

CY 100 ENGINEERING CHEMISTRY



**NEHRU COLLEGE OF ENGINEERING AND RESEARCH CENTRE
(NAAC Accredited)**

(Approved by AICTE, Affiliated to APJ Abdul Kalam Technological University, Kerala)



DEPARTMENT OF MECHATRONICS ENGINEERING

COURSE MATERIALS



CY 100 ENGINEERING CHEMISTRY

VISION OF THE INSTITUTION

To mould true citizens who are millennium leaders and catalysts of change through excellence in education.

MISSION OF THE INSTITUTION

NCERC is committed to transform itself into a center of excellence in Learning and Research in Engineering and Frontier Technology and to impart quality education to mould technically competent citizens with moral integrity, social commitment and ethical values.

We intend to facilitate our students to assimilate the latest technological know-how and to imbibe discipline, culture and spiritually, and to mould them in to technological giants, dedicated research scientists and intellectual leaders of the country who can spread the beams of light and happiness among the poor and the underprivileged.

CY 100 ENGINEERING CHEMISTRY

ABOUT DEPARTMENT

- ◆ Established in: 2013
- ◆ Course offered: B.Tech Mechatronics Engineering
- ◆ Approved by AICTE New Delhi and Accredited by NAAC
- ◆ Affiliated to the University of Dr. A P J Abdul Kalam Technological University.

DEPARTMENT VISION

To develop professionally ethical and socially responsible Mechatronics engineers to serve the humanity through quality professional education.

DEPARTMENT MISSION

- 1) The department is committed to impart the right blend of knowledge and quality education to create professionally ethical and socially responsible graduates.
- 2) The department is committed to impart the awareness to meet the current challenges in technology.
- 3) Establish state-of-the-art laboratories to promote practical knowledge of mechatronics to meet the needs of the society

PROGRAMME EDUCATIONAL OBJECTIVES

- I. Graduates shall have the ability to work in multidisciplinary environment with good professional and commitment.
- II. Graduates shall have the ability to solve the complex engineering problems by applying electrical, mechanical, electronics and computer knowledge and engage in lifelong learning in their profession.
- III. Graduates shall have the ability to lead and contribute in a team with entrepreneur skills, professional, social and ethical responsibilities.
- IV. Graduates shall have ability to acquire scientific and engineering fundamentals necessary for higher studies and research.

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PROGRAM OUTCOME (PO'S)

Engineering Graduates will be able to:

PO 1. Engineering knowledge: Apply the knowledge of mathematics, science, engineering fundamentals, and an engineering specialization to the solution of complex engineering problems.

PO 2. Problem analysis: Identify, formulate, review research literature, and analyze complex engineering problems reaching substantiated conclusions using first principles of mathematics, natural sciences, and engineering sciences.

PO 3. Design/development of solutions: Design solutions for complex engineering problems and design system components or processes that meet the specified needs with appropriate consideration for the public health and safety, and the cultural, societal, and environmental considerations.

PO 4. Conduct investigations of complex problems: Use research-based knowledge and research methods including design of experiments, analysis and interpretation of data, and synthesis of the information to provide valid conclusions.

PO 5. Modern tool usage: Create, select, and apply appropriate techniques, resources, and modern engineering and IT tools including prediction and modeling to complex engineering activities with an understanding of the limitations.

PO 6. The engineer and society: Apply reasoning informed by the contextual knowledge to assess societal, health, safety, legal and cultural issues and the consequent responsibilities relevant to the professional engineering practice.

PO 7. Environment and sustainability: Understand the impact of the professional engineering solutions in societal and environmental contexts, and demonstrate the knowledge of, and need for sustainable development.

PO 8. Ethics: Apply ethical principles and commit to professional ethics and responsibilities and norms of the engineering practice.

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PO 9. Individual and team work: Function effectively as an individual, and as a member or leader in diverse teams, and in multidisciplinary settings.

PO 10. Communication: Communicate effectively on complex engineering activities with the engineering community and with society at large, such as, being able to comprehend and write effective reports and design documentation, make effective presentations, and give and receive clear instructions.

PO 11. Project management and finance: Demonstrate knowledge and understanding of the engineering and management principles and apply these to one's own work, as a member and leader in a team, to manage projects and in multidisciplinary environments.

PO 12. Life-long learning: Recognize the need for, and have the preparation and ability to engage in independent and life-long learning in the broadest context of technological change.

PROGRAM SPECIFIC OUTCOME(PSO'S)

PSO 1: Design and develop Mechatronics systems to solve the complex engineering problem by integrating electronics, mechanical and control systems.

PSO 2: Apply the engineering knowledge to conduct investigations of complex engineering problem related to instrumentation, control, automation, robotics and provide solutions.

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COURSE OUTCOME

After the completion of the course the student will be able to

COURSE OUTCOMES	
CO1	Understand various spectroscopic techniques like UV-Visible , IR , NMR, and its applications
CO2	Apply the basic concepts of electrochemistry to explore its possible applications in various engineering fields
CO3	Apply the knowledge of analytical method for characterizing a chemical mixture of a compound
CO4	Apply the knowledge of conducting polymers and advanced polymers in engineering
CO5	Understand about calorific value of fuels and lubricants and its properties
CO6	Acquire knowledge about various types of water treatment methods to develop skills for treating waste water

CO VS PO'S MAPPING

CO Vs PO														
SUBJECT														
COURSE OUTCOME	PO1	PO2	PO3	PO4	PO5	PO6	PO7	PO8	PO9	PO10	PO11	PO12	PSO1	PSO2
C103.1	3	2	-	3	-	3	-	-	-	-	-	2	-	-
C103.2	3	3	3	-	-	2	-	-	-	-	-	2	-	-
C103.3	2	-	2	3	-	-	-	-	-	-	-	2	-	2
C103.4	2	-	-	-	-	3	3	-	-	-	-	2	2	-
C103.5	3	3	3	2	-	3	3	2	-	-	-	3	-	-
C103.6	3	1	3	3	2	3	3	3	-	-	-	3	-	-
C103	2.7	2.25	2.75	2.75	2	2.8	3	2.5	-	-	-	2.3	2	2
CO ATTAINMENT	2.7	2.25	2.75	2.75	2	2.8	3	2.5	-	-	-	2.3	2	2

Note: H-Highly correlated=3, M-Medium correlated=2, L-Less correlated=1

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SYLLABUS

Course No.	Course Name	L-T-P-Credits	Year of Introduction
CY100	ENGINEERING CHEMISTRY	3-1-0-4	2016
Course Objectives			
To enable the students to acquire knowledge in the concepts of chemistry for engineering applications and to familiarize the students with different application oriented topics like new generation engineering materials, storage devices, different instrumental methods etc. And to develop abilities and skills that are relevant to the study and practice of chemistry.			
Syllabus			
Spectroscopy - Principles and Applications, Electrochemistry - Electrodes, Electrochemical series and applications, Nernst Equation, Potentiometric titration and application, Cells, Instrumental Methods- Thermal Analysis, Chromatography; Conductivity, Chemistry of Engineering Materials, Copolymers, Conducting Polymers, Advanced Polymers, Nano materials, Fuels and Calorific value; Lubricants and their properties, Water Technology - Hardness, Water softening methods, Sewage water Treatment.			
Expected outcome			
The student will be able to apply the knowledge of chemistry and will be equipped to take up chemistry related topics as part of their project works during higher semester of the course.			
References Books:			
<ul style="list-style-type: none"> • Ahad, J., Engineering Chemistry, Jai Publications • Dara, S. S., Engineering Chemistry, S Chand Publishers • Fernandez, A., Engineering Chemistry, Owl Book Publishers, ISBN 9788192863382 • Jain and Jain, Engineering Chemistry, Dhanpat Rai Publishers • Kaurav, Engineering Chemistry with Laboratory Experiments, PHI, ISBN 9788120341746 • Manjooran K. S., Modern Engineering Chemistry, Kannatheri Publication • Seymour, R. B., Introduction to Polymer Chemistry, McGraw Hill • Rath, P., Engineering Chemistry, Cengage Learning, ISBN 9788131526699 • Wiley India, Engineering Chemistry, ISBN 9788126543205 			
Course Plan			
Module	Contents	Hours	Sem. Exam Marks
I	Spectroscopy: Introduction, Beer Lamberts Law (no derivations)(Numericals)	1	15%
	UV-visible spectroscopy - Principle, Instrumentation and applications	2	
	IR spectroscopy - Principle and applications (Numericals)	2	
	¹ H NMR spectroscopy - Principle, chemical shift - spin - spin splitting and applications including MRI(brief), Spectral Problems	4	
II	Electrochemistry: Different types of electrodes (general) – SHE, Calomel electrode, Glass electrode and determination of E ⁰ using SHE & Calomel	2	15%

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	electrode		
	Electrochemical series and its applications.(Numericals)	1	
	Nernst equation - Derivation, application & numericals	2	
	Potentiometric titration - Acid-base and redox titration	2	
	Lithium ion cell and Fuel cell.	1	
FIRST INTERNAL EXAM			
III	Instrumental Methods: Thermal analysis - Principle, instrumentation and applications of TGA and DTA.	3	15%
	Chromatographic methods - Basic principles, column, TLC. Instrumentation and principles of GC and HPLC.	4	
	Conductivity - Measurement of conductivity	1	
IV	Chemistry of Engineering Materials: Copolymers - BS, ABS - Structure and Properties.	1	15%
	Conducting Polymers - Polyaniline, Polypyrrole - Preparation, Structure and Properties.	2	
	OLED – An introduction	1	
	Advanced Polymers – Kevlar, Polybutadiene rubber and silicone rubber: Preparation, Structure and Properties.	2	
	Nanomaterials – Definition, Classification, chemical methods of preparation - hydrolysis and reduction	2	
	Properties and Applications – Carbon Nano Tubes and fullerenes.	1	
SECOND INTERNAL EXAM			
V	Fuels and Lubricants: Fuels - Calorific Value, HCV and LCV - Determination of calorific value of a solid and liquid fuel by Bomb calorimeter - Dulong's formula and Numericals.	3	20%
	Liquid fuel - Petrol and Diesel - Octane number & Cetane number	1	
	Biodiesel - Natural gas.	2	
	Lubricant - Introduction, solid, semisolid and liquid lubricants.	1	
	Properties of lubricants - Viscosity Index, Flash point, Fire point, Cloud point, Pour point and Aniline point.	2	
VI	Water Technology: Types of hardness, Units of hardness, Estimation of Hardness – EDTA method. Numericals based on the above	3	20%
	Water softening methods - Ion exchange process - Principle. Polymer ion exchange.	2	
	Reverse Osmosis - Disinfection method by chlorination and UV	1	
	Dissolved oxygen, BOD and COD.	2	
	Sewage water Treatment - Trickling Filter and UASB process.	1	
END SEMESTER EXAM			

6. Raymond B. Seymour, Charles E. Carraher, "Polymer Chemistry: An Introduction", Marcel Dekker Inc; 4th Revised Edition, 1996.
7. MuhammedArif, Annette Fernandez, Kavitha P. Nair "Engineering Chemistry", Owl Books, 2019.
8. Ahad J., "Engineering Chemistry", Jai Publication, 2019.
9. Roy K. Varghese, "Engineering Chemistry", Crownplus Publishers, 2019.
10. Soney C. George, RinoLaly Jose, "Text Book of Engineering Chemistry", S. Chand & Company Pvt Ltd, 2019.

No	Topic	No. of Lectures (hrs)
1	Electrochemistry and Corrosion	9
1.1	Introduction - Differences between electrolytic and electrochemical cells- Daniel cell- redox reactions - cell representation. Different types of electrodes (brief) - Reference electrodes- SHE - Calomel electrode - Glass Electrode - Construction and Working	2
1.2	Single electrode potential – definition - Helmholtz electrical double layer - Determination of E^\ominus using calomel electrode. Determination of pH using glass electrode. Electrochemical series and its applications. Free energy and EMF - Nernst Equation – Derivation - single electrode and cell (Numericals) -Application -Variation of emf with temperature.	3
1.3	Potentiometric titration - Introduction -Redox titration only. Lithium ion cell - construction and working. Conductivity- Measurement of conductivity of a solution (Numericals).	2
1.4	Corrosion-Electrochemical corrosion – mechanism. Galvanic series- cathodic protection - electroless plating –Copper and Nickel plating.	2
2	Spectroscopic Techniques and Applications	9
2.1	Introduction- Types of spectrum - electromagnetic spectrum - molecular energy levels - Beer Lambert's law (Numericals).	2
2.2	UV-Visible Spectroscopy – Principle - Types of electronic transitions - Energy level diagram of ethane, butadiene, benzene and hexatriene. Instrumentation of UV-Visible spectrometer and applications.	2
2.3	IR-Spectroscopy – Principle - Number of vibrational modes -Vibrational energy states of a diatomic molecule and -Determination of force constant of diatomic molecule (Numericals) –Applications.	2
2.4	^1H NMR spectroscopy – Principle- Relation between field strength and frequency - chemical shift - spin-spin splitting (spectral problems) - coupling constant (definition) - applications of NMR- including MRI (brief).	3
3	Instrumental Methods and Nanomaterials	9
3.1	Thermal analysis –TGA- Principle, instrumentation (block diagram) and applications – TGA of $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$ and polymers. DTA-Principle, instrumentation (block diagram) and applications- DTA of $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$.	2

3.2	Chromatographic methods- Basic principles and applications of column and TLC- Retention factor.	2
3.3	GC and HPLC-Principle, instrumentation (block diagram) - retention time and applications.	2
3.4	Nanomaterials - Definition - Classification - Chemical methods of preparation - Hydrolysis and Reduction - Applications of nanomaterials - Surface characterisation - SEM – Principle and instrumentation (block diagram).	3
4	Stereochemistry and Polymer Chemistry	9
4.1	Isomerism-Structural, chain, position, functional, tautomerism and metamerism - Definition with examples - Representation of 3D structures>Newman, Sawhorse, Wedge and Fischer projection of substituted methane and ethane. Stereoisomerism - Geometrical isomerism in double bonds and cycloalkanes (cis-trans and E-Z notations).	2
4.2	R-S Notation – Rules and examples - Optical isomerism, Chirality, Enantiomers and Diastereoisomers-Definition with examples	1
4.3	Conformational analysis of ethane, butane, cyclohexane, mono and di methyl substituted cyclohexane.	2
4.4	Copolymers - Definition - Types - Random, Alternating Block and Graft copolymers - ABS - preparation, properties and applications. Kevlar-preparation, properties and applications. Conducting polymers - Doping -Polyaniline and Polypyrrole - preparation properties and applications. OLED - Principle, construction and advantages.	4
5	Water Chemistry and Sewage Water Treatment	9
5.1	Water characteristics - Hardness- Types of hardness-Temporary and Permanent - Disadvantages of hard water -Units of hardness- ppm and mg/L -Degree of hardness (Numericals) - Estimation of hardness-EDTA method (Numericals). Water softening methods-Ion exchange process-Principle, procedure and advantages. Reverse osmosis – principle, process and advantages.	3
5.2	Municipal water treatment (brief) - Disinfection methods - chlorination, ozone andUV irradiation.	2
5.3	Dissolved oxygen (DO) -Estimation (only brief procedure-Winkler's method), BOD and COD-definition, estimation (only brief procedure) and significance (Numericals).	2
5.4	Sewage water treatment - Primary, Secondary and Tertiary - Flow diagram - Trickling filter and UASB process.	2

QUESTION BANK

MODULE I –ELECTROCHEMISTRY

1. Define standard electrode potential? Explain Helmholtz electrical double layer.
2. What is metal – metal insoluble salt electrode? Give example?
3. Give an example for Gas – ion electrode and represent the electrode?
4. What do you mean by a reference electrode? Mention any two?
5. What is an electrochemical series? Give its applications.
6. Explain Standard Hydrogen Electrode? Write down its merits and limitations?
7. Explain Saturated Calomel Electrode? Give its applications
8. What are the advantages of Potentiometric titration? Discuss Redox titration in detail.
9. Derive Nernst equation for Daniel cell
10. Explain Lithium ion cell? Give its advantages
11. What do you mean by glass electrode? How can we determine the P^H of a solution? Explain its merits and limitation?
12. Give the differences between electrochemical cells and electrolytic cells
13. What is Nernst equation? Derive Nernst equation for electrode and write its application?
14. Write a note on electrochemical cell.
15. Explain variation of EMF with temperature.
16. What is meant by single electrode potential? How is it measured?
17. Define the term specific conductance .Explain the procedure for conductivity measurements.

