution?
24. How many gms of  $Na_2CO_3$  are required to prepare one litre of its decimolar solution?
25. Obtain a relationship between molarity and normality.
26. Convert 0.01 M  $H_2SO_4$  in to normality.
27. Convert  $10^{-2}$  N  $H_2SO_4$  in to molarity.
28. Define  $P^H$  and  $P^{OH}$ .
29. The  $P^H$  of a basic solution is 12. What is its hydroxyl ion concentration in moles/lit?
30. Define ionic product of water. What is its value at  $25^\circ C$ ?
31. What is the importance of  $P^H$  in sugar industry?
32. Write down the importance of  $P^H$  in textile industries.
33. Find the  $P^H$  value of 0.001 M HCl solution.
34. Find the  $P^H$  value of 0.01 M NaOH solution.
35. Find the  $P^H$  value of 0.01 M  $H_2SO_4$  solution.

## 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 are called electrolytes. Example: All acids, all alkalies and all salts.

### **Non-electrolyte:**

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

### **Classification of Electrolytes:**

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

- i. Strong electrolytes
- ii. Weak electrolytes

i. **Strong electrolytes:** These are the electrolytes which undergo almost complete ionization in aqueous solution.

- Example: a) acids like  $\text{HCl}$ ,  $\text{HNO}_3$ ,  $\text{H}_2\text{SO}_4$ , etc.  
b) alkalies like  $\text{NaOH}$ ,  $\text{KOH}$ ,  $\text{Ca(OH)}_2$ ,  $\text{Mg(OH)}_2$ , etc.  
c) salts like  $\text{NaCl}$ ,  $\text{KCl}$ ,  $\text{CaCl}_2$ ,  $\text{MgCl}_2$ , etc.

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

- Example: a) Organic acids like  $\text{CH}_3\text{COOH}$ ,  $\text{HCOOH}$ ,  $(\text{COOH})_2$ , etc.  
b) Inorganic acids like  $\text{H}_2\text{CO}_3$ ,  $\text{HCN}$ , etc.  
c) Base like  $\text{NH}_4\text{OH}$

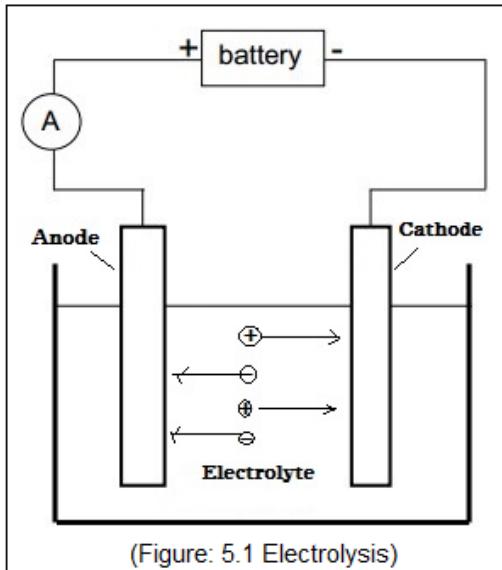
## **ELECTROLYSIS:**

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

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

### **Working Process:**

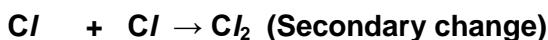
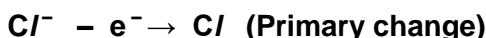
Electrolytes exist in the ionic form in their molten, fused or solution state. When electricity is allowed to pass through the electrolytic solution, the ions migrate towards the oppositely charged electrodes. Cations migrate towards the cathode while anions migrate towards the anode. While reaching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



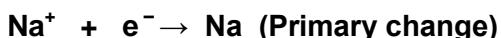
### **Example 1: Electrolysis of molten NaCl.**

Molten NaCl exists in the ionic form  $\text{Na}^+$  and  $\text{Cl}^-$ . During the process of electrolysis,  $\text{Na}^+$  ions migrate towards the cathode while  $\text{Cl}^-$  ions migrate towards the anode. During electrolysis the following changes take place at different electrodes.

#### **At Anode:**



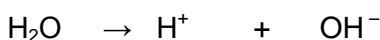
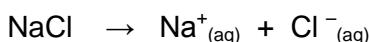
#### **At Cathode:**



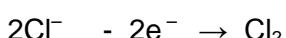
Thus, electrolysis of molten NaCl liberates chlorine gas at the anode while metallic sodium at the cathode.

### **Example 2: Electrolysis of aqueous NaCl solution.**

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



Out of  $\text{Cl}^-$  and  $\text{OH}^-$  ions, the former has lower discharge potential and hence preferably gets discharged at the anode.



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



Thus electrolysis of aqueous NaCl solution liberates chlorine gas at the anode and hydrogen gas at the cathode.

### **Faraday's 1<sup>st</sup> Law of Electrolysis:**

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

Mathematically,

$$W \propto Q$$

$$\text{But, } Q = I \times T$$

$$\Rightarrow W \propto I \times T$$

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

Where, W = Amount of substance in gram

Q = Quantity of electricity or Charge in coulomb

I = Current in ampere

t = time of flow of current in second.

Z = Electrochemical equivalent (ECE)

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

$$W = Z$$

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

A bigger unit of charge is Faraday.

1 Faraday = 96500 coulomb

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

96500 Coulomb of charge deposits 1 gram equivalent

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

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

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  $\text{AgNO}_3$  for 1 hour?

**Solution:**

Given Data:  $I = 10 \text{ Ampere}$

$t = 1 \text{ hr} = 3600 \text{ Sec.}$

$$Z = \frac{1 \text{ gram equivalent}}{96500 C} = \frac{\text{Atomic mass / Valency}}{96500} = \frac{108/1}{96500} = \frac{108}{96500} = 0.0011$$

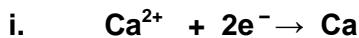
Applying Faraday's 1<sup>st</sup> Law of electrolysis

$$W = ZIt = 0.0011 \times 10 \times 3600 = 39.6 \text{ gram.}$$

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

- One mole  $\text{Ca}^{2+}$  into  $\text{Ca}$ .
- Two moles of  $\text{Al}^{3+}$  into  $\text{Al}$ .

**Solution:**



1 mole of electrons carries 96500 coulombs.

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



1 mole of electrons carries 96500 coulombs.

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

**Question 3:** How many coulombs of charge are required to get 10 grams of calcium from molten  $\text{CaCl}_2$ ?

**Solution:**

$$W = 10 \text{ gm, } Q = ?$$

$$W = ZQ$$

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

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

### Assignment

- Find the ECE of Ca and Al.
- How many coulombs of charges are required to reduce 10 gm of calcium ions into calcium?
- How many coulombs of charge are required to get 3.6 grams of aluminium from molten alumina?
- How many grams of copper will be deposited at the cathode by the passage of 20 ampere of current through an aqueous solution of  $\text{CuSO}_4$  for half an hour?

## **Faraday's 2<sup>nd</sup> Law of Electrolysis:**

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

Mathematically,

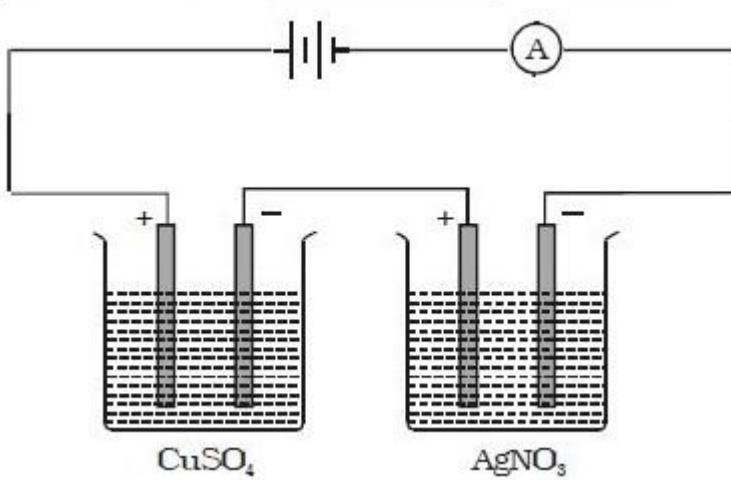
$$W \propto E$$

Let us consider two electrolytic solutions  $\text{AgNO}_3$  and  $\text{CuSO}_4$  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 2<sup>nd</sup> law of electrolysis,

$$W_{\text{Ag}} \propto E_{\text{Ag}} \quad \dots \dots \dots (1)$$

$$W_{\text{Cu}} \propto E_{\text{Cu}} \quad \dots \dots \dots (2)$$



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

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

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

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

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

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

Equivalent weight of hydrogen  $E_{H_2} = 1.008$

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

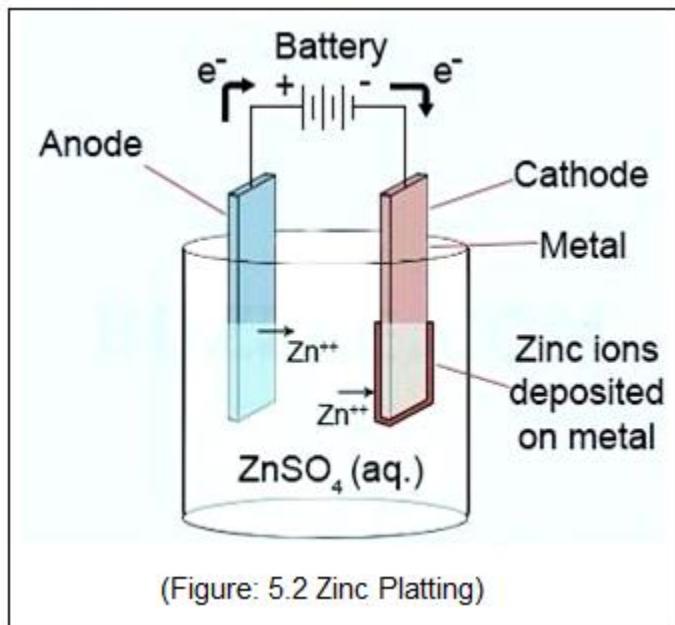
Applying Faraday's 2<sup>nd</sup> law of electrolysis,

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

## **Industrial Application of Electrolysis:**

- 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 Plating:** Normally iron gets rusted when exposed to moist air. Rusting of iron can be prevented by applying a coating of zinc or chromium over it. The process of applying a coating of zinc over iron with a view to protect it from rusting is called **Galvanization**.



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

## **Exercise**

### **(02 Marks Questions)**

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

### **(05 Marks Questions)**

1. Define electrolyte and electrolysis. What are strong and weak electrolytes? Give examples.
2. Define electrolysis. Explain the process of electrolysis of molten NaCl.
3. Define Faraday's 1<sup>st</sup> law of electrolysis. How many grams of calcium will be deposited at the cathode by passing 15 ampere of currents through molten  $\text{CaCl}_2$  for 30 minutes?
4. Define electrochemical equivalent. Find the ECE of Ca and Al.
5. Define and explain Faraday's 2<sup>nd</sup> law of electrolysis.
6. Explain the process of applying a coating of zinc over an iron article by the process of electrolysis.
7. Explain the electro refining process of a crude copper bar.
8. Define and explain electrometallurgy.
9. Explain the electrolysis of acidulated water.
10. Define and explain Galvanisation.
11. Define Faraday's 1<sup>st</sup> law of electrolysis. How many coulombs of charges are required to get 36 grams of magnesium from molten magnesium chloride?

## 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

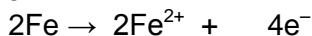
i. **Atmospheric corrosion:** The process of development of undesirable substances usually oxide over the surface of a metal when exposed to atmosphere is called *atmospheric corrosion*. Example: (a) rusting of iron, (b) tarnishing of silver, (c) developing of green coating over copper and bronze.

### 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  $\text{CO}_2$ ,  $\text{SO}_2$ , etc. The following changes take place on the surface of iron during the process of corrosion (Fig. 6.1).

### At Anode:

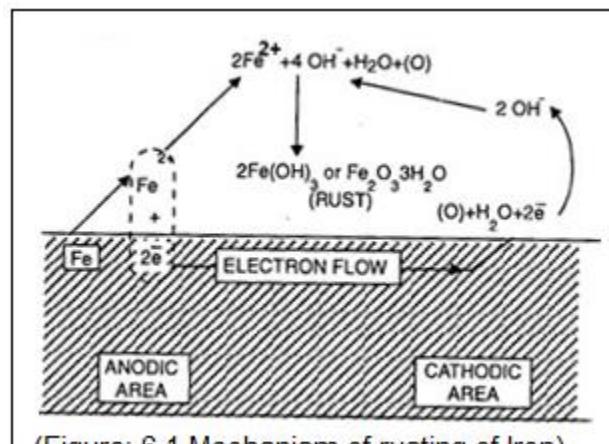
At anode iron gets oxidized into ferrous ion.



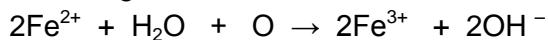
The electrons thus formed migrate towards the cathodic part of the piece of iron.

### At Cathode:

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



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

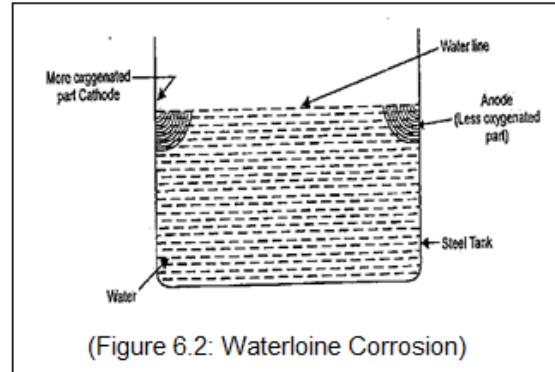


Note:

- ☞ Rust is nothing but hydrated ferric oxide ( $\text{Fe}_2\text{O}_3 \cdot n\text{H}_2\text{O}$ )
- ☞ Presence of  $\text{CO}_2$  in water or trace of Cu or Zn in iron accelerates the process of corrosion. Also, corrosion process is accelerated in saline water.
- ☞ Presence of alkalis in water or Cr, Ni in iron slows down the process of corrosion.

**ii. Water line Corrosion:** This type of corrosion occurs due to differential oxygen concentration above and below the level of water. When water is stored in a steel tank, it is noticed that corrosion occurs along the line just below the level of water (Fig. 6.2).

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



(Figure 6.2: Waterline Corrosion)

#### **Protection of Corrosion:**

**1. Alloying:** Corrosion can be prevented by alloying a metal. Alloying prevent corrosion in two ways.

i. **Homogeneity:** Alloying increases the homogeneity of the metal for which the rate of corrosion is reduced. Rusting of iron can be prevented by alloying it with chromium. It is important to note that only uniform alloy can prevent corrosion to a maximum extent.

ii. **Oxide film:** In some cases, the oxide film formed at the surface of the metal prevents corrosion. Duriron is a silica-iron alloy. It is resistant to acids as a layer of silicon oxide is formed at the surface of iron.

**2. 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 **Galvanization**.

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

## **Exercise**

### **(02 Marks Questions)**

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

### **(05 Marks Questions)**

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

## **CHAPTER – 7** **METALLURGY**

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

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

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

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

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

### Difference between Minerals and Ores

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

### SOME IMPORTANT METALS AND THEIR MINERALS:

<b>Metals</b>	<b>Minerals</b>	<b>Formula</b>
Na	Rock Salt Borax	NaCl Na <sub>2</sub> B <sub>4</sub> O <sub>7</sub>
K	Carnallite Niter	KCl.MgCl <sub>2</sub> .6H <sub>2</sub> O KNO <sub>3</sub>
Mg	Magnesite Dolomite Epsom salt Carnallite	MgCO <sub>3</sub> MgCO <sub>3</sub> .CaCO <sub>3</sub> MgSO <sub>4</sub> .7H <sub>2</sub> O KCl.MgCl <sub>2</sub> .6H <sub>2</sub> O
Ca	Limestone Dolomite Gypsum	CaCO <sub>3</sub> MgCO <sub>3</sub> .CaCO <sub>3</sub> CaSO <sub>4</sub> .2H <sub>2</sub> O
Cu	Copper pyrite Copper glance Cuprite	CuFeS <sub>2</sub> Cu <sub>2</sub> S Cu <sub>2</sub> O
Ag	Silver glance Horn silver	Ag <sub>2</sub> S AgCl
Zn	Zinc blend Zincite Calamine	ZnS ZnO ZnCO <sub>3</sub>

Hg	Cinnabar	HgS
Al	Bauxite Cryolite	$\text{Al}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$ $\text{Na}_3\text{AlF}_6$
Sn	Tin stone	$\text{SnO}_2$
Pb	Galena	$\text{PbS}$
Cr	Chromite	$\text{FeO} \cdot \text{Cr}_2\text{O}_3$
Fe	Haematite Magnetite Limonite	$\text{Fe}_2\text{O}_3$ $\text{Fe}_3\text{O}_4$ $\text{Fe}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$

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

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

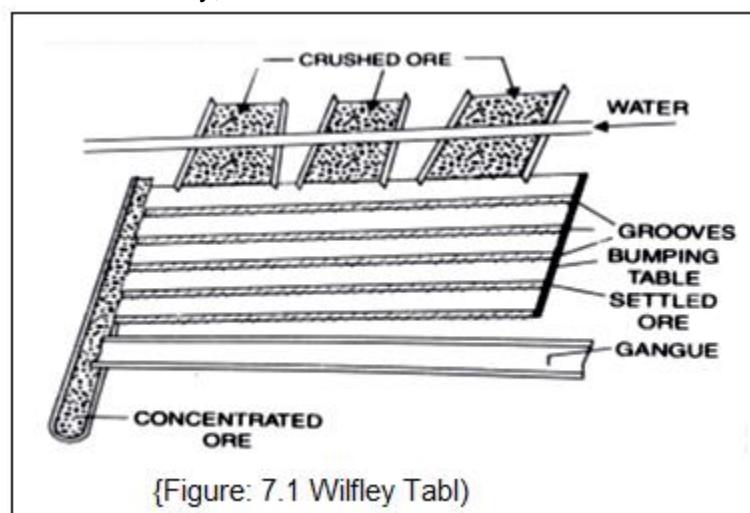
1. Crushing and Grinding.
2. Concentration or Ore dressing.
3. Oxidation.
4. Reduction.
5. Refining.

**1. CRUSHING AND GRINDING:** - The ores obtained from mines are in the form of solid rocks. These are first crushed into small pieces with the help of jaw crusher and then grinded into their powder form with the help of stamp mill or ball mill. The powdered form of ore is called pulverized ore.

**2. CONCENTRATION OR ORE DRESSING:** - The process of removal of maximum impurities (gangue or matrix) from the powdered ore is called ore concentration. The method of concentration to be followed depends upon the nature of the impurities present. Following are the different methods of concentration:

**(i) Gravity Separation Method:** - This method of concentration is adopted only when there is a gravity difference between the ore and impurities. Normally, Carbonate and oxide ores are heavier than the impurities associated with them and hence they are concentrated by this method. In this method the powdered ores are kept in some containers over a specially designed table called Wilfley table (Fig. 7.1).

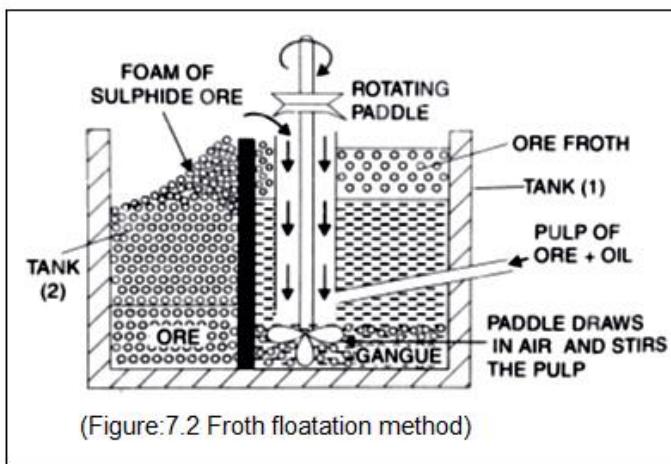
The table contains a number of horizontal grooves. The table is kept slightly inclined in position and is provided with a rocking motion. When water is spread over the ore, lighter impurities are washed away while heavier ore particles get deposited in the grooves, which are finally carried out into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



{Figure: 7.1 Wilfley Tabl}

#### (ii) Froth Flotation Method: -

This method is suitable for the concentration of Sulphide Ores only. In this method, two interconnected tanks are used (Fig. 7.2). In one of the tanks, a mixture of ore, oil (pine oil), water and a little quantity of mineral acid is agitated strongly by blowing air through it.



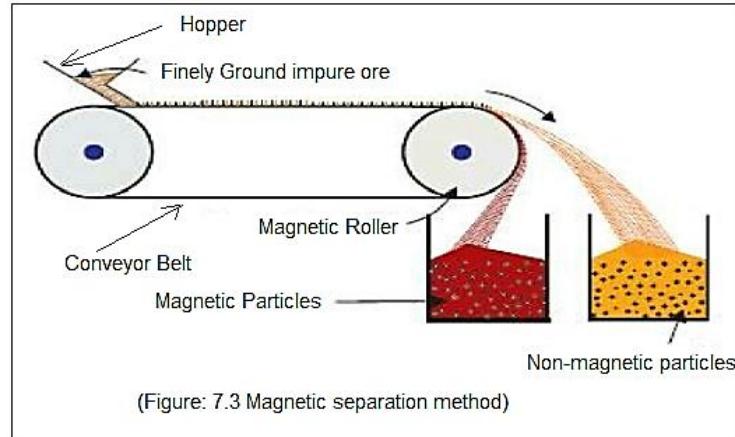
(Figure: 7.2 Froth floatation method)

Due to the preferential wetting of the sulphide ores by oil than by water, a layer of oil gets covered over the surface of sulphide ores. These sulphide ores become lighter and float over the surface of the mixture, which are carried out into the second container along with the foam formed due to agitation.

#### (iii) Magnetic Separation method: -

This method of concentration is suitable only when there is a difference in the magnetic behavior between the ores and the impurities.

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



(Figure: 7.3 Magnetic separation method)

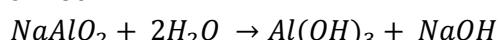
#### (iv) Leaching: -

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

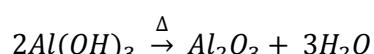
For example: Impure bauxite ore is treated with dil NaOH solution which dissolves Bauxite to form soluble sodium meta-aluminate.



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



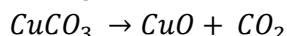
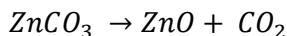
The precipitate obtained is dried and heated strongly to get pure alumina from which aluminium is extracted.



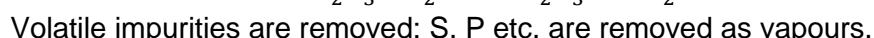
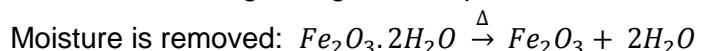
**3. OXIDATION:** - In this step of metallurgical operation, the concentrated ores are converted into their respective metal oxides. This is achieved by the following two methods:

**(i) Calcination:**

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

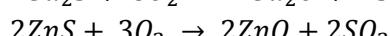
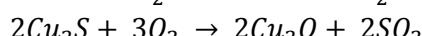
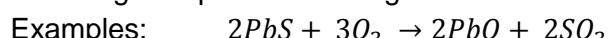


- During calcination following changes takes place:



**(ii) Roasting:**

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

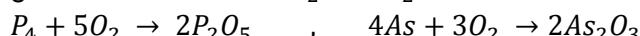


- The changes taking place during roasting are:

Moisture is removed.

Volatile impurities are removed.

Impurities like sulphur, Arsenic, Phosphorous, etc. are removed in the form of their gaseous oxides:  $\text{S} + \text{O}_2 \rightarrow \text{SO}_2$



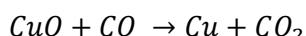
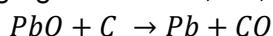
It makes the ore porous.

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

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

**(i) Smelting:** - The process of heating a roasted ore strongly above its melting point with a suitable quantity of coke or charcoal is called smelting. During the process of smelting, metal oxides are reduced into their respective metals. For the reduction of the oxides of less electropositive metals such as Zn, Fe, Cu, Cr etc., the reducing agents like Co, Na, K, H<sub>2</sub>O etc. are used.

Examples:



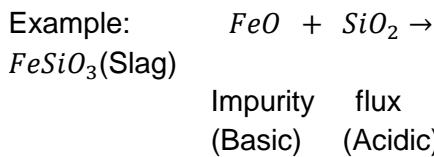
During the process of smelting, an additional chemical substance called 'flux' is added which combines with the solid impurities to form fusible 'slag'.

**Impurity + Flux → Slag**

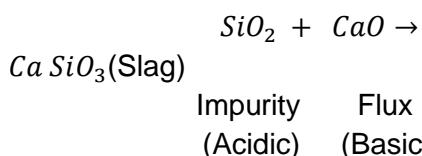
**Flux:** A substance added during the process of smelting to convert the solid gangue into fusible mass (slag) is called flux.

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

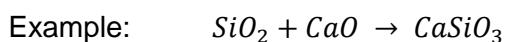
**Acidic Flux:** It is used to remove basic impurities such as metallic oxides.



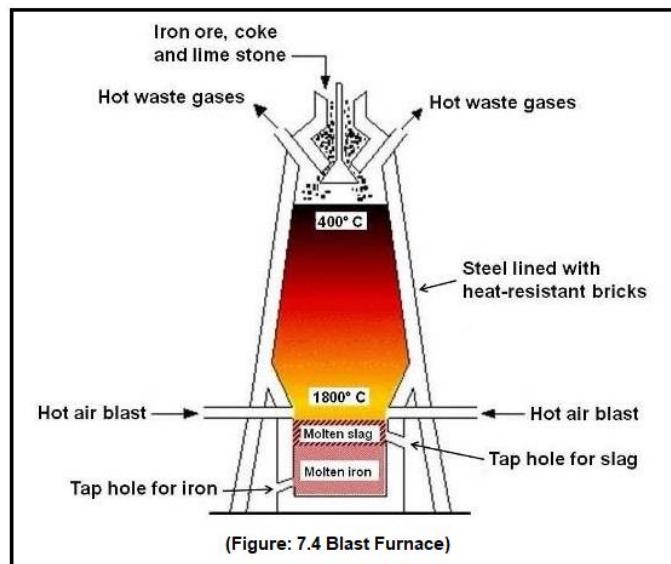
**Basic flux:** It is used to remove acidic impurity such as sand.



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

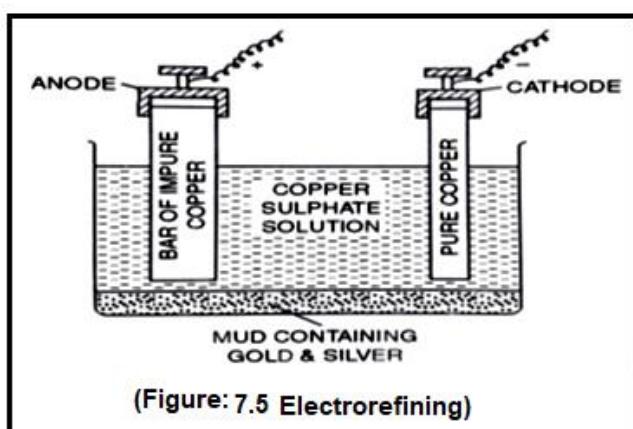


Smelting is carried out in a blast furnace (fig. 7.4) which is a tall cylindrical furnace made of steel plates lined inside with fire bricks. Since the density of slag is lower, it floats over the molten metal. The molten metal is tapped out at the bottom of the furnace.