18. Explain the mechanism of electrochemical corrosion (wet corrosion)
19. Distinguish between Galvanic series and Electrochemical series
20. Describe in detail electroless plating of nickel. Give its advantages & applications
21. Describe in detail electroless plating of copper. Give its advantages & applications
22. problems

SUBJECT: ENGINEERING CHEMISTRY

Code: CYT100

QUESTION BANK-MODULE- II (SPECTROSCOPY)

1. Which of the following nuclei can give NMR spectrum? Give reason.
a) ${}^1_1\text{H}$ b) ${}^{12}_6\text{C}$ c) ${}^{19}_9\text{F}$ d) ${}^{16}_8\text{O}$
2. The vibrational frequency of HCl molecule is 2886 cm^{-1} . Calculate the force constant of the molecule. Reduced mass of HCl is $1.63 \times 10^{-27}\text{ Kg}$.
3. How can you distinguish NMR spectrum of $\text{CH}_3\text{CH}_2\text{Cl}$ and CH_3CHCl_2 . Apply the concept of spin spin splitting.
4. Which of the following molecules show UV Visible absorption? Give reason.
a) ethane b) butadiene c) benzene d) phenol
5. Write the principle components of UV Visible spectrometer & Explain the instrumentation procedure
6. Sketch the various modes of vibrations possible for CO_2 . Which are IR active. Write the reason for your answer.
7. Chemical shift value of methyl chloride is lower compared to that of methyl fluoride. Give reason.
8. List all the electronic transitions possible for CH_3Cl and HCHO .
9. Briefly explain chemical shift and factors affecting it. (5)
10. Which of the following molecules can give IR absorption? Give reason.
a) O_2 b) HCl c) N_2 d) CO_2
11. The fundamental vibrational frequency of CO is 2140 cm^{-1} . Calculate the force constant of the bonds if reduced mass of CO is $1.14 \times 10^{-26}\text{ Kg}$.
12. Explain spin-spin splitting. Write the splitting pattern in the NMR spectrum of $\text{CH}_3\text{CH}_2\text{OH}$
13. Explain the various modes of vibrations possible for H_2O which of them are IR active. Give reasons.
14. Why TMS is used as reference compound to measure chemical shift (δ)
15. A solution shows a transmittance of 20% when taken in a cell of 2.5 cm thickness. Calculate its concentration when its molar absorption coefficient is $12000\text{ dm}^2\text{ mol}^{-1}$.

16. What is the principle of UV-Visible spectroscopy . Explain electronic transitions in detail

17. Distinguish between Absorption spectrum and Emission spectrum

QUESTION BANK-CHEMISTRY

MODULE III - INSTRUMENTAL METHODS & NANOMATERIALS

1. What do you mean by R_f value?
2. Give any two applications of TLC
3. Define elution ?How elution can be done in column chromatography
4. What are the requirements of a good adsorbent in column chromatography?
5. How the TLC plate is prepared and developed in TLC.
6. Give the principle & any three applications of DTA.
7. Differentiate retention time and retention factor.
8. Give the applications of TGA.
9. Briefly explain the columns and detectors used in HPLC
10. Explain the basic principle & instrumentation of TGA
11. Briefly explain Differential Thermal analysis.
12. Gas Chromatography is the most efficient and convenient tool in recent days. Comment.
13. Explain TGA & DTA Thermogram
14. Write short note on column chromatography.
15. How HPLC becomes a superior analytical tool? Explain.
16. Give the visualization techniques used in TLC
17. Discuss the TGA & DTA thermogram of hydrated calcium oxalate
 $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$
18. Discuss the classification of nanomaterials
19. Give different chemical methods of preparation of nanoparticles
20. Write a note on sol gel method
21. Explain Electro reduction & chemical reduction methods for the production of nanoparticles
22. Give the applications of nanomaterial
23. Explain the instrumentation of **SEM**. Give its advantages, disadvantages & applications.

Question bank –module 4

STEREOCHEMISTRY & POLYMERS

1. Write notes on i) position isomers ii) chain isomers ii) functional group isomers
2. Explain keto-enol tautomerism with proper examples
3. Define Metamerism with example
4. Write a note on geometrical isomers
5. Draw the structure of 2R,3S-Dihydroxy butanoic acid
6. How many isomers are possible for i) C_4H_8 ii) C_6H_{14} iii) $C_4H_{10}O$
7. Write the rule for assigning E –Z notation
8. Explain R,S notation with proper examples
9. Discuss the conformations of ethane
10. Discuss the conformations of Butane
11. Write a note on optical isomerism
12. Draw the structure of Cis 1,4 –dimethyl cyclohexane and Trans-1,4 – dimethyl cyclohexane
13. Discuss Enantiomers and Diastereomers with suitable examples

Polymers

1. What are co-polymers .Discuss different types
2. Give the preparation,properties & applications of the following polymers
i) ABS II) KEVLAR
3. Explain the classification of conducting polymers
4. Give the preparation,properties & uses of
I) polyaniline ii) poly pyrrole
5. Explain the conduction mechanism in polyaniline
6. Discuss the construction and working of OLED? Give its advantages, disadvantages & applications

MODULE V (Water Technology)

EACH QUESTION CARRIES 3 MARKS EACH

1. What do you understand by hardness of water? How are they represented?
2. What are the different units in which hardness is expressed?
3. What are ion exchange resins? Give examples for cation exchange resins and anion exchange resins?
4. Why do we express hardness of water in terms of CaCO_3 equivalents?
5. Write the significance of BOD & COD
6. What are disinfectants? Give examples
7. Differentiate between aerobic and anaerobic oxidation
8. What are the defects of using hard water in boilers?
9. Explain the terms hard water and soft water; Give the cause of hardness.
10. What is meant by desalination of water?
11. Explain the principle of EDTA method
12. Explain BOD & COD. Indicate their significance in sewage treatment.
13. Explain break point of chlorination
14. What is disinfection? Give the advantages and disadvantages of UV disinfection of water
15. What is reverse osmosis? Where it is applied?
16. What are the problems of using hard water in industries?
17. Describe briefly disinfection of water using UV
18. Give any four points of differences between BOD & COD
19. Describe disinfection by chlorine. What are its advantages?

EACH QUESTION CARRIES 10 MARKS EACH

1. Discuss the different steps involved in sewage treatment
2. How hardness is determined by EDTA method
3. Explain the method used for demineralization of water
4. i) With the help of a neat diagram outline reverse osmosis process
ii) What do you mean by UASB process? How is it useful in waste water treatment?
5. i) What is the importance of DO
ii) Explain trickling filter method for sewage treatment.

MODULE I

ELECTROCHEMISTRY AND CORROSION

The branch of chemistry which deals with two forms of energy such as electrical energy and chemical energy and the inter-conversion of one form to another is called electrochemistry. Thus there are two types of electro chemical changes. On the basis of electrochemical changes, cells are of two types.

1. Electrolytic cell
2. Galvanic cell (Voltaic cell) (Electro chemical cell)

Differences between electrolytic cell & galvanic cell

Electrolytic cell	Electro chemical cell
<ul style="list-style-type: none"> • It is used for the conversion of electrical energy to chemical energy. • It requires EMF. • Anode is +ve and cathode is -ve. • Discharges of ions occur at both the electrodes. • Non-spontaneous reaction occurs. • These are irreversible. 	<ul style="list-style-type: none"> • It is used for the conversion of chemical energy to electrical energy. • It produces EMF. • Anode is -ve and cathode is +ve. • Discharges of ions occur only at cathode. • Spontaneous reaction occurs. • These may be reversible.

Comparison of electrolytic cell & galvanic cell

Electrolytic cell	Electro chemical cell
<ul style="list-style-type: none"> • Oxidation takes place at the anode and reduction at the cathode. • Flow of electrons from anode to cathode. • Electrons leave the cell at anode and enter the cell at cathode. 	<ul style="list-style-type: none"> • Oxidation takes place at the anode and reduction at the cathode. • Flow of electrons from anode to cathode. • Electrons leave the cell at anode and enter the cell at cathode.

Electrode potential and its origin

When a metal rod is immersed in a solution of its own ion, it will either undergo oxidation or reduction. As a result metal rod attains positive or negative charge. If the metal rod attains the positive charge, then it can attract the negatively charged free ions from the solution & if the metal rod attains negative charge, then it can attract the positively charged free ions from the solution. As a result a layer of both positive and negative charge is produced on the metal rod. This will lead to the development of a potential and is called electrode potential.

Electrode potential (E) is defined as the tendency of an electrode to lose or gain electrons when it is immersed in a solution of its own ions. Electrode potential is of two types. They are

1. Oxidation potential
2. Reduction potential

Oxidation potential

It is defined as the tendency of an electrode to lose electrons when it is immersed in a solution of its own ions.

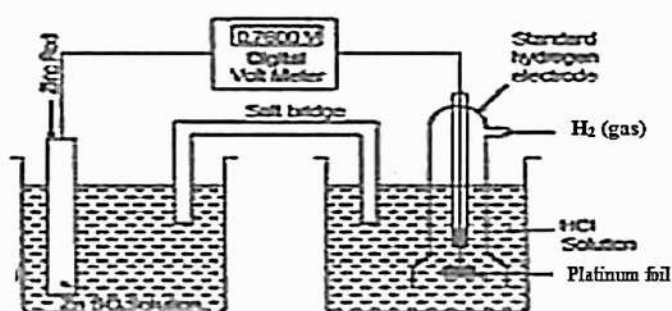
Reduction potential

It is defined as the tendency of an electrode to gain electrons when it is immersed in a solution of its own ions.

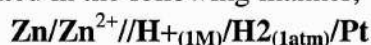
Electrode potential becomes constant at equilibrium then it is called standard electrode potential (E^0). It is defined as the tendency of an electrode to lose or gain electrons when it is immersed in a solution of its own ions of 1M concentration, 1atm pressure and 298K or 25°C.

It is not possible to find out the absolute value of electrode potential, since neither oxidation nor reduction takes place independently both occur simultaneously. Hence we can find out the relative value of electrode potential by coupling it with universally accepted reference electrode such as SHE or NHE. Its potential is arbitrarily fixed as zero. It can function as an anode or cathode depending on the nature of the other electrode to which it is connected.

In order to measure the standard electrode potential of Zn rod, (Zn rod dipped in 1M ZnSO₄ solution) Zn electrode is coupled with SHE internally using salt bridge and externally using volt meter. Zn has greater tendency for oxidation than SHE. So Zn can function as anode and SHE can function as the cathode. The resultant cell potential can be read directly from the volt meter.



The resultant cell can be represented in the following manner,



$$E^0 \text{ Cell} = E^0_{\text{cathode}} - E^0_{\text{anode}}$$

$$= E^0_{\text{SHE}} - E^0_{\text{Zn/Zn}^{2+}}$$

$$0.76 \text{ V} = 0 - E^0_{\text{Zn/Zn}^{2+}}$$

$$(E^0_{\text{Zn/Zn}^{2+}} = -0.76\text{V})$$

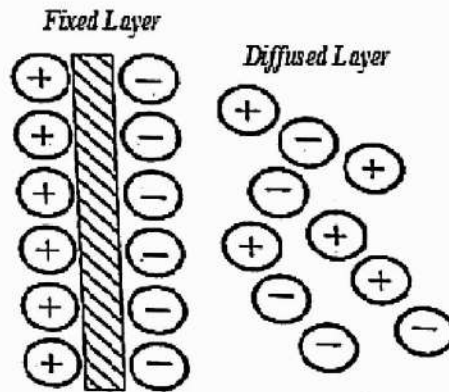
Helmholtz electrical double layer

When an electrode is immersed in a solution of its own ions an electrical double layer is produced. It is the double layer of both positive and negative charges. Electrical double layer corresponds to an electrical capacitor. Electrical properties can be explained qualitatively by using the concept of electrical double layer at the solid liquid interphase. This concept was proposed by the scientist, Helmholtz. He considered that electrical double layer is produced at the surface of separation between the two phases, i.e. the solid electrode and liquid electrolyte. Electrical double layer consists of two parts.

- 1). Fixed part
- 2) Diffused part

Fixed part: It is fixed to the solid electrode. It contains either positive or negative ions.

Diffused part: It extends some distance into the solution. It contains both positive and negative ions. The existence of charges of opposite signs on the diffused to the fixed part of the electrical double layer develops a potential between the two layers. This potential is called electro kinetic potential or zeta potential.



According to electrostatic theory, the potential difference between the two layers (Φ) is given by

$$\Phi = \frac{\sigma a}{\epsilon_0 \epsilon}$$

Where ' σ ' is the charge density, i.e. *Charge/Unit area*

' a ' is the distance between the layers of positive and negative charges.

' ϵ ' is the dielectric constant of the medium and ϵ_0 that of free space.

Electrochemical series

An electrochemical series is a series in which the electrodes are arranged in the increasing order of reduction potential or decreasing order of oxidation potential. On moving down the series, reduction potential increases and oxidation potential decreases. Thus this series gives the increased tendency of electrodes to get reduced or decreases tendency of electrodes to get oxidised. The electrodes present at the top of the series can function as anode and those present at the bottom of the series can function as cathode. This series is also called activity series, since the electrodes at the top of the series is more reactive than those present at the bottom.

Anodic (Active)



Cathodic (Noble)

Hydrogen has zero reduction potential. Above hydrogen, all the electrodes have negative reduction potential and below hydrogen, all the electrodes have positive reduction potential.

Applications of electrochemical series

1. To know the relative ease of oxidation and reduction:

Greater the reduction potential, more easily the substance undergoes reduction and is a better oxidising agent. (Eg. Fluorine). Similarly greater the oxidation potential, more easily the substance undergoes oxidation and is a better reducing agent. (Eg. Pottasium).

2. To predict whether the metal will react with acid to give hydrogen gas:

Metals present above hydrogen in the electrochemical series can react with acids to give hydrogen gas. This is because these metals have greater tendency to undergo oxidation with respect to hydrogen, since they have negative reduction potential.

3. To calculate the standard emf of the cell:

$$E^{\circ}_{\text{Cell}} = E^{\circ}_{\text{Cathode}} - E^{\circ}_{\text{Anode}}$$

If we know the position of electrodes in the electrochemical series, we can easily predict which electrode can function as anode and which one can function as cathode.

4. Displacement reactions

A metal with lower reduction potential can displace a metal with higher reduction potential from its salt solution. Zn can displace Cu from CuSO_4 solution.

5. To predict the spontaneity of any redox reaction

For any spontaneous reaction, free energy change (ΔG) should be negative. $\Delta G = -nFE_{\text{cell}}$
Hence, E_{cell} should be positive for spontaneous reaction. E_{cell} of the cell can be calculated from the redox potentials by using the relation $E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}}$

Relationship between electrical energy and free energy

The electrical energy produced by the working of the cell is the product of quantity of electricity passed through the cell and emf of the cell. If in a particular cell reaction, 'n' is the number of electrons get transferred, then the quantity of electricity passed through the cell is 'nF' and E is the emf of the cell.

$$\text{Then electrical energy} = nFE$$

But Gibbs and Helmholtz suggested that electrical energy produced due to the working of the cell is always accompanied with decrease in free energy.

$$\text{Then electrical energy} = nFE = -\Delta G$$

$$\Delta G = -nFE$$

Criteria for spontaneity in terms of cell emf

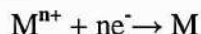
Case 1: If $\Delta G < 0$ or ΔG is -ve, then $E_{\text{cell}} > 0$ or E_{cell} is +ve and the reaction will be spontaneous.

Case 2: If $\Delta G = 0$, then $E_{\text{cell}} = 0$ and the reaction will be in equilibrium.

Case 3: If $\Delta G > 0$ or ΔG is +ve, then $E_{\text{cell}} < 0$ or E_{cell} is -ve and the reaction will be non-spontaneous.

Nernst equation

Nernst equation is the fundamental equation that gives the relationship between electrode potential and concentration of electrolyte. To derive Nernst equation, consider a general reversible reaction.



For a reversible reaction, free energy change (ΔG) is related to the equilibrium constant (K) by an expression.

$$\Delta G = \Delta G^{\circ} + RT \ln K \quad (1)$$

Where ΔG is the free energy change, ΔG° is the standard free energy change, R is the universal gas constant, K is the equilibrium constant and T is the temperature in Kelvin.

$$K = \frac{[\text{M}]}{[\text{M}^{n+}]}$$

According to Gibbs-Helmholtz suggestion,

$$\Delta G = -nFE \text{ \& } \Delta G^0 = -nFE^0 \quad (2)$$

Substituting equation (2) in equation (1)

$$-nFE = -nFE^0 + RT \ln \frac{[M]}{[M^+]}$$

Dividing above equation by $-nF$, on both sides and convert natural log into base 10, we get

$$E = E^0 - 2.303 \frac{RT}{nF} \log \frac{[M]}{[M^+]}$$

Since $[M] = 1$, then the equation becomes;

$$E = E^0 - 2.303 \frac{RT}{nF} \log \frac{1}{[M^+]}$$

$$E = E^0 + 2.303 \frac{RT}{nF} \log [M^{n+}]$$

On substituting $R = 8.314\text{J/K}$, $T = 298\text{K}$ & $F = 96500\text{C}$, we get simplified form of Nernst equation;

$$E = E^0 + \frac{0.0591}{n} \log [M^{n+}]$$

Where E is the electrode potential, E^0 is the standard electrode potential.

For a reaction of the type $aA + bB \rightleftharpoons cC + dD$, Nernst equation becomes,

$$E = E^0 + \frac{2.303RT}{nF} \log \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

From the above equation, it can be concluded that

- (1) When $[M^{n+}]$ increases E increases
- (2) The electrode potential E decreases as the increase in temperature.
- (3) The electrode potential normally refers to the reduction reaction at an electrode.