**5. REFINING:** The metals obtained after reduction still contain some impurities. The process of removal of impurities from crude metal is called refining. The method of refining to be followed depends upon the nature of the metal and the impurity contaminated with it. The following are the methods of refining:

(i) **Distillation Method:** - This method of refining is suitable for volatile metals like Hg, Zn, Pb contaminated with non-volatile impurities. The impure metal is heated in a distillation flask attached with a water condenser. During heating the volatile metal gets evaporated and condensed which is collected in a separate container while the non-volatile impurities are left at the bottom of the distillation flask.



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

## **ASSIGNMENT**

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

## **Exercise**

### **(02 Marks Questions)**

1. What do you mean by gangue?
2. Mention the basic steps involved in the metallurgical operation.
3. What do you mean by concentration of ore?
4. What happens during oxidation step of metallurgical operation?
5. What happens during reduction step of metallurgical operation?
6. Why only sulphide ores are concentrated by froth floatation method?
7. Which types of ores are concentrated by magnetic separation?
8. Which types of ores are concentrated by gravity separation method?
9. What is leaching?
10. What is the purpose of adding charcoal or coke during smelting?
11. What do you mean by smelting?
12. Define calcinations and roasting.
13. What is slag?
14. What is the principle of distillation method of refining of crude metals?
15. What is electrometallurgy?
16. What is the purpose of addition of flux during smelting?

### **(05 Marks questions)**

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

## CHAPTER – 8

### ALLOYS

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

Types of alloys:

1. **Ferro Alloys:** The alloy containing iron as the main constituent is called a ferro alloy.

Example: Stainless Steel, Manganese Steel etc.

2. **Non-Ferro Alloy:** The alloy which does not contain iron as the main constituent is called as non-ferro alloy.

Example: Brass, Bronze, Gun metal etc.

3. **Amalgam:** Alloys containing mercury as one of the constituents is called amalgam.

Example: Silver Amalgam, Sodium amalgam, Copper amalgam is used for filling dental cavities; Tin amalgam is used for silvering cheap mirrors.

#### COMPOSITION AND USES OF BRASS, BRONZE, ALNICO AND DURALUMIN

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

#### ASSIGNMENT

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

## **Exercise**

### **(02 Marks Questions)**

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

### **(05 Marks Questions)**

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

## **CHAPTER – 9** **HYDROCARBONS**

### **Introduction:**

The branch of chemistry which deals with the study of covalently bonded compounds of carbon except, oxides of carbon ( $\text{CO}$ ,  $\text{CO}_2$ ), carbonates, bicarbonates, nitriles, and carbides ( $\text{Na}_2\text{CO}_3$ ,  $\text{NaHCO}_3$ ,  $\text{NaCN}$ ,  $\text{KCN}$ ,  $\text{CaC}_2$ , etc.) of certain metals is called organic chemistry.

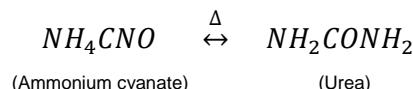
Lemery classified all the substances in to three categories.

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

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

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

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

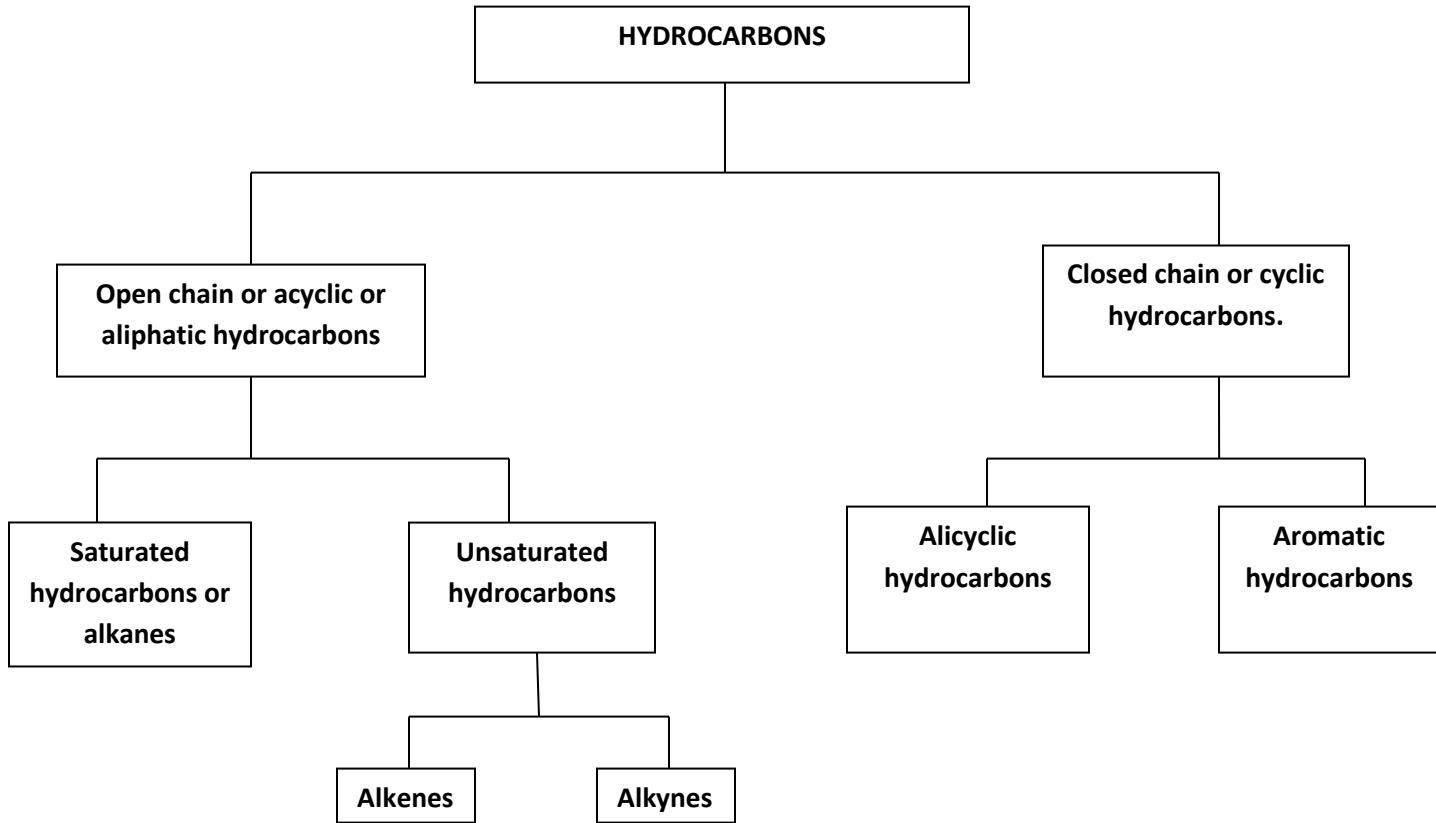


Later, Berthelot synthesized methane ( $\text{CH}_4$ ) starting from the carbon and hydrogen. Again, Lavoisier synthesized acetic acid ( $\text{CH}_3\text{COOH}$ ) starting from the constituent elements C, H & O. soon after these syntheses, the whole idea about organic chemistry has changed and the 'vital force theory' got a strong blow.

### **Hydrocarbons:**

The compounds containing carbon and hydrogen are called hydrocarbons. For example:  $\text{CH}_4$ ,  $\text{C}_2\text{H}_6$ ,  $\text{C}_2\text{H}_4$ ,  $\text{C}_2\text{H}_2$ ,  $\text{C}_6\text{H}_6$ , etc.

## Classification of hydrocarbons: -



**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 ≡ C).

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

## IUPAC SYSTEM OF NOMENCLATURE: -

IUPAC stands for “International Union of Pure and Applied Chemistry”. According to this system an organic compound may contain the following four parts.

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

**1. ROOT WORD:** It refers to the number of carbon atoms present in the parent chain of an organic compound.

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

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

Group	Prefix
-F	Fluoro
-Cl	Chloro
-Br	Bromo
-I	Iodo
-NO <sub>2</sub>	Nitro
-R	Alkyl
-OR	Alkoxy

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

Nature of Bond	Primary Suffix
All C—C bond	-ane
One C=C	-ene
Two C=C bond	-a-----diene
Three C=C bond	-a-----triene
One C≡C bond	-yne
Two C≡C bond	-a-----diyne

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

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

### CLASS OF COMPOUNDS:

- (i) Alkanes
- (ii) Alkenes
- (iii) Alkynes
- (iv) Alkyl halides
- (v) Alcohol

**1. Alkanes:** These are the saturated hydrocarbons in which the carbon atoms are linked by single bonds (C—C). These are also called Paraffins.

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

**Primary Suffix:** ane

n (No. of carbon atoms)	Molecular Formula	Structural formula	Common name	IUPAC name
1	$CH_4$	<pre>       H         H - C - H               H     </pre>	Methane	Methane
2	$C_2H_6$	<pre>       H   H             H - C - C - H                   H   H     </pre>	Ethane	Ethane
3	$C_3H_8$	<pre>       H   H   H                 H - C - C - C - H                       H   H   H     </pre>	Propane	Propane

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

**General Formula:**  $C_nH_{2n}$  where 'n' is the no. of carbon atoms.

**Primary Suffix:** ene

n (No. of carbon atoms)	Molecular Formula	Structural formula	Common name	IUPAC name
2	$C_2H_4$	<pre>       H - C = C - H                   H   H     </pre>	Ethylene	Ethene
3	$C_3H_6$	<pre>       H         H - C = C - C - H                   H   H     </pre>	Propylene	Propene

3. **Alkynes:** These are the unsaturated hydrocarbons which have a carbon-carbon triple bond ( $C\equiv C$ ) in their molecules. These are also called Acetylenes.

**General Formula:**  $C_nH_{2n-2}$  where 'n' is the no. of carbon atoms.

**Primary Suffix:** yne

n (No. of carbon atoms)	Molecular Formula	Structural formula	Common name	IUPAC name
2	$C_2H_2$	$H - C \equiv C - H$	Acetylene	Ethyne
3	$C_3H_4$	<pre>       H         H - C \equiv C - C - H               H     </pre>	Methyl acetylene	Propyne

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

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

n (No. of carbon atoms)	Molecular Formula	Structural formula	Common name	IUPAC name
1	$CH_3-Cl$	<pre>       H               H - C - Cl               H     </pre>	Methyl Chloride	Chloromethane
2	$C_2H_5-Br$	<pre>       H   H                   H - C - C - Br                   H   H     </pre>	Ethyl Bromide	Bromoethane

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

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

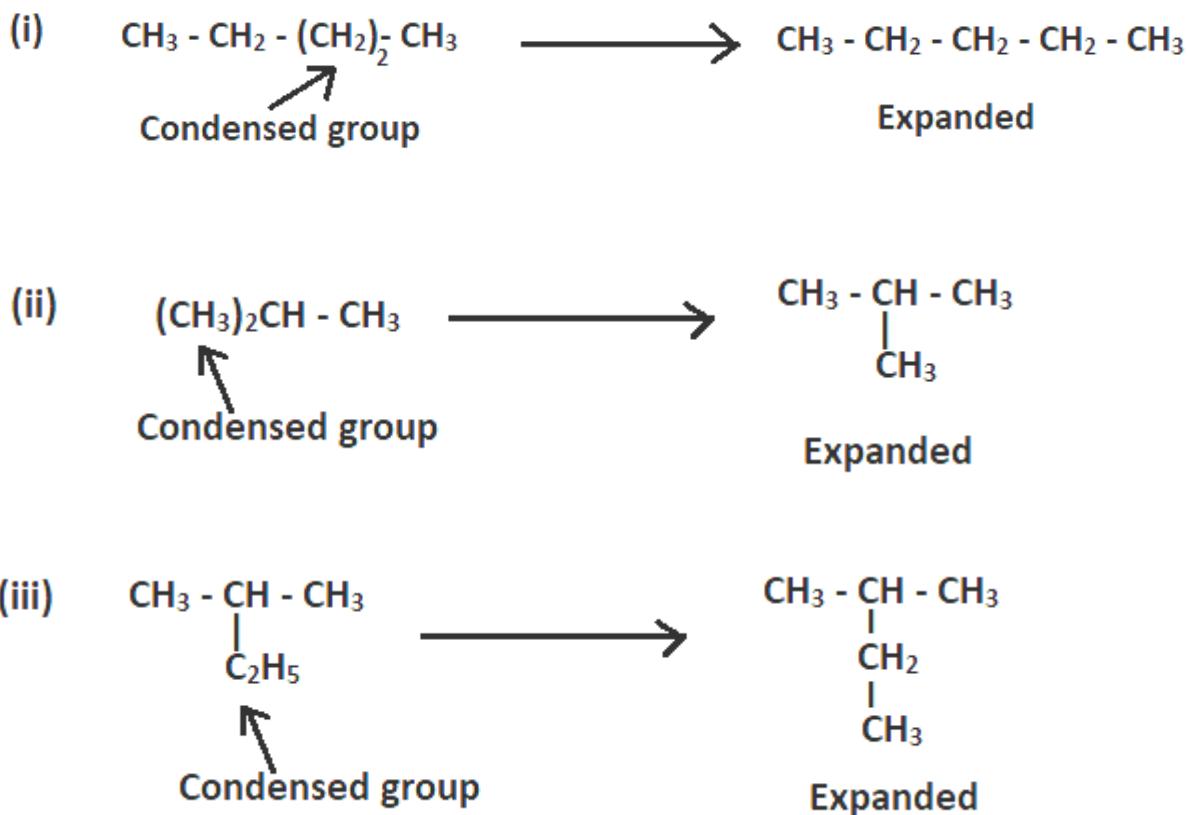
**Suffix:** ol

n (No. of carbon atoms)	Molecular Formula	Structural formula	Common name	IUPAC name
1	$CH_3-OH$	<pre>       H               H - C - OH               H     </pre>	Methyl alcohol	Methanol
2	$C_2H_5-OH$	<pre>       H   H                   H - C - C - OH                   H   H     </pre>	Ethyl alcohol	Ethanol

## **RULES FOR IUPAC SYSTEM OF NOMENCLATURE:**

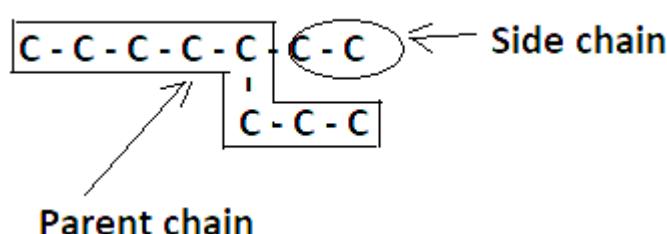
1. **Expansion of chain:** Sometimes condensed groups are present in organic compounds. These condensed groups are to be separated.

Examples:



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

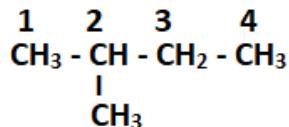
Example:



**3. Numbering of Carbon atoms: (Lowest number rule or lowest sum rule).**

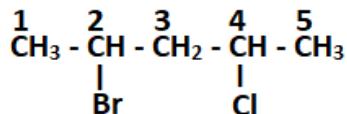
- a. **Presence of one substituent or one side chain:** The numbering of carbon atoms in the continuous carbon chain is done from one end to the other end, so that the carbon atom carrying the substituent get the lowest number.

Examples:



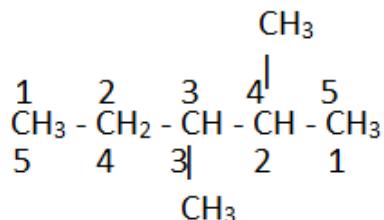
- b. **Presence of 2 Substituents at the same position from either end:** In this case minimum number is given to the carbon containing the substituent which comes first in alphabetical order.

Example:



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

Example:



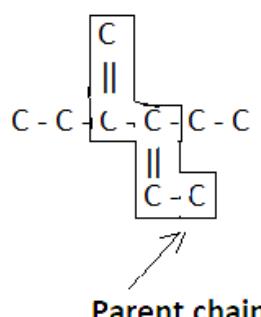
$$\text{L} \rightarrow \text{R}: \text{Sum} = 3 + 4 = 7 \times$$

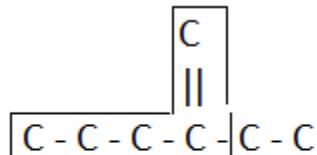
$$\text{R} \rightarrow \text{L}: \text{Sum} = 2 + 3 = 5 \checkmark$$

**4. Presence of Multiple bonds (double and triple bonds):**

- (i) Select the longest continuous carbon chain as the principal chain which contains the maximum number of multiple bonds.

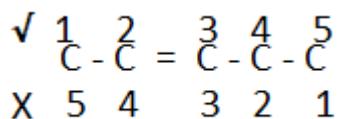
Example:



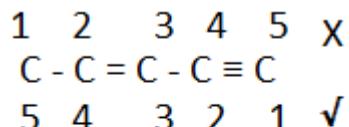


**Parent chain**

- (ii) If a compound contains a multiple bond, then minimum number is given to the carbon containing the multiple bonds, irrespective of the position of the substituent or the side chain.  
Example:

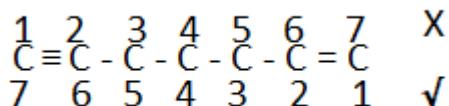


- (iii) If the principal chain (parent chain) contains 2 or more multiple bonds, then number the principal chain from one end so that the multiple bonds get the lowest set of numbers.  
Example:



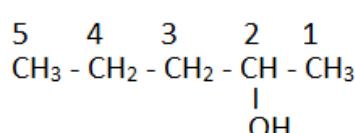
$$\begin{aligned} L \rightarrow R: \text{Sum} &= 2 + 4 = 6 \\ R \rightarrow L: \text{Sum} &= 1 + 3 = 4 \end{aligned}$$

- (iv) If the numbering of principal chain from both the ends gives the same set of numbers to multiple bonds, then select the set which gives lower number to the double bond.  
Example:



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

Example:

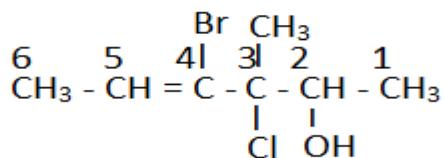


- 6. Arrangement of Prefixes:** In an organic compound the WR, Prefix, PS and SS are arranged in the following way.

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

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

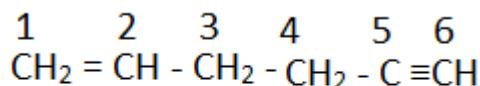
Example:



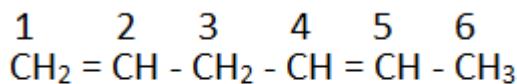
IUPAC Name: 4-Bromo-3-chloro-3-methylhex-4-en-2-ol

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

Examples:



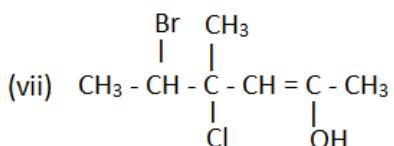
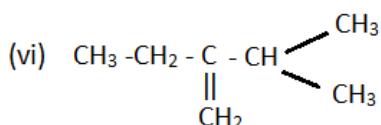
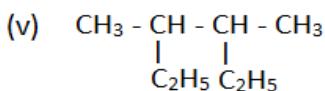
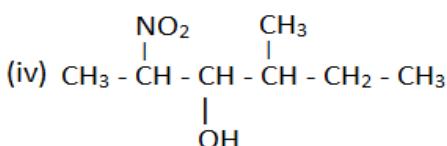
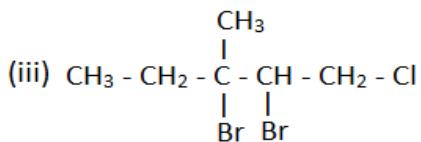
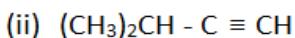
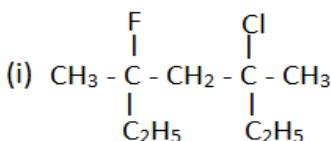
Hex-1-en-5-yne



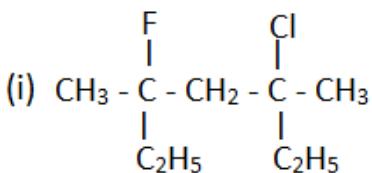
Hexa-1,4-diene

**EXAMPLES:**

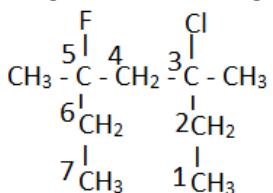
Write the I.U.P.A.C names of the following organic compounds:



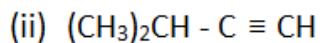
Solution:



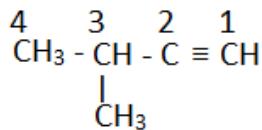
On expanding the condensed groups, we have



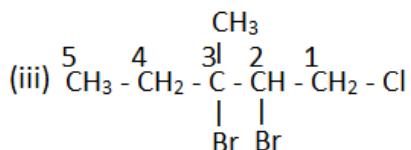
3-Chloro-5-fluoro-3,5-dimethylheptane



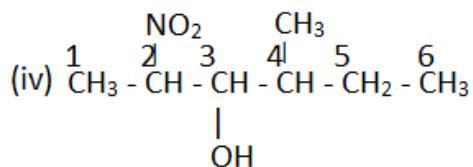
On expanding the condensed groups, we have



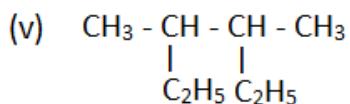
3-Methylbut-1-yne



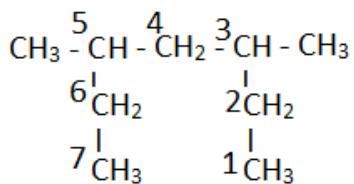
1-Chloro-2,3-dibromo-3-methylpentane



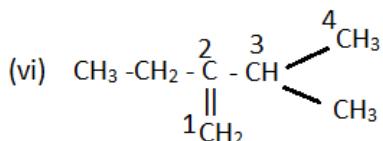
4-Methyl-2-nitrohexan-3-ol



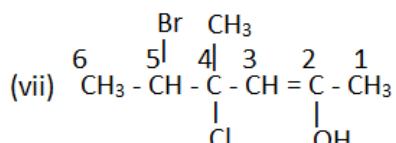
On expanding the condensed groups, we have



3,5-Dimethylheptane



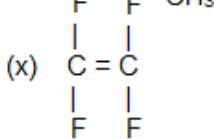
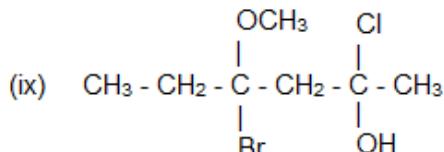
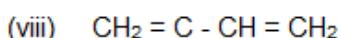
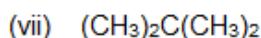
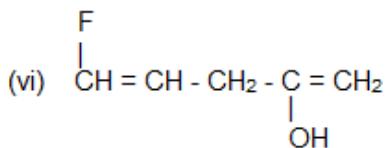
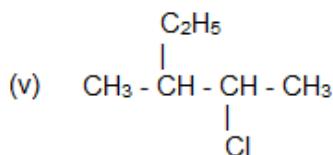
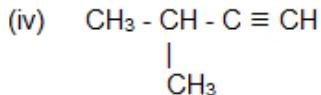
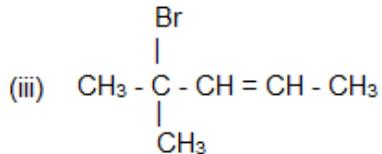
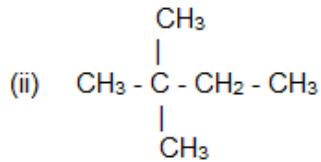
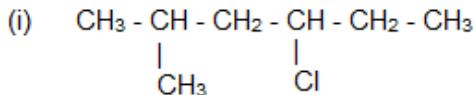
2-Ethyl-3-methylbut-1-ene



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

### **ASSIGNMENT:**

Write the IUPAC names of the following:



### **WRITING STRUCTURAL FORMULA FROM IUPAC NAMES:**

Steps to be followed:

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

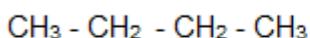
### **TYPES OF CARBON ATOMS IN ALKANES:**

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

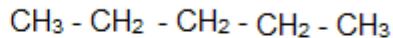
## **RULES FOR WRITING THE COMMON NAMES OF SOME SIMPLE ALKANES:**

The simple branched chain alkanes can be assigned common names. According to common system of nomenclature, all the isomeric alkanes (having same molecular formula but different structural formula) have the same parent name but are distinguished by prefixes. The prefix indicates the type of branching in the molecule.

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

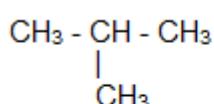


n - butane

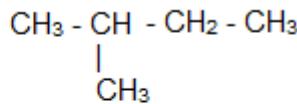


n - pentane

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



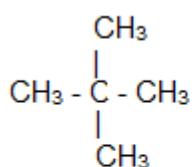
iso-butane



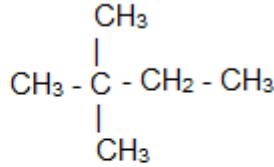
iso-pentane

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

Examples:



neo-pentane

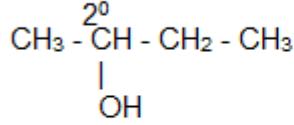


neo-hexane

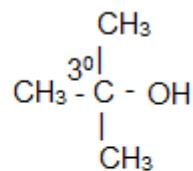
(If the branching occurs at any other position then these prefixes are not used.)

- (iv) The prefixes **sec** and **tert** before the name of the alkyl group indicates the removal of H-atom from  $2^\circ$  and  $3^\circ$  carbon atoms respectively.