Applications of Nernst equation

1. Nernst equation can be used to study the effect of electrolyte concentration on electrode potential.
2. It can be used for the calculation of the potential of a cell under nonstandard conditions
3. Determination of unknown concentration of one of the ionic species in a cell is possible with the help of Nernst equation, if $E^0_{\text{(cell)}}$ and concentration of the other ionic species are known
4. The P^H of a solution can be calculated from the measurement of electrode potential

Nernst equation can be used for finding the valency of an ion or the number of electrons involved in the electrochemical reaction.

- Calculate the equilibrium constant for Daniel cell at 25^0C . $E_{0\text{cell}} = 1.1\text{V}$.

$$\text{Log } K = \frac{nE_{0\text{cell}}}{0.0591} = \frac{2 \times 1.1}{0.0591} = 37.22$$

$$K = 1.68 \times 10^{37}$$

- Calculate the standard emf of $\text{H}_2 - \text{O}_2$ fuel cell. (E^0 values for hydrogen and oxygen half cells are -0.40V & 0.83V respectively).

$$E^0_{\text{cell}} = E^0_{\text{Cathode}} - E^0_{\text{Anode}} = E^0_{\text{O}_2} - E^0_{\text{H}_2} = 0.83 - (-0.40) = 1.23\text{V}$$

- At 25^0C the standard emf of a cell having reaction involving two electron charge is found to be 0.295V . Calculate the equilibrium constant of the reaction.

$$\text{Log } K = \frac{nE_{0\text{cell}}}{0.0591} = \frac{2 \times 0.295}{0.0591} = 10$$

$$K = 10^{10}$$

- What is the concentration of Ni^{2+} in the cell at 25^0C , if the emf is 0.601V ? Given that $E_0 \text{Ni(s)/Ni}^{2+}$ is -0.25V & $E_0 \text{Cu(s)/Cu}^{2+}$ is 0.34V . $\text{Ni(s)/Ni}^{2+} \text{ (a=?)} // \text{Cu}^{2+} \text{ (0.75M)/Cu(s)}$.

$$E_{\text{cell}} = E^{\circ}_{\text{cell}} + \frac{0.0591}{2} \log \frac{[\text{Cu}^{2+}]}{[\text{Ni}^{2+}]}$$

Where $E^{\circ}_{\text{cell}} = 0.34 - (-0.25) = 0.59$, $E_{\text{cell}} = 0.601\text{V}$

$$0.601 = 0.59 + 0.0295 \log \frac{0.75}{[\text{Ni}^{2+}]}$$

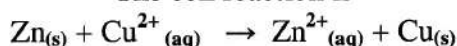
$$\frac{0.011}{0.0295} = \log \frac{0.75}{[\text{Ni}^{2+}]}$$

$$\frac{0.75}{[\text{Ni}^{2+}]} = 2.356.$$

Therefore $[\text{Ni}^{2+}] = 0.3183\text{M}$

- Calculate the emf of the cell $\text{Zn}/\text{Zn}^{2+} (0.01\text{M})//\text{Cu}^{2+} (0.1\text{M})/\text{Cu}$. Write its half-cell reactions is E°_{Zn} is -0.76V and E°_{Cu} is $+0.34\text{V}$.

The cell reaction is



Nernst equation for this cell reaction is

$$E_{\text{cell}} = E^{\circ}_{\text{cell}} + \frac{0.0591}{2} \log \frac{[\text{Cu}^{2+}]}{[\text{Zn}^{2+}]}$$

$$\text{But } E^{\circ}_{\text{cell}} = E^{\circ}_{\text{R}} - E^{\circ}_{\text{L}} = 0.34 + 0.76 = 1.1\text{V}$$

$$\text{Therefore } E_{\text{cell}} = 1.1 + \frac{0.0591}{2} \log \frac{[0.1]}{[0.01]} = 1.1295\text{V}$$

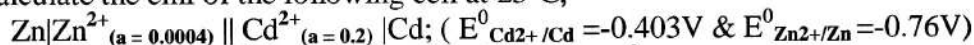
- Calculate the equilibrium constant of the reaction, $\text{Cu} + 2\text{Ag}^+ \rightarrow \text{Cu}^{2+} + 2\text{Ag}$ ($E^{\circ}_{\text{Ag}(\text{s})/\text{Ag}^+}$ is 0.80V & $E^{\circ}_{\text{Cu}^{2+}/\text{Cu}(\text{s})}$ is 0.34V .)

$$E^{\circ}_{\text{cell}} = E^{\circ}_{\text{Ag}(\text{s})/\text{Ag}^+} - E^{\circ}_{\text{Cu}^{2+}/\text{Cu}(\text{s})} = 0.80 - 0.34 = 0.46$$

$$\log K = \frac{nE^{\circ}_{\text{cell}}}{0.0591} = \frac{2 \times 0.46}{0.0591} = 15.57$$

$$K = 3.775 \times 10^{15}$$

- Calculate the emf of the following cell at 25°C ,



$$E^{\circ}_{\text{cell}} = E^{\circ}_{\text{cathode}} - E^{\circ}_{\text{anode}} = E^{\circ}_{\text{Cd}^{2+}/\text{Cd}} - E^{\circ}_{\text{Zn}^{2+}/\text{Zn}} = -0.403 + 0.76 = 0.357\text{V}$$

$$E_{\text{cell}} = E^{\circ}_{\text{cell}} + \frac{0.0591}{2} \log \frac{[\text{Cd}^{2+}]}{[\text{Zn}^{2+}]} = 0.357 + \frac{0.0591}{2} \log \frac{[0.2]}{0.0004} = 0.4367\text{V}$$

- Find the single electrode potential for copper metal in contact with 0.1M Cu^{2+} solution at 298K . $E^{\circ}_{\text{Cu}^{2+}/\text{Cu}} = 0.34\text{V}$

$$E_{\text{Cu}} = E^{\circ}_{\text{Cu}} + \frac{0.0591}{2} \log [\text{Cu}^{2+}] = 0.34 + \frac{0.0591}{2} \log [0.1] = 0.31045\text{V}$$

- Determine the standard emf of the cell and standard free energy change of the cell reaction. $\text{Zn}, \text{Zn}^{2+} || \text{Ni}^{2+}, \text{Ni}$. The standard reduction potentials of $\text{Zn}^{2+}, \text{Zn}$ and $\text{Ni}^{2+}, \text{Ni}$ half cells are -0.76V and -0.25V respectively.

$$E^{\circ}_{\text{cell}} = E^{\circ}_{\text{cathode}} - E^{\circ}_{\text{anode}} = -0.25 - (-0.76) = +0.51\text{V}$$

E°_{cell} is +ve and ΔG° should be -ve.

$$\Delta G^{\circ} = -nFE^{\circ}_{\text{cell}}$$

$$\Delta G^{\circ} = -(2 \times 96500 \times 0.51) = -98430\text{ Joules}$$

- Calculate the amount of electrical energy available from dry cell of EMF 1.5V which consumes 10g Zn . (At wt. of $\text{Zn} = 65.5\text{g}$)

$$\Delta G = -nFE = -2 \times 96500 \times 1.5 = 289500\text{J}$$

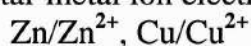
$$\text{Therefore electric energy available for } 10\text{g } \text{Zn} = \frac{289500 \times 10}{65.5} = 44198\text{ J}$$

Types of electrodes

- 1) Metal-metal ion electrode
- 2) Gas electrode
- 3) Metal-metal insoluble salt electrode
- 4) Redox electrode
- 5) Ion selective electrode

1. Metal-metal ion electrode

A metal is immersed in its own ionic solution, resultant electrode is called metal-metal ion electrode.

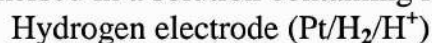


$$E_{\text{cell}} = E^0_{\text{cell}} + 0.0591 \log [\text{Zn}^{2+}]$$

Here the electrode potential depends on the $[\text{M}^{n+}]$

2. Gas electrode

In gas electrode, gas is passed through an inert electrode like platinum which is immersed in a solution containing its own ion.



Here the electrode potential depends on the [ion] and the pressure at which gas is bubbled.

3. Metal-metal insoluble salt electrode

In metal-metal insoluble salt electrode, metal is covered with a paste of its insoluble metal salt which is in contact with a solution containing a common ion with the insoluble salt.

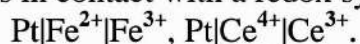


$$E_{\text{cal}} = E^0_{\text{cal}} - \frac{2.303RT}{2F} \log [\text{Cl}^-]^2 = E^0_{\text{cal}} - \frac{2.303RT}{F} \log [\text{Cl}^-]$$

Here the electrode potential depends on the [common ion]

4. Redox electrode

An electrode is in contact with a redox system is called redox electrode.



$$E_{\text{cell}} = E^0_{\text{cell}} + 0.0591 \log \frac{[\text{Fe}^{3+}]}{[\text{Fe}^{2+}]}$$

In these electrodes the electrode potential depends on the ratio of concentration of all ionic species involved in the redox reaction.

5. Ion selective electrode

In this electrode, the sensing part of the electrode is made up of an ion selective membrane.

Eg. Glass electrode consists of an ion selective membrane sensitive to H^+ ions.

Reference electrode

It is not possible to find out the absolute value of electrode potential, since neither oxidation nor reduction takes place independently both occur simultaneously. Hence we can find out the relative value of electrode potential by coupling it with universally accepted reference electrode.

An ideal reference electrode is one whose potential is accurately known, constant and is completely sensitive to the concentration of analyte solution.

Types of reference electrodes

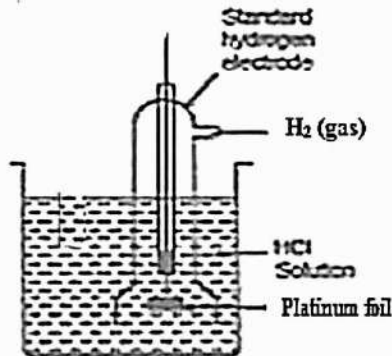
Reference electrodes are of two types. They are

1. Primary reference electrode (SHE)
-

2. Secondary reference electrode (Calomel electrode and glass electrode)

Standard Hydrogen Electrode (SHE)

It consists of platinum foil coated with Pt black which is immersed in a solution of 1M HCl. Hydrogen gas at 1atm pressure is bubbled over the electrode



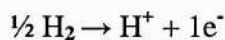
Characteristics of SHE

1. Its potential is arbitrarily fixed as zero.
2. It is reversible electrode, i.e. it can function as an anode or cathode depending on the nature of the other electrode to which it is connected.

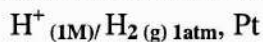
If it functions as an anode, it can be represented as



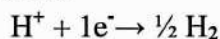
Cell reaction:



If it functions as a cathode, it can be represented as



Cell reaction:

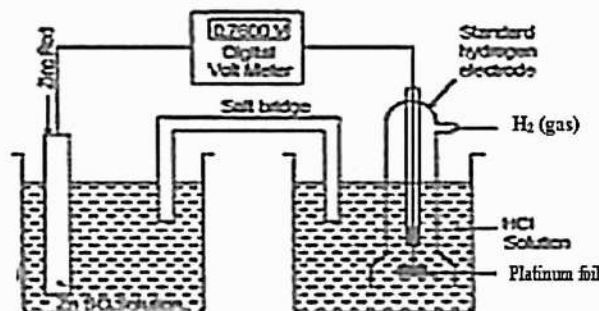
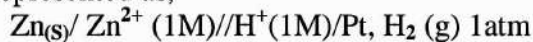


Uses:

It is used for determining unknown potential of an electrode.

Working of SHE (Determination of E° using SHE)

Consider a Zinc rod dipped in ZnSO4 solution of 1M concentration which is coupled with SHE externally using voltmeter and internally through salt bridge. Now, the resultant cell can be represented as,



$$\begin{aligned} E^0_{\text{Cell}} &= E^0_{\text{cathode}} - E^0_{\text{anode}} \\ &= E^0_{\text{SHE}} - E^0_{\text{Zn/Zn}^{2+}} \\ 0.76 \text{ V} &= 0 - E^0_{\text{Zn/Zn}^{2+}} \end{aligned}$$

$$E^{\circ}_{\text{Zn}/\text{Zn}^{2+}} = -0.76\text{V}$$

E° Cell can be directly read out from the voltmeter and E° Cathode is zero. Hence we can find out $E^{\circ}_{\text{Anode}}(E^{\circ}_{\text{Zn}})$.

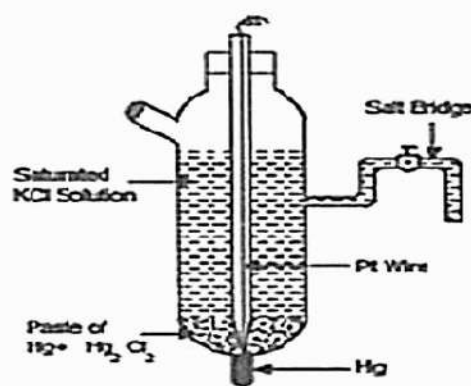
Draw backs of SHE

1. It is very difficult to set up.
2. It cannot be used as a reference electrode if the solution contains reducible substances such as copper, silver etc.
3. It causes poisoning of the Pt foil.

Secondary Reference Electrode

Secondary Reference Electrode is a reference electrode with known constant potential and can be coupled with other electrodes to determine the unknown potential.

Calomel Electrode



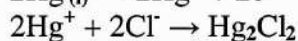
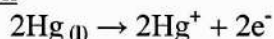
Calomel electrode consists of a glass having side tube on both sides. Mercury covered with a paste of Hg_2Cl_2 is taken at the bottom the glass tube. Inside the glass tube 0.1N or 1N or saturated KCl solution is taken. A Pt wire is dipped into the glass tube containing Hg, which helps for electrical contact. Potential of calomel electrode depends on the concentration of KCl solution taken in the glass tube.

Calomel electrode can be represented as, $\text{Pt, Hg}_{(l)} | \text{Hg}_2\text{Cl}_{2(s)} | \text{KCl}(\text{sat})$

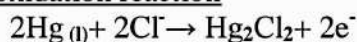
$$E_{\text{cal}} = E^{\circ}_{\text{cal}} - \frac{2.303RT}{2F} \log [\text{Cl}^-]^2 = E^{\circ}_{\text{cal}} - \frac{2.303RT}{F} \log [\text{Cl}^-] = E^{\circ}_{\text{cal}} - \frac{0.0591}{1} \log [\text{Cl}^-]$$

Saturated Calomel Electrode is generally used, since it is easy to set up and its emf will not change with chemical reaction.

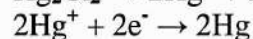
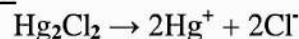
Oxidation



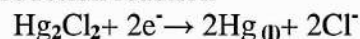
Overall oxidation reaction



Reduction



Overall reduction reaction



Overall reaction when oxidation takes place is just reverse of the overall reaction when reduction takes place. Hence calomel electrode is reversible with respect to chloride ions.

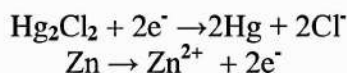
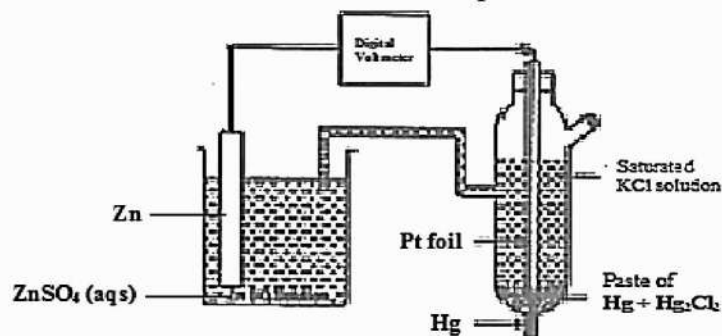
Potential of calomel electrode depends on the concentration of KCl solution.

Concentration	0.1N	1N	Saturated
E	0.3335 V	0.2810 V	0.2422 V

If the calomel electrode is filled with 0.1 N or 1 N KCl, then the calomel electrode is called Normal Calomel Electrode (NCE) and if it is filled with saturated KCl, then it is called Saturated Calomel Electrode (SCE)

Working of Calomel electrode (Determination of electrode potential using calomel electrode)

In order to measure the electrode potential of an electrode, (Zn electrode) it is coupled with SCE using a digital volt meter. The volt meter reading will give the cell emf. The reduction potential of SCE is 0.2422V is higher than the reduction potential of Zn²⁺/Zn (-0.76V). Therefore reduction reaction takes place at SCE.



The resultant cell can be represented as

$$\text{Zn}/\text{Zn}^{2+}/\text{KCl}_{(\text{sat})}/\text{Hg}_2\text{Cl}_{2(\text{s})}/\text{Hg(l)}/\text{Pt}$$

$$E_{\text{cell}} = E_{\text{R}} - E_{\text{L}} = E_{\text{cal}} - E_{\text{Zn}/\text{Zn}^{2+}} = 0.2422 - E_{\text{Zn}/\text{Zn}^{2+}}$$

$$E_{\text{Zn}/\text{Zn}^{2+}} = 0.2422 - E_{\text{cell}}$$

E_{cell} can be read directly from volt meter.

Advantages of Calomel electrode

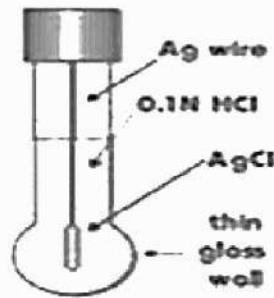
1. It is very easy to set up.
2. Its emf will not change with chemical reaction.

Glass electrode

Glass electrode is a secondary reference electrode. Corning 015 glass has been used for making glass electrode. It is a special type of glass with low melting point and high electrical conductivity. It consists of 72% SiO₂, 6% CaO & 22% Na₂O.

Construction;

It consists of a thin glass bulb in which Ag wire coated AgCl is used as an internal reference electrode. It is then filled with 0.1N HCl solution.



Glass electrode works on the principle that potential difference between the surface of the glass membrane and a solution is a linear function of P^H . Here the glass membrane acts as an ion selective membrane sensitive to $[H^+]$. So an ion exchange reaction occurs between singly charged cations of glass (Na^+) & H^+ ions of solution. Finally an equilibrium is established between (Na^+) ions of glass & H^+ ions of solution.

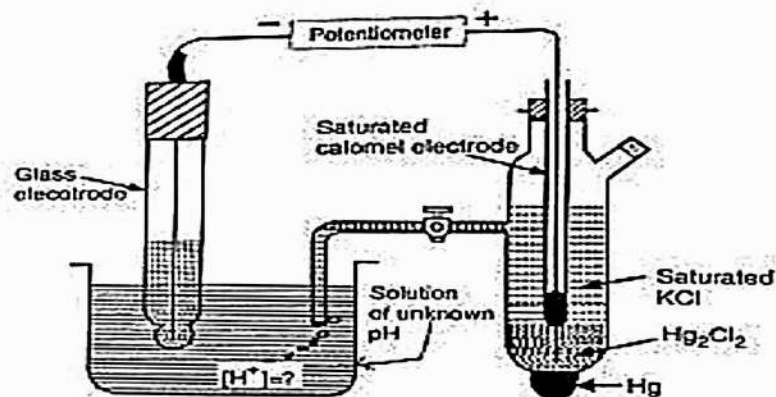


The potential of glass electrode varies with concentration of H^+ ions. E_G^0 is constant and it depends on the nature of the glass and also the P^H of the solution taken inside the glass bulb.
 $E_G^0 = 0.6990 \text{ V}$

The concentration of H^+ ion inside the glass is constant, i.e. P^H is constant. But when it is dipped into a solution of unknown P^H , concentration of H^+ ion inside the glass bulb changes. As a result, P^H changes. This results in the development of a potential difference.

Determination of PH using glass electrode

Glass electrode is used as an internal reference electrode. In order to determine the unknown PH of a solution, glass electrode is coupled with SCE and the resultant cell can be represented like this, $\text{Ag, AgCl(s)/0.1N HCl/Glass/Solution of Unknown } P^H // \text{KCl}_{(sat)}/\text{Hg}_2\text{Cl}_2(\text{s})/\text{Hg(l)}/\text{Pt}$



$$E_{\text{cell}} = E_R - E_L = E_{\text{SCE}} - E_G$$

$$= 0.2422 - (E_G^0 - 0.0591 P^H)$$

$$= 0.2422 - E_G^0 + 0.0591 P^H$$

E_G^0 of glass electrode can be determined by using a solution of known P^H .

$$0.0591 P^H = E_{\text{cell}} + E_G^0 - 0.2422$$

$$P^H = \frac{E_{\text{cell}} + E_G^0 - 0.2422}{0.0591}$$

Advantages of glass electrode

1. It is very simple to operate.

2. It can be used to find the P^H of oxidising, reducing and even coloured solutions.
3. Glass electrode works effectively in the P^H range of 1-9 and is unaffected by oxidising, reducing and poisoning agents.
4. Electrodes made of special glasses can be used upto a P^H of 12.

Draw backs of glass electrode

1. It cannot be used as a reference electrode for solutions having P^H greater than 12.
2. Glass membrane has very high resistance. So ordinary potentiometers cannot be used for determining potential of electrode instead special electronic potentiometers has to be used.

- Find out the pH of a solution measured using Hydrogen electrode which is coupled with saturated calomel electrode. EMF of the combined cell is 0.523V at 25°C. Given that $E_{SCE} = 0.2422V$.

$$E_{cell} = E_{cal} - E_{H_2} = 0.2422 + 0.0591 P^H = 0.523V$$

$$P^H = \frac{0.523 - 0.2422}{0.0591} = 4.75$$

- Potential of H_2 electrode set up in acid solution of unknown strength is 0.295 volts at 25°C when coupled with SHE. Find the P^H of the solution.

$$E_{H_2} = E^0_{H_2} + 0.0591 \log [H^+] = -0.0591 P^H$$

$$E_{Cell} = E_{Cathode} - E_{Anode} = E_{SHE} - E_{H_2} = 0 + 0.0591 P^H = 0.0591 P^H$$

$$P^H = \frac{E_{H_2}}{0.0591} = \frac{0.295}{0.0591} = 4.99$$

- Find out the P^H of a solution in which a glass electrode is dipped and is coupled with SCE. The EMF of the combined cell is 0.205V at 25°C. Given that $E_{SCE} = 0.2422V$ and $E^0_{Glass} = 0.57V$.

$$P^H = \frac{E_{Cell} + E^0_G - 0.2422}{0.0591} = \frac{0.205 + 0.57 - 0.2422}{0.0591} = 9.02$$

Primary and secondary cells

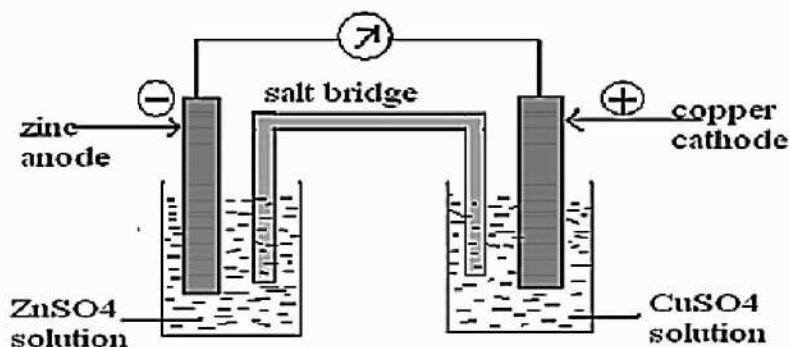
Cells which become dead over a period of time, because the chemical reaction occurs only once. After that the cell becomes exhausted or discharged. They cannot be recharged or reused again.

Eg. Dry cell, Daniel cell, mercury cell etc.

Daniel cell

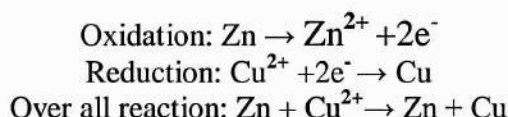
It is also called electrochemical cell or voltaic cell

It consists of Zn rod dipped in $ZnSO_4$ solution and Cu rod dipped in $CuSO_4$ solution. These two electrodes are connected externally using a volt meter and internally using salt bridge. The resultant cell can be represented like this.



DANIELL CELL





Temperature dependance of emf of a Daniel cell or effect of concentration on emf of a daniel cell.

Consider the Daniel cell reaction, $\text{Zn}_{(s)} + \text{Cu}^{2+} \rightarrow \text{Cu}_{(s)} + \text{Zn}^{2+}$,

Nernst equation is given as, $E_{\text{cell}} = E^{\circ}_{\text{cell}} + \frac{2.303RT}{nF} \log \frac{[\text{Cu}^{2+}]}{[\text{Zn}^{2+}]}$

Case I, When $[\text{Cu}^{2+}] = [\text{Zn}^{2+}]$, logarithmic term becomes zero. Then $E_{\text{cell}} = E^{\circ}_{\text{cell}}$ & emf of the cell is independent of temperature.

Case II, When $[\text{Cu}^{2+}] < [\text{Zn}^{2+}]$, logarithmic term becomes negative. Then $E_{\text{cell}} < E^{\circ}_{\text{cell}}$ & emf of the cell decreases with rise in temperature.

Case III, When $[\text{Cu}^{2+}] > [\text{Zn}^{2+}]$, logarithmic term becomes positive. Then $E_{\text{cell}} > E^{\circ}_{\text{cell}}$ & emf of the cell increases with rise in temperature.

Salt Bridge

It is U-shaped tube containing semisolid paste prepared by adding agar-agar or gelatin to aqueous solution of strong electrolyte like KCl, KNO₃, K₂SO₄, NH₄NO₃ etc. Electrolyte should be inert.

Functions of the salt bridge

- It provides cations and anions to replace the ions lost or produced in the two half cells.
- It maintains electrical neutrality of the two solutions in the two half cells.
- It allows the flow of current by completing the electrical circuit.
- It prevents intermixing of solution as well as ions in the two half cells, which may lead to a precipitation reaction.

Variation of Emf of hydrogen electrode with P^H of the solution

For H₂ electrode, $E_{\text{H}_2} = E^{\circ}_{\text{H}_2} + 0.0591 \log [\text{H}^+] = -0.0591\text{P}^{\text{H}}$

At P^H = 0, $E_{\text{H}_2} = -0.0591\text{P}^{\text{H}} = 0.0591 \times 0 = 0 \text{ V}$

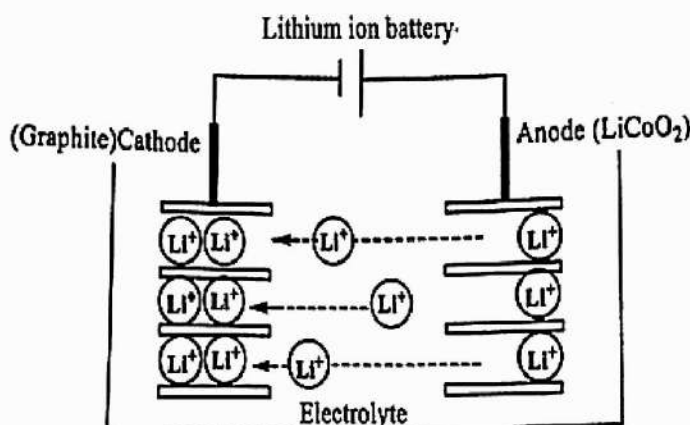
At P^H = 7, $E_{\text{H}_2} = -0.0591\text{P}^{\text{H}} = 0.0591 \times 7 = 0.4137\text{V}$

At P^H = 14, $E_{\text{H}_2} = -0.0591\text{P}^{\text{H}} = 0.0591 \times 14 = 0.8274 \text{ V}$

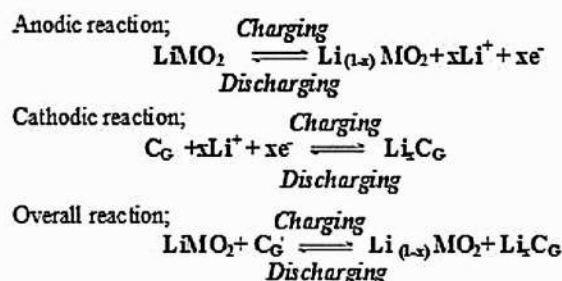
Secondary cell (Accumulators) (Storage cells)

Cells which can be recharged again and again by passing direct current through them. They can be reused. So they are called repeated action cells. They can store electrical energy in the form of chemical energy. Hence they are called storage cells (accumulators).

Lithium ion cell.



Lithium ion cell is a secondary cell in which lithium ions moves between cathode and anode during charging and recharging. In this cell, anode is LiMO_2 , cathode is graphite & electrolyte is an aprotic organic solution.



Thus there is the movement of lithium ions between the cathode and anode during charging and recharging. The main electrochemical reaction in lithium ion cell is the uptake of lithium ion at the cathode and their release during discharging

Cell representation; $\text{Li}_x\text{C}_G | \text{LiX in PC-EC} | \text{Li}_{(1-x)}\text{MO}_2$

Where LiX is lithium salt such as LiClO_4 , PC-EC is a mixed poly propylene carbonate and ethylene carbonate solvent & M is a transition metal such as Co, Mn or Ni.

Uses:

- It is used in lap tops.
- It is used in mobile phones.
- It is used in iPods.
- It is used in MP³ players.

Potentiometric titrations

Titrations which involve the measurement of potential of an indicator electrode with the addition of a titrant is called potentiometric titrations.

Merits of potentiometric titrations;

- No external indicator is required.
- Titrations of weak acids & bases can be carried out potentiometrically.

Principle;

The potential of an electrode dipping into the solution of an electrolyte depends upon the concentration of ions with which it is in equilibrium. Potentiometric titrations are based on the fact that potential of suitable indicator electrode is measured relative to that of a reference electrode and is related to the concentration changes in the solution being titrated. Near the end point, there is a sharp change in the potential of indicator electrode.

Types of potentiometric titrations

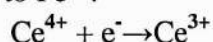
Three types of potentiometric titrations are

1. Acid – base titrations
2. Redox titrations
3. Precipitation titrations

Potentiometric redox titrations

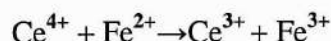
In order to explain the potentiometric titration, let us consider the oxidation of Fe^{2+} to Fe^{3+} by Ce^{4+} in acid medium.

The Ce^{4+} ions having greater reduction potential (1.60V) will undergo reduction & Fe^{2+} ions (0.77V) get oxidized to Fe^{3+} .





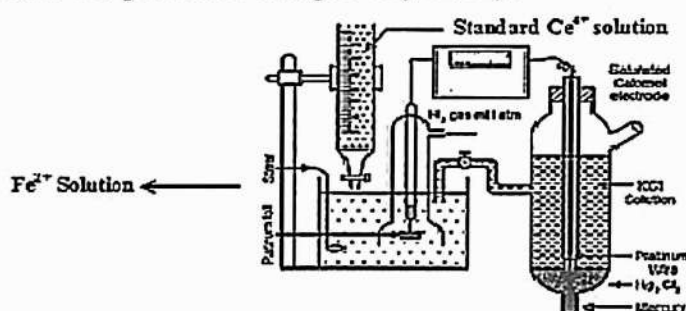
Over all reaction;



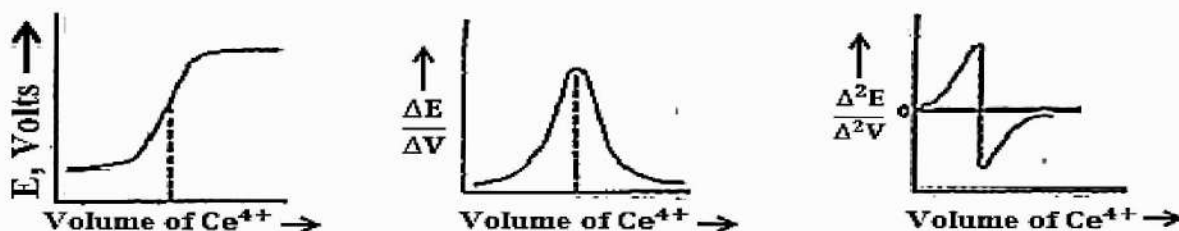
The potential of indicator electrode is

$$E = E_0 + \frac{0.0591}{n} \log \frac{[\text{oxidised state}]}{[\text{reduced state}]} = E_0 + \frac{0.0591}{1} \log \frac{[\text{Fe}^{3+}]}{[\text{Fe}^{2+}]}$$

20 ml ferrous sulphate solution is mixed with 20ml 4N H₂SO₄ in a beaker. A platinum electrode is then inserted into it. It is then coupled with SCE. The electrodes are then connected using a potentiometer. Then standard ceric ammonium sulphate solution is added from the burette. After each addition emf is noted. Emf is then plotted against volume of ceric solution. Emf initially increases with the addition of titrant due to the oxidation of Fe²⁺. Near the end point potential changes sharply. After the end point emf changes very slowly.



Emf is then plotted against volume of Ce⁴⁺ solution, we get an 'S' shaped curve. More and most accurate results are obtained by plotting $\frac{\Delta E}{\Delta V}$ against volume of Ce⁴⁺ solution and $\frac{\Delta^2 E}{\Delta^2 V}$ against volume of Ce⁴⁺ solution, the following curves are obtained.



Uses of potentiometric titration

- There is no need of any external indicator.
- We can conduct the titration of coloured solutions.
- It is useful for the titration of very dilute solution with high degree of accuracy.
- It is useful for the titration of solution contains CN⁻, Cl⁻ etc.