Examples:



Sec-butyl alcohol



Tert-butyl alcohol

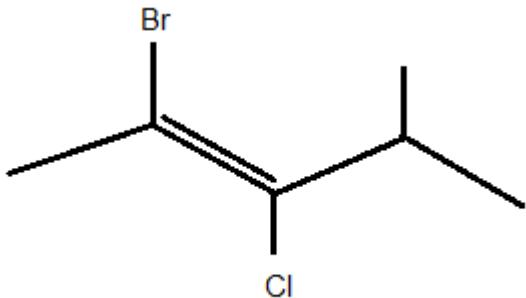
### **ASSIGNMENT:**

Write the structural formulae of the following organic compounds:

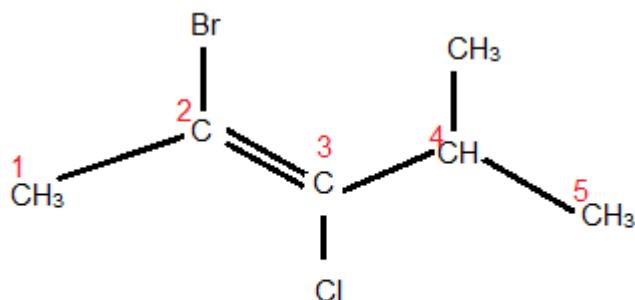
- (i) Tert-butyl alcohol
- (ii) But-1-en-3-yne
- (iii) 3,4-dimethyl pentan-2-ol
- (iv) 1,1,2,2-tetrafloro ethene
- (v) 2,3-dibromo-1,4-dichloro but-2-ene
- (vi) Iso-hexane
- (vii) n-propyl iodide
- (viii) n-butyl bromide
- (ix) iso-pentyl alcohol
- (x) 4,5-dimethoxy hex-2-ene
- (xi) Propylene
- (xii)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

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

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



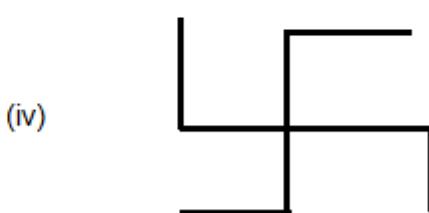
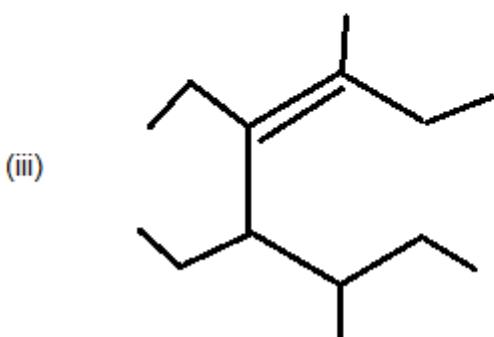
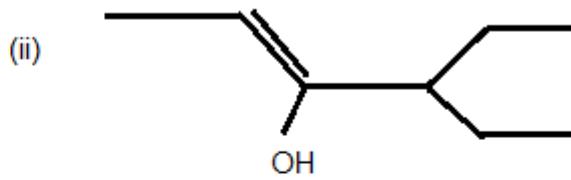
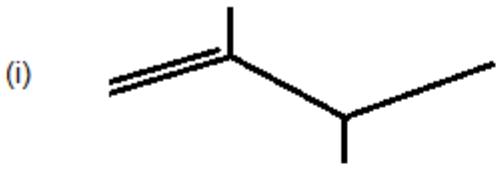
Substituting the carbon hydrogen atoms, we have,



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

### ASSIGNMENT:

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

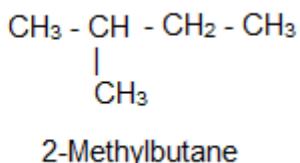
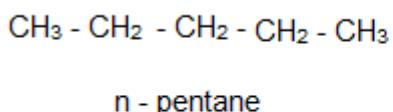


### DISTINCTION BETWEEN SATURATED AND UNSATURATED HYDROCARBONS:

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

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

Example:



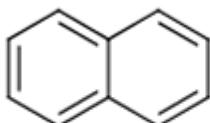
**Aromatic hydrocarbons:** These are the closed chain or cyclic hydrocarbons. They obey Huckel's rule of aromaticity.

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

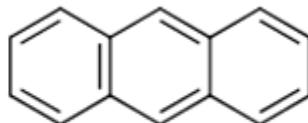
For example:



benzene



naphthalene



anthracene

### **DISTINCTION BETWEEN ALIPHATIC & AROMATIC HYDROCARBONS.**

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

### **USE OF SOME IMPORTANT AROMATIC COMPOUNDS:**

**1. Benzene:** It is used:

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

**2. Toluene:** It is used:

- (a) as a solvent for paint, paint thinner, printer ink etc.
- (b) used in the synthesis of Trinitrotoluene (TNT) explosives.
- (c) in making elastic.
- (d) as a radiator fluid.
- (e) in breaking of RBC in order to extract the hemoglobin in biochemistry experiments.

**3. BHC (Benzene Hexachloride):** Also called gammoxene. It is used:

- (a) as an important insecticide.
- (b) as medication to remove head lice.

**4. Phenol:** It is used:

- (a) as disinfectant in household cleaners and in mouthwash when used in small quantity.

- (b) as surgical antiseptic.
  - (c) in the manufacturing of cough syrups and other antiseptics.
  - (d) as a starting material to make plastics and drugs such as aspirin.
  - (e) in the study and extraction of biomolecules.
- 5. Naphthalene:** It is used:
- (a) in the form of mothballs and toilet deodorant blocks.
  - (b) in making dyes, resins, insecticides.
  - (c) in manufacturing of PVC (polyvinyl chloride).
- 6. Anthracene:** It is used:
- (a) in wood preservatives, insecticides.
  - (b) as a scintillator for detectors of high energy photons, electrons and alpha particles.
- 7. Benzoic acid:** It is used:
- (a) as a food preservative.
  - (b) in mouthwash, toothpaste, facial cleanser.
  - (c) in making dyes and insect repellents.
  - (d) a constituent of Whitfield's ointment which is used for the treatment of fungal skin disease.

### **ASSIGNMENT:**

1. Define Saturated and Unsaturated hydrocarbons with examples.
2. Differentiate between Aromatic and Aliphatic hydrocarbons.
3. State Huckel's rule.
4. To which class the organic compound  $C_8 H_{16}$  belong and how?
5.  $C_4H_8$  belongs to which homologous series?
6. Distinguish between Saturated and Unsaturated hydrocarbons.

## **Exercise**

### **(02 Marks Questions)**

1. To which class of compound  $C_4H_{10}$  belongs and how?
2. To which class of compound  $C_5H_{10}$  belongs and how?
3. To which class of compound  $C_6H_{10}$  belongs and how?
4. What are saturated hydrocarbons?
5. What are unsaturated hydrocarbons?
6. How  $C_4H_8$  is unsaturated?
7. What are aliphatic hydrocarbons? Give any two examples of it.
8. What is the IUPAC name of isopropyl alcohol?
9. What is the IUPAC name of tertiary butyl alcohol?
10. What is the IUPAC name of isobutyl chloride?
11. Give the structural formula of 4-Chloro-5-methylpent-2-en-2-ol.
12. Define Huckel's rule for aromativity.
13. How benzene is aromatic?
14. What is tertiary alkyl halide? Give an example of it.
15. What is the general formula of monohydric alcohols? Five a suitable example of it.

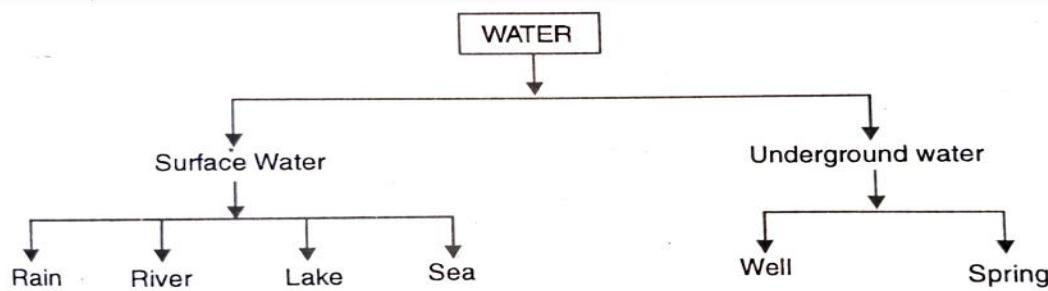
### **(05 Marks Questions)**

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

## CHAPTER – 10 WATER TREATMENT

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

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



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

### 1. Rainwater:

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



### 2. River water:

- A river is a naturally flowing watercourse, usually freshwater, flowing towards a sea lake or another river.
- Rivers are nourished by precipitation, by surface runoff, through springs or from melting of glaciers.
- It contains high percentage of dissolved minerals like  $\text{NaCl}$ ,  $\text{KCl}$ ,  $\text{NaNO}_3$ ,  $\text{CaCO}_3$ ,  $\text{NaHCO}_3$  etc.

### 3. Lake water:

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

### 4. Sea water:

- Sea water is the water from sea or ocean and is the most impure form of natural water.

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

### **B. Underground Water:**

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

Underground water is of two types.

## **1. Spring water:**

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

## **2.Well water:**

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

## **Types of water**

Water is of 02 types:

(1) Soft water & (2) Hard water.

**1. Soft water:** - Water which forms lather with soap solution is called soft water.

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

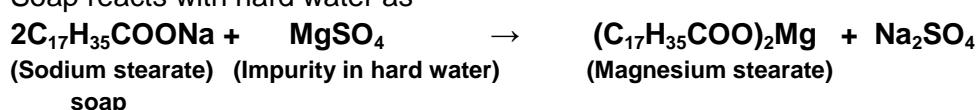
**2. Hard water:** - Water which does not form lather with soap solution is called hard water. Instead, it forms a curdy white precipitate.

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

### **Hardness of water:**

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

Soap reacts with hard water as



## **Types of hardness:**

Hardness of water is of two types:

- A. Temporary or Carbonate hardness
  - B. Permanent or Non-carbonate hardness

- A. Temporary hardness:** The temporary hardness of water arises due to the presence of bicarbonates of Ca and Mg,  $\text{Ca}(\text{HCO}_3)_2$ ,  $\text{Mg}(\text{HCO}_3)_2$ .

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

- B. Permanent hardness:** The permanent hardness of water arises due to the presence of chlorides of Ca, Mg ( $\text{CaCl}_2$ ,  $\text{MgCl}_2$ ). It is named permanent hardness because such a hardness cannot be removed by simply boiling the water.

### **Unit of hardness**

- (1) PPM – Parts per million.

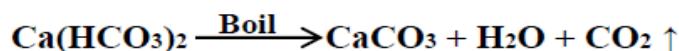
- (2) mg/L – Milligrams per Litre.

### **Softening of water or removal of hardness:**

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

#### **Removal of temporary hardness:**

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



## Hard Water (insoluble)

(soluble)

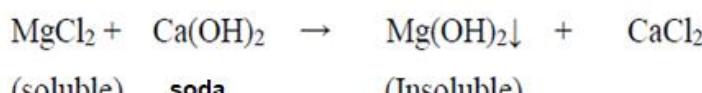
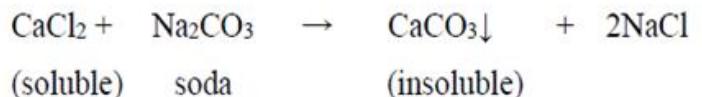


## Hard Water (insoluble)

(Soluble)

#### **Removal of permanent hardness:**

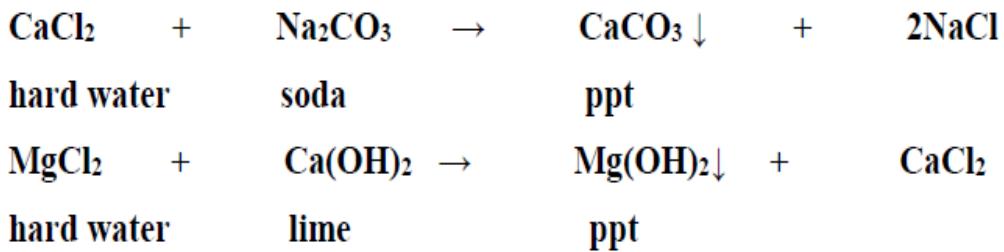
- A. Lime Soda Process:** In this process hard water is treated with a calculated quantity of lime and soda. Lime and soda convert the soluble hardness causing chemicals present in hard water into insoluble substances called sludges. The precipitate or sludge formed is then removed by filtration to get soft water.



(a) Cold Lime soda process (b) Hot lime soda process

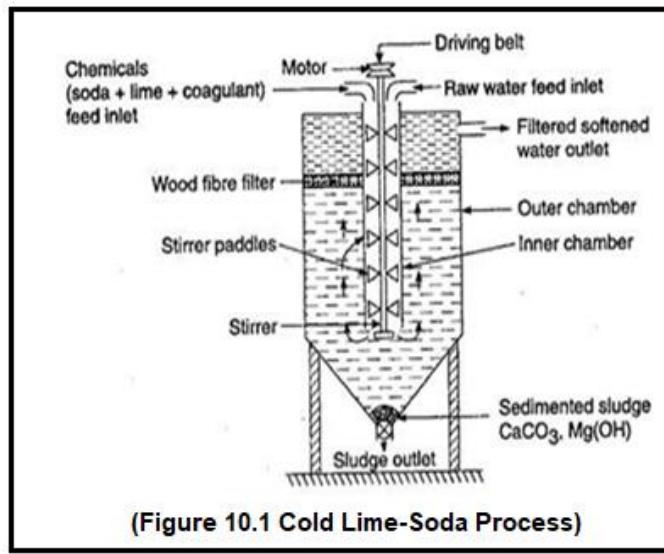
### (a) Cold Lime Soda Process:

**Principle:** When hard water is treated with calculated amount of lime  $[\text{Ca}(\text{OH})_2]$  and soda  $(\text{Na}_2\text{CO}_3)$  at room temperature  $25^\circ\text{C}$ , the soluble Ca and Mg salt present in hard water are chemically converted into ppt. of calcium carbonate  $(\text{CaCO}_3)$  and magnesium hydroxide  $[\text{Mg}(\text{OH})_2]$ . These ppts are removed by filtration. Thus, soft water is obtained.



### Process:

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



(Figure 10.1 Cold Lime-Soda Process)

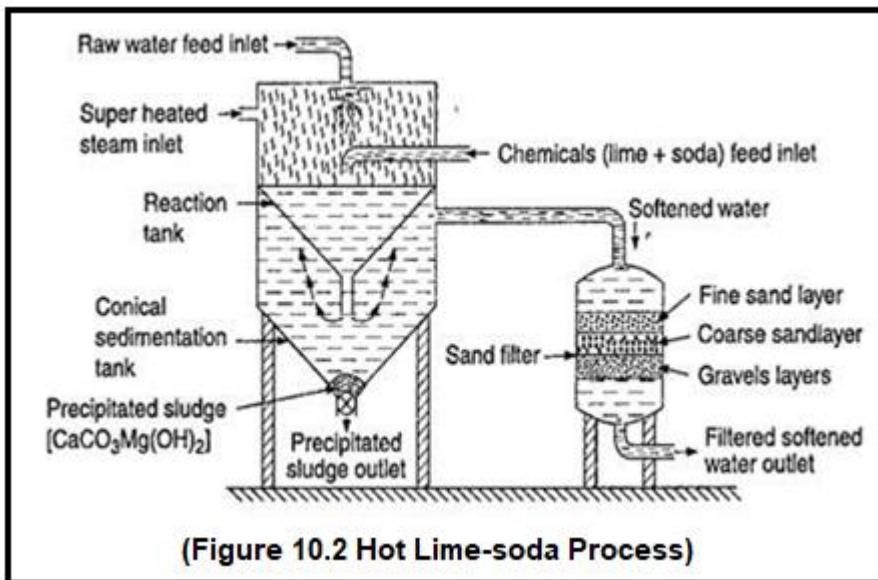
### Dis-advantages:

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

### (b) Hot Lime Soda process:

**Principle:** This process involves treatment of hard water with lime and soda at a temp. of  $80-150^\circ\text{C}$ .

**Process:** In the hot lime soda process, the reactions take place at higher temperature near about boiling point of water. The chemical mixing process is same as the cold lime soda process, but steam is applied in mixture tank. As a result, precipitation becomes almost complete very quickly.



### **Apparatus:**

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

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

### **Advantages:**

- It is much economical.
- The reaction is completed within a short period.
- The reaction proceeds faster. Hence the softening capacity is increased.
- No coagulant is required, as the sludge settles down easily.
- Dissolved gasses like  $\text{CO}_2$ , air etc. are removed.
- Under hot condition viscosity of water is lowered. Thus, filtration becomes easier.
- Pathogenic bacteria are destroyed.
- The residual hardness left in this process is much lower (15-30 ppm) as compared to that in the cold L-S process (50-60 ppm).

### **Dis-advantages:**

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

### Difference between cold lime soda process & hot lime soda process

Cold Lime soda process	Hot lime soda process
1. This process is conducted at room temp. ( $25^{\circ}\text{C}$ )	This process is conducted at $80^{\circ}$ to $150^{\circ}\text{C}$ .
2. It is costlier.	It is much economical.
3. The process takes longer time to complete.	It takes comparatively less time for completion.
4. The reaction is slower.	The reaction proceeds faster. Hence the softening capacity is increased.
5. Coagulant like alum is required.	No coagulant is required, as the sludge settles down easily.
6. Dissolved gases are not escaped.	Dissolved gasses like $\text{CO}_2$ , air etc. are removed.
7. Filtration is comparatively slower.	Under hot condition viscosity of water is lowered. Thus, filtration becomes easier.
8. Pathogenic bacteria are not destroyed.	Pathogenic bacteria if any are destroyed.
9. The residual hardness left is more, i.e., 50 – 60 ppm.	The residual hardness left in this process is much lower (15-30 ppm) as compared to that in the cold L-S process (50-60 ppm).

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

- (i) The precipitation reaction becomes almost complete.
- (ii) The reaction takes place faster.
- (iii) The sludge settles rapidly.
- (iv) No coagulant is needed.
- (v) Dissolved gases are removed.
- (vi) Residual hardness is low as compared to the cold lime-soda process.

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

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

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

These are organic polymers having:

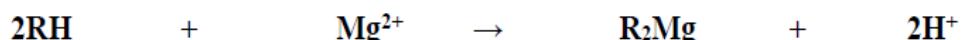
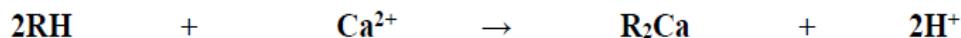
- (i) high molecular weight.
- (ii) Open and permeable molecular structure.
- (iii) acidic (-COOH,  $-\text{SO}_3\text{H}$ ) or basic groups ( $-\text{OH}^-$ ,  $-\text{NH}_2$ ) attached with them.

Ion-exchange resins are of two types:

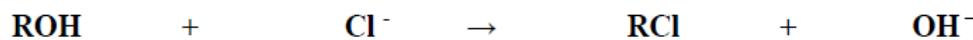
**(a) Cation-exchange resin(R-H<sup>+</sup>):** If the active ion in ion-exchanger is a cation, generally acidic functional groups, the resin is called cation-exchange resin, Ex – (Resin-H<sup>+</sup>)

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

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



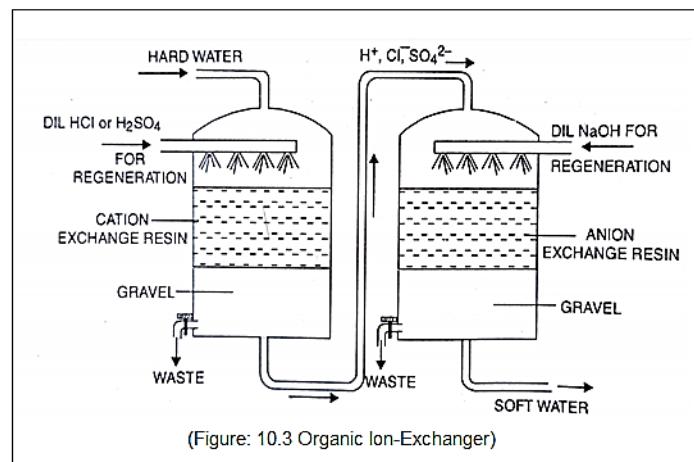
Then the hard water is passed through the column of anion exchange resin. All the anions present in water get exchanged with OH- ions of the resin.



$\text{H}^+$  and  $\text{OH}^-$  ions released from the cation and anion exchange columns respectively get combined to produce water molecules.



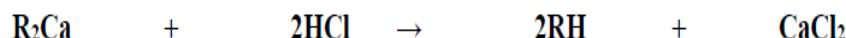
Thus, the water coming out from the exchanger is free from cations as well as anion. Such water is known as deionized or demineralized water.



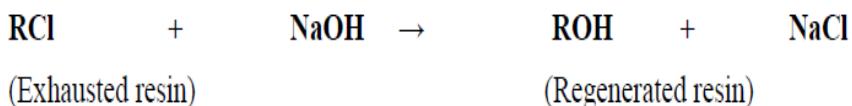
## **Regeneration of resins:**

When all the  $H^+$  and  $OH^-$  ions of the resins are exchanged by the cations and anions present in hard water, then the resins are said to be exhausted and regeneration can be done.

The cation-exchange resin can be regenerated by the treatment with dilute acids like dil. HCl or dil. $H_2SO_4$ .



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



The regenerated resins may be used again.

#### **Advantages of Ion – Exchange Process –**

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

#### **Dis-advantages of Ion – Exchange Process:**

- ☞ The equipment is costly and more expensive chemicals are needed.
- ☞ If water contains turbidity, then output of the process is reduced.

## **Exercise**

### **(02 Marks Questions)**

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

### **(05 Marks Questions)**

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

## CHAPTER – 11

# LUBRICANTS

### Introduction:

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

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

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

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

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

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

### Uses of graphite:

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

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

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

**Uses of liquid lubricants:** Liquid lubricants are used when,

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

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

Example-greases, Vaseline, waxes, etc.

### Uses of Grease:

- ☞ Used where oil cannot remain in place due to high load, low speed, sudden jerks like rail axle.
- ☞ In bearings and gears which work at high temperature.

☞ Where dropping of oil affects the machine or products like production of paper, textile etc.

#### **Purpose of lubrication or Functions of lubricants:**

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

## **Exercise**

### **(02 Marks Questions)**

1. Define lubricant. Give an example of a semi-solid lubricant.
2. Give example of solid lubricants. Write the uses of graphite.
3. What are liquid lubricants?

### **(05 Marks Questions)**

1. What is a lubricant? Write the major functions of lubricants.
2. Define lubricant. Write the classification of lubricants with examples.

## CHAPTER – 12

# FUEL

### Introduction:

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

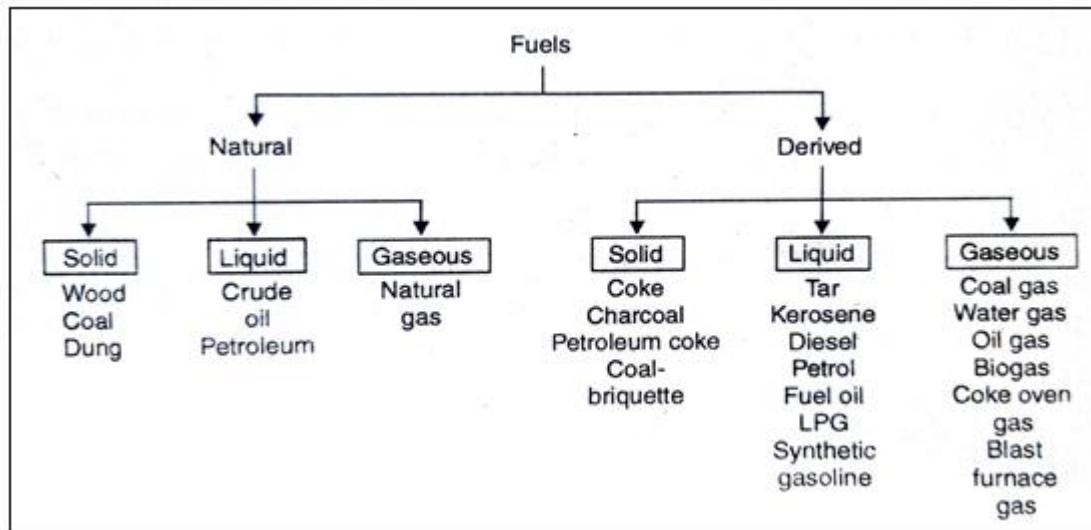
The heat energy released by reactions of fuels is converted into mechanical energy via a heat engine. Other times the heat itself is valued for warmth, cooking, or industrial processes, as well as the illumination that comes with combustion. Fuels are also used in the cells of organisms in a process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

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

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



### Classification of Fuels:



A. On the basis of their occurrence, fuels may be classified into two categories: -

1. **Natural Fuels:** Such fuels are found in nature.

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

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

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

**B.** Based on their physical state, fuels may be classified into three categories:

1. **Solid Fuels:** Fuels which are found in their solid state at room temperature are generally referred to as Solid Fuels.

Ex-Wood, coal, charcoal, straw etc.

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

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

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

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

#### **Calorific value of fuel:**

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

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

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

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

#### **Composition and uses of some liquid fuels:**

##### **Diesel**

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

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

##### **Petrol or Gasoline**

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

**Uses:**

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

**Kerosene**

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

**Uses:**

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

**Composition and uses of some gaseous fuels:****1. Water Gas**

- (i) It is a mixture of combustible gases CO and  $H_2$  with a little quantity of non-combustible gases like  $CO_2$  and  $N_2$ .
- (ii) The average composition of water gas is  $H_2$ = 51 %, CO = 41 %,  $CO_2$  = 4% &  $N_2$  = 4%,
- (iii) Its calorific value is 2800 Kcal /  $m^3$ .

**Uses:** It is used:

- ☞ as a source of  $H_2$  Gas.
- ☞ as a fuel.
- ☞ as an illuminating gas.
- ☞ for welding purposes.

**2. Producer Gas:**

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

**Uses:** It is used:

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

**3. Coal gas:**

- (i) It is a mixture of a number of hydrocarbons along with  $N_2$ ,  $H_2$ , CO &  $CO_2$ .
- (ii) It is a colourless gas and burns with a sooty flame.
- (iii) The average composition of coal gas is  
 $H_2$ =40%,  $CH_4$ =32%, CO=7%,  $C_2H_2$ =2%,  $C_2H_4$ =3%,  $N_2$ =4%,  $CO_2$ =1% & rest=11%
- (iv) Its calorific value is 4900 Kcal / $m^3$ .

**Uses:** It is used:

- ☞ as a fuel.
- ☞ as a reducing agent in metallurgical operations.
- ☞ as an illuminant.

#### **4. LPG (Liquified petroleum gas):**

- (i) It is mainly C<sub>3</sub>, C<sub>4</sub> hydrocarbons of alkane & alkene.
- (ii) It is highly inflammable.
- (iii) It is colourless and odourless but a smelling agent called ethyl mercaptan(C<sub>2</sub>H<sub>5</sub>SH) is added to it to detect the leakage.
- (iv) The average composition of LPG is  
n-butane=27%, iso-butane=25%, butene=43%, propene=2.5% & propane=2.5%.
- (v) Its calorific value is 27,800 Kcal /m<sup>3</sup>.

**Uses:** It is used:

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

#### **5. CNG (Compressed Natural Gas):**

- (i) It is a colourless, odourless gas and burns with a pale blue flame.
- (ii) The average composition of CNG is:  
CH<sub>4</sub>=70-90%, C<sub>2</sub>H<sub>6</sub>=4-9% & traces of propane and butane.
- (iii) Its calorific value is 12500 Kcal /m<sup>3</sup>.

**Uses:** It is used:

- ☞ as a fuel in low emissive vehicles like ULEV (ultra-low emission vehicles).
- ☞ as a domestic and industrial fuel.
- ☞ as a source of carbon in tyre industry.
- ☞ for the production of H<sub>2</sub> gas needed in fertilizer industry.

## **Exercise**

### **(02 Marks Questions)**

1. Define fuel. Write the characteristics of a good fuel in terms of calorific value and moisture.
2. What is calorific value of fuel? Write its unit.
3. What is CNG?
4. Write the composition of coal gas.
5. Write the composition of producer gas.
6. What are derived fuels? Give two examples.

### **(05 Marks Questions)**

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

## CHAPTER – 13

# POLYMERS

### Introduction:

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

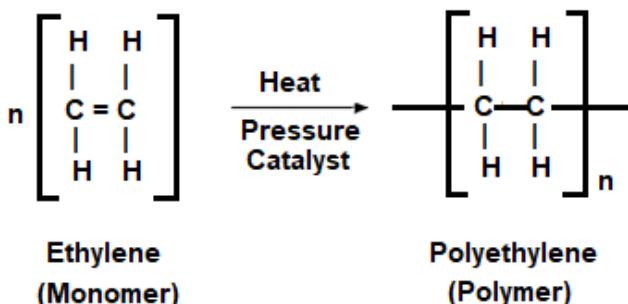
Product made from polymers are all around us: clothing made from synthetic fibers, polyethylene cups, fiberglass, nylon bearings, plastic bags, polymer-based paints, epoxy glue, polyurethane foam cushion, silicone heart valves, and Teflon-coated cookware. The list is almost endless.

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

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

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

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



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

- (i) Natural Polymers:** These are the polymers which occur in the nature. Ex. Natural rubber, silk, polysaccharides, starch, cellulose, etc.
- (ii) Synthetic Polymers:** These are the polymers which are manufactured in industries. Ex. Polythene, PVC, Bakelite, Teflon, Nylon, Buna-S, Buna-N, etc.