Fundamentals for the measurement of conductivity

Ohm's law:

It states that current passing through the conductor is directly proportional to the potential difference.

$$I \propto V$$

$$V = IR$$

Resistance:

It is the measure of obstruction to the flow of current. Its unit is Ω

$$R \propto l \text{ and } R \propto \frac{1}{A}$$

$$R = \rho \times \frac{l}{A}$$

Conductance:

It is the reciprocal of resistance.

$$C = \frac{1}{R}$$

Specific Resistance (Resistivity):

It is the resistance of a conductor of unit length and unit area of cross section. Or it is the resistance of unit volume of a conductor. Its unit is Ωcm

$$\rho = R \times \frac{A}{l}$$

Specific Conductance (Conductivity):

It is the reciprocal of resistivity. It is also defined as the conductance of unit length and unit area of cross section of a conductor. Its unit is Scm^{-1}

$$K = \frac{1}{R} \times \frac{l}{A} = C \times \frac{l}{A}$$

Molar conductance:

Molar conductance is the conductance of a solution containing 1mol of an electrolyte which is placed between two electrodes which are separated by unit distance. It is denoted by the letter λ_m . Its unit is $\text{Scm}^{-1}\text{mol}^{-1}$.

$$\lambda_m = \frac{1000K}{C}$$

Equivalent conductance:

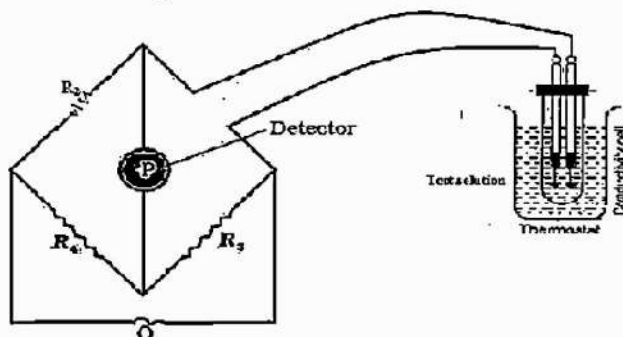
Equivalent conductance is the conductance of a solution containing 1gram equivalent of an electrolyte which is placed between two electrodes which are separated by unit distance. It is denoted by the letter λ . Its unit is $\text{Scm}^{-1}\text{equi}^{-1}$.

$$\lambda = \frac{1000K}{M}$$

The experimental arrangement and procedure for measuring conductance of an electrolytic solution

$$\text{Conductivity of the solution} = C \times \frac{l}{A} = \frac{1}{R} \times \frac{l}{A}$$

Thus for the measurement of conductivity of solution resistance of the solution is to be determined. Wheat stone bridge method is used for this purpose. In this method, a conductivity cell containing the solution is made one arm of the wheat stone bridge apparatus. The electrodes of the cell are made up of platinum coated with platinum black. Then the conductivity cell is placed in a thermostat to keep the temperature constant. In order to prevent electrolysis, an Alternating Current is used. When current passes through the circuit, the resistors R2, R3 and R4 are so adjusted that a null point is obtained in the detector.



At the null point,

$$\frac{R_{\text{solution}}}{R_2} = \frac{R_3}{R_4}$$

$$R_{\text{solution}} = \frac{R_2 R_3}{R_4}$$

The reciprocal of this resistance will give the conductance of the solution. From the conductance we get the specific conductance of the solution. Since conductivity of the solution = $C \times \frac{l}{A}$, where 'l' is the distance between the electrodes and 'A' is the area of cross section of electrodes. For a particular conductivity cell, $\frac{l}{A}$ is constant and is called cell constant.

$$K = C \times \text{Cell constant}$$

$$\text{Cell constant} = \frac{\text{Conductivity}}{\text{Conductance}} = \frac{K}{C}$$

PROBLEMS

1. The specific conductivity of $N/50$ KCl solution at 25°C is $0.0002765\text{ohm}^{-1}\text{cm}^{-1}$. If the resistance of the cell containing this solution is 500Ω , what is its cell constant?

$$K = C \times \frac{l}{A} = \frac{1}{R} \times \frac{l}{A}$$

$$\text{Cell constant} = K \times R = 0.0002765 \times 500 = 0.13825\text{cm}^{-1}$$

2. The specific conductance of a decinormal solution of KCl at 18°C is $0.0112\Omega^{-1}\text{cm}^{-1}$. The resistance of the cell containing the solution at 18°C was found to be 55Ω . What is cell constant.

$$K = C \times \frac{l}{A} = \frac{1}{R} \times \frac{l}{A} = \frac{1}{55} \times \text{cell constant} = 0.0112\Omega^{-1}\text{cm}^{-1}$$

$$\text{Cell constant} = K \times R = 0.0112 \times 55 = 0.616\text{cm}^{-1}$$

3. Find the specific conductance of a given solution at 298K . The resistance of the solution and 0.1M KCl solution are found to be $75\text{k}\Omega$ and $300\text{k}\Omega$ respectively at 298K in the same conductivity cell. Specific conductance of KCl is 0.012Scm^{-1} .

$$K = C \times \frac{l}{A} = \frac{1}{R} \times \frac{l}{A} = \frac{1}{300} \times \text{cell constant} = 0.012\text{Scm}^{-1}$$

$$\text{Cell constant} = K \times R = 0.012 \times 300 = 3.6\text{cm}^{-1}$$

$$K = C \times \frac{l}{A} = \frac{1}{R} \times \text{Cell constant} = \frac{1}{75} \times 3.6 = 0.048\text{Scm}^{-1}$$

4. The decinormal solution of an electrolyte in a conductivity cell whose electrodes are 2.1cm apart and 4.2cm^2 in area offered a resistance of 32Ω . Find the equivalent conductance of the solution.

$$\lambda_{\text{Eq}} = \frac{1000K}{C} = \frac{1000 \times l}{C \times R \times A} = \frac{1000 \times 2.1}{0.1 \times 32 \times 4.2} = 156.25\text{S cm}^{-1}\text{Eq}^{-1}$$

5. Calculate the conductivity of given NaCl solution at 298K , which shows a conductance of $560\mu\Omega^{-1}$ in the given cell at 298K . A standard solution of 0.1M KCl shows a conductance of $1200\mu\Omega^{-1}$ in that cell. Given that conductivity of 0.1M KCl at 298K is $0.01288\Omega^{-1}\text{cm}^{-1}$.

$$K_{\text{KCl}} = C_{\text{KCl}} \times \text{Cell constant}$$

$$\text{Cell constant} = \frac{K_{\text{KCl}}}{C_{\text{KCl}}} = \frac{0.01288}{1200 \times 10^{-6}} = 10.73\text{cm}^{-1}$$

$$K_{\text{NaCl}} = C_{\text{NaCl}} \times \text{Cell constant} = 560 \times 10^{-6} \times 10.73 = 6.01 \times 10^{-3}\Omega^{-1}\text{cm}^{-1}$$

Corrosion

Corrosion is the slow process of deterioration or destruction of the metal through the chemical or electrochemical changes taking place at its surface. Corrosion reactions are of two types. On the basis of this, theories of corrosion are of two types.

I. Dry corrosion (Chemical corrosion)

II. Wet corrosion (Electrochemical corrosion)

I. Dry corrosion:

Corrosion of this type gases occurs by the direct chemical attack of atmospheric gases on the metal in the absence of moisture. They are of three types.

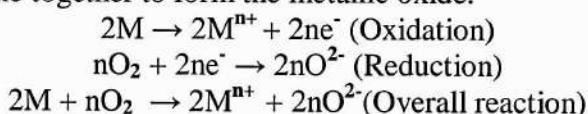
1. Oxidation corrosion
2. Corrosion by other gases
3. Liquid metal corrosion

1. Oxidation corrosion:

It occurs due to the direct action of oxygen on metals in the absence of moisture to form metal oxide. Alkali metals and alkaline earth metals undergo this type of corrosion even at low temperature, whereas noble metals like gold, silver and platinum undergo oxidative corrosion only at high temperature.

Mechanism:

Oxidation occurs at the surface of the metal to form the metal oxide. On oxidation, the metal atoms change to metal ions (M^{n+}) and oxygen changes to oxide ions (O^{2-}). These oppositely charged ions then combine together to form the metallic oxide.



Thus a thin layer of metal oxide is formed on the surface of the metal. The nature of the oxide film determines the further destruction of the metal. Films can be of different types.

a) Stable film:

Stable films can adhere tightly to the metal surface. This film can act as a protective coating to prevent further deterioration of the metal. Oxide films of Al, Sn, Cu, Pb etc. are included in this film.

b) Unstable films:

Unstable films readily decompose back to metal and oxygen. In this case metal will not undergo further deterioration. This type of film is obtained in the case of metals like gold, silver and platinum.

c) Volatile film:

This type of film volatilises off as soon as it is formed. Hence the underlying metal surface again becomes exposed for further attack of oxygen and this process continues. Here corrosion becomes a continuous process and the observed destruction will be maximum. Molybdenum can produce volatile oxide film.

d) Porous oxide film:

If the oxide film formed is porous, then the atmospheric oxygen can penetrate through the film to attack the underlying metal. Here also corrosion becomes a continuous process leading to the total destruction of the metal. Iron can produce this type of film.

2. Corrosion by other gases:

Similar to oxygen, some other gases also bring dry corrosion. They are SO_2 , CO_2 , Cl_2 , H_2S , F_2 , H_2 etc. Extent of corrosion is determined by its chemical affinity towards the metal. It also depends upon the nature of the film, whether the film is porous or protective.

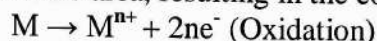
3. Liquid metal corrosion:

This type of corrosion is seen in nuclear power stations. It occurs due to the chemical action of flowing liquid metal on solid metal or alloys at high temperature. In such cases, solid metal may dissolve in the liquid metal or liquid metal may penetrate into the internals of solid metals.

II. Wet corrosion (Electrochemical corrosion)

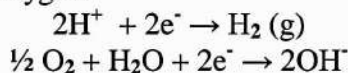
This type of corrosion can occur when a conducting liquid is in contact with a metal or when two dissimilar metals or alloys are partially immersed in a conducting solution.

Oxidation takes place at the anodic area, resulting in the corrosion of the metal.



The M^{n+} ions so formed dissolves in the solution.

Reduction occurs at the cathodic area. At the cathodic area, the dissolved constituents in the conducting medium accept electrons to form ions like OH^- , O^{2-} etc. The non-metallic ions so formed combine with the M^{n+} to form corrosion product. The electrons released at the anode flow through the metal and get consumed in the cathodic reaction, either for the evolution of hydrogen or for the absorption of oxygen.

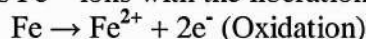


Corrosion with evolution of H_2 occurs, when the anodic area is very large and cathodic area is small and it usually occurs in acidic environments. Absorption of O_2 occurs in neutral or slightly alkaline medium.

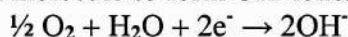
Rusting of iron

In this initially a thin film of iron oxide is formed on the surface of iron metal. Some cracks are developed on the iron oxide film. The surface of the metal acts as the anodic area, whereas the interior of the metal behaves as cathode.

At the anodic area, Fe dissolves as Fe^{2+} ions with the liberation of electrons.

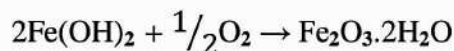


The electrons thus released from the anode move to the cathodic area through the metal. These electrons are then taken up oxygen molecule to form OH^- ions.

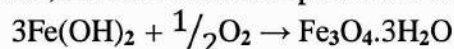


The Fe^{2+} ions formed at the anodic area and the OH^- ions formed at the cathodic area combine to form $\text{Fe}(\text{OH})_2$ precipitate.

In the presence of excess of oxygen, $\text{Fe}(\text{OH})_2$ precipitate easily oxidises to get yellow rust having the formula, $\text{Fe}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$



If the amount of oxygen is limited, then the corrosion product is black rust (Hydrated magnetite)



Galvanic series


Relative corrosion affinities of metals and alloys can be explained by using a series called galvanic series. This series can be prepared by studying the corrosion affinities of metals and alloys in unpolluted sea water without their oxide films. A metal high in this series is more anodic and undergoes corrosion faster than the metal below it. The position of a metal in the form of an alloy is different from that of the pure metal in this series.

Comparison of electrochemical series and galvanic series

Electrochemical Series	Galvanic series
<ul style="list-style-type: none"> • E^0 is measured only for metals and non-metals. • E^0 is measured by dipping pure metals in their 1M salt solution. • SHE is used as the reference electrode. • Position of the metals is fixed. • It predicts the relative displacement tendencies. 	<ul style="list-style-type: none"> • E^0 is measured only for metals and alloys. • E^0 is measured by dipping metals and alloys in unpolluted sea water. • Calomel electrode is used as the reference electrode. • Position of the metal and alloys may change. • It predicts the corrosion tendencies.

Galvanic series of metals and alloys

Active or Anodic

- 
1. Mg
 2. Mg Alloy
 3. Zn
 4. Al
 5. Cd
 6. Al Alloy
 7. Mild Steel
 8. Cast Iron
 9. High Ni Cast Iron
 10. Pb-Sn Solder
 11. Pb
 12. Sn
 13. Inconel
 14. Ni-Mo-Fe Alloys
 15. Brass
 16. Monel (30% Cu, 7% Ni and rest Fe)
 17. Ag Solder
 18. Cu
 19. Ni
 20. Cr Stainless steel
 21. 18-8 Stainless Steel
 22. 18-8 Mo Stainless Steel
 23. Ag
 24. Ti
 25. Graphite
 26. Au
 27. Pt

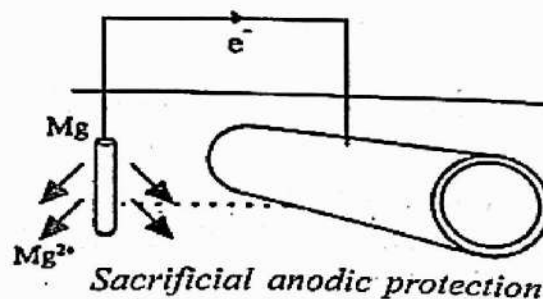
Noble or Cathodic

Cathodic Protection:

In this method, the metal to be protected is made as cathode so that corrosion will not occur. The following methods are employed for cathodic protection.

a) Sacrificial anodic protection:

In this method, the metal to be protected is connected by a wire to a more anodic or active metal. Then the more active metal will undergo corrosion and the cathode remains protected.

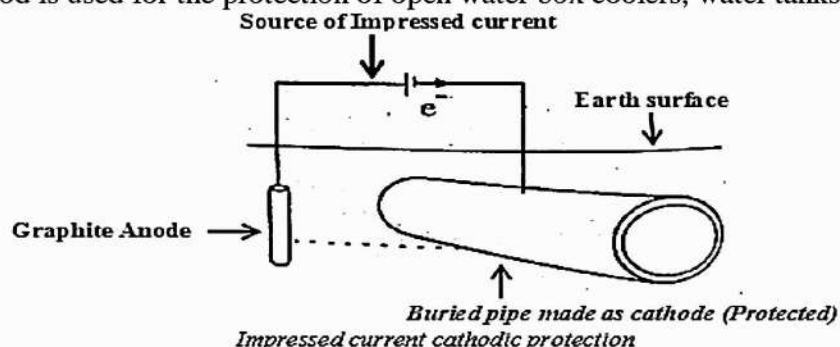


Here the more active anodic metal sacrifices for the protection of cathodic metal and is called sacrificial anode. Metals commonly used for this purpose are Mg, Zn, Al and their alloys.

b) Impressed current cathode protection:

In this method an impressed current is applied in opposite direction to nullify the corrosion current. As a result corroding metal is converted from anode to cathode. The impressed current

required can be obtained from a battery with an insoluble anode made of graphite or high silica iron. This method is used for the protection of open water box coolers, water tanks etc.



Comparison of sacrificial anode protection and impressed current cathodic protection

Sacrificial anode protection	Impressed current cathodic protection
<ul style="list-style-type: none"> • No external power supply is required. • Economical for short term protection. • Investment is less. • Requires periodical replacement of anodic material. • Suitable when current requirements and resistivity of the electrolyte are relatively low. 	<ul style="list-style-type: none"> • External power supply is required. • More suitable for long term protection. • High investment is required. • Anodes are relatively stable and do not corrode. • Suitable when current requirements and resistivity of the electrolyte are relatively high.

Electroless plating (Autocatalytic plating)

It is the method of depositing a metal from its salt solution on the catalytically active surface of the metal to be plated using a suitable reducing agent without using electrical energy.

In this process, metal piece to be plated is immersed in a mixture of reducing agent and a complex compound. The reducing agent reduces metal ion into metal which gets plated over the catalytically active surface of the metal to produce a thin uniform coating. This process is a controlled chemical reduction and is catalyzed by the metal or alloy being deposited. This method allows the easy preparation of films of low thickness using simple equipments. Most common electroless plating is electroless nickel plating.

Electroless Nickel plating

Pretreatment and activation of the surface

The surface to be plated is first degreased by using organic solvents or alkali. It is then followed by acid treatment. Surface of stainless steel is then activated by dipping in a hot solution of 50% dil. H_2SO_4 . Mg alloy surface can be activated by thin coating of Zn and Copper over it. Metals like Cu, Al and alloys like brass can be directly Ni plated without activation. Non-metallic articles like plastics, glasses are activated by dipping them in the solution of $SnCl_2$ and HCl followed by dipping in $PdCl_2$ solution. A thin layer of Pd will be formed on the surface upon drying.