**(B)** Depending upon the nature of monomers present, polymers may be classified into the following types.

#### i. Homo-polymer:

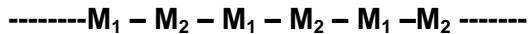
The polymer containing monomer units of identical chemical composition is called a homo-polymer. In other words, the polymer formed from one type of monomer is called a homo-polymer. Example: polythene, PVC, Polystyrene etc.

-----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.



(Copolymer)

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

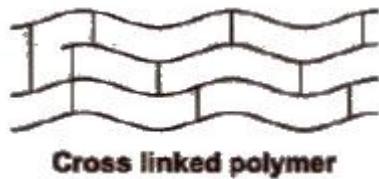
**(i) Linear polymers:** These are the polymers in which the monomer units are linked to one another to form long linear chains. These linear chains are closely packed in space. The close packing results in high densities, tensile strength and high melting and boiling points. e.g., high density polyethene,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



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



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



### Classification of Polymers Based on Mode of Polymerization

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

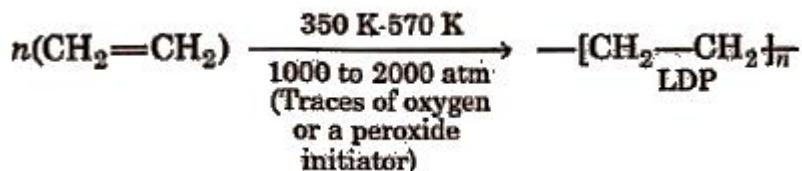
**(ii) Condensation Polymers:** The polymers which are formed by the combination of monomers with the elimination of small molecules such as water, alcohol, hydrogen chloride etc., are known as condensation polymers. Examples: Nylon-6,6 is formed by the condensation of hexamethylene diamine with adipic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

## **Distinction between Thermoplastics & Thermosetting.**

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

## Polythene:

### **(i) Low density polythene (LDP)**

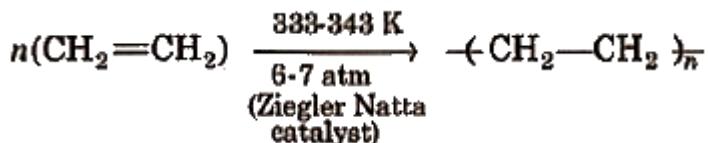


It is tough, flexible, transparent, chemically inert as well as poor conductor of electricity. It has moderate tensile strength but good tearing strength.

**Uses:** It is used

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

#### **(ii) High density polyethylene (HDP)**



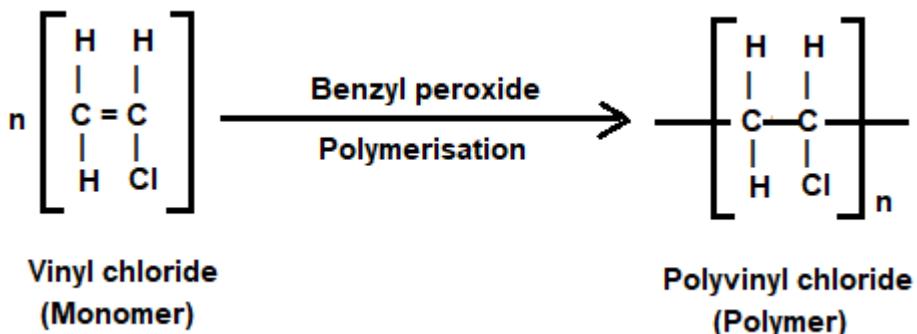
It has high density due to close packing. It is also chemically inert, tougher, and harder.

**Uses:** It is used

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

### PVC (Poly Vinyl Chloride):

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

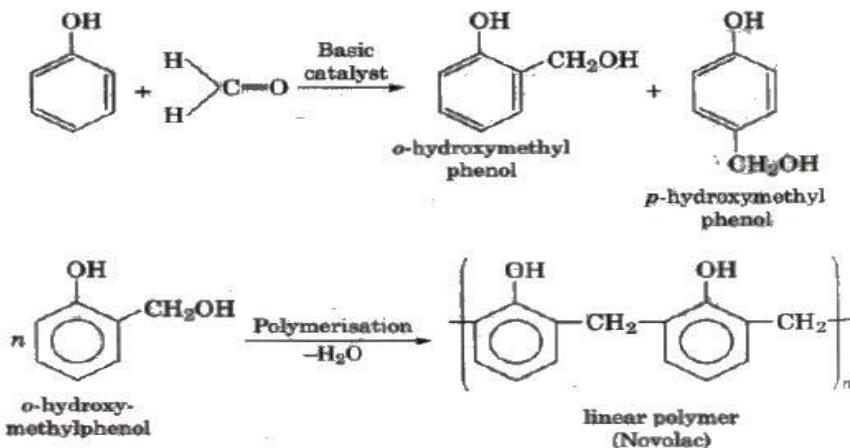


**Uses:** It is used for making:

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

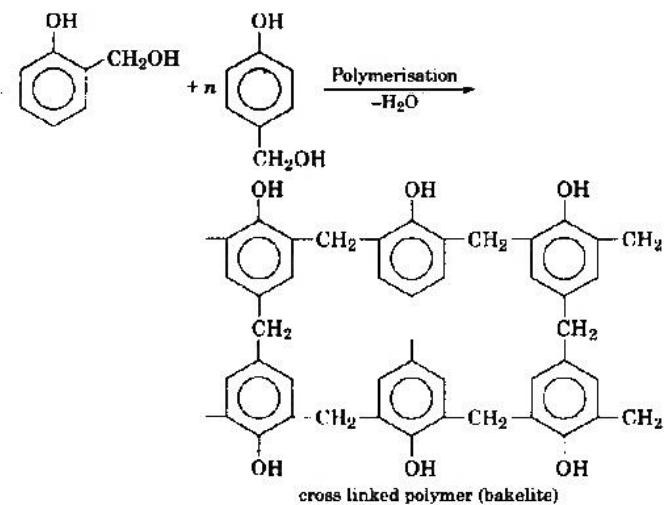
### Bakelite (Phenol-Formaldehyde Resin):

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



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

During the process of polymerization, a little quantity of hexamethylene tetraamine  $[(\text{CH}_2)_6\text{N}_4]$  is added which converts 'novolac' into a hard resinous mass **called Bakelite**.



**Uses:** It is used in the manufacture of:

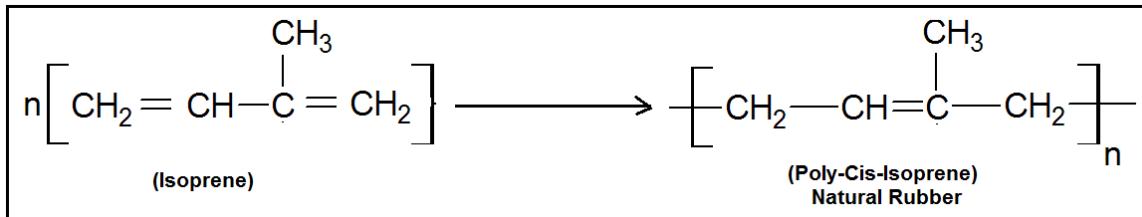
- i. Electrical insulators like plug, switch etc.
- ii. Cabinets for Radio and TV
- iii. Telephone parts
- iv. Paints, varnishes
- v. Hydrogen exchange resin for softening of hard water.

### RUBBER:

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

Rubber is obtained from rubber plants like '*Hevea brasiliensis*' generally found in the tropical regions of *Brazil, Indonesia, Malaysia* etc. Certain saps are cut on the rubber plants and the thick milky liquid called **Latex** is collected. It is then diluted with water and filtered to remove any impurities present in it. Then, the latex is treated with acetic acid ( $\text{CH}_3\text{COOH}$ ) which coagulates the latex. The coagulated latex is then passed through a creeping machine to obtain sheets of rubber. These sheets of rubber are then put into moulding machine to get moulded articles.

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



### Draw backs of natural rubber:

Natural rubber or raw rubber has the following drawbacks:

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

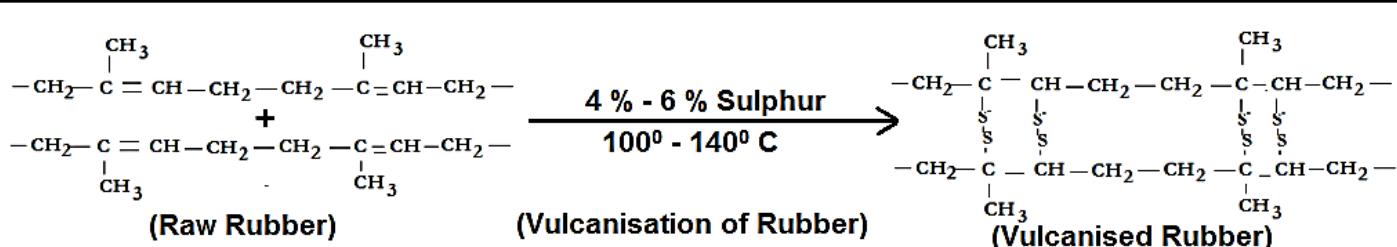
v. It is attacked by acids and alkalis.

vi. It has the property of tackiness.

### Vulcanization of rubber:

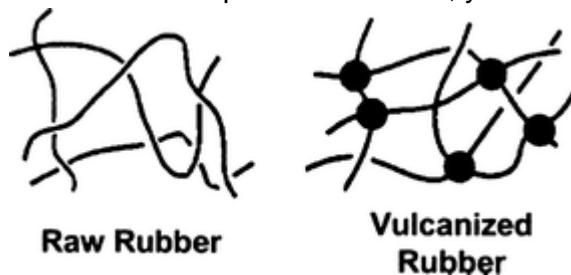
Natural rubber is a thermoplastic. There are no cross links between the polymer chains. It becomes soft and sticky when heated. It is not hard and tough. The properties of natural rubber can be modified and improved by the process of vulcanization. To improve the properties of natural rubber, it is heated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

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



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

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



### Advantages of Vulcanization:

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

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

## **Exercise**

### **(02 Marks Questions)**

1. Define monomer and polymer with example.
2. Define homopolymer and copolymer.
3. What is degree of polymerization?
4. Name the monomer of PVC. Write its two important applications.
5. Name the monomers of Bakelite. Write its two uses.
6. What is natural rubber?
7. Write two advantages of vulcanization.

### **(05 Marks Questions)**

1. Explain the terms monomer, polymer, homopolymer, co-polymer & degree of polymerization with examples.
2. What is a polymer? Write the composition and uses of Bakelite.
3. Define polymer? Write the composition and uses of PVC.
4. What is vulcanization of rubber. Write the advantages of vulcanization.
5. What are the differences between thermoplastic and thermosetting polymers?

## CHAPTER – 14

### CHEMICALS IN AGRICULTURE

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

The term pesticide includes all the following:

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

**Insecticides:** Insecticides are substances used to kill insects.

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

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

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

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

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

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

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

Ex- Bleaching powder, CuSO<sub>4</sub> solution, aluminium phosphide, Copper oxychloride, Carbendazim, Carboxin, Mancozeb, etc.

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

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

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

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

**Uses-**

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

## **Exercise**

### **(02 Marks Questions)**

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

### **(05 Marks Questions)**

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

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**UNIT – I – INTRODUCTION TO SPECTROSCOPY – SCY1612**

## **Introduction**

Spectroscopy is the branch of science dealing with the study of interaction of electromagnetic radiation with matter like atoms and molecules. The interaction of EMR with matter gives rise to two types of spectra namely atomic spectra and molecular spectra.

Atomic spectrum arises from the transition of electrons from one energy level to another due to changes of energy in the atom.

Molecular spectrum involves transition of electrons between rotational and vibrational energy levels in addition to electronic transition. Therefore molecular spectrum is much more complicated than the atomic spectrum.

Molecular Spectroscopy provides a clear image of how diatomic and polyatomic molecules interact by looking at the Frequency, Wavelength, Wave number, Energy, and molecular process also provides most useful information regarding the shape and size of molecules, the bond angles, bond lengths, strength of bonds and bond dissociation energies.

Hence molecular spectroscopy is of great use in determining the structure and constitution of compounds.

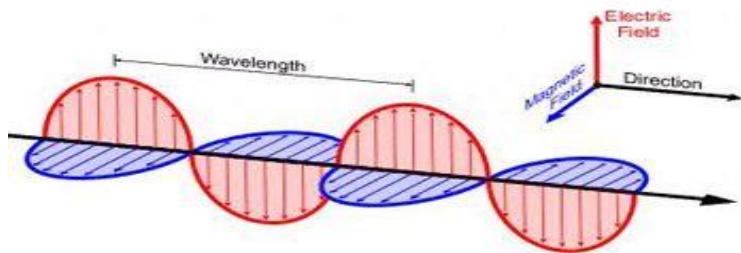
## **Electromagnetic Radiations (EMR)**

EM radiation is created when a subatomic particle, such as an electron, is accelerated by an electric field. The movement produces oscillating electric and magnetic fields, which travel at right angles to each other in a bundle of light energy called a photon. Photons travel as harmonic waves at the fastest speed possible in the universe: 186,282 miles per second (299,792,458 meters per second) in a vacuum, also known as the speed of light.

The EM waves are characterized by frequency, wavelength, wave number and energy.

Electromagnetic (EM) radiation is a form of energy that is all around us and takes many forms, such as radio waves, microwaves, X-rays and gamma rays.

Visible light is only a small portion of the EM spectrum, which contains a broad range of electromagnetic wavelengths.



Electromagnetic waves are formed when an electric field (shown in red arrows) couples with a magnetic field (shown in blue arrows). Magnetic and electric fields of an electromagnetic wave are perpendicular to each other and to the direction of the wave.

### **The four main electromagnetic interactions:**

The force of attraction or repulsion between electric charges is inversely proportional to the square of the distance between them.

Magnetic poles come in pairs that attract and repel each other, similar to that of electrical charges.

An electric current in a wire produces a magnetic field, the direction of which depends on the direction of the current.

A moving electric field produces a magnetic field, and vice versa.

### **Characterization of EMR**

**Wavelength ( $\lambda$ ) :** It is the distance between two consecutive peaks of a wave (crests). Unit = m.

**Frequency ( $\nu$ ):** It is the number of waves that are formed in a given length of time. Unit = number of wave cycles per second or hertz (Hz).

A short wavelength means that the frequency will be higher and a longer wavelength has a lower frequency.

**Wavenumber ( $\bar{\nu}$  ):** It is the number of waves per unit distance. Unit = cm<sup>-1</sup>       $\bar{\nu} = 1/\lambda$

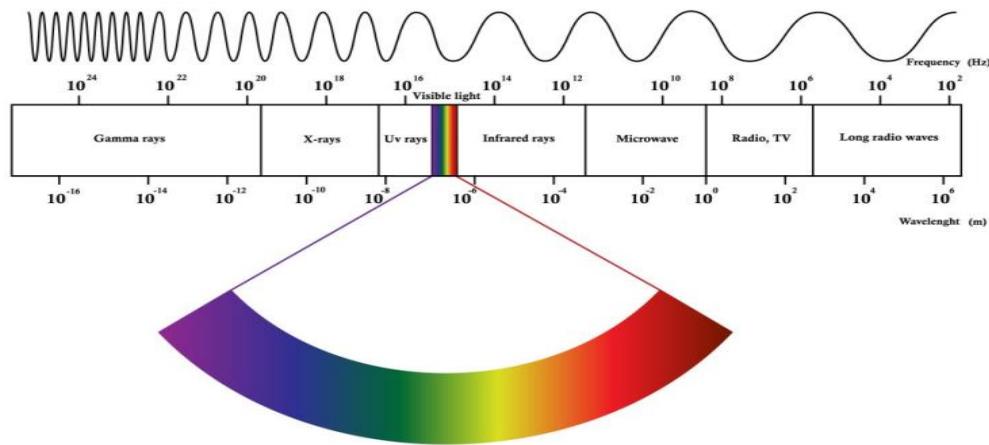
**Energy of EMR (E):** Electromagnetic radiations consists of particles having small packets of energies called quanta or photons. Photons possess the characteristic of wave and travel with the speed of light. The amount of energy corresponding to one photon is expressed by Planck's equation as

$$E = hv \text{ or } E = \frac{hc}{\lambda}$$

where  $h$  = Planck's constant ( $6.62 \times 10^{-34} \text{ Js}$ )

$\nu$  - frequency in Hz

$\lambda$  - wavelength in cm/m.



$$\text{Energy (E)} = hc/\lambda$$

$$E = h\nu$$

$$E = hc\nu$$

### Interaction of EMR with matter

EMR interacts with matter only when the matter has some electric and magnetic effect and are influenced by the electric and magnetic components of the EM radiation.

The net change in the electric/magnetic dipole moment in the molecule or nuclear spin, interact with the magnetic/electrical component of the EMR by either absorption or emission of the EMR.

Total energy of molecules = Translational + rotational + vibrational + electronic

Absorption or emission of EMR causes a change in any of these types of energies.

In molecular spectroscopy, we measure the change in these energy states.

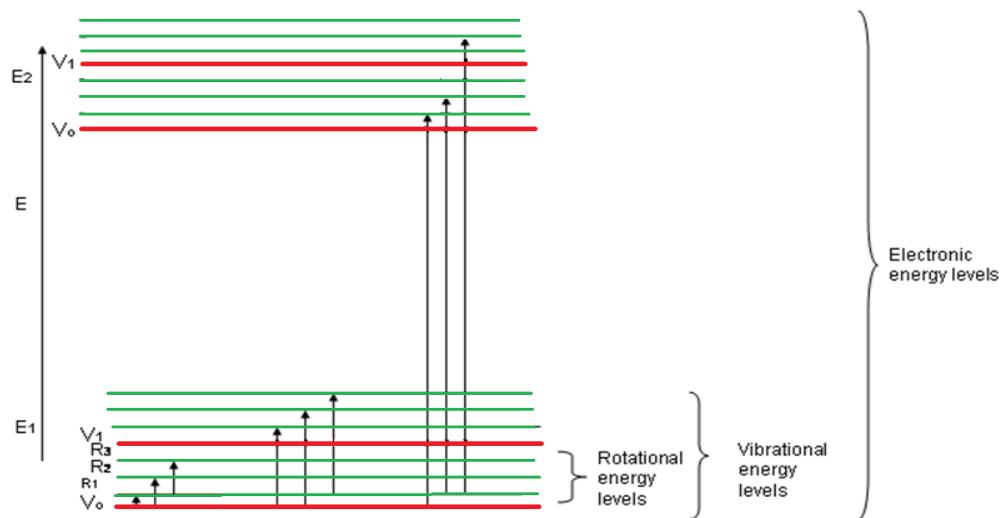
**Translational energy** – It is due to the overall movement of the molecule. Energy levels are not quantized . Hence no spectroscopy.

**Rotational energy** – It is due to spinning of molecules about the axis passing through the centre of gravity - Rotational Levels are quantized – **Rotational spectroscopy (Microwave spectroscopy)**

**Vibrational energy** – It is due to vibrations in molecules – Vibrational Levels are Quantized – **IR Spectroscopy (Vibrational spectroscopy)**

**Electronic energy** – Consists of electronic levels which are quantized – **UV/visible spectroscopy (Electronic spectroscopy)**

If  $E$  is the total energy of a molecule, it can be expressed as the sum of translational, rotational, vibrational and electronic contributions.  $E = E_{\text{trans}} + E_{\text{rot}} + E_{\text{vib}} + E_{\text{elec}}$



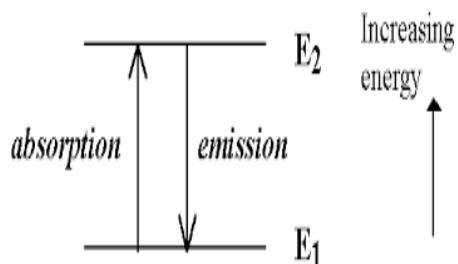
## Spectra

Molecular spectra result from either the absorption or the emission of electromagnetic radiation as molecules undergo changes from one quantized energy state to another.

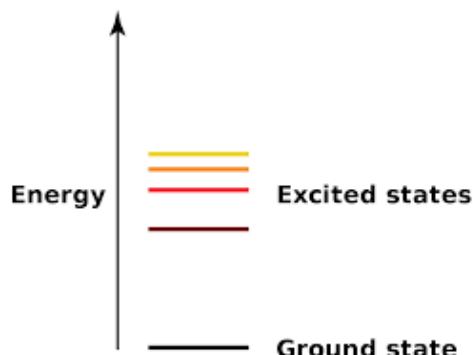
- The electrons in a molecule possess kinetic energy due to their motions and potential energy arising from their attraction by the positive nuclei and their mutual repulsion. These two energy factors, along with the potential energy due to the mutual electrostatic repulsion of the positive nuclei, constitute the electronic energy of a molecule.
- Molecules are not rigid structures, and the motion of the nuclei within the molecular framework gives rise to **vibrational energy levels**.
- In the gas phase, where they are widely separated relative to their size, molecules can undergo free rotation and as a result possess quantized amounts of **rotational energy**.
- In theory, the translational energy of molecules through space is also quantized, but in practice the quantum effects are so small that they are not observable, and the motion appears continuous.

- The interaction of electromagnetic radiation with these molecular energy levels constitutes the basis for Electronic, IR and Microwave spectroscopy.

## Absorption and Emission Spectra

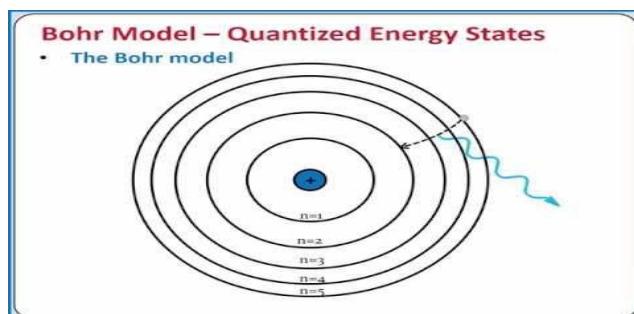


Absorption of electromagnetic radiation by compounds gives absorption spectrum and spectrum obtained by the emission of absorbed radiation is called emission spectrum.



Ground level/state is the lowest energy state. Higher energy levels/states are called excited states.

## QUANTIZATION OF ENERGY LEVELS



## **Relative Population : Boltzmann Distribution Formula**

Relative population in different energy levels is given by  $N_2/N_1$

$N_2$  = number of molecules in the higher energy state  $E_2$

$N_1$  = number of molecules in the lower energy state  $E_1$

$$N_2/N_1 = e^{-(E_2 - E_1)/kT}$$

$k$  = Boltzmann constant,  $T$  = temperature

.

Thermodynamic equilibrium condition:  $N_1 > N_2$  ; There is observed absorbance of electromagnetic radiation

For emission spectra :  $N_2 > N_1$  ; There is population inversion

Saturation condition :  $N_1 = N_2$  ; There is no absorption or emission of radiation

## **Selection Rule in Spectroscopy**

Selection rules describe the allowed transitions between energy states in quantum systems. They are determined by which final states are accessible given an initial state and perturbing potential.

Atomic and molecular species contain a very large number of states in which energy can be distributed, although generally only the states lying lowest in energy will be thermally populated.

If electromagnetic radiation could effectively stimulate transitions between any one of these states, atomic and molecular spectra would be complex.

Selection rules, limit the possible transitions and render these spectra amenable to analysis.

Some transitions are “allowed” by the selection rules, while others are “forbidden”.

- The selection rules may differ according to the technique used to observe the transition.
- In quantum mechanics the basis for a spectroscopic selection rule is the value of the *transition moment integral*

$$\int \psi_1^* \mu \psi_2 d\tau$$

- where  $\Psi_1$  and  $\Psi_2$  are the wave functions of the two states, "state 1" and "state 2", involved in the transition, and  $\mu$  is the transition moment operator. This integral represents the propagator (and thus the probability) of the transition between states 1 and 2; if the value of this integral is *zero* then the transition is "forbidden".
- In practice, to determine a selection rule the integral itself does not need to be calculated: It is sufficient to determine the symmetry of the *transition moment function*. If the transition moment function is symmetric over all of the totally symmetric representation of the point group to which the atom or molecule belongs, then the integral's value is (in general) *not* zero and the transition *is* allowed. Otherwise, the transition is "forbidden".
- The transition moment integral is zero if the *transition moment function*, is anti-symmetric or odd.

## Width of Spectral lines

Spectral lines are broadened because of two reasons:

1. Energy levels are not sharp.
2. Atoms are moving relative to observer.

Three mechanisms determine the line profile –

1. Quantum mechanical uncertainty in the energy  $E$  of levels with finite lifetimes. Determines the natural width of a line (generally very small).
2. Collisional broadening: Collisions reduce the effective lifetime of a state, leading to broader lines. High pressure gives more collisions (eg stars).
3. Doppler or thermal broadening, due to the thermal (or large-scale turbulent) motion of individual atoms in the gas relative to the observer.

## Signal-to-Noise Ratio (SNR)

The ability of the spectrometer to make accurate measurements depends on the quality of the signal obtained from the detector and the subsequent electrical circuits. The signal-to-noise ratio (SNR) provides a measure of the signal quality. The SNR compares the average power available in

the signal to the average power contained in the noise, which includes any signal from sources other than the target signal source. In a spectrometer, the desired signal consists of the optical power at a given wavelength directed by the diffraction grating (and by the DMD, in a DLP-based system) to the detector. The noise signal arises from a number of sources, both electrical and optical.

In order to improve the SNR in a spectrometer, the design choices must increase the power in the measurement signal while at the same time minimize the noise sources as much as possible.

- Thermal energy provided by ambient heating generates the additional carriers that contribute to the noise current.
- Additional electronic noise, sometimes referred to as the readout noise, arises from the circuitry directly behind the detector that provides the initial filtering and scaling of the signal.
- Fixed pattern noise arises from the variation in the response to incident light of the detectors in a detector array. The variation originates primarily from differences in quantum efficiency caused by differences in the aperture area and the thickness of the detectors that occurred during fabrication. Only spectrometers employing a linear detector array for discriminating between wavelengths suffers from this source of noise.

## Improving SNR

Several methods of spectrometer design and measurement, based on the nature of the noise sources, can improve the SNR of the spectrometer and lead to higher quality measurements.

- The use of holographic gratings, which have much fewer imperfections than ruled gratings, can reduce the stray light generated by the optical system. For this reason, holographic gratings are commonly used in UV spectrometers that suffer signal losses in the optical system due to absorption and are thus more susceptible to noise from stray light.
- A thermo-electric cooler (TEC) attached to any detector reduces the effective temperature of the detector and thus can reduce the impact of on the SNR.

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## **Question Bank**

### **Part A**

1. What is electromagnetic radiation?
2. Mention the important characteristics of electromagnetic radiation.
3. Define wavelength, frequency and wavenumber.
4. Give the equation relating energy and frequency of EMR.
5. Relate energy and wavelength of EMR.
6. What are the different quantized energy levels?
7. Compare absorption and emission spectra.
8. What is SNR in spectroscopic techniques?
9. List out the important conditions for spectral line broadening.
10. Give any two methods of improving SNR.
11. Give the expression for Boltzmann Distribution Law.

### **Part B**

1. Explain EMR and how are they characterized?
2. Elaborate on energy level quantization and the different spectroscopic method of analysis.
3. Write short note on Boltzmann Distribution Law and give its significance.
4. Discuss the signal to noise ratio related to spectroscopy.
5. Explain the various factors causing spectral line broadening.
6. Elaborate on selection rule in spectroscopic method of analysis.



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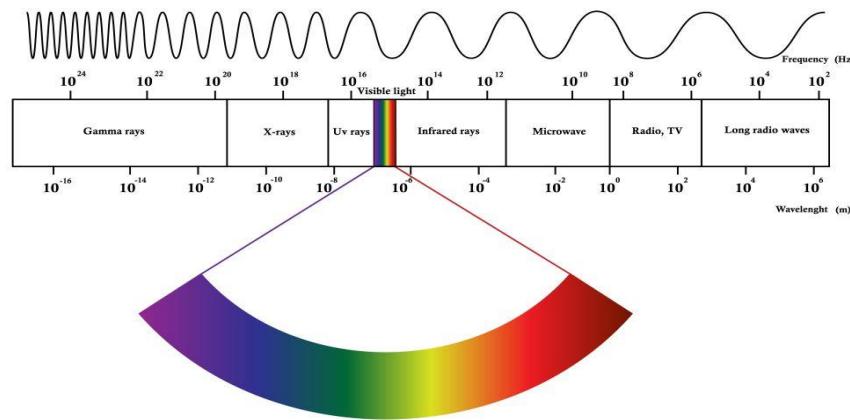
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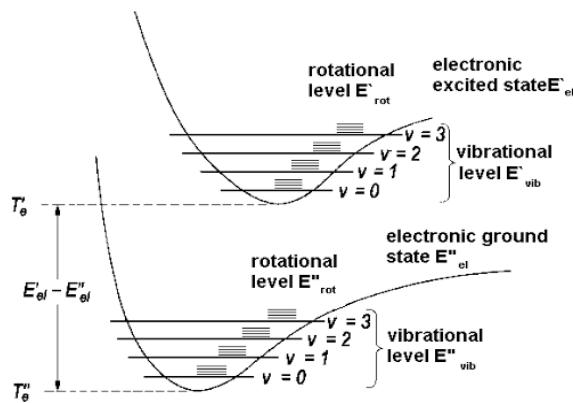
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**UNIT – II –UV-VISIBLE SPECTROSCOPY – SCY1612**

## Electromagnetic Spectrum– UV-Visible range



The UV-Visible range in the electromagnetic spectrum is from 200 – 800nm. The range 200 – 400 nm is the UV range and from 400 – 800 nm is the Visible range.

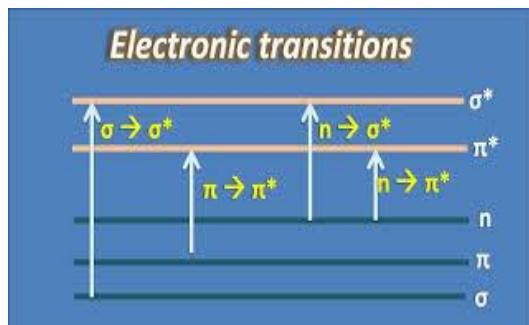


The electronic transitions are accompanied by vibrational and rotational transitions. Therefore the electronic absorption bands are broad in the spectrum.

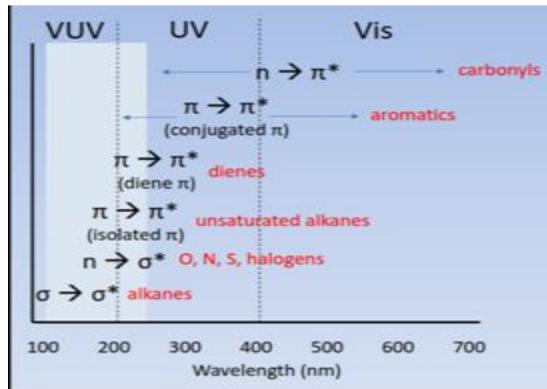
### Characteristics of electronic transitions

- Electronic transitions are appeared as broad bands due to the accompanying vibrational and rotational transitions.
- During electronic transition there should be change in the dipole moment of the molecule (i.e. Ground state and Excited state dipole moment should not be the same)
- During electronic transition change in angular momentum should be zero or  $+/- 1$

## Types of Electronic Transitions



## Examples of molecules exhibiting various electronic transitions



## Types of electronic transitions

- $\sigma \rightarrow \sigma^*$  transition: The energy required for this transition is high (i.e. very short wavelengths; 150nm). The saturated alkanes will undergo this type of transition.
- $n \rightarrow \sigma^*$  transition: The saturated hydrocarbons attached to hetero atoms will undergo this type of transition. Example: Alcohols, amines, ether and water. The energy required for this transition is 180-190 nm.
- $\pi \rightarrow \pi^*$  transition: The unsaturated hydrocarbons, carbonyl compounds, cyanides and azo compounds will undergo this type of transition around 250 nm. Ex: Alkenes, Alkynes, Aldehyde and Ketone. The energy required for this transition is very low (i.e. very longer wavelengths).
- $n \rightarrow \pi^*$  transition: The carbonyl compounds will undergo this type of transition around 275 nm. Ex: Aldehydes, Ketone and cyanide.

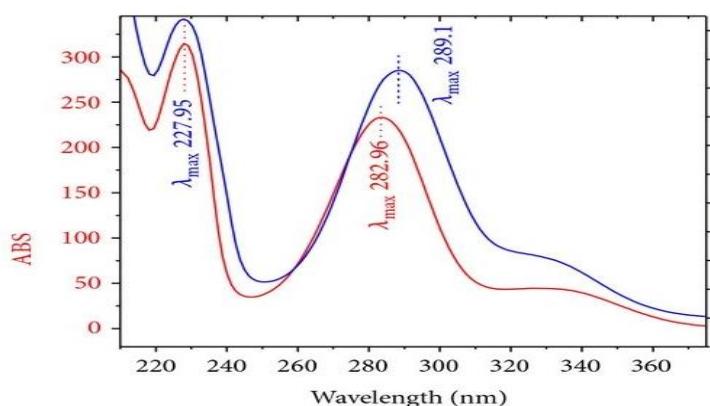
**Table illustrates the type of transition and the resulting maximum wavelength.**

Molecule	Transition	$\lambda_{\text{max}}$ (nm)
Ethane	$\sigma \rightarrow \sigma^*$	135
Methanol	$\sigma \rightarrow \sigma^*$ $\pi \rightarrow \sigma^*$	150 183
Ethylene	$\pi \rightarrow \pi^*$	175
Benzene	$\pi \rightarrow \pi^*$	254
Acetone	$\pi \rightarrow \pi^*$	290

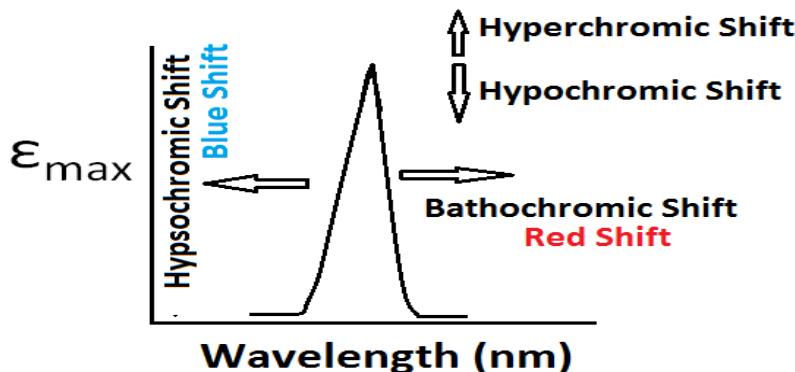
Differences between  $\pi \rightarrow \pi^*$  and  $n \rightarrow \pi^*$  transitions

S.No.	$\pi \rightarrow \pi^*$	$n \rightarrow \pi^*$
1	Allowed transition	Forbidden transition
2	High energy transition	Lower energy transition
3	Molar extinction coefficient ( $\epsilon$ ) value lies between 100 to 10000	Molar extinction coefficient ( $\epsilon$ ) value is < 100
4	More intense than $n \rightarrow \pi^*$	More intense than $\pi \rightarrow \pi^*$

$\lambda_{\text{max}}$  is the wavelength corresponding to maximum absorbance and  $\epsilon_{\text{max}}$  is the molar absorption coefficient which is a constant for a particular molecule and proves the identity of the molecule.

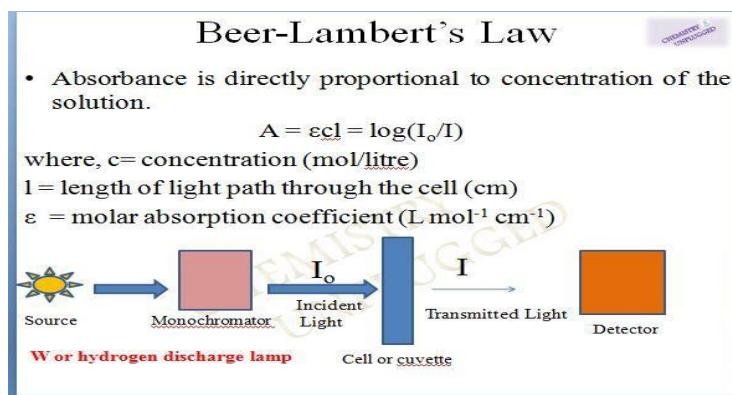


## Effect of Substituents on Absorption Spectra



- Bathochromic shift :- Absorption maximum of a compound shift to longer wavelength, it is known as Bathochromic shift or red shift.
- Hypsochromic shift:- Absorption maximum of a compound shifts to a shorter wavelength it is called a Hypsochromic shift or Blue shift.
- Hyperchromic shift :- Intensity of the absorption band increases.
- Hypochromic shift :- Intensity of the absorption band decreases.

## UV-Visible spectroscopy – Instrumentation



A spectrophotometer is an instrument which uses monochromatic light. It measures the absorbance of various solutions at different wavelengths. This instrument scans the entire UV-visible regions.

In a double beam spectrophotometer, radiation from hydrogen lamp or tungsten lamp enters the monochromator, which produces very narrow band widths. The beam is then passed through a

reference cell and the sample cell by means of rotating mirrors. The photomultiplier tube is used as a detector which receives alternate pulses of radiation from the reference and sample beam.

**Sources:** Commonly used sources of UV radiation are the hydrogen lamp and the deuterium lamp. Tungsten filament lamp is used for the visible range.

**Filters and Monochromators:** Tinted glass filters are used to produce monochromatic radiations. Filters resolve polychromatic light into a relatively wide bandwidth to produce monochromatic radiations. Monochromator is a device which resolves polychromatic radiation into its individual wavelength and isolates them into very narrow bands.

**Prism:** A prism disperses polychromatic light from a source into its constituent wavelengths. Cornu quartz and littro prisms are used. Glass prisms are used for visible range while silica, fused silica or quartz prisms are used for the UV range.

**Sample Holder (Cells / Cuvette) :** The sample container should be transparent to the UV-visible radiation. Cuvettes are made ordinary glass or quartz. Fused silica cells are used for the UV range. The path length of these cuvettes is usually 1 cm.

**Solvents:** A solvent is selected in such a way that it does not absorb in the UV-visible range. The solvents that are frequently used are water, methanol, ethanol, hexane, chloroform etc.

**Detectors:** The commonly used detectors are photocells, phototubes and photomultiplier tubes.

**Amplification and Read out:** The transmitted radiation is converted into electrical signal and the electrical signals are interpreted using ammeters, amplifiers and potentiometers.

### **Mathematical Derivation of Beer- Lambert's Law:**

When a beam of monochromatic radiation passes through a transparent absorbing medium, the rate of decrease of intensity of radiation with the thickness of the absorbing medium is proportional to the intensity of the incident radiation and concentration of the medium.

$$-\frac{dI}{dx} \propto cI$$

where  $-\frac{dI}{dx}$  = decrease of intensity of radiation with the thickness of the absorbing medium

c = concentration of the absorbing medium

dI = Change in intensity of incident light (range is from  $I_0$  to I)

$dx$  = Change in thickness of medium (range is from 0 to b)

$$-\frac{dI}{I} = \epsilon c dx$$

$\epsilon$  = Molar extinction coefficient

$$-\frac{dI}{I} = c dx$$

$$\int_{I_o}^I \frac{dI}{I} = - \int_{x=0}^{x=b} \epsilon c dx$$

$$\log[I]_I = -\epsilon c [x]_0^b$$

$$\log I - \log I_o = -\epsilon bc$$

$$\log \frac{I}{I_o} = -\epsilon bc$$

$$T = -\epsilon bc, \quad T = \text{Transmittance}$$

$$\log \frac{I_o}{I} = \epsilon bc$$

$$A = \epsilon bc, \quad A = \text{Absorbance or Optical density}$$

Transmittance (T) : It is the fraction of the incident light that is transmitted by a sample.  $T = I/I_o$

Absorbance (A) : It is the negative logarithm to the base 10 of the transmittance of the solution.

$$A = -\log T \quad (\text{no unit})$$

Molar absorptivity ( $\epsilon$ ): It is the absorbance of a one molar solution placed in a cell of one cm path length.  $A = \epsilon bc \quad (\text{unit} = \text{dm}^3 \text{mol}^{-1} \text{cm}^{-1})$

## Chromophore

It is a covalently unsaturated group which is responsible for absorption of UV or visible radiation and may or may not have an impact on the colour of the compound.

A compound which contains chromophore it is called chromogen. In unsaturated linkage such as –C=C-, -N=N-, the  $\pi$  electron are loosely bound. These loosely bound electron required less energy for electronic transition and the absorption band occur in near UV region.

Example: Acetylene possess -C=C- in structure its  $\lambda_{\text{max}}$  is 175-180 nm.

## Auxochrome

It is saturated and unsaturated group which consists of one or more pair of non-bonded electron. This group when attached to a Chromophore help in altering the wavelength by increasing the intensity of absorption and increases  $\lambda_{\text{max}}$ .

Examples of Auxochrome are: -OH, -NH<sub>2</sub>, -OR etc.

## Problems and Solutions

### Problem 1

If the transmittance of a solution is 19%, what is its absorbance or optical density?

Solution

$$\%T = 19.4$$

$$T = 0.194$$

$$\text{Absorbance} = -\log T$$

$$= \log 1/T$$

$$= 0.712$$

### Problem 2

A solution of a transmittance of 20% when taken in a cell of 2.5cm thickness. Calculate its concentration if the molar absorption coefficient is 12,000 dm<sup>2</sup>mol<sup>-1</sup>cm<sup>-1</sup>

**Solution:**

$$\log 1/T = \epsilon bc$$

$$T = I/I_0$$

$$\%T = 20, T = 0.2, b = 2.5 \text{ cm} \quad \log T = \log I/I_0$$

$$\epsilon = 12000 \text{ dm}^3\text{mol}^{-1}\text{cm}^{-1}$$

$$-\log T = \log I_0/I$$

$$\log 1/0.2 = 12000 \times 2.5 \times c \quad -\log T = \epsilon b c$$

$$c = 2.33 \times 10^{-5} \text{ mol dm}^{-3}$$

**Problem 3:** A solution of thickness 2 cm transmits 40% incident light. Calculate the concentration of the solution given that  $\epsilon = 6000 \text{ dm}^3 \text{mol}^{-1} \text{cm}^{-1}$

$$\log 1/T = \epsilon b c$$

$$\%T = 40, T = 0.4, b = 2 \text{ cm}$$

$$\log 1/0.4 = 6000 \times 2 \times c$$

$$c = 3.31 \times 10^{-5} \text{ mol/dm}^3$$

**Problem 4:** The transmittance of a  $2 \times 10^{-4} \text{ M}$  solution of a substance was found to be 76.2% at a wavelength of 360nm, when placed in a cell of 1 cm length. Calculate A and  $\epsilon$ .

$$\%T = 76.2, T = 0.762$$

$$A = -\log T \text{ or } A = \log 1/T$$

$$A = \log 1/0.762 = 0.118$$

$$A = \epsilon b c \text{ or } \epsilon = A/bc$$

$$\epsilon = 0.118/1 \times 2 \times 10^{-4}$$

$$\epsilon = 0.059 \times 10^4 \text{ dm}^3 \text{mol}^{-1} \text{cm}^{-1}$$

**Problem 5:** The molar extinction coefficient of a solute is  $1.4 \times 10^4 \text{ dm}^3 \text{mol}^{-1} \text{cm}^{-1}$ . If a solution of a substance has an absorbance of 0.85, in a cell of 1cm path length, calculate T and c of the solution.

$$\log 1/T = A = 0.85$$

$$1/T = 7.0794$$

$$T = 0.1412$$

$$A = \epsilon b c$$

$$c = A/\epsilon b$$

$$c = 0.85/1 \times 1.4 \times 10^4$$

$$c = 6.07 \times 10^{-5} \text{ M}$$

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1. Barrow G. M., Introduction to Molecular Spectroscopy, McGraw-Hill, 1962.
2. Willard H. H., Merritt Jr. L. L., Dean J. A., and Settle Jr. A. F., Instrumental methods of analysis, 6th Edition, Van Nostrand, 1981.

## **Question Bank**

### **Part A**

1. What is electronic spectroscopy?
2. Mention the different types of electronic transitions in UV-visible spectroscopy.
3. Differentiate chromophore and auxochrome.
4. Write on solvent selection in electronic spectroscopy.
5. Give the important parts of an UV-visible spectrophotometer.
6. Write the principle behind UV-visible spectroscopy.
7. What are the limitations of electronic spectroscopy?
8. What is Beer-Lambert's Law?
9. Compare bathochromic and hypsochromic shifts.
10. Differentiate hyperchromic and hypochromic shifts.
11. Give one example of a molecule showing  $\sigma \rightarrow \sigma^*$  and  $\pi \rightarrow \pi^*$  transitions.
12. Differentiate  $\pi \rightarrow \pi^*$  and  $n \rightarrow \pi^*$  transitions in electronic spectroscopy.
13. Define  $\lambda_{\max}$  and  $\epsilon_{\max}$  in electronic spectroscopy.

### **Part B**

1. Write short on the different types of electronic transitions in molecules.
2. Explain the instrumentation of UV-visible spectroscopy in a block diagram
3. Derive the expression for Beer – Lambert's Law.
4. Explain the effect of substituents on  $\lambda_{\max}$  and  $\epsilon_{\max}$  values in electronic spectroscopy.
5. Discuss the effect of chromophoric and auxochromic groups in molecules.



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**UNIT – III –IR AND RAMAN SPECTROSCOPY– SCY1612**

## VIBRATIONAL SPECTROSCOPY (IR spectroscopy)

Vibrational spectroscopy is due to the interaction of matter with the Infra red region of the electromagnetic spectrum.

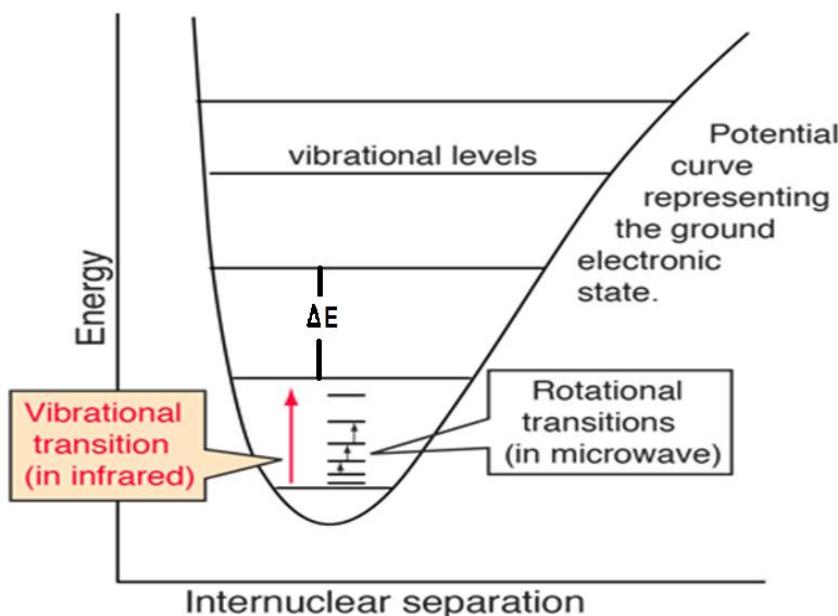
### Spectral Range of IR Radiation:

- Near IR:  $12000\text{ cm}^{-1}$  to  $4000\text{ cm}^{-1}$
- MID IR:  $4000\text{ cm}^{-1}$  to  $620\text{ cm}^{-1}$
- Far IR:  $300\text{ cm}^{-1}$  to  $10\text{ cm}^{-1}$

The mid IR region is used for the sample analysis in IR spectroscopy.

### Quantum Approach

Irradiation of sample with IR radiation brings about vibrational changes in molecules. The transition of molecule is from lower vibrational energy level to higher vibrational energy level. The transition is induced by absorption of photon of the IR radiation of appropriate frequency, which matches with energy gap between the two levels.



IR absorption by molecules happens only when there is a change in the dipole moment of the molecule.

$$\text{Dipole Moment } (\mu) = \text{Charge } (Q) * \text{distance of separation } (r)$$

Measured in Debye units denoted by 'D'.

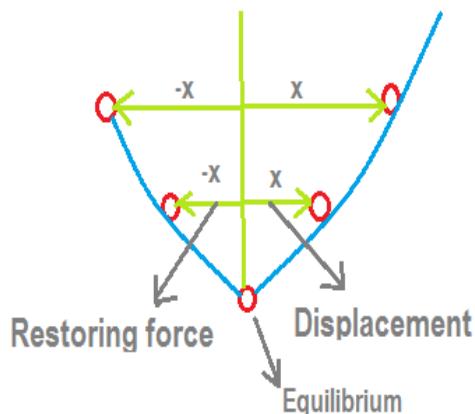
$$1\text{ D} = 3.33564 \times 10^{-30}\text{ Cm, where C is Coulomb and m is meter.}$$

The bond dipole moment that arises in a chemical bond between two atoms of different electronegativities can be expressed as follows:

$$\mu = \delta \cdot d$$

where  $\mu$  is the bond dipole moment,  $\delta$  is the magnitude of the partial charges  $\delta^+$  and  $\delta^-$ ,

and  $d$  is the internuclear distance between  $\delta^+$  and  $\delta^-$ .



The bond between the atoms is considered as a spring which can undergo stretching and bending vibrations. During vibration, there is a change in the dipole moment of the molecule as a result of the change in the distance between the atoms. When an atom in a molecule is stretched over a certain distance keeping the other atom stationary, the atom gets displaced from its equilibrium position by distance “ $x$ ” . To attain equilibrium, the atom tries to move back to the original position, by applying a restoring force which is equal the displaced distance but will be in the opposite direction and has a negative value. According to Hook's Law:

$$-\text{restoring force} \propto x$$

$$-F \propto x$$

$$-F = kx \quad k = \text{force constant}$$

### Harmonic Oscillator – vibrating pendulum

$$\frac{1}{2\pi}\sqrt{\frac{k}{\mu}}$$

$\omega_{\text{osc}}$  = vibrational frequency =

$$\overline{\omega}_{\text{osc}} = \frac{1}{2\pi c}\sqrt{\frac{k}{\mu}}$$

## VIBRATIONS OF POLYATOMIC MOLECULES

### Degrees of freedom:

The number of degrees of freedom is equal to the sum of coordinates necessary to locate all the atoms of a molecule in space. Each atom has three degrees of freedom corresponding to the three Cartesian coordinates (X, Y, Z) which is necessary to describe its position on relative to other atoms in a molecule.

The total number of degrees of freedom in a molecule containing  $N$ -atoms is equal to  $3N$  which includes rotational, vibrational and translation degrees of freedom.

Total number of degrees of freedom ( $3N$ ) = Translational + Vibrational + Rotational

The number of degrees of freedom for H atom = 3

The number of degrees of freedom for Methane ( $\text{CH}_4$ ) molecule =  $3N = 3 \times 5 = 15$

S.No.	degrees of freedom	Monoatomic	Poly atomic	
			Linear molecule	Non linear molecules
1	Total	3	$3N$	$3N$
2	Translational	3	3	3
3	Rotational	0	2	3
4	Vibrational	0	$3N-5$	$3N-6$

### Vibrational Degrees of freedom for Linear molecule

Total degrees of freedom for a polyatomic molecule = Translational + Rotational + Vibrational

$$3N = 3 + 2 + \text{Vibrational}$$

- Vibrational Degrees of freedom =  $3N-5$
- For example: CO<sub>2</sub>, CO, HCl, Acetylene
- Vibrational Degrees of freedom for CO =  $3N-5 = 1$
- Vibrational Degrees of freedom for C<sub>2</sub>H<sub>2</sub> =  $3N-5 = 7$
- Vibrational Degrees of freedom for CO<sub>2</sub> =  $3N-5 = 4$

### Degrees of freedom of vibration for Non-linear molecule

Total degrees of freedom for polyatomic molecule = Translational + Rotational + Vibrational

$$3N = 3 + 3 + \text{Vibrational}$$

$$\text{Vibrational Degrees of freedom} = 3N-6$$

$$\text{Vibrational Degrees of freedom for H}_2\text{O} = 3N-6 = 3$$

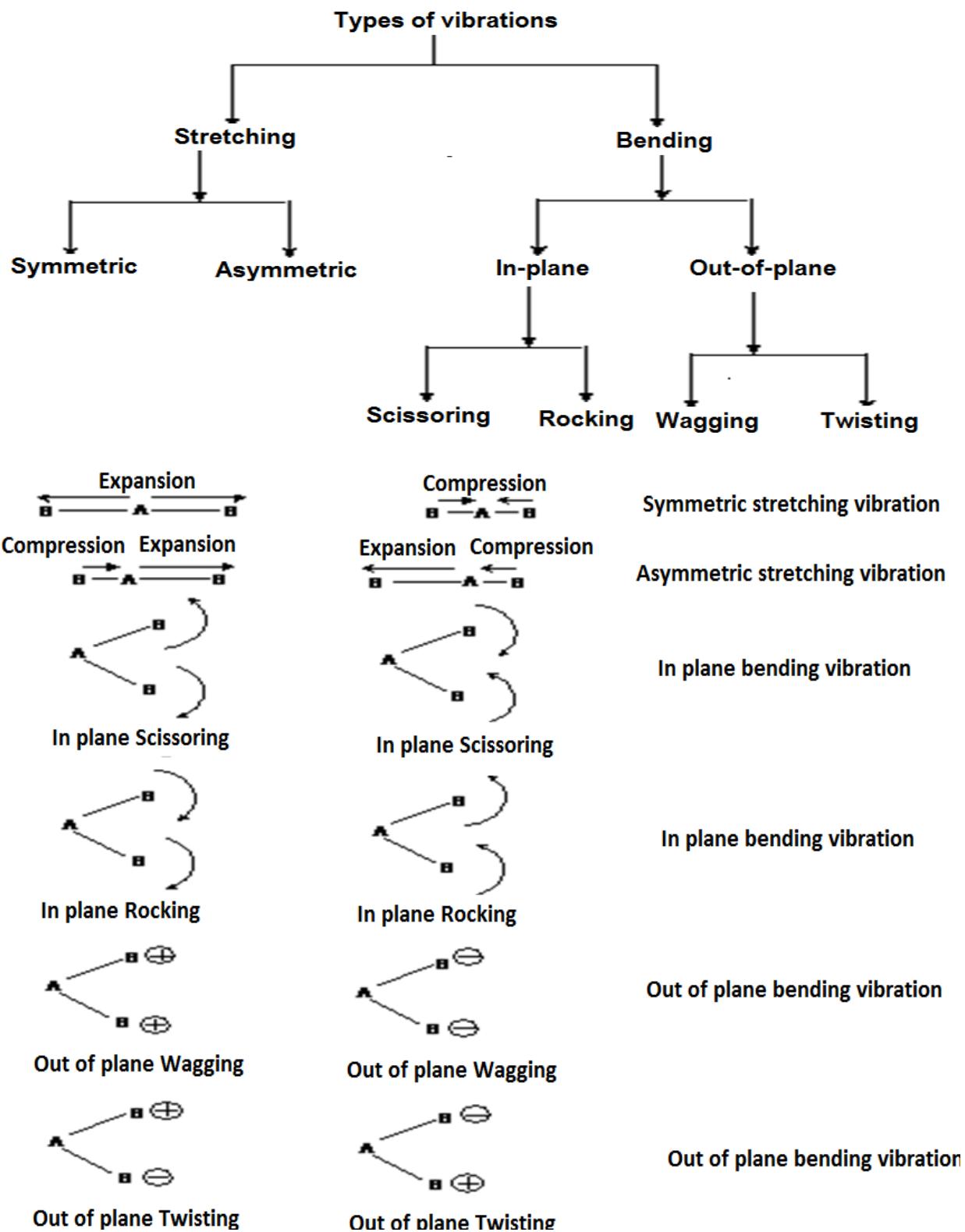
$$\text{Vibrational Degrees of freedom for CH}_4 = 3N-6 = 9$$

$$\text{Vibrational Degrees of freedom for NH}_3 = 3N-6 = 6$$

$$\text{Vibrational Degrees of freedom for C}_6\text{H}_6 = 3N-6 = 30$$

### Types of Vibrations

Vibration is periodic displacement of atoms or nuclei from their equilibrium position.