Procedure

The pretreated object is immersed in the plating bath containing Nickel sulphate salt (Coating), hypophosphate reducing agent (Metal deposition), complexing agent like Sodium succinate (Quality improvement) and a buffer like Sodium Acetate (P^H maintenance). Air is then applied and heated. Electroless plating of Ni takes place as follows.



Applications of electroless Ni plating

- It is extensively used in electronic applications.
- Electroless Ni plated polymers like ABS are used for decoration purpose.
- It is also used automotive fields.

Advantages

- No electricity is required.
- This can be carried out on insulators on insulators and semiconductor materials.
- This can be used to obtain uniform coating on irregular shaped objects.
- These deposits are more compact and highly adherent.

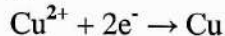
Electroless Copper plating

In this method, article to be plated is immersed in a plating bath containing CuSO_4 (As a source of Cu), formaldehyde (Reducing Agent), buffer solution of NaOH and Rochelle salt and a complexing reagent. Air is bubbled slowly through the medium to control the formation of cuprous oxide. Electroless plating of Cu takes place as follows.

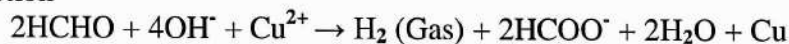
Oxidation



Reduction



Net reaction



Applications of electroless Cu plating

- Widely used for metalizing printed circuit boards.
- Used for plating on non-conductors.
- It is also used for making decorative plating on plastics.

Advantages

- This method produces even coatings.
- It does not use electrical power.
- This coating is having improved hardness, strength, ductility and resistance to corrosion.

Disadvantages

- The reducing agent, formaldehyde is a human health hazard.
- The instability of the electroless copper bath creates difficulties in process control.

MODULE II
SPECTROSCOPIC TECHNIQUES AND APPLICATIONS

The study of interaction of electromagnetic radiation with matter is called spectroscopy.

Absorption laws

The absorption of light by molecules is governed by certain laws. They are collectively known as absorption laws. They are

1. Beer's law
2. Lambert's law
3. Beer – Lambert's law

Beer's law

When a monochromatic light is incident on a homogeneous medium, then the intensity of transmitted light decreases with increase in concentration of absorbing solution.

$$\text{Log } \frac{I_0}{I_t} \propto c$$
$$\text{Log } \frac{I_0}{I_t} = kc$$

Lambert's law

When a monochromatic light is incident on a homogeneous medium, then the intensity of transmitted light decreases with increase in thickness of the medium.

$$\log \frac{I_0}{I_t} \propto t$$
$$\log \frac{I_0}{I_t} = kt$$

Beer – Lambert's law

When a monochromatic light is incident on a homogeneous medium, then the intensity of transmitted light decreases with increase in concentration of absorbing solution as well as thickness of the medium.

$$\log \frac{I_0}{I_t} \propto ct$$
$$\log \frac{I_0}{I_t} = \epsilon ct$$

Where I_0 is intensity of incident radiation, I_t that of transmitted radiation, ϵ is the molar extinction (absorption) coefficient, c is the concentration and t is the thickness of the medium.

Absorbance (A)

It is the logarithm of ratio of intensity of incident radiation to that of transmitted radiation.

$$A = \log \frac{I_0}{I_t}$$

Transmittance (T)

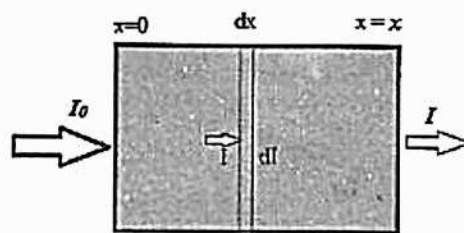
It is the ratio of intensity of transmitted radiation to that of incident radiation.

$$T = \frac{I_t}{I_0}$$
$$\log \frac{1}{T} = \epsilon ct$$
$$-\log T = \epsilon ct$$

Derivation of Beer – Lambert's law

When a mono-chromatic light is passed through the homogeneous medium of concentration (C), the rate of decrease in intensity of radiation (-dI) with thickness of the medium (dt) is proportional to the intensity of incident radiation (I) and also the concentration (C).

$$\frac{-dI}{dt} \propto IC$$
$$\frac{-dI}{I} = KCdt, \text{ where K is the proportionality constant.}$$



Light beam passing through a solution

Let I_0 be the intensity of incident radiation and I_t that of transmitted radiation passing through any finite thickness (t) of the medium, then

$$-\int_{I_0}^{I_t} \frac{dI}{I} = KC \int_0^t dt$$

$$-\ln \frac{I_t}{I_0} = KCt$$

$$\ln \frac{I_0}{I_t} = KCt$$

This is the integrated form of Beer-Lambert's law.

$$2.303 \log \frac{I_0}{I_t} = KCt \quad \log \frac{I_0}{I_t} = \frac{K}{2.303} Ct$$

$$A = \log \frac{I_0}{I_t} = \epsilon Ct$$

Where ϵ is the molar extinction (absorption) coefficient. It depends on the nature of medium and also the extent of absorption.

- The absorbance of a 0.01M dye solution in ethanol is 0.62 in a 2cm cell for light of wave length 5000 \AA . If the path length of light through the sample is doubled and the concentration is made half, what will be the value of absorbance?

$$A = \epsilon ct$$

$$\frac{A_1}{A_2} = \frac{c_1 t_1}{c_2 t_2} = \frac{c_1 t_1}{\frac{c_1}{2} 2t_1} = 1, \text{ absorbance remains same}$$

- A dye solution of concentration 0.04M shows absorbance of 0.045 at 530nm; while a test solution of same dye shows absorbance 0.022 under same conditions. Find the concentration of test solution.

$$A = \epsilon Ct, \text{ Here } \epsilon \text{ and } t \text{ are constants}$$

$$\frac{A_1}{A_2} = \frac{C_1}{C_2}$$

$$\frac{0.045}{0.022} = \frac{0.04}{C_2}$$

$$C_2 = 0.0195M$$

- The percentage transmittance of a 0.01m dye solution in ethanol is 20% in a 2cm cell for light of wave length 5000 \AA . Find the absorbance and molar absorption coefficient.

$$A = \log \frac{I_0}{I_t} = \epsilon Ct$$

$$A = \log \frac{100}{20} = 0.6989$$

$$\epsilon = \frac{A}{Ct} = \frac{0.6989}{0.01 \times 2} = 34.945 \text{ M}^{-1} \text{ cm}^{-1}$$

- A 50ppm standard solution of Fe^{3+} after developing red colour with ammonium thio-cyanate shows a transmittance of 0.2 at 620nm. While an unknown solution of Fe^{3+} after developing colour with the same amount of ammonium thio-cyanate gives a transmittance of 0.4. Find the concentration of unknown Fe^{3+} solution.

$-\log T = \epsilon Ct$, where ϵ & t are constants.

$$\frac{\log T_1}{\log T_2} = \frac{C_1}{C_2}$$

$$\frac{\log 0.2}{\log 0.4} = \frac{50}{C_2}$$

$$C_2 = 28.4 \text{ ppm}$$

- A solution shows a transmittance of 20% when taken in a cell of 2.5 cm thickness. Calculate its concentration if molar absorption coefficient is $12000 \text{ dm}^2 \text{ mol}^{-1}$.

$$A = \log \frac{I_0}{I_t} = \epsilon ct = 0.6986$$

$$\log \frac{100}{20} = 12000 \times c \times 2.5$$

$$c = \frac{A}{\epsilon t} = \frac{0.6986}{12000 \times 2.5} = 2.3296 \times 10^{-4} \text{ mol dm}^{-3}$$

Fundamentals of spectroscopy

Interaction of electromagnetic radiations with matter produces spectrum. Spectrum can be explained in terms of energy levels present in the matter.

Interaction of electromagnetic radiations with atom produces atomic spectrum. Atomic spectrum can be explained in terms of energy levels present in the atom. When an electron jumps from one energy level to another energy level, energy can be emitted or absorbed. When the electron jumps from higher energy level E_2 to the lower energy level E_1 , the excess energy can be emitted in the form of radiation of definite frequency (ν).

$$\Delta E = E_2 - E_1$$

$$h\nu = E_2 - E_1$$

$$\nu = \frac{E_2 - E_1}{h}$$

where 'h' is the Planck's constant. The frequency of emitted radiation produces a bright line. Spectrum consists of bright lines produced by the emission of electromagnetic radiation by atoms is called atomic emission spectra or line spectra.

Types of spectrum

Based on the nature of interaction, the spectra can be broadly divided into absorption spectra and emission spectra.

Absorption Spectra

When an atom or molecule undergoes transition from lower energy level E_1 to the higher energy level E_2 , absorption of energy occurs in the form of radiation of definite frequency and the resultant spectrum is called absorption spectrum.

Emission Spectrum

When an atom or molecule undergoes transition from lower energy level E_1 to the higher energy level E_2 , absorption of energy occurs in the form of radiation of definite frequency and the resultant spectrum is called absorption spectrum.

Based on the nature of the interacting species, the spectra can be divided into two categories, atomic spectra and molecular spectra.

Atomic Spectra

Interaction of electromagnetic radiations with atoms produces transition of electrons between the atomic energy levels and the resultant spectrum is called atomic spectra.

Molecular Spectra

Interaction of electromagnetic radiations with molecules produces transition of electrons between the molecular energy levels and the resultant spectrum is called molecular spectra.

Electromagnetic radiations

Radiations having electric and magnetic field associated with them are called electromagnetic radiations. They are radio waves, micro waves, IR (far IR, middle IR, near IR), visible light, UV light (ordinary UV, vacuum UV), X- rays, γ – rays and cosmic rays. They are arranged in the increasing order of their frequency or the decreasing order of wave length. This is known as *electromagnetic spectrum*. They do not require any medium for their propagation. They possess wave like characteristics.

Characteristics of electromagnetic radiations

1. Wave length (λ)

It is the distance between two adjacent crests or two adjacent trough of a wave. Unit is nanometer and \AA .

$$1\text{nm} = 10^{-9}\text{ meter}$$
$$1\text{\AA} = 10^{-10}\text{ meter}$$

2. Frequency (ν)

Number of waves which pass through a given point in 1 second is called frequency. Its unit is Hertz or Cycles per Second (CPU).

$$1\text{ Hertz} = 1\text{ Cycles per Second (CPU)}$$

3. Velocity (v or c)

Distance travelled by a wave in 1 second is called velocity. Its unit is m/S. Velocity of all electromagnetic radiations in space is constant and is $3 \times 10^8 \text{ ms}^{-1}$

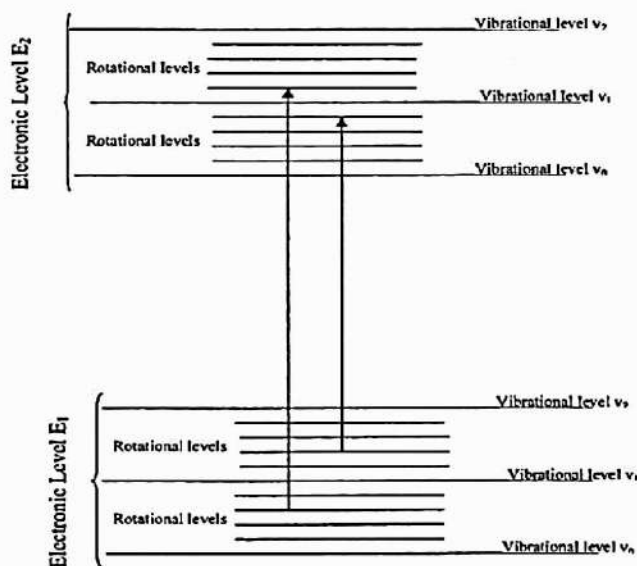
4. Wave number ($\bar{\nu}$)

It is the reciprocal of wave length. Its unit is cm^{-1} or m^{-1} .

$$\bar{\nu} = 1/\lambda$$

Molecular spectra

Interactions of electromagnetic radiation with molecules produce molecular spectra. In a molecule three types of energy levels are present. They are rotational, vibrational & electronic energy levels. The transition between these energy levels results in the emission or absorption of energy in the form of radiation of definite frequency. Generally large numbers of such transitions are possible.



Within the same electronic energy level, there are large numbers of vibrational energy levels and within the same vibrational energy level, there are large number of rotational energy levels. The electronic, vibrational and rotational energy levels are represented by n, v, j .

Total energy of a molecule = $E_{\text{ele}} + E_{\text{vib}} + E_{\text{rot}}$

When a molecule emit or absorb radiation, it may results in the electronic vibrational and rotational energy changes. All these changes are quantized and give rise to three types of molecular spectra. They are rotational spectra, vibrational spectra and electronic spectra.

The energy involved in these transitions is in the following order.

$$E_{\text{ele}} - E_{\text{ele}}^1 > E_{\text{vib}} - E_{\text{vib}}^1 > E_{\text{rot}} - E_{\text{rot}}^1$$

Because of the change in energy level between the rotational, vibrational and electronic energy levels, molecular spectrum is obtained at three different regions of the electronic spectra.

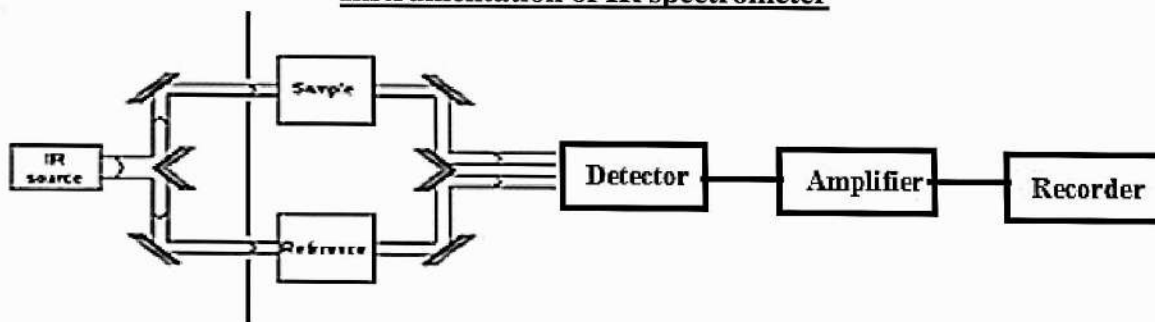
Vibrational Spectra (IR Spectra)

IR spectroscopy is concerned with the study of absorption of IR radiation (800nm-1mm), which causes vibrational transition in the molecule. When a gaseous molecule absorbs IR radiation, it produces transition between the vibrational energy levels. Resultant spectrum is called vibrational spectra.

The essential requirement for a molecule to produce IR spectrum is that **the dipole moment of the molecule must change during vibration**. Thus vibrational spectrum is given by hetero nuclear diatomic molecules. Polyatomic molecules with and without dipole moment also produces IR spectrum. Homo nuclear diatomic molecules such as O_2 , N_2 , H_2 etc. will not produce IR spectrum, since they have zero dipole moment. But molecules like HCl , HBr , NO_2 , H_2O , CO_2 , NH_3 , CH_3Cl and SO_2 can produce IR spectra and they are IR active molecules. In the case of polyatomic molecules without dipole moment, the exciting radiations can induce an oscillating dipole moment. Hence they are also IR active.

When a gaseous molecule having dipole moment vibrates, it generates an electric field which can interact with electrical component of IR radiation. During this interaction energy can be emitted or absorbed in the form of radiation of definite frequency. Thus the vibration of the molecule produces IR spectrum.

Instrumentation of IR spectrometer



Theory of IR spectra

In order to explain the theory of IR spectra, consider the vibration of hetero nuclear diatomic molecule. It is similar to the vibration of a simple harmonic oscillator.

Vibrational energy of simple harmonic oscillator = Vibrational energy of diatomic molecule

$$E_{\text{vib}} = (v + \frac{1}{2}) h\omega$$

Fundamental frequency of vibration, $\omega = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}}$, where 'k' is the force constant and it gives an idea about the strength of the bond.

$$\text{Reduced mass } (\mu) = \frac{m_1 m_2}{m_1 + m_2}$$

When the molecule is in the vibrational ground level ($v = 0$), $E_{\text{vib}} = \frac{1}{2} h\omega$. This is the lowest vibrational energy level and it is called **zero point energy**.