Regions of the Infrared spectrum

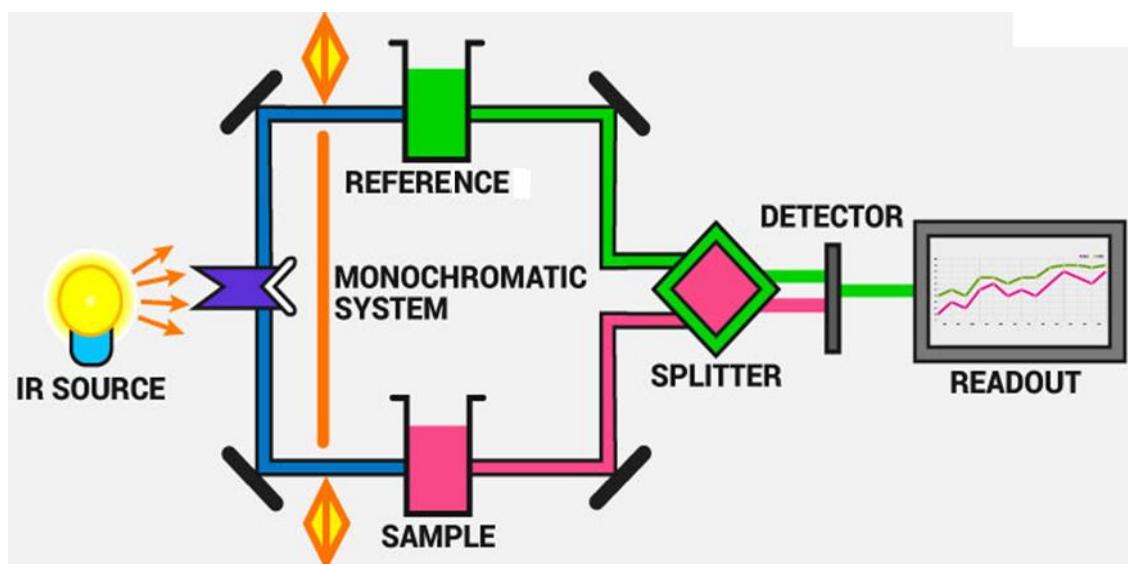
- Most of the bands that indicate what functional group is present are found in the region from  $4000\text{ cm}^{-1}$  to  $1300\text{ cm}^{-1}$ . Their bands can be identified and used to determine the functional group of an unknown compound.
- Bands that are unique to each molecule, similar to a fingerprint, are found in the fingerprint region, from  $1300\text{ cm}^{-1}$  to  $400\text{ cm}^{-1}$ . These bands are only used to compare the spectra of one compound to another.



## IR – Sampling Techniques

- The samples used in IR spectroscopy can be either in the solid, liquid, or gaseous state.
- Solid samples can be prepared by crushing the sample with a mulling agent (KBr) which has an oily texture. A thin layer of this mull can now be applied on a salt plate to be measured.
- Liquid samples are generally kept between two salt (NaCl) plates and measured since the plates are transparent to IR light. Salt plates can be made up of sodium chloride, calcium fluoride, or even potassium bromide.
- Since the concentration of gaseous samples can be in parts per million, the sample cell must have a relatively long pathlength, i.e. light must travel for a relatively long distance in the sample cell.
- Thus, samples of multiple physical states can be used in Infrared Spectroscopy.

## IR Spectroscopy – Instrumentation



- A beam of IR light from the source (Nernst Glower / Globar) is split into two and passed through the reference and the sample respectively.

- Now, both of these beams are reflected to pass through a splitter and then through a detector. Finally, the required reading is printed out after the processor deciphers the data passed through the detector.

### Vibrational Frequencies

Bond	Stretching frequency ( $\text{cm}^{-1}$ )	Intensity
O-H (alcohol)	3200-3650	Medium, broad
O-H (carboxylic acid)	2500-3300	Strong, broad
N-H	3100-3550	Medium
C-H (alkane)	2850-3000	Medium
C-H (alkene)	3000-3100	Medium to strong
C-H (alkyne)	3300	Weak to medium
C≡C	2100-2250	Weak
C=C	1600-1680	Weak to medium
C=O (aldehyde/ketone)	1630-1820	Strong
C=O (ester)	1735-1800	Strong
C=O (carboxylic acid)	1700-1725	Strong
C-O	1000-1250	Strong

### Selection rules for Infrared transitions

For a particular vibration to be infrared active there must be a change in the dipole moment of the molecule during the vibration. In other words transition dipole moment must not be zero.

Homonuclear diatomic molecules are inactive in the infrared spectrum. They do not have a dipole moment and during the vibration also the dipole moment is zero. eg: H<sub>2</sub>, O<sub>2</sub>, N<sub>2</sub> etc.

Heteronuclear diatomic molecules such as CO, NO are active in IR.

Symmetrical polyatomic molecules such as CO<sub>2</sub>, the symmetric stretching vibration is infrared inactive where as the asymmetric stretching vibration is IR active  $\Delta v = \pm 1$ , transition can take place between Adjacent vibrational levels, 0 to 1, 1 to 2 etc.

- IR spectrum shows bands rather than line spectrum due to coupling of various rotational transitions within a given vibrational transition. IR spectrum is generally complex and contains many bands in addition to the ones corresponding to fundamental vibrational transitions
- Overtones: Bands corresponding to integral multiple of fundamental vibration. They are due to transition from ground state to higher vibrational states. They are very weak bands. An absorption band at 1050  $\text{cm}^{-1}$  may well have an accompanying band at 2100 (2 v) and 3150 (3 v)  $\text{cm}^{-1}$ .

- Combination bands: Two vibrational frequencies in a molecule couple to give a new frequency within the molecule. This band is a sum of the two interacting bands.
- Difference bands: Similar to combination bands. The observed frequency is the difference between the two interacting frequencies.
- Fermi resonance: When a fundamental vibration couples with overtone or combination Band, the coupled vibration is called a Fermi resonance.

## Raman Spectroscopy

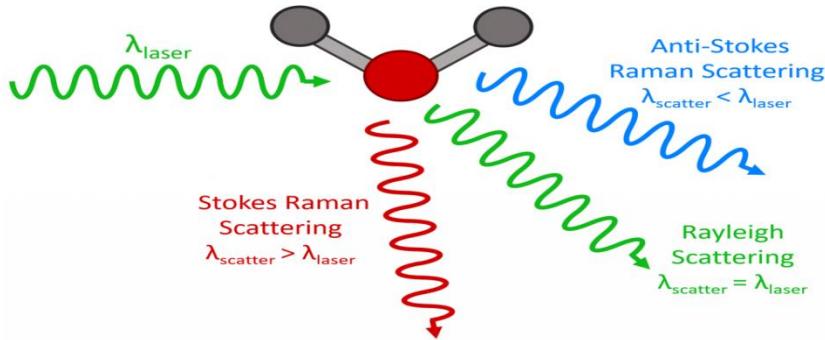
Raman spectroscopy is an analytical technique where scattered light is used to measure the vibrational energy modes of a sample. It is named after the Indian physicist C. V. Raman who, together with his research partner K. S. Krishnan, was the first to observe Raman scattering in 1928.

Raman spectroscopy can provide both chemical and structural information, as well as the identification of substances through their characteristic Raman ‘fingerprint’. Raman spectroscopy extracts this information through the detection of Raman scattering from the sample.

### Raman Scattering

When light is scattered by a molecule, the oscillating electromagnetic field of a photon induces a polarisation of the molecular electron cloud which leaves the molecule in a higher energy state with the energy of the photon transferred to the molecule. This can be considered as the formation of a very short-lived complex between the photon and molecule which is commonly called the virtual state of the molecule.

The virtual state is not stable and the photon is re-emitted almost immediately, as scattered light.



### Rayleigh scattering

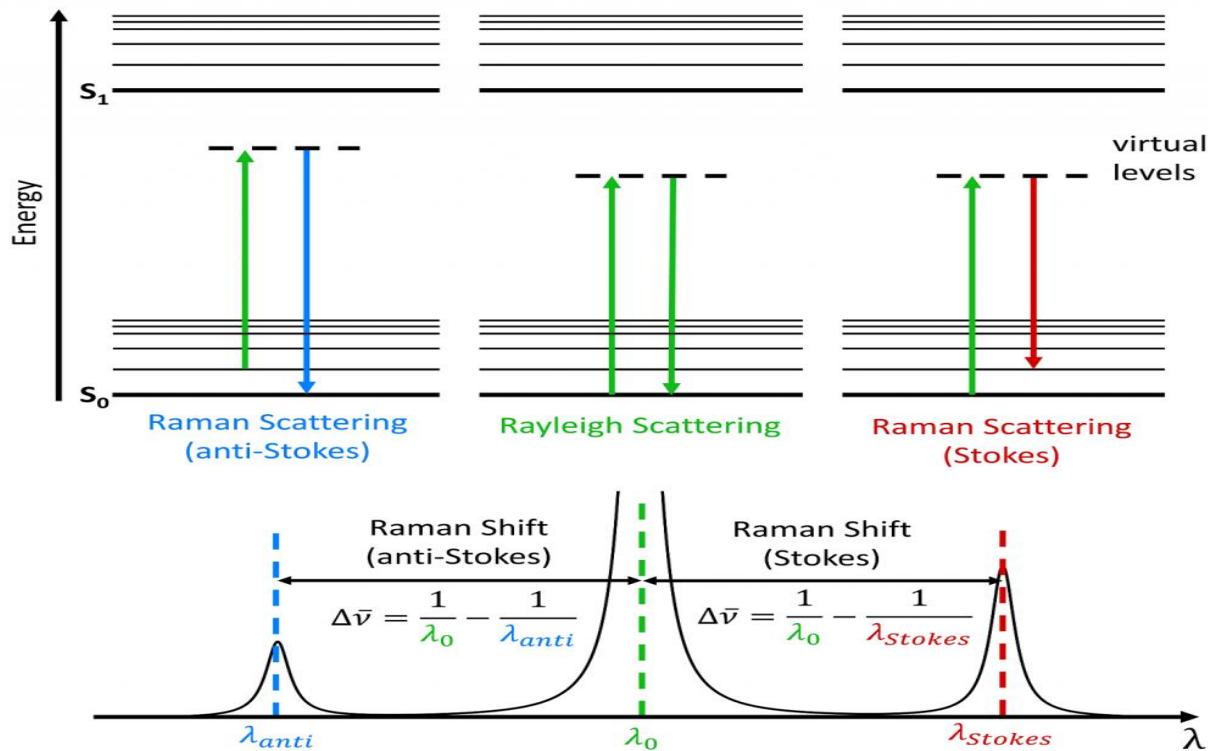
In the vast majority of scattering events, the energy of the molecule is unchanged after its interaction with the photon; and the energy, and therefore the wavelength, of the scattered photon is equal to that of the incident photon. This is called elastic (energy of scattering particle is conserved) or Rayleigh scattering and is the dominant process.

### Stokes and Antistokes lines

In a much rarer event (approximately 1 in 10 million photons) Raman scattering occurs, which is an inelastic scattering process with a transfer of energy between the molecule and scattered photon. If the molecule gains energy from the photon during the scattering (excited to a higher vibrational level) then the

scattered photon loses energy and its wavelength increases which is called Stokes Raman scattering (after G. G. Stokes). Inversely, if the molecule loses energy by relaxing to a lower vibrational level the scattered photon gains the corresponding energy and its wavelength decreases; which is called Anti-Stokes Raman scattering.

Quantum mechanically Stokes and Anti-Stokes are equally likely processes. However, with an ensemble of molecules, the majority of molecules will be in the ground vibrational level (Boltzmann distribution) and Stokes scatter is the statistically more probable process. As a result, the Stokes Raman scatter is always more intense than the anti-Stokes and for this reason, it is nearly always the Stokes Raman scatter that is measured in Raman spectroscopy.



#### Differences between IR and Raman methods

RAMAN	IR
It is due to the scattering of light by the vibrating molecules.	It is the result of absorption of light by vibrating molecules.
The vibration is Raman active if it causes a change in polarisability.	Vibration is IR active if there is change in dipole moment.
The molecule need not possess a permanent dipole moment.	The vibration concerned should have a change in dipole moment due to that vibration.
Water can be used as a solvent.	Water cannot be used due to its intense absorption of IR.
Sample preparation is not very elaborate, it can be in any state.	Sample preparation is elaborate Gaseous samples can rarely be used.
Gives an indication of covalent character in the	Gives an indication of ionic character in the

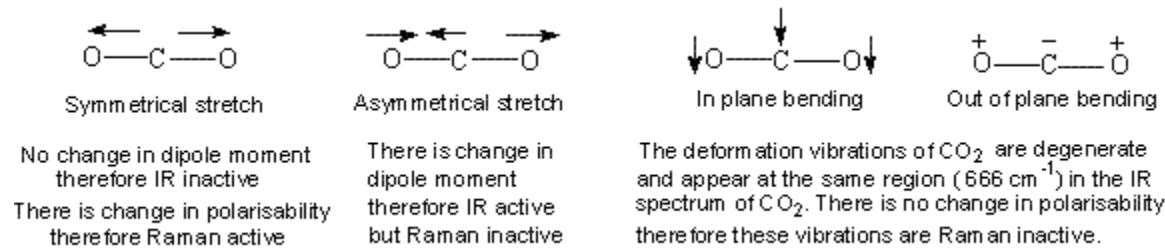
molecule.	molecule.
Cost of instrumentation is very high	Comparatively inexpensive.

### Mutual Exclusion Principle

In molecules with a center of symmetry it is observed that vibrations that are Raman active are IR inactive and vice-versa, this is called the Principle of mutual exclusion (eg: CO<sub>2</sub>). In molecules with different elements of symmetry, certain bands may be active in IR, Raman, both or neither. For a complex molecule that has no symmetry except identity element, all of the normal modes are active in both IR and Raman. In both types the neighbouring strong bands may obscure weak bands, while others may be intrinsically too weak to be observed even if they are theoretically “allowed”.

In general the strong bands in the IR spectrum of a compound corresponds to weak bands in the Raman and vice versa. This complimentary nature is due to the electrical characteristic of the vibration. If a bond is strongly polarised, a small change in its length such as that occurs during a vibration, will have only a small additional effect on polarisation. Vibrations involving polar bonds (C-O , N-O , O-H) are therefore, comparatively weak Raman scatterers. Such polarised bonds, however, carry their charges during the vibrational motion, (unless neutralised by symmetry factors), which results in a large net dipole moment change and produce strong IR absorption band. Conversely, relatively neutral bonds ( C-C , C-H , C=C ) suffer large changes in polarisability during a vibration. But the dipole moment is not similarly affected and vibrations that predominantly involve this type of bond are strong Raman scatterers but weak in the IR.

In molecules having inversion center, none of the normal modes of vibrations will be both Raman and IR active. This is known as “mutual exclusion principle”. A simple molecule which obeys this principle is CO<sub>2</sub>. Carbon dioxide has an inversion center or center of symmetry. The following are its normal modes of vibrations. The IR and Raman active modes are indicated below each type of vibration.



## **References**

1. Kemp W., Applications of Spectroscopy, English Language Book Society, 1987.
2. Skoog D. A., West D. M., Holler f. J., and Crouch S. R., Fundamentals of Analytical Chemistry, 9th Edition, Wadsworth Publishing Co. Inc., 2012

## **Question Bank**

### **Part A**

1. Mention the use of IR radiation in vibrational spectroscopy.
2. Write the important conditions for IR absorption by molecules.
3. Calculate the number of vibrational degree of freedom in CO<sub>2</sub>, H<sub>2</sub>O molecules
4. Give the expression relating force constant and wavenumber used in IR spectroscopy.
5. Differentiate functional and finger print regions in vibrational spectroscopy.
6. What is Rayleigh scattering?
7. What is Raman scattering?
8. Compare Stokes and anti-Stokes lines in IR spectroscopy.
9. What is mutual exclusion principle?
10. Compare Raman and IR spectroscopic techniques.

### **Part B**

1. Discuss the different types of vibrational transitions.
2. Explain the instrumentation of IR spectroscopy with a neat block diagram.
3. Elaborate on the structural determination of molecules by Raman spectroscopy.
4. Write short note on mutual exclusion principle.
5. Compare and contrast IR and Raman spectroscopic methods of analysis.
6. Write briefly on the selection rule in IR spectroscopy.



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**UNIT – IV– NMR SPECTROSCOPY – SCY1612**

## Introduction

Nuclear Magnetic Resonance (NMR) spectroscopy takes advantage of the magnetic properties of certain nuclei and records the absorption of energy between quantized nuclear energy levels. In an NMR experiment, the spectrometer is tuned to the frequency of a *particular* nucleus and the spectrum reveals all such nuclei in the molecule being investigated. It is thus a very powerful technique, the closest analogy being a powerful microscope that allows the chemist to "see" the structure of molecules in solution.

## Theory

NMR is possible owing to the magnetic properties of certain nuclei. In addition to charge and mass, which all nuclei have, various nuclei also possess a property called *nuclear spin*, which means that they behave as if they were spinning. Since nuclei have a charge, they generate a magnetic field with an associated *magnetic moment*.

There are useful empirical rules relating mass number, atomic number ( $Z$ ) and *nuclear spin quantum number* ( $I$ ):

Mass Number	$Z$	$I$
even	even	0
odd	even or odd	$\frac{1}{2}, \frac{3}{2}, \frac{5}{2}, \dots$
even	odd	$1, 2, 3, \dots$

Since NMR depends on the existence of a nuclear spin, nuclei with  $I = 0$  have no NMR spectrum (e.g.,  $^{12}\text{C}$ ,  $^{16}\text{O}$ ,  $^{18}\text{O}$ ). From standpoint of generating NMR spectra, the most important class of nuclei are those with  $I = \frac{1}{2}$ . Nuclei with  $I > \frac{1}{2}$  (e.g.,  $^{11}\text{B}$ ,  $I = \frac{3}{2}$ ;  $^{14}\text{N}$ ,  $I = 1$ ) have *quadrupole moments*, a non-spherical distribution of nuclear charge, which results in broad absorption lines and makes observation of spectra more difficult. The quadrupole moment can even affect the lineshape of neighbouring nuclei. For example, resonances of protons bonded to nitrogen or boron atoms are generally broad in  $^1\text{H}$  NMR spectra. We shall thus be primarily concerned with nuclei where  $I = \frac{1}{2}$ , but the effect that quadrupolar nuclei can have on the NMR spectra of  $I = \frac{1}{2}$  nuclei should be remembered. A listing of isotopes with  $I = \frac{1}{2}$  is provided in Table 1.

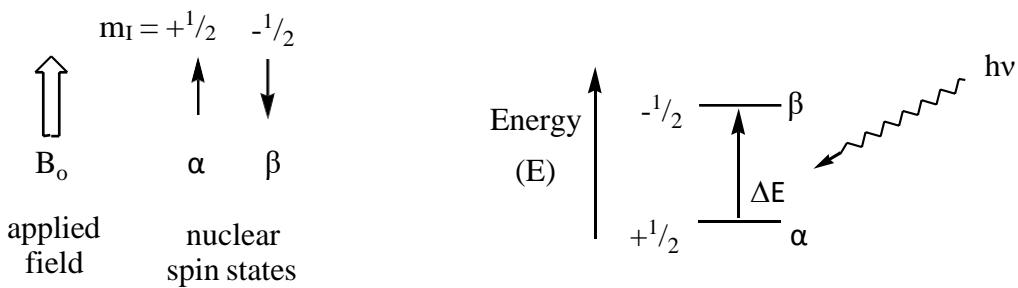
**Table 1:** Natural abundances of isotopes with  $I = \frac{1}{2}$ .

Isotope	Natural Abundance (%)	Isotope	Natural Abundance (%)	Isotope	Natural Abundance (%)
$^1\text{H}$	100	$^{107}\text{Ag}$	51.35	$^{129}\text{Xe}$	26.44
$^{13}\text{C}$	1.108	$^{109}\text{Ag}$	48.65	$^{169}\text{Tm}$	100

<sup>15</sup> N	0.365	<sup>111</sup> Cd	12.75	<sup>183</sup> W	14.4
<sup>19</sup> F	100	<sup>113</sup> Cd	12.26	<sup>187</sup> Os	1.64
<sup>29</sup> Si	4.71	<sup>115</sup> Sn	0.34	<sup>195</sup> Pt	33.8
<sup>31</sup> P	100	<sup>117</sup> Sn	7.57	<sup>199</sup> Hg	16.84
<sup>57</sup> Fe	2.17	<sup>119</sup> Sn	8.58	<sup>203</sup> Tl	29.50
<sup>77</sup> Se	7.58	<sup>123</sup> Te	0.87	<sup>205</sup> Tl	70.50
<sup>89</sup> Y	100	<sup>125</sup> Te	6.99	<sup>207</sup> Pb	21.7
<sup>103</sup> Rh	100				

In an NMR experiment, the sample is placed in a strong magnetic field,  $B_o$ . Since the spins of the magnetic nuclei are quantized, they can have only certain well-defined values. If we have nuclei with  $I = 1/2$  (e.g., <sup>1</sup>H, <sup>31</sup>P), the spins can orient only in two directions: either with ( $m_I = +1/2$ ,  $\alpha$ ) or against ( $m_I = -1/2$ ,  $\beta$ ) the applied field. NMR transitions are allowed for cases where  $\Delta m_I = \pm 1$ . There is an energy difference,  $\Delta E$ , between the two states, and this is given by

$$\Delta E = h\nu = (h/2\pi\gamma) B_o \text{ or } \nu = (1/2\pi\gamma) B_o$$



where  $h$  is Planck's constant,  $\gamma$  is the gyromagnetic ratio (a constant characteristic of each nucleus)\*, and  $B_o$  is the applied magnetic field. When the energy of the incoming radiation matches (is in *resonance* with) the energy difference between the spin states, energy is absorbed and the nucleus is promoted from the lower  $+^{1/2}$  to the higher  $-^{1/2}$  spin state. Since the sign of  $m_I$  changes, this is sometimes referred to as a "spin flip". NMR transitions occur in the *radio frequency* (rf) range of the electromagnetic spectrum. The absorption of rf energy is electronically detected and is displayed as an NMR spectrum.

The above equation is very important since it shows that  $\Delta E$  depends only on  $\gamma$  and  $B_o$ . The gyromagnetic ratio,  $\gamma$ , is an intrinsic property of the magnetic nucleus. Therefore, each type of nucleus has a distinct and characteristic value of  $\gamma$ . Accordingly, the NMR experiment must be tuned for a *specific nucleus* and one must record a *different* NMR spectrum for each NMR active nucleus of interest. Conversely, you do not have to worry about observing signals from different nuclei on the same NMR spectrum. In order to gather all NMR knowledge about a molecule such as  $\text{PH}_3$ , we would record two different NMR spectra - a  $^1\text{H}$  NMR spectrum to observe the  $^1\text{H}$  nuclei and a  $^{31}\text{P}$  NMR spectrum to observe the  $^{31}\text{P}$  nucleus. We would not observe the  $^{31}\text{P}$  nucleus in a  $^1\text{H}$  NMR spectrum and *vice-versa*.

The above equation also reveals that  $\Delta E$  is directly proportional to  $B_o$ , the external magnetic field. The higher the external field, the greater is the energy separation between the  $\alpha$  ( $m_I = +^{1/2}$ ) and  $\beta$  ( $m_I = -^{1/2}$ ) spin states. Recalling that  $E = hv$ , another way of saying this is that the *resonance frequency* of the nucleus increases with increasing  $B_o$  since if  $E$  increases, so does  $v$ . This is shown in the following table.

$B_o$ (tesla) <sup>‡</sup>	Resonance Frequency ( $v$ , MHz)				
	$^1\text{H}$	$^{13}\text{C}$	$^{11}\text{B}$	$^{19}\text{F}$	$^{31}\text{P}$
2.35	100	25.2	32.1	94.1	40.5
4.70	200	50.4	64.2	188.2	81.0

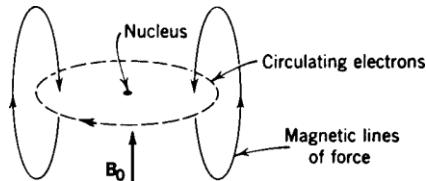
<sup>‡</sup>a *tesla* is a unit describing magnetic field strength

Note that *all*  $I = \frac{1}{2}$  nuclei behave according to the same theoretical principles - although  $^1\text{H}$  NMR spectroscopy is the most commonly practiced,  $^{19}\text{F}$  and  $^{31}\text{P}$  NMR spectra are generated in exactly the same way as a  $^1\text{H}$  NMR spectrum. The main difference between the different  $I = \frac{1}{2}$  nuclei is that the resonance frequency is changed when recording the spectrum.

### Chemical Shift

The resonance frequency is determined only by  $\gamma$  and  $B_0$ , therefore, all atoms of a given nucleus in a molecule (*e.g.*, all  $^1\text{H}$  nuclei) should resonate at the same frequency. If this were the case, the only thing NMR could tell us is whether a molecule contains NMR active nuclei ( $^1\text{H}$ ,  $^{31}\text{P}$ ,  $^{13}\text{C}$ , etc.). Fortunately, the frequency of the NMR absorptions of a given nucleus also depends on the *chemical environment* of the nucleus. The variation of the resonance frequency with chemical environment is termed the *chemical shift*, and herein lies the power of the NMR method.

The origin of the chemical shift can be traced to the electrons surrounding the nucleus, and the interaction of the electron cloud with the applied field,  $B_0$ . The reason for this is that circulating electrons also generate a magnetic field that orients itself in the *opposite direction* to the applied field.



The actual field ( $B_{\text{local}}$ ) "felt" by a nucleus is thus *less* than  $B_0$ , and the ability of the electrons to alter the field felt at the nucleus can be expressed by  $\theta$ , the *shielding constant*.

$$B_{\text{local}} = B_0 (1-\theta)$$

Nuclei are said to be *shielded* or *deshielded* depending on the presence or absence of electron density surrounding them. For example, the introduction of an *electron withdrawing group* (*e.g.*, halogen, O, etc.) will reduce the electron density around a nucleus (*deshielding*;  $\delta$  is small) and the resonance frequency will increase. Conversely, an *electron donating substituent* (*e.g.*,  $\text{CH}_x$ ,  $\text{SiH}_x$ ) will cause increased *shielding* ( $\delta$  is large) and lower the resonance frequency.

In reporting chemical shifts, one could use absolute field or absolute frequency, but this would be cumbersome and would result in the chemical shift being dependent upon the applied field. A simpler scale for chemical shifts has been devised. Chemical shifts ( $\delta$ ) are expressed in units of parts per million (ppm) of the spectrometer frequency with respect to a *reference material* whose position is arbitrarily assigned a value of 0.0 ppm.

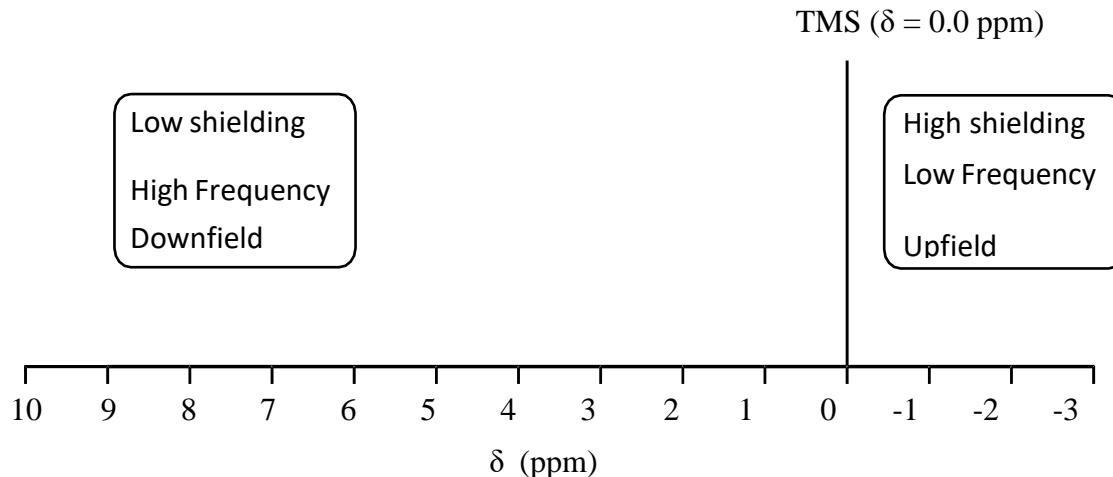
$$\delta = \frac{\text{frequency of signal} - \text{frequency of standard}}{\text{spectrometer frequency}} \times 10^6$$

When expressed in such dimensionless units ( $\delta$  in ppm), the chemical shifts are *invariant of the frequency of the spectrometer* and can be used as molecular parameters. For example, 1.0 ppm at 60 MHz is equal to a separation of 60 Hz, and at 200 MHz, 1.0 ppm equals 200 Hz. Thus, the same two resonances that are separated by 1 ppm at 60 MHz are still 1 ppm apart at 200 MHz, because  $\delta = 60 \text{ Hz}/60 \text{ MHz} = 200 \text{ Hz}/200 \text{ MHz} = 1 \text{ ppm}$ . Therefore, if the *same sample* is run at two different spectrometer frequencies, the chemical shifts of the resonances will be *identical*. Naturally, this statement is only true if the same reference material is used for each spectrum. Different references are used for different nuclei. The most widely accepted reference for  $^1\text{H}$  and  $^{13}\text{C}$  NMR is tetramethylsilane ( $\text{Si}(\text{CH}_3)_4 = \text{TMS}$ ). For  $^{11}\text{B}$  NMR,  $\text{F}_3\text{B} \cdot \text{OEt}_2$  is commonly used, as are  $\text{CFCl}_3$  for  $^{19}\text{F}$  NMR and 85%  $\text{H}_3\text{PO}_4$  for  $^{31}\text{P}$  NMR spectroscopy.

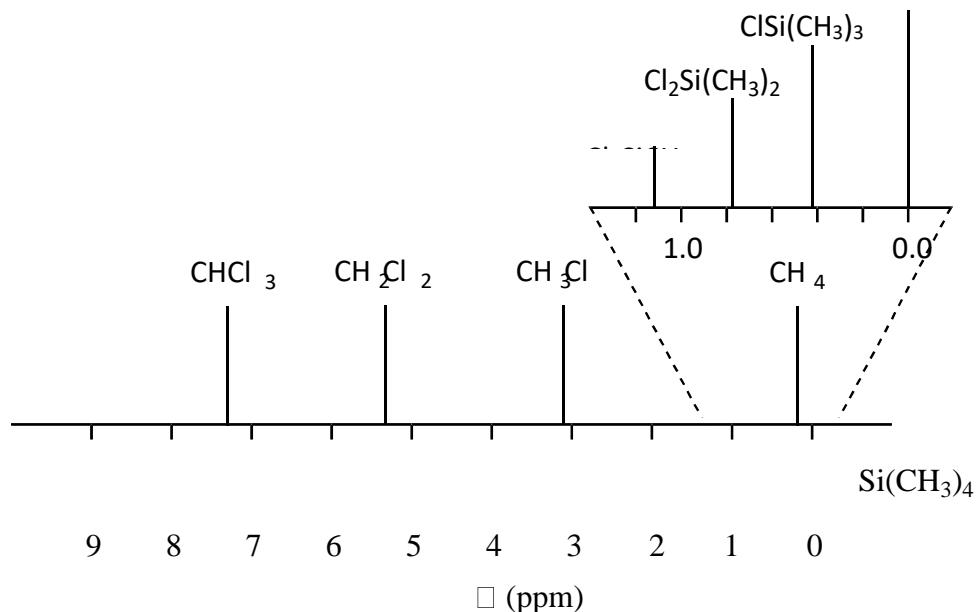
In the past, NMR spectra were obtained by varying the applied field and measuring the chemical shift as a function of the field strength. This gave rise to the terminology of a *downfield shift* for nuclei that were *deshielded* (as they required a lower applied field to bring the nucleus into resonance) and *upfield shift* for *shielded* nuclei. For example, one would say that a resonance at  $\delta$  8.0 ppm is downfield of one at  $\delta$  2.0 ppm, and conversely that the signal at  $\delta$  2.0 ppm was upfield of the signal at  $\delta$  8.0 ppm.

More modern NMR spectrometers generate spectra by varying the frequency,  $\gamma$ , while keeping the magnetic field strength,  $B_o$ , constant. Nevertheless, the upfield/downfield terminology remains in common use. Unfortunately, this results in the confusing situation that  $\delta$  is *positive* in the *downfield* direction (to the left of the standard on spectra) where *resonance*

*frequencies are higher.* Resonances that are *upfield* of the reference appear at *lower frequencies* and have *negative  $\delta$*  values.



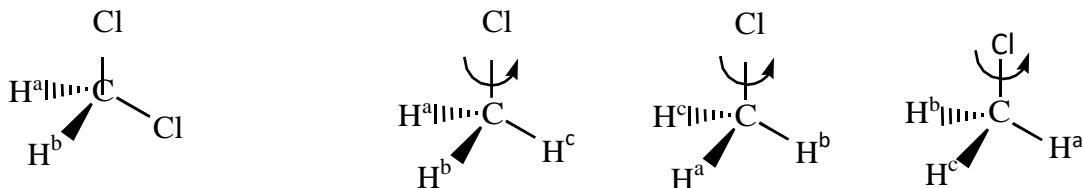
The concept of chemical shift is illustrated in Figure 8. As the hydrogens of methane are increasingly substituted by electron withdrawing chlorine atoms, the chemical shift of the remaining hydrogens shifts further *downfield* as the hydrogens become increasingly *deshielded*. Substitution of the methyl groups of tetramethylsilane (TMS) by chlorine has similar, but far less dramatic, results. In this case, the electron withdrawing chlorine atoms are separated from the hydrogens by carbon and silicon, resulting in less significant deshielding of the  $^1\text{H}$  nuclei.



$^1\text{H}$  NMR Spectra of  $\text{CH}_x\text{Cl}_y$  and  $\text{Cl}_y\text{Si}(\text{CH}_3)_x$ .

One important consequence of chemical shift is that each *chemically different* type of NMR-active nucleus in a molecule will give rise to *its own signal* in an NMR spectrum. Nuclei

are thus referred to as *chemically equivalent* or *chemically inequivalent* in determining how many signals will be observed in an NMR spectrum. For example, both  $\text{CH}_3\text{Cl}$  and  $\text{CH}_2\text{Cl}_2$  provided one resonance each in the  $^1\text{H}$  NMR spectrum in the figure. From this, we can infer that the individual hydrogens in each of these molecules are *chemically equivalent*. From the viewpoint of chemical structure, the reason for this is that hydrogens are related by symmetry elements (reflection through a mirror plane or rotation about an axis) and are thus identical.

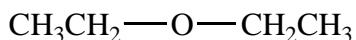


mirror in the plane of the page renders  $\text{H}^{\text{a}} = \text{H}^{\text{b}}$

three-fold rotation axis demonstrates  
 $\text{H}^{\text{a}} = \text{H}^{\text{b}} = \text{H}^{\text{c}}$

Sometimes, determining chemical equivalence or inequivalence is straightforward. The methyl hydrogens in ethanol ( $\text{CH}_3\text{CH}_2\text{OH}$ ) are different from the methylene hydrogens and that both of these are different than the hydroxyl hydrogen; we would thus anticipate three signals in the  $^1\text{H}$  NMR spectrum. Upon further reflection though, why should the hydrogens of the methyl group all be equivalent? The answer is simple when it is recognized that methyl groups rotate freely and rapidly, with the result that each hydrogen experiences the same overall chemical shift as it completes one rotation, a situation analogous to  $\text{CH}_3\text{Cl}$  described above. Therefore, all methyl groups generally give rise to one signal in  $^1\text{H}$  NMR spectra. This concept can generally be applied to analogous groups such as *tert*-butyl,  $\text{C}(\text{CH}_3)_3$ , trimethylsilyl,  $\text{Si}(\text{CH}_3)_3$ , and trifluoromethyl,  $\text{CF}_3$  (in  $^{19}\text{F}$  NMR spectra).

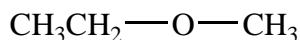
The most general method of determining whether nuclei are chemically equivalent to other nuclei in a molecule is to determine whether they are in the same environment, and whether one nucleus can be related to the other through a symmetry transformation such as rotation or reflection through a mirror plane. Some examples are provided below for illustration.



The  $\text{CH}_2$  groups are equivalent and the  $\text{CH}_3$  groups are equivalent. 2 signals in either the  $^1\text{H}$  or  $^{13}\text{C}$  NMR spectra



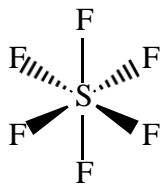
The  $\text{CH}_2$  groups are inequivalent. 3 signals in either the  $^1\text{H}$  or  $^{13}\text{C}$  NMR spectra



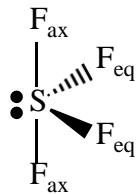
The  $\text{CH}_3$  groups are inequivalent. 3 signals in either the  $^1\text{H}$  or  $^{13}\text{C}$  NMR spectra



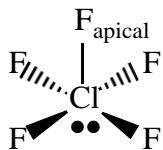
There are two distinct sets of  $\text{CH}_2$  groups. 2 signals in either the  $^1\text{H}$  or  $^{13}\text{C}$  NMR spectra



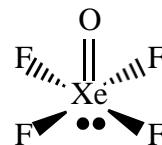
$\text{SF}_6$  is a highly symmetrical octahedral molecule. 1 signal in the  $^{19}\text{F}$  NMR spectrum



The axial (ax) and equatorial (eq) fluorines are chemically inequivalent 2 signals in the  $^{19}\text{F}$  NMR spectrum



The apical fluorine is chemically distinct from the four fluorines in the square base 2 signals in the  $^{19}\text{F}$  NMR spectrum



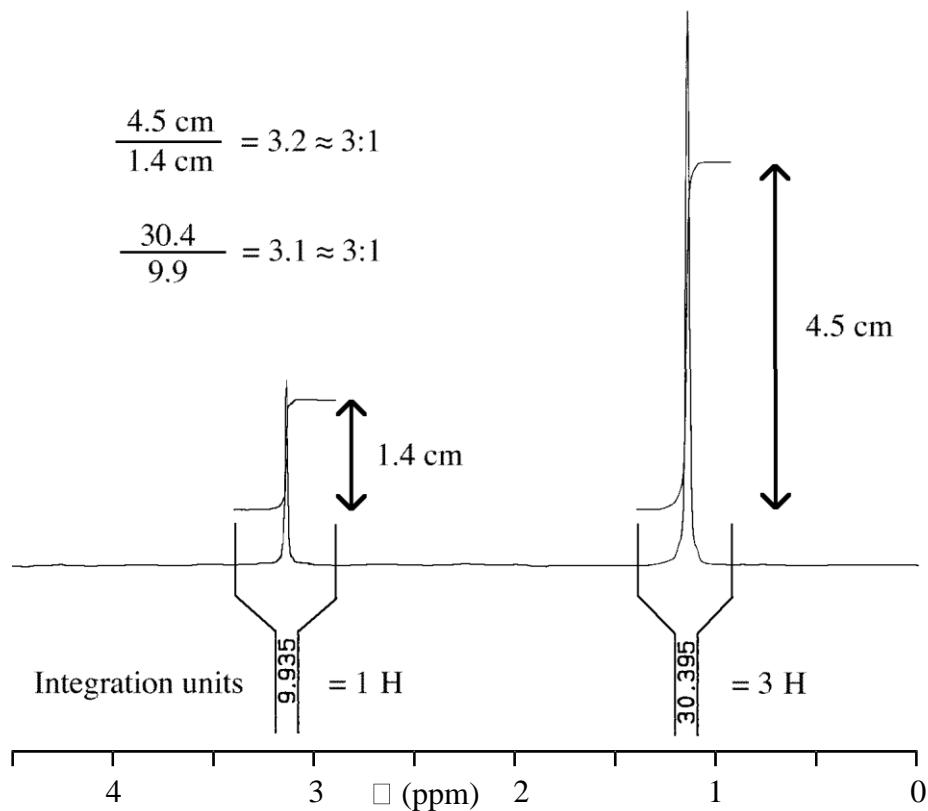
The four fluorine nuclei in the square base are chemically equivalent 1 signal in the  $^{19}\text{F}$  NMR spectrum

## Integration

The area under each NMR absorption peak can be electronically *integrated* to determine the *relative number of nuclei* responsible for each peak. The integral of each peak can be provided numerically, and is often accompanied by a line that represents the integration graphically. Intensities of signals can be compared within a particular NMR spectrum only. For example,  $^1\text{H}$  intensities cannot be compared to those of  $^{19}\text{F}$  or  $^{31}\text{P}$  nuclei. It is important to note that the integration of a peak is a relative number and does not give the *absolute number* of nuclei that cause the signal. Thus, the  $^1\text{H}$  NMR spectrum of  $\text{H}_3\text{C}-\text{SiH}_3$  will show two peaks in a 1:1 ratio, as will the  $^1\text{H}$  NMR spectrum of  $(\text{H}_3\text{C})_3\text{C}-\text{Si}(\text{CH}_3)_3$ . This is simply because the ratios  $3:3 = 9:9 = 1:1$ . Nonetheless, the integrated intensities of the signals in an NMR spectrum are a vital piece of the puzzle.

The concept of integration, and also that of chemical shift, is illustrated by Figure 9. Determining integration ratios is an exercise in finding the greatest common divisor for the series of peaks (the largest whole number divisor that will produce a whole number ratio). In the above example, this value is either 1.4 cm or 9.9 integration units. It should be remembered that integration is a measurement that is subject to error; it is common for the error in integrated intensity to approach 5 - 10 %. The ratio of the integrated peak intensities is  $1:3 = 3:9$ , allowing us to assign the resonance at  $\delta$  3.21 to the methyl group and that at  $\delta$  1.20 to the  $(\text{CH}_3)_3\text{C}$  group. It is important to note that the hydrogens of the  $(\text{CH}_3)_3\text{C}$  group are more *shielded* than the  $\text{CH}_3$

group. This occurs because the  $\text{CH}_3$  group is directly adjacent to the electron withdrawing oxygen, but the corresponding methyl protons in the  $(\text{CH}_3)_3\text{C}$  group are separated from oxygen by a second intervening carbon center.



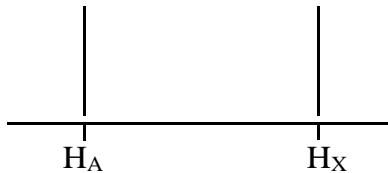
**Figure 1.**  $^1\text{H}$  NMR Spectrum of  $\text{CH}_3\text{OC}(\text{CH}_3)_3$ .

At this stage, we can begin to appreciate how NMR resembles a molecular microscope. For example, at one frequency we could "see" the various protons, while the carbons, fluorines, phosphorus, and even certain metal nuclei could be observed at other frequencies. Within one spectrum, we can make use of the position (*chemical shift*) and *integrated intensity* of the different signals to assign particular molecular fragments responsible for them, and to build up a model of the molecule. There is one more aspect of NMR that is extremely helpful in determining how to connect the parts together.

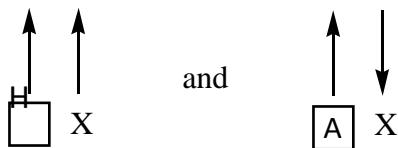
### Spin-Spin Splitting (Coupling)

The appearance of a resonance may be very different when there are other *neighbouring* magnetic nuclei. The reason for this is that the nucleus under observation will interact with the magnetic spins of the different neighbouring nuclei.

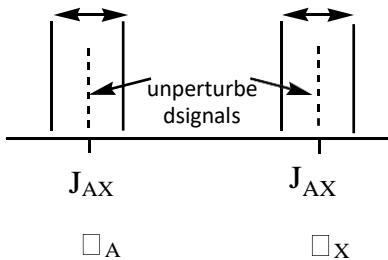
The simplest case is that of two protons having significantly different chemical shifts (designated A and X). Considering chemical shift and integration only, we could represent the spectrum as:



Both protons have a spin of  $1/2$ , and both can exist in the  $+1/2$  and  $-1/2$  spin states. Now, it turns out that the magnetic environment of  $H_A$  is slightly different when  $H_X$  is in the  $+1/2$  state than when it is in the  $-1/2$  state. This can be represented pictorially with arrows (pointing either up or down) representing the two spin states of  $H_X$ .

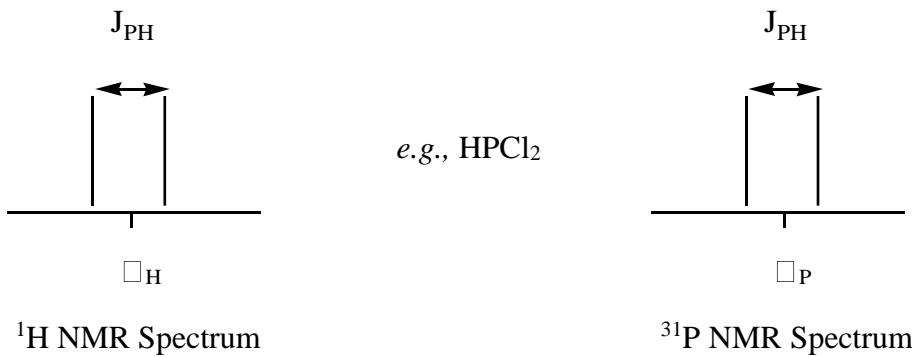


As a result,  $H_A$  will split into two lines, each half the intensity of the unperturbed signal. Similarly,  $H_A$  will influence  $H_X$  which becomes a *doublet* also. The *splitting*, or *coupling*, is symmetrical about the unperturbed resonances  $H_A$  and  $H_X$ , and is described by the means of a *coupling constant*,  $J_{AX}$ , which has units of Hz.



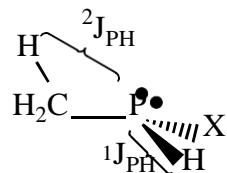
Note that the magnitude of  $J_{AX}$  is *identical* at both signals - coupled nuclei must share the *same* coupling constant.

In a similar way, the resonance of a proton attached to phosphorus will be a doublet, since the phosphorus nucleus has  $I = 1/2$  and may be in the  $+1/2$  or  $-1/2$  state. However, the key distinction here is that we are dealing with two different nuclei, and thus two different NMR spectra. *Each* NMR spectrum ( $^1H$  and  $^{31}P$ ) will show *one doublet* with a  $J_{PH}$  coupling constant that is identical in magnitude. Recall that we cannot "see" a  $^{31}P$  nucleus in a  $^1H$  NMR spectrum and vice-versa. Nonetheless, the splitting of the peaks into doublets in each spectrum tells us that the  $^1H$  and  $^{31}P$  nuclei are interacting.

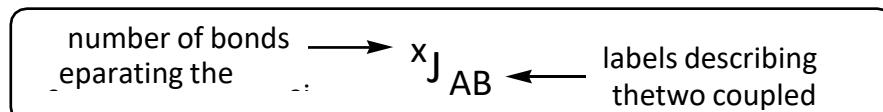


To review, the influence of the neighbouring spins is called *spin-spin coupling* and NMR peaks are split into *multiplets* as a result. The separation between the two peaks is called the *coupling constant*, J, which is expressed in Hz. Spin-spin coupling has the following characteristics:

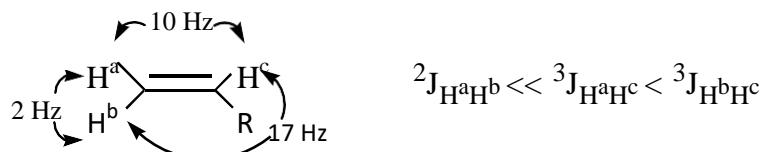
- the *magnitude* of J measures how strongly the nuclear spins interact with each other.
- coupling is normally a through-bond interaction, and is proportional to the product of the gyromagnetic ratios of the coupled nuclei. For example,  $^1J_{CH} = 124$  Hz for  $^1H$ - $^{13}C$  coupling in CH<sub>4</sub>, and  $^1J_{SnH} = 1931$  Hz for  $^{119}Sn$ -H coupling in SnH<sub>4</sub>. This happens because  $\delta(^{119}Sn)$  is much larger than  $\delta(^{13}C)$ .
- since coupling occurs through chemical bonds, the magnitude of J normally falls off rapidly as the number of intervening bonds increases. e.g.,  $^1J_{PH} \sim 700$ ;  $^2J_{PH} \sim 20$  Hz in



Coupling constants are thus labeled to show the *types of nuclei* and the *number of bonds separating the nuclei* that give rise to spin-spin splitting.



- since spin-spin coupling is a through-bond interaction, it is sensitive to the orientation of the bonds between two interacting nuclei. *This is particularly important for two-bond coupling constants.* The influence of the orientation of the two coupled nuclei can occasionally render  $^2J < ^3J$ . For example,



$^1J$  is *not* affected by the orientation of the coupled nuclei, so it is generally true that  $^1J \gg ^2J$  or  $^3J$ , but it is *not* always true that  $^2J > ^3J$ .

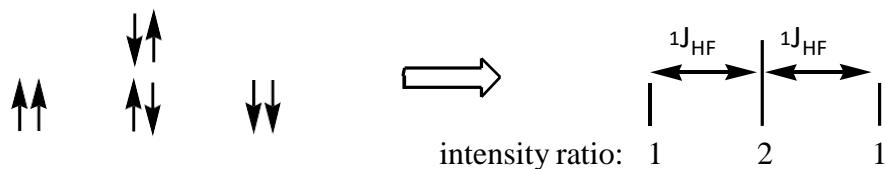
- spin-spin interactions are *independent of the strength of the applied field*. The spacing (in Hz) between lines at two different field strengths *will be the same if it is due to coupling*, but will be proportional to the field strength if it is due to a difference in chemical shift.

**Table 2:** Typical Coupling Constant Ranges (in Hz)

x	Coupled Nuclei (AB in ${}^xJ_{AB}$ )			
	HH	CH	PH <sup>b</sup>	PC <sup>b</sup>
1	—	115 - 250	630 - 710	120 - 180
2 <sup>a</sup>	2 - 30	5 - 60	7 - 13	5 - 40
3	2 - 17	2 - 20	6 - 11	5 - 11
4	—	—	0 - 1	—

<sup>a</sup>Two bond couplings are particularly sensitive to the geometrical arrangement of the nuclei, which in some cases may render  $^2J_{AB} < ^3J_{AB}$ . <sup>b</sup>Restricted to acyclic compounds.

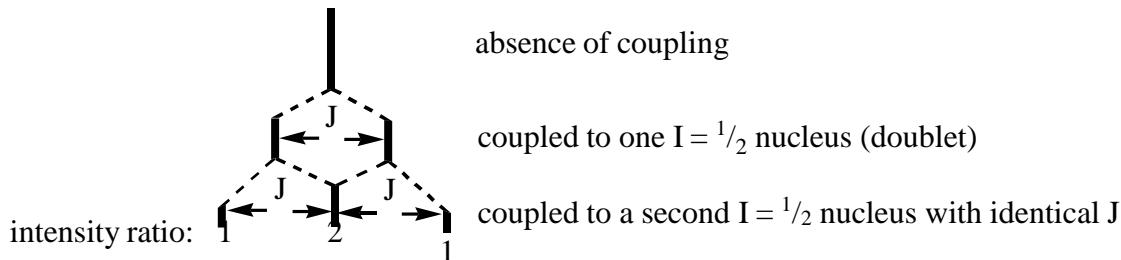
Cases involving more than two nuclei with  $I = 1/2$  are direct extensions of the above. However, because there are more nuclear spins interacting, the *pattern* of lines observed in the NMR spectrum becomes more complicated. For example, let's consider the  $^1H$  NMR spectrum of the  $HF_2^-$  anion (*i.e.*,  $[F-H-F]^-$ ). We are observing the  $^1H$  nucleus, but it is coupled to two chemically equivalent  $^{19}F$  ( $I = 1/2$ ) nuclei. There are four ways that we can arrange the nuclear spins of the two fluorine nuclei, but only three different energy states are created, as is explained below:



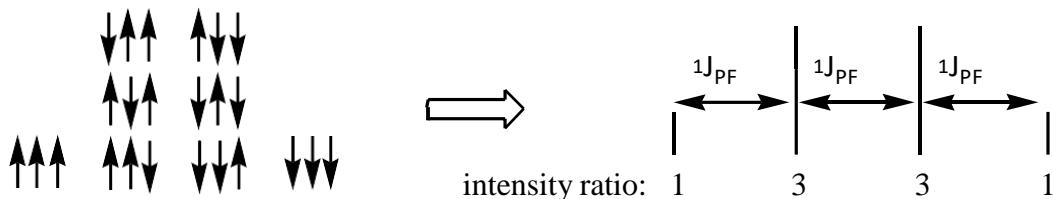
Extending what we learned about the generation of a doublet, we can clearly see that the  $^1H$  environment where both  $^{19}F$  spins are “up” is different from that where both  $^{19}F$  spins are “down”. However, we can also arrange things so that one  $^{19}F$  spin is “up” and the other is “down”. The latter case is *degenerate*; that is, there is more than one way of accomplishing an “up/down” arrangement of nuclei, but each “up/down” arrangement has the same energy. As a result, a pattern of three peaks (or *triplet*) with an intensity pattern of 1:2:1 is generated as shown above. It is important to note that each line in the triplet is separated by the same  $^1J_{HF}$  coupling

constant. As we would expect, the  $^{19}\text{F}$  NMR spectrum of  $\text{HF}_2^-$  would show a doublet because the fluorine nuclei are chemically equivalent and couple to one  $^1\text{H}$  nucleus.