Let us consider the vibrational transition from lowest vibrational (v^1) to the next higher vibrational energy level (v).

$$\begin{aligned} \text{Energy change during vibrational transition } (\Delta E_{\text{vib}}) &= E_{v_2} - E_{v_1} \\ &= (v + 1/2) h\omega - (v^1 + 1/2) h\omega \\ &= (v - v^1) h\omega = \Delta v h\omega \end{aligned}$$

The selection rule for vibrational spectrum is

$$\Delta v = \pm 1$$

$$\Delta E_{\text{vib}} = h\omega$$

Spectrum can be explained in terms of wave number.

$$\text{Thus the wave number of absorbed line } (\bar{\nu}) = \frac{\Delta E_{\text{vib}}}{ch} = \frac{h\omega}{ch} = \frac{\omega}{c} = \frac{1}{2\pi c} \sqrt{\frac{k}{\mu}}$$

According to Hooke's law,

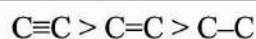
$$\bar{\nu} = \frac{1}{2\pi c} \sqrt{\frac{k}{\mu}}$$

$$K = 4\pi^2 c^2 \bar{\nu}^2 \mu$$

Thus the frequency or wave number of absorbed line depends on

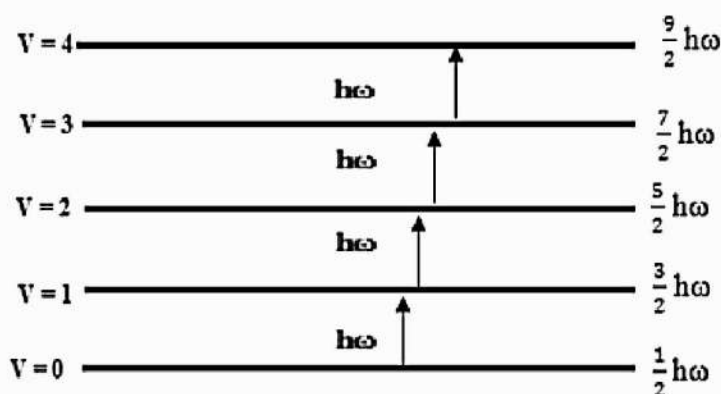
- Force constant(k)
- Reduced mass(μ)

Stretching frequency for $\text{C}\equiv\text{C}$, $\text{C}=\text{C}$, $\text{C}-\text{C}$ bond are in the following order etc.



Since the force constant for each type of bond follows the order.

$$k_{\text{C}\equiv\text{C}} > k_{\text{C}=\text{C}} > k_{\text{C}-\text{C}}$$



Different vibrational transitions are possible between the vibrational energy levels, but all the vibrational energy levels are equally spaced with a spacing of ' $h\omega$ '. So all the lines in the spectrum would fall in the same region. **Hence vibrational spectrum is expected to consist of a single line.**

At ordinary conditions of temperature and pressure, most of the molecules are in the vibrational ground level ($V = 0$). So only one transition is possible according to the selection rule, i.e. $0 \rightarrow 1$ transition and the resultant lines are called **fundamental lines** and are **highly intense lines**. But in actual practice molecular vibrations are **not harmonic**. Such an oscillator is called **anharmonic oscillator**. For an anharmonic oscillator ΔV is rarely unity. Sometimes it is +2 and sometimes it is +3. If $\Delta V = +2$, then the most probable transition is **$0 \rightarrow 2$ transition** and the resultant lines are called **first overtones**. They have lesser intensity than the fundamental

lines. If $\Delta V = +3$, then the most probable transition is **0 \rightarrow 3 transition** and the resultant lines are called **second overtones**. They have least intensity.

- Calculate the force constant of HCl molecule, if it gives IR absorption at 3050cm^{-1} . (Given that atomic masses of H = 1 amu and Cl = 35 amu)

$$\bar{\nu} = 3050\text{cm}^{-1} = 3050 \times 100 \text{ m}^{-1}$$

$$\mu = \frac{m_1 m_2}{m_1 + m_2} \times 1\text{u} = \frac{1 \times 35}{1 + 35} \times 1.67 \times 10^{-27} \text{ kg} = 1.63 \times 10^{-27} \text{ Kg.}$$

$$k = 4\pi^2 c^2 \bar{\nu}^2 \mu = 4\pi^2 \times (3 \times 10^8)^2 (3050 \times 100 \text{ m}^{-1})^2 \times 1.63 \times 10^{-27} \text{ kg} \\ = 532.8 \text{ Nm}^{-1}$$

- CO molecule absorbs at 2140cm^{-1} . Calculate the force constant of the molecule. Given atomic masses of C & O are 12u and 16u respectively. ($1\text{u} = 1.67 \times 10^{-27} \text{ kg}$).

$$\bar{\nu} = \frac{1}{2\pi c} \sqrt{\frac{k}{\mu}}$$

$$\mu = \frac{m_1 m_2}{m_1 + m_2} \times 1\text{U} = \frac{12 \times 16}{12 + 16} \times 1.67 \times 10^{-27} \text{ kg}$$

$$k = 4\pi^2 c^2 \bar{\nu}^2 \mu$$

$$k = 1853 \text{ Nm}^{-1}$$

- The vibrational frequency of HCl molecule is 2886cm^{-1} . Calculate the force constant of the molecule. Reduced mass of HCl is $1.63 \times 10^{-27} \text{ Kg}$.

$$\bar{\nu} = \frac{1}{2\pi c} \sqrt{\frac{k}{\mu}} \text{ cm}^{-1}$$

$$k = 4\pi^2 c^2 \bar{\nu}^2 \mu = 4\pi^2 \times (3 \times 10^8)^2 (2886 \times 100)^2 \times 1.63 \times 10^{-27} \text{ Kg.}$$

$$k = 481.8 \text{ Nm}^{-1}$$

- The fundamental vibrational frequency of $^{12}\text{C}^{16}\text{O}$ is 2140 cm^{-1} . Without calculating force constant, find the fundamental frequency of $^{13}\text{C}^{17}\text{O}$ in cm^{-1} .

$$k = 4\pi^2 c^2 \bar{\nu}^2 \mu$$

$$\mu^{12\text{C}^{16}\text{O}} = \frac{12 \times 16}{12 + 16} \times 1.67 \times 10^{-27} = 1.145 \times 10^{-26} \text{ kg}$$

$$\mu^{13\text{C}^{17}\text{O}} = \frac{13 \times 17}{13 + 17} \times 1.67 \times 10^{-27} = 1.23 \times 10^{-26} \text{ kg}$$

$$\frac{\bar{\nu}^{13\text{C}^{17}\text{O}}}{\bar{\nu}^{12\text{C}^{16}\text{O}}} = \sqrt{\frac{\mu^{12\text{C}^{16}\text{O}}}{\mu^{13\text{C}^{17}\text{O}}}}$$

$$\bar{\nu}^{13\text{C}^{17}\text{O}} = \bar{\nu}^{12\text{C}^{16}\text{O}} \times \sqrt{\frac{\mu^{12\text{C}^{16}\text{O}}}{\mu^{13\text{C}^{17}\text{O}}}}$$

$$\bar{\nu}^{13\text{C}^{17}\text{O}} = 2140 \times \sqrt{\frac{1.145 \times 10^{-26}}{1.23 \times 10^{-26}}} = 2065 \text{ cm}^{-1}$$

- Calculate the force constant of HF molecule, if it shows IR absorption at 4138 cm^{-1} . Given that atomic masses of hydrogen and fluorine are 1u and 19u respectively. What would be the wave number if hydrogen atoms are replaced by deuterium atoms?

$$k = 4\pi^2 c^2 \bar{\nu}^2 \mu$$

$$\mu = \frac{m_1 m_2}{m_1 + m_2} \times 1\text{U} = \frac{1 \times 19}{1 + 19} \times 1.66 \times 10^{-27} \text{ kg} = 1.577 \times 10^{-27} \text{ kg}$$

$$k = 4\pi^2 c^2 \bar{\nu}^2 \mu = 4\pi^2 \times (3 \times 10^8)^2 (4138 \times 100)^2 \times 1.577 \times 10^{-27} \text{ Kg} = 958.3 \text{ Nm}^{-1}$$

When deuterium is substituted for hydrogen, k remains constant.

$$\bar{\nu}^2 \propto 1/\mu$$

$$\frac{\bar{\nu}_1^2}{\bar{\nu}_2^2} = \frac{\mu_2}{\mu_1}$$

$$\frac{4138^2}{\bar{\nu}_2^2} = \frac{2 \times 19}{1 \times 19}$$

$$\bar{\nu}_2 = 2998 \text{ cm}^{-1}$$

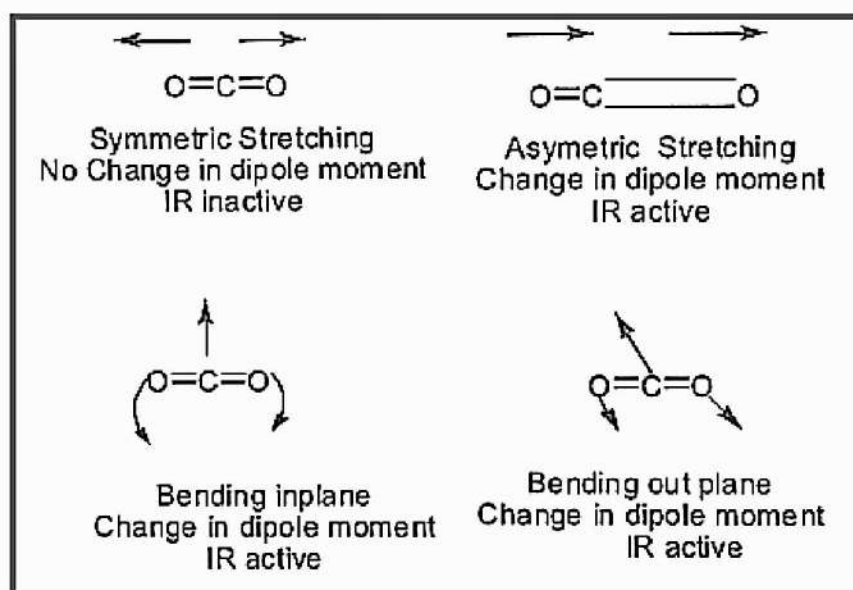
IR Spectrum of polyatomic molecules

In the case of polyatomic molecules, IR spectrum depends on the number of vibrational modes. But the number of vibrational modes depends upon the structure.

For linear molecules (CO_2), number of vibrational modes = $3n-5$ and for non-linear molecules (H_2O , SO_2), number of vibrational modes = $3n-6$.

CO_2 has four vibrational modes symmetric stretching, asymmetric stretching and two bending vibrations in two mutually perpendicular planes. Out of the four vibrational modes only three are IR active. The symmetric stretching does not involve the change of di-pole moment and is not IR active.

For CO_2 , which is a linear molecule, there are $3(3) - 5 = 4$ fundamental vibrations:

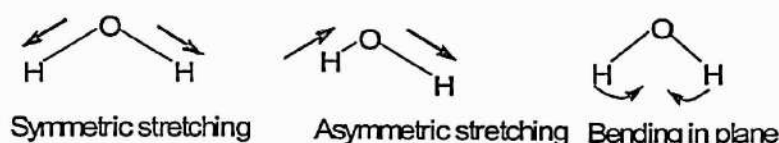


Asymmetric stretching and bending modes of vibration of $\text{O}=\text{C}=\text{O}$ molecule results in the variations of dipole moment. Hence these vibrational modes are IR active.

H_2O is a non-linear molecule.

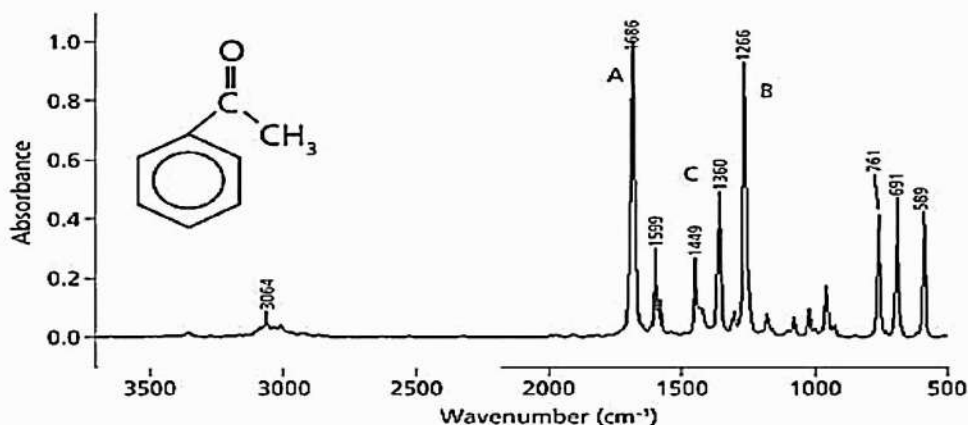
So number of vibrational modes = $3n - 6 = 3 \times 3 - 6 = 3$.

They are symmetric stretching, asymmetric stretching and bending in plane vibrational modes. In all these cases there is a change in dipole moment. So all are IR active.



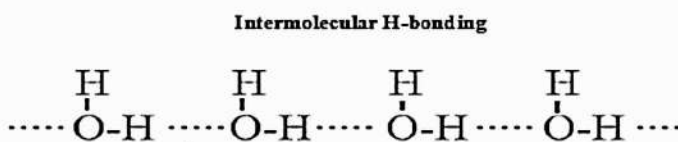
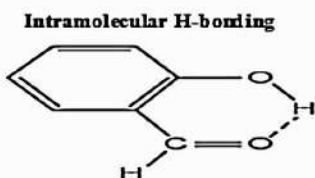
Features of IR spectrum

In order to explain the features of IR spectrum, let us consider the IR spectrum of acetophenone. Spectrum can be divided into two regions. First region lies in between 1600 – 4000 cm^{-1} . This region is called functional group region, since the vibrational modes of most of the functional groups occur in this region. A few broad bands in the functional group region show the presence of a functional group. Second region lies between 600 – 1600 cm^{-1} . A few broad bands in this region show the presence of an aliphatic group. Large numbers of sharp bands in this region show the presence of an aromatic group. Hence this region provides the confirmation of identity and this region is called finger print region.



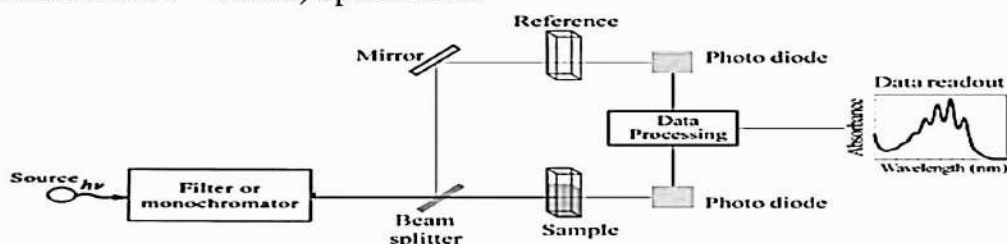
Applications of IR spectroscopy;

- The identity of unknown substance can be explained by considering the IR spectrum of unknown substance with that of a known substance.
- This will give valuable information about molecular symmetry and force constant.
- This can be used to detect the presence of impurities, since the impurities give rise to extra absorption bands.
- This can be used to distinguish intra molecular H-bonding & inter molecular H-bonding. This can be done by taking the IR spectrum at different dilutions. As the dilution increases intensity of absorption band diminishes when it is due to inter molecular H-bonding and as the dilution increases intensity of absorption band remains unchanged when it is due to intra molecular H- bonding.



Electronic (UV –Visible) Spectroscopy

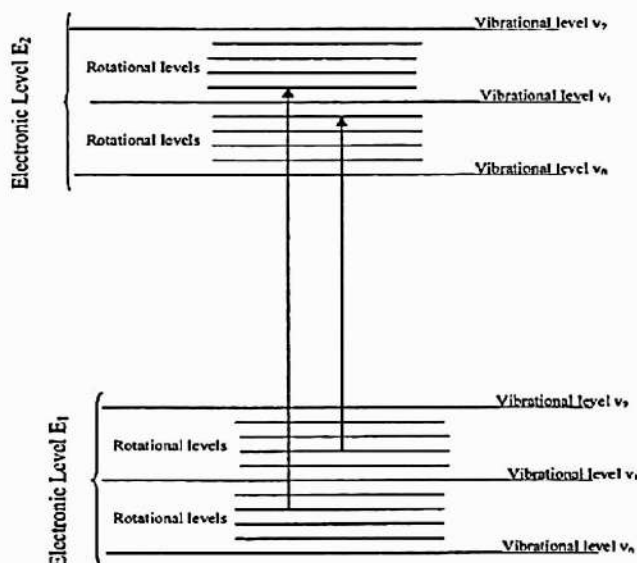
Instrumentation of UV –Visible) Spectrometer



Electronic spectrum of a molecule

Electronic spectrum of molecule arises due to the transition between electronic energy levels. Electronic transitions are highly energetic transitions. Hence it produces spectrum in the UV – Visible region.

In a molecule three types of energy levels are present. They are rotational, vibrational & electronic energy levels. Within the same electronic energy level, there are large numbers of vibrational energy levels and within the same vibrational energy level, there are large number of rotational energy levels. So electronic transitions are always followed by simultaneous vibrational and rotational transitions. Hence we get a broad spectrum consisting of lines for electronic, vibrational and rotational transitions.



Suppose $E^1_{(ele)}$, $E^1_{(vib)}$, $E^1_{(rot)}$ be the electronic, vibrational and rotational energy of the molecule before transition and $E_{(ele)}$, $E_{(vib)}$, $E_{(rot)}$ be the electronic, vibrational and rotational energy of the molecule after transition.