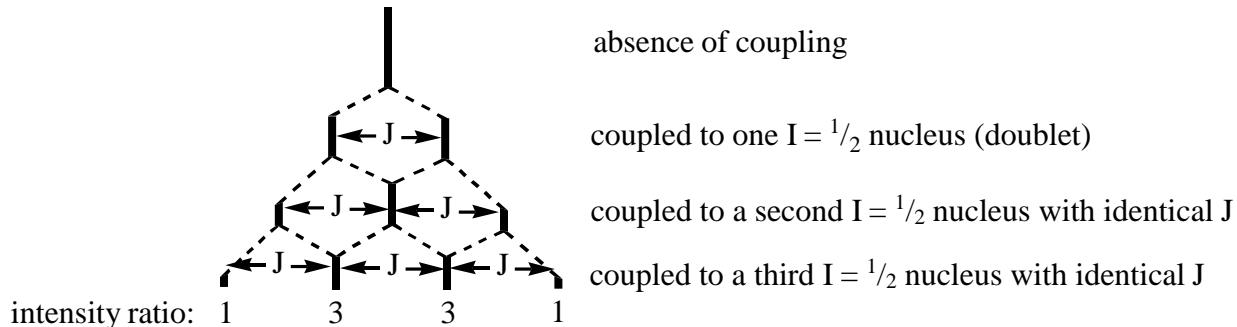
Another way of looking at this is to begin with a singlet for the  $^1\text{H}$  nucleus and then couple each  $^{19}\text{F}$  nucleus one step at a time. The coupling of the first  $^{19}\text{F}$  nucleus generates a doublet. When each line in this doublet is *split again* into a doublet, they overlap identically at the center of the signal, generating a single line of intensity two relative to each outer line of intensity one:



When a similar exercise is undertaken for the  $^{31}\text{P}$  NMR spectrum of  $\text{PF}_3$ , the nuclear spins of the three equivalent  $^{19}\text{F}$  nuclei can be arranged in four ways to generate a *quartet*:



or we can split a singlet into doublets three times to accomplish the same transformation:



In this case, when each line at the triplet stage is split again into doublets, the intensity of the overlapping peaks is not identical; a signal of relative intensity two (from the middle peak) overlaps with a signal of intensity one (from the outer peak) to create a peak of intensity three.

Fortunately, the pattern of peaks generated by the interaction of  $I = 1/2$  nuclei can be easily generated by remembering that *one nucleus is split by (n) equivalent nuclei into (n+1) peaks*, each separated by the coupling constant,  $^XJ_{AB}$ . The number of peaks is referred to as the *multiplicity*. The intensity pattern is a direct consequence of the number of combinations of the various nuclear spins that are possible and is described by a series of binomial coefficients. In practice, it is easiest to determine the intensity pattern by use of a mnemonic device such as Pascal's triangle.

<u>n</u>	<u>n+1</u>	<u>Intensity</u>	<u>Multiplicity</u>	<u>Pattern</u>	<u>Example</u>
0	1	1	singlet (s)		$\text{CH}_4$
1	2	1 : 1	doublet (d)		$(\text{CH}_3)_2\text{CHCl}$
2	3	1 : 2 : 1	triplet (t)		$\text{CH}_3\text{CH}_2\text{Cl}$
3	4	1 : 3 : 3 : 1	quartet (q)		$\text{CH}_3\text{CH}_2\text{Cl}$
4	5	1 : 4 : 6 : 4 : 1	quintet		$^{29}\text{SiF}_4$
5	6	1 : 5 : 10 : 10 : 5 : 1	sextet		$\text{PF}_5$
6	7	1 : 6 : 15 : 20 : 15 : 6 : 1	septet		$(\text{CH}_3)_2\text{CHCl}$
			etc.		

The phenomenon of spin-spin coupling and its effect on the appearance and interpretation of NMR spectra is best described by example, several of which appear on the following pages.

### Analyzing NMR Spectra and Reporting Results

NMR spectra contain a wealth of information and must be analyzed in a methodical way. Much like a jig-saw puzzle, all of the pieces (*i.e.*, chemical shift, integration, multiplicity, and coupling constants) must fit together properly. As with a puzzle, you may find that your initial conclusion is incorrect because several “pieces” are out of place. It is important to approach the problem in a creative way and investigate alternate solutions. The most straightforward method for analyzing NMR spectra is:

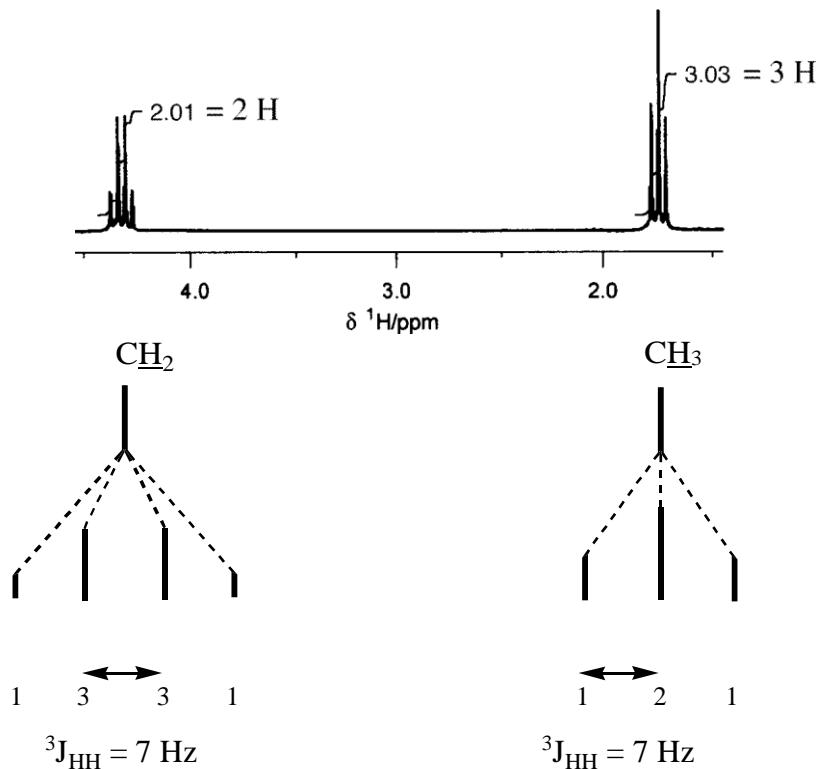
- 1) identify signals by chemical shift and determine their relative integration
- 2) identify the multiplicity of the peaks and calculate coupling constants.

Many students are tempted to “leap in” and attempt to analyze coupling patterns first, but the coupling pattern may not correlate if the integration ratio of the coupled multiplets has not already been deduced. Above all else, remember to double-check that the assignments make sense. It is often a good practice to use your results to generate a simple stick-diagram of the

NMR spectrum. If the stick-diagram matches the actual spectrum exactly, then you have correctly analyzed the NMR spectrum.

Chemical shifts should generally be reported to two decimal places. Multiplicities may be written out (*e.g.*, “triplet”) or expressed in terms of common abbreviations (*e.g.*, “t”). Coupling constants are commonly reported as whole numbers, but may be expressed to one decimal place if the spectrum is of sufficiently high resolution. The coupling constants should be properly labeled (*i.e.*,  ${}^xJ_{AB}$ ) to show the nuclei that are coupled; if there is more than one NMR active isotope for a nucleus (*e.g.*,  ${}^{117}\text{Sn}/{}^{119}\text{Sn}$ ), it should be clearly defined which is involved in the coupling interaction you are describing.

**Example :**  $^1\text{H}$  NMR spectrum of  $(\text{CH}_3\text{CH}_2\text{O})_4\text{Si}$ .



1. On the basis of chemical shift and integration, a  $\text{CH}_2$  signal of intensity two appears downfield of a  $\text{CH}_3$  signal of intensity three.
2. The  $\text{CH}_3$  signal will be split into a triplet by interaction with the two equivalent methylene protons ( $n = 2$  and thus  $n+1 = 3$ ). The  $\text{CH}_2$  signal is split into quartet by the three equivalent  $\text{CH}_3$  protons ( $n = 3$  and thus  $n+1 = 4$ ).
3. The spacing is  $^3\text{J}_{\text{HH}} = 7 \text{ Hz}$ , and is the same in both regions.
4. The relative peak heights in the methyl triplet will be  $1 : 2 : 1$  and will be  $1 : 3 : 3 : 1$  for the methylene quartet. Recalling the overall integration, the methyl absorption must be  $^{3/2}$  as intense as methylene absorption as the total signal intensity is proportional to the number of nuclei; the integration ratio is  $3.03 \div 2.01 \sim ^{3/2}$ .

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## Question Bank

### Part A

1. What type of EMR is used in NMR. Why?
2. Differentiate shielding and deshielding in NMR.
3. Mention the use of chemical shift in NMR.
4. Define spin-spin coupling in NMR spectroscopy.
5. Give the significance of splitting of signals in NMR.
6. Relate the effect of spin quantum number in NMR spectroscopy.
7. What is spin flip in NMR spectroscopy?
8. What is shielding constant and bring out its role in NMR spectroscopy.
9. What is the principle of NMR spectroscopy?

**Part B**

1. Discuss shielding and deshielding effects in NMR spectroscopy.
2. Explain chemical shift in NMR.
3. Elaborate on spin spin coupling in NMR with examples.
4. Explain the role of reference compounds in NMR.
5. Explain the significance of spin quantum number values in NMR spectroscopy.



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**SCHOOL OF SCIENCE AND HUMANITIES**

**DEPARTMENT OF CHEMISTRY**

**UNIT – V– MASS SPECTROMETRY – SCY1612**

Mass spectrometry is an analytical tool useful for measuring the **mass-to-charge ratio** ( $m/z$ ) of one or more molecules present in a sample.

These measurements can be used to calculate the **exact molecular weight** of the sample components.

Mass spectrometers can be used to identify unknown compounds via molecular weight determination, to quantify known compounds, and to determine structure and chemical properties of molecules.

**Mass spectrometer consists of at least these three components:**

- Ionization Source
- Mass Analyzer
- Ion Detection System

### 1. The Ionization Source

Molecules are converted to **gas-phase ions** so that they can be moved about and manipulated by external electric and magnetic fields.

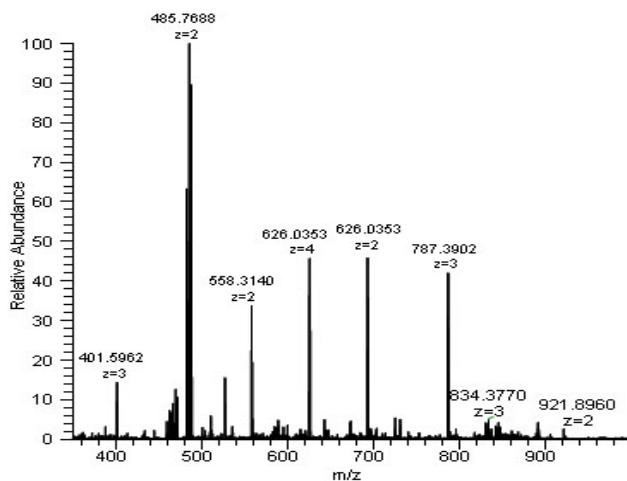
### 2. The Mass Analyzer

Once ionized, the ions are sorted and separated according to **mass-to-charge** ( $m/z$ ) ratios.

### 3. Ion Detection System

The separated ions are then measured and sent to a data system where the  $m/z$  ratios are stored together along with their relative abundance.

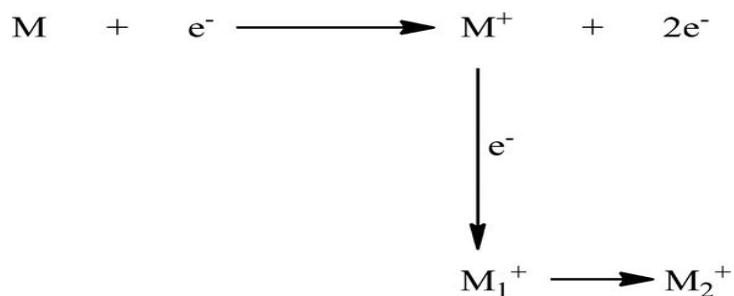
A **mass spectrum** is simply the  $m/z$  ratios of the ions present in a sample plotted against their intensities. Each peak in a mass spectrum shows a component of unique  $m/z$  in the sample, and heights of the peaks gives the relative abundance of the various components in the sample. A mass spectrum of a sample is given below:



## Principle

The mass spectroscopy is based on the positive ion generation. In electron impact ionization technique, the sample under investigation is converted into vapor phase and bombarded with electrons having energy sufficient to knock out one electron from it ( $>10\text{ eV}$ ) to produce a positively charged ion called molecular ion or parent ion which is denoted by  $\text{M}^+$ .

Positively charged molecule  $\text{M}^+$  is often unstable, and with increase in energy (10–70 eV) according to bond strength, they break into fragments called fragment or daughter ion which is denoted by  $\text{M}^{+1}$ . Ions formed are separated in analyzer under the influence of electric and magnetic field and are recorded by the detector to give rise a mass spectrum.



Where,

$\text{M}^+$  = molecular ion

$\text{M}_1^+$  and  $\text{M}_2^+$  = Fragment ions

When a high energy electron collides with a molecule it often ionizes it by knocking away one of the molecular electrons (either bonding or non-bonding). This leaves behind a **molecular ion** (colored red in the following diagram). Residual energy from the collision may cause the molecular ion to fragment into neutral pieces (colored green) and smaller **fragment ions** (colored pink and orange). The molecular ion is a radical cation, but the fragment ions may either be radical cations (pink) or carbocations (orange), depending on the nature of the neutral fragment. An animated display of this ionization process will appear if you click on the ion source of the mass spectrometer diagram.

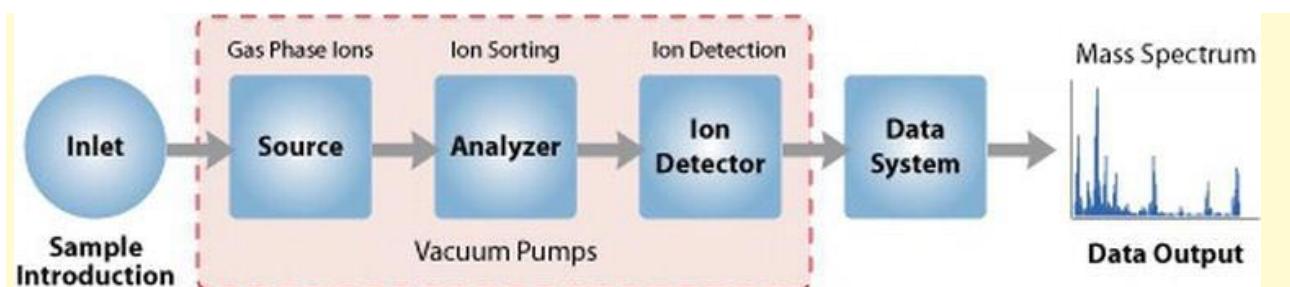
A mass spectrum will usually be presented as a vertical bar graph, in which each bar represents an ion having a specific mass-to-charge ratio ( $\text{m}/\text{z}$ ) and the length of the bar indicates the relative abundance of the ion. The most intense ion is assigned an abundance of 100, and it is referred to as the **base peak**. Most of the ions formed in a mass spectrometer have a single charge, so the  $\text{m}/\text{z}$  value is equivalent to mass itself. Modern mass spectrometers easily distinguish (resolve) ions differing by only a single atomic mass unit (amu), and thus provide completely accurate values for the molecular mass of a compound. The highest-mass ion in a spectrum is normally considered to be the molecular ion, and lower-mass ions are fragments from the molecular ion, assuming the sample is a single pure compound.

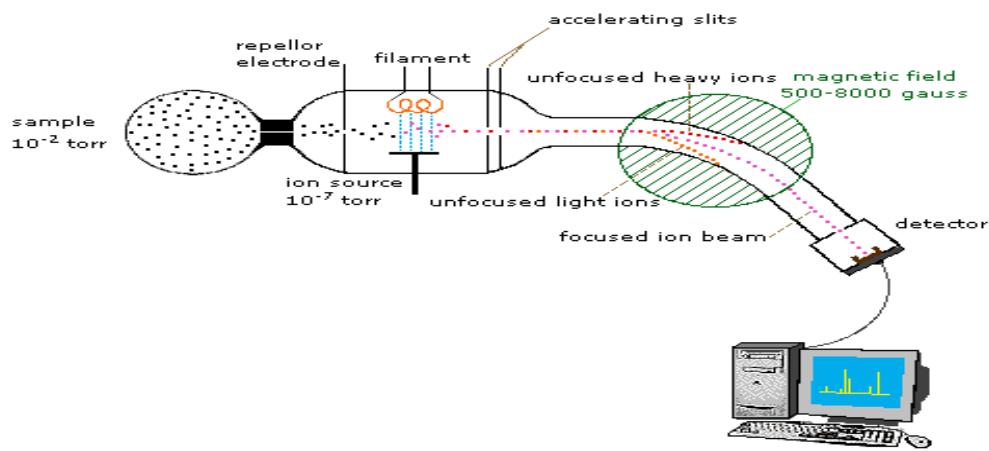
## Components of mass spectrometer

Mass spectrometer mainly consists of following components:

1. Inlet system
2. Ion generation chamber
3. Analyzer tube
4. Ion collector
5. Data collection system

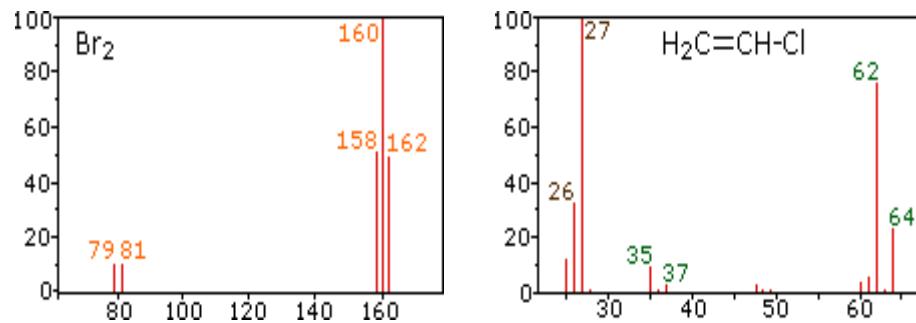
The inlet system transfers the gaseous form of sample into the vacuum of the ion generation chamber of mass spectrometer. In the ion generation chamber, neutral sample molecules are ionized and then accelerated into the mass analyzer tube. The mass analyzer tube is the most important part on which a range of the mass spectrometer depends. This segment separates generated ions, either in space or in time, according to their mass-to-charge ratio ( $m/z$ ). Once the ions are separated, they are collected and detected in ion collector chamber. Then, the signal is transferred to a data collection system for data investigation. The high vacuum is applied between the ion generation chamber, analyzer tube and ion collector. The vacuum system is maintaining the low pressure which minimizes the chances of ion-molecule reaction, scattering and neutralization of the ions. Components of a mass spectrometer are shown in the figure given below.





## Isotopes

Since a mass spectrometer separates and detects ions of slightly different masses, it easily distinguishes different isotopes of a given element. This is manifested most dramatically for compounds containing bromine and chlorine, as illustrated by the following examples. Since molecules of bromine have only two atoms, the spectrum on the left will come as a surprise if a single atomic mass of 80 amu is assumed for Br. The five peaks in this spectrum demonstrate clearly that natural bromine consists of a nearly 50:50 mixture of isotopes having atomic masses of 79 and 81 amu respectively. Thus, the bromine molecule may be composed of two  $^{79}\text{Br}$  atoms (mass 158 amu), two  $^{81}\text{Br}$  atoms (mass 162 amu) or the more probable combination of  $^{79}\text{Br}$ - $^{81}\text{Br}$  (mass 160 amu). Fragmentation of  $\text{Br}_2$  to a bromine cation then gives rise to equal sized ion peaks at 79 and 81 amu.



## Metastable ions

Metastable ions are those that dissociate en route from an ion source, through a mass analyser to an ion detection device. The term metastable refers only to ions that are able to fragment in flight by virtue of internal energy that they acquired within the ion source, not after acceleration therefrom,

nor by collisions with a target gas, nor by radiative excitation as they traverse the apparatus. They are thus unimolecular dissociations.

The ions resulting from decomposition between the source region and magnetic analyzer are called as metastable ions. These appear as broad peaks called metastable ion peaks.

Characteristics of metastable peaks are:

1. These peaks are much broader, that is, they spread over several mass units.
2. These peaks appear in the mass spectrum usually at non-integral m/e values.
3. These peaks are of relatively low abundance or low intensity
4. The metastable ions can be detected by a double focussing mass spectrometer.

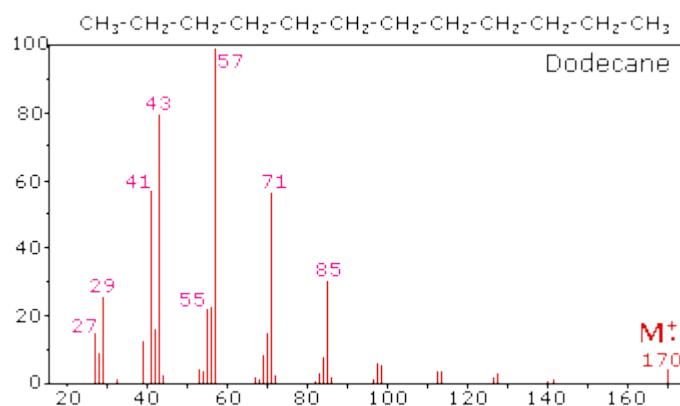
Metastable peaks in the mass spectrum greatly contribute in structure elucidation

### **Fragmentation patterns**

The fragmentation of molecular ions provides a clue to the molecular structure, but if the molecular ion has a lifetime of less than a few microseconds it will not survive long enough to be observed. Without a molecular ion peak as a reference, the difficulty of interpreting a mass spectrum increases markedly. Fortunately, most organic compounds give mass spectra that include a molecular ion, and those that do not often respond successfully to the use of milder ionization conditions. Among simple organic compounds, the most stable molecular ions are those from aromatic rings, other conjugated pi-electron systems and cycloalkanes. Alcohols, ethers and highly branched alkanes generally show the greatest tendency toward fragmentation.

The mass spectrum of dodecane illustrates the behavior of an unbranched alkane. Since there are no heteroatoms in this molecule, there are no non-bonding valence shell electrons. Consequently, the radical cation character of the molecular ion ( $m/z = 170$ ) is delocalized over all the covalent bonds. Fragmentation of C-C bonds occurs because they are usually weaker than C-H bonds, and this produces a mixture of alkyl radicals and alkyl carbocations. The positive charge commonly resides on the smaller fragment, so we see a homologous series of hexyl ( $m/z = 85$ ), pentyl ( $m/z = 71$ ), butyl ( $m/z = 57$ ), propyl ( $m/z = 43$ ), ethyl ( $m/z = 29$ ) and methyl ( $m/z = 15$ ) cations. These are accompanied by a set of corresponding alkenyl carbocations (e.g.  $m/z = 55, 41 \& 27$ ) formed by loss of 2 H. All of the significant fragment ions in this spectrum are even-electron ions. In most alkane spectra the propyl and butyl ions are the most abundant.

The presence of a functional group, particularly one having a heteroatom Y with non-bonding valence electrons (Y = N, O, S, X etc.), can dramatically alter the fragmentation pattern of a compound.



## The Nitrogen Rule

If the molecular mass of an unknown compound to the nearest integer value is an odd number, the compound contains an odd number of nitrogens in its molecular formula. Correspondingly, if the molecular mass is an even number, the compound contains zero or an even number of nitrogens in its molecular formula. This rule, illustrated below, results from nitrogen having a valence of three and an even atomic mass. Consistent with the nitrogen rule, a correct molecular formula for a molecule with an odd molecular mass in the nearest integer value will have the sum of the number of hydrogens plus halides as an odd number. Correspondingly, a correct molecular formula for a molecule with an even molecular mass will have the sum of the number of hydrogens plus halides as an even number.

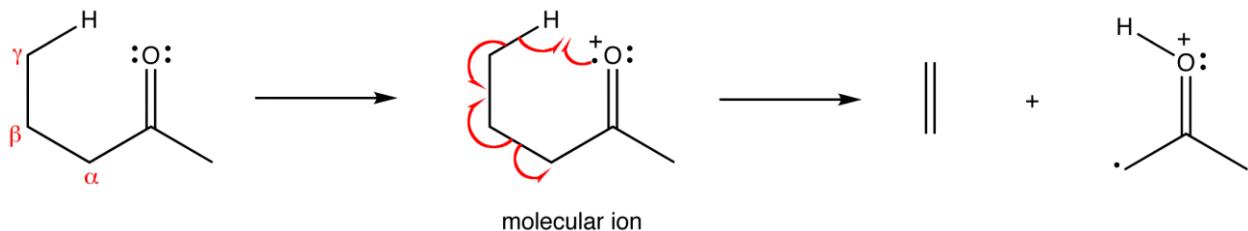
## Examples

The molecular ion for aminoethane (ethylamine),  $[\text{CH}_3\text{CH}_2\text{NH}_2]^+$ , is  $m/z=45$  amu, an odd number; the number of hydrogens is five, also an odd number.

The molecular ion for 1,2-diaminoethane,  $[\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2]^+$ , is  $m/z=60$  amu, an even number; the number of hydrogens is eight, also an even number.

## McLafferty rearrangement

McLafferty rearrangement is a characteristic fragmentation of the molecular ion of a carbonyl compound containing at least one gamma hydrogen, eg:



## **Applications**

### **1. Phytochemical analysis**

Mass spectroscopy is widely employed in phytochemical analysis due to its capability to identify and measure metabolites having very low molecular weight at very low concentration ranges below nanogram per milliliter (ng/mL). Therefore, it is considered as trace analysis methodology.

### **2. Structure elucidation**

Mass spectroscopy has major use in structure elucidation of compounds. Mass spectrum is produced in the form of bar graph which is interpreted by using the following peaks: Base peak, Molecular ion peak, fragment ion peak, metastable ion peak.

### **3. Peptide and protein sequence/structure analysis**

Mass spectroscopy has an important application in analysis of sequence of amino acids in proteins and peptides, that is, analysis of structure of proteins and peptides, and this is employed increasingly. This can be performed by stepwise hydrolysis accompanied with chromatography.

### **4. Clinical studies**

Greater degree of sensitivity is required when analyte quantity is too low and mass spectroscopy due to its higher sensitivity marks a valuable place in clinical analysis.

### **5. Pharmaceutical analysis**

Mass spectroscopy now becomes an irreplaceable tool in all types of drug discoveries due to its high sensitivity, speed, versatility and selectivity.

### **6. Forensic applications**

In forensic study, sample is in minute quantity; therefore, high sensitivity is required for analysis. Mass spectroscopy coupled with gas chromatography emerged as an indispensable tool in forensic field as well as LC–MS has also wide utility in forensic study. In forensic studies, the use of mass spectroscopy is becoming significant because of increase in the demand to investigate use of illegal drugs through analyzing body fluids and tissues.

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## **Question Bank**

### **Part A**

1. What is a molecular ion peak?
2. What are metastable ions?
3. What is m/z value in mass spectrometry?
4. Give the principle of mass spectrometry.
5. Compare molecular ion and base peak in mass spectrometry.
6. Write short note on nitrogen rule.
7. What is McLafferty rearrangement?
8. List out the applications of mass spectrometry.

### **Part B**

1. Explain the instrumentation of mass spectrometry with a neat block diagram.
2. Discuss nitrogen rule in mass spectrometry.
3. Elaborate on fragmentation pattern in mass spectrometry quoting an example.
4. Discuss the formation of molecular ion and base peaks in mass spectrometry.
5. Explain McLafferty rearrangement with examples in mass spectrometry.