Total energy of the molecule before transition (E^1) = $E^1_{(ele)} + E^1_{(vib)} + E^1_{(rot)}$

Total energy of the molecule after transition (E) = $E_{(ele)} + E_{(vib)} + E_{(rot)}$

Change in energy during transition (ΔE) = $(E - E^1)$
 $= (E_{(ele)} + E_{(vib)} + E_{(rot)}) - (E^1_{(ele)} + E^1_{(vib)} + E^1_{(rot)})$

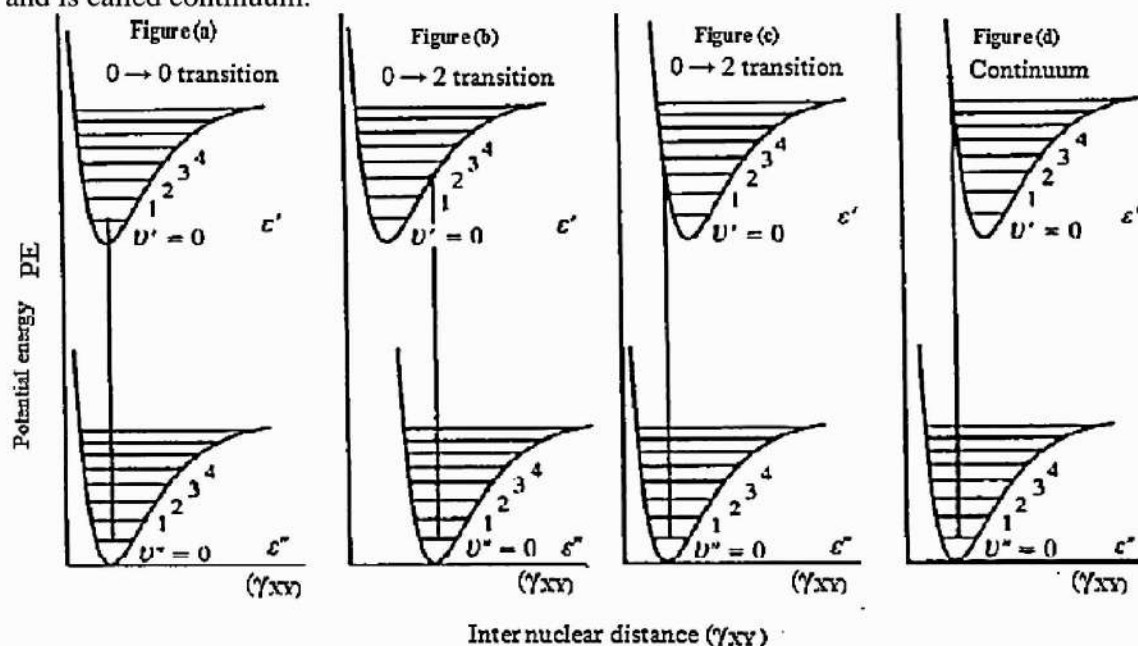
Principle of electronic spectroscopy

In order to explain the principle of electronic spectra, let us consider the Frank Condon principle. According to Frank Condon principle, **during an electronic transition internuclear distance remains constant**. Since the electrons move much more rapidly than the nucleus.

The figure shows the potential energy versus inter nuclear distance curve of ground state and first excited state of the diatomic molecule XY. Quantum mechanically molecule is at the

center of the ground vibrational level of ground electronic state. Electronic transitions are always represented by a vertical line.

In **figure (a)**, upper and lower inter nuclear distance is same. According to Frank Condon principle, most probable transition is $0 \rightarrow 0$ transitions. In **figure (b)**, upper state inter nuclear distance is slightly lesser than the lower state. According to Frank Condon principle, most probable transition is $0 \rightarrow 2$ transitions. In **figure (c)**, upper state inter nuclear distance is slightly greater than the lower state. According to Frank Condon principle, most probable transition is $0 \rightarrow 2$ transitions. In **figure (d)**, upper state inter nuclear distance is considerably greater than the lower state. Here there is no specific electronic transition; instead we get some dark faded lines and is called continuum.



Fundamentals of electronic spectroscopy

Chromophore

Any isolated covalently bonded group that shows characteristic absorption in the UV Visible region irrespective of the fact that whether colour is produced or not.

Eg: $>C=C<$, $-C \equiv C-$, $-N \equiv N-$ etc.

Types of chromophores $\sigma - \sigma^*$, $\pi - \pi^*$, $n - \pi^*$ & $n - \sigma^*$

Chromophores are of two types

1. Chromophores containing π bond undergoes $\pi - \pi^*$ transition

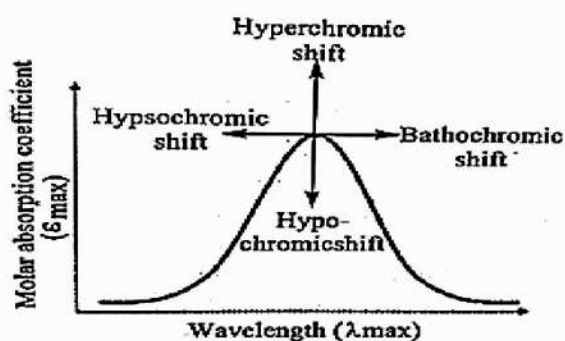
Eg. Ethylene, acetylene etc.

2. Chromophores containing both π and n electrons undergoes $\pi - \pi^*$, $n - \pi^*$ transitions.

Eg. CH_3-CH_2-CHO

Auxochromes

These are substituent on the Chromophore which leads to red shift. eg. NH_2^- , SH^- , OH^- etc.



Bathochromic shift (Red shift)

Shift of absorption band towards longer wavelength region (red region) is called Bathochromic shift. Reason for red shift is the presence of auxochrome and change in solvent.

Hypsochromic shift (Blue shift)

Shift of absorption band towards shorter wavelength region (blue region) is called Hypsochromic shift. Reason for blue shift is the presence of removal of conjugation and change in polarity of solvent.

Hyper chromic shift

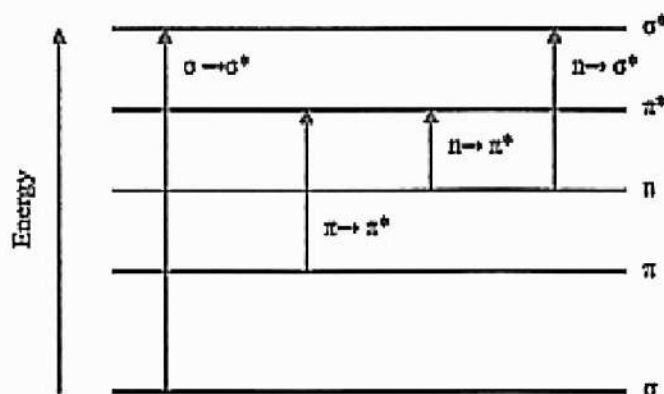
Shift in which there is an increase in intensity of absorption band is called hyper chromic shift.

Hypo chromic shift

Shift in which there is a decrease in intensity of absorption band is called hypo chromic shift.

Electronic spectrum of polyatomic molecules

In the case of polyatomic molecules, electronic transitions give rise to absorption spectra in the UV-Visible region. From the investigations of UV-Visible spectra we get information about various energy levels in the molecule depending on the energy of the molecular orbitals. The electronic transitions are $\sigma - \sigma^*$, $\pi - \pi^*$, $n - \pi^*$ & $n - \sigma^*$ respectively.



Electronic transitions in molecules

1) $\sigma - \sigma^*$ transitions

The energy required for this transition is very high. Since the σ electrons are held more strongly in the molecule and are highly energetic. Hence the absorption band occurs in far UV region. All saturated hydrocarbons will undergo this transition. These types of transitions occur only below 150nm. The ordinary UV spectrometers can take spectra only from 200 – 780nm. Hence saturated hydrocarbons cannot be detected using UV-Visible spectra.

2) $\pi - \pi^*$ transition

Unsaturated hydrocarbons containing π bonds can produce this type of transition. But C=C of $\text{CH}_2=\text{CH}_2$ molecule gives absorption maxima at 169nm. So it cannot be detected using ordinary UV spectrometer. But in compounds containing conjugated double bonds, due to the presence of conjugated double bonds absorption occurs in visible region. In such molecules $\pi - \pi^*$ transition produces absorption bands in the UV-Visible region.

(eg. Butadiene, absorption occurs at 217nm). Due to this transition high intensity absorption bands are produced in the near UV region. Benzene also produces these transitions, due to the presence of three conjugated double bonds. In the case of lycopene red coloured of tomato, there are eleven double bonds in conjugation, its λ_{max} is 505 nm. For every double bond in conjugation, there is an increment of 30 nm.

3) $n - \pi^*$ transition

Unsaturated compounds containing atoms such as O, N, S, X etc, containing lone pair of electrons produces absorption band due to $n - \pi^*$ transition and the absorption bands are observed in the visible region. (eg., aldehydes and ketones containing C=C and C \equiv C bonds)

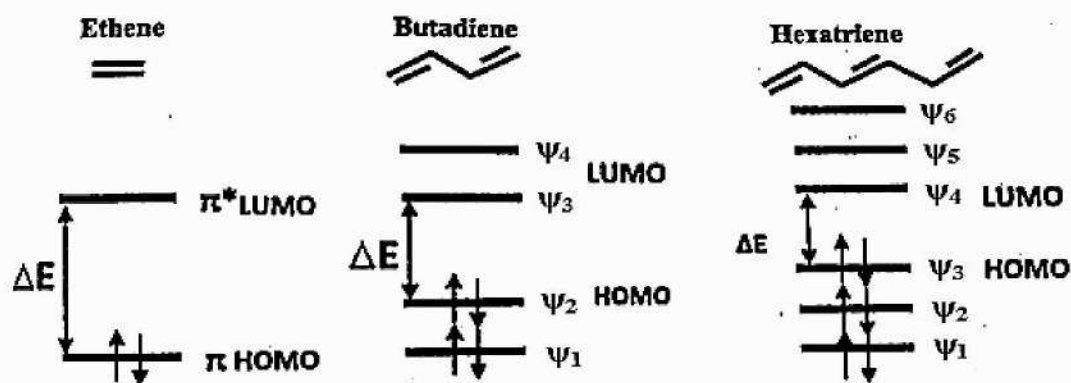
4) $n - \sigma^*$ transition

Saturated compounds containing atoms such as O, N, S, X etc, containing lone pair of electrons produces absorption band due to $n - \sigma^*$ transition and the absorption bands are observed in the near UV region. Generally absorption takes place below 200nm. (eg., CH_3OH , CH_3NH_2 & $(\text{CH}_3)_2\text{NH}$ etc.)

UV- VIS energy level diagram of conjugated systems

The energy levels of π molecular orbitals of conjugated systems can be obtained from Huckel's molecular orbital theory. In such molecules, the ground state electrons occupy the low energy Huckel molecular orbital in spin paired state. Out of the occupied orbitals, the one with higher energy is termed as HOMO (highest occupied molecular orbital). Similarly, out of the unoccupied orbitals, the one with lower energy is termed as LUMO (lowest unoccupied molecular orbital). If the molecule absorbs electromagnetic radiation in the UV - VIS region, electrons get promoted from HOMO to LUMO and the wavelength of absorption depends upon HOMO-LUMO energy gap.

UV- VIS energy level diagram of ethylene, butadiene and hexa-triene

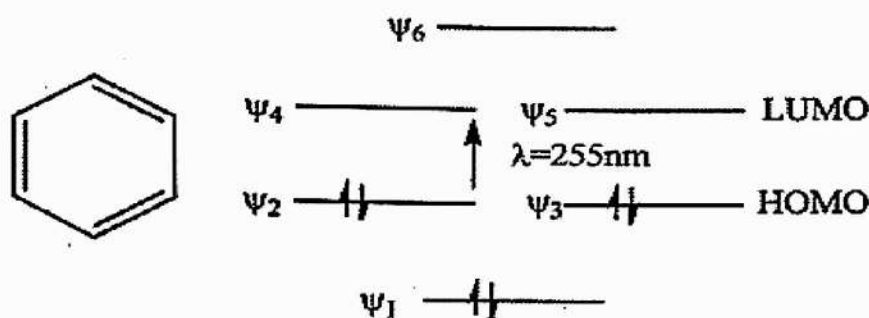


Note that the energy gap ΔE (HOMO-LUMO gap) decreases (becomes smaller) as the number of conjugated pi orbitals increases

Ethylene contains a simple isolated C=C bond, but the other two have conjugated double bonds. In the case of ethylene, there is one π bonding molecular orbital and one π^* antibonding molecular orbital. So $\pi \rightarrow \pi^*$ transition occurs and ethylene gives an absorption maxima at 169 nm. In 1, 3-butadiene, there are two double bonds in conjugation. So it has four π molecular orbitals ($\psi_1, \psi_2, \psi_3, \psi_4$) formed by the linear combination of four atomic orbitals (p orbitals). Here ψ_1 & ψ_2 are the bonding π molecular orbitals and ψ_3 & ψ_4 are the antibonding π^* molecular orbitals. In the ground state the four π electrons occupy bonding molecular orbitals. Here the transition takes place from HOMO (ψ_2) to LUMO (ψ_3) and absorption occurs at 217nm. In 1, 3, 5-hexatriene, there are three double bonds in conjugation. So it has six π molecular orbitals ($\psi_1, \psi_2, \psi_3, \psi_4, \psi_5, \psi_6$) formed by the linear combination of six atomic orbitals (p orbitals). In the ground state the six π electrons occupy bonding molecular orbitals. Here the transition takes place from HOMO (ψ_3) to LUMO (ψ_4) and absorption occurs at 247nm.

UV- VIS energy level diagram of benzene

In benzene, there are three double bonds in conjugation. So it has six π molecular orbitals ($\psi_1, \psi_2, \psi_3, \psi_4, \psi_5, \psi_6$) formed by the linear combination of six atomic orbitals (p orbitals). In the ground state the six π electrons occupy bonding molecular orbitals. Here the transition takes place from HOMO to LUMO and absorption occurs at 255nm. Here ψ_2, ψ_3 are degenerate orbitals and ψ_4, ψ_5 are also degenerate orbitals



Applications of UV – Visible spectroscopy

- In medical lab test for determining cholesterol and blood sugar.
 - For the characterization of dyes and colourants
 - For the detection of aromatic compounds
 - Detection of impurities. (Benzene is present as an impurity in cyclohexane can be detected)
- Write three points of comparison between UV & IR spectrum.

UV-VIS spectroscopy	IR-spectroscopy
Electronic spectrum is due to the electronic transitions in atoms and molecules.	Vibrational spectrum is due to the vibrational motions of atoms and molecules.
It arises by the interaction of EMR with matter	It arises by the interaction of EMR with matter.
EMR in the UV-Vis region is responsible for electronic spectrum	EMR in the IR region is responsible for electronic spectrum

All molecules gives this spectrum	Molecules with a permanent and fluctuating dipole moment give this spectrum.
Examples are organic, inorganic and coordination compounds.	Examples HCl, HBr, HF, H ₂ O, CO ₂ , NH ₃ , CO, CH ₃ Cl

NMR (Nuclear Magnetic Resonance) Spectra

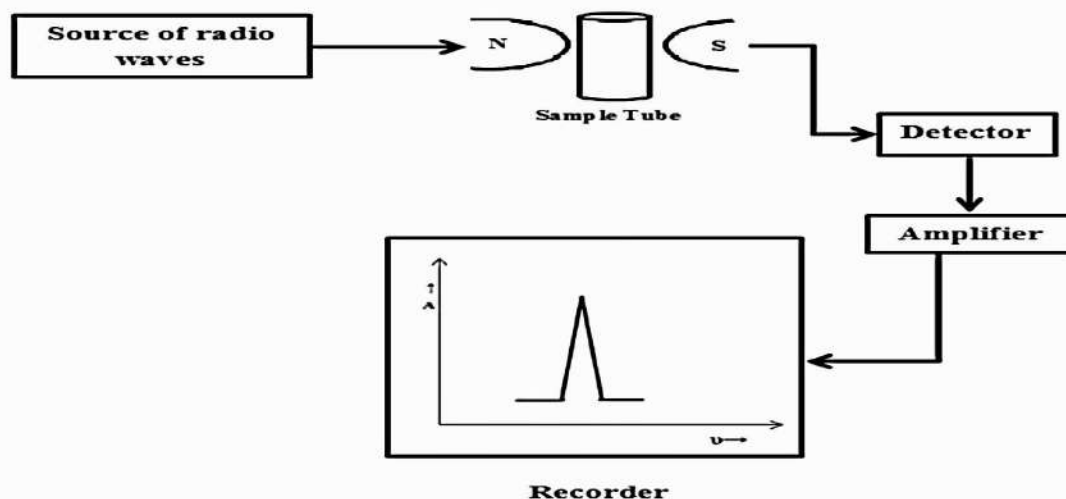
NMR spectrum is obtained by the interaction of radio waves on the nuclei of molecules. In the absence of magnetic field, spin states of nuclei are degenerate, ie, they possess same energy. Hence no transition is possible. When the nucleus is placed in a magnetic field, the spin states lost its degeneracy and are splitted into magnetic energy levels. Then the interaction of radio waves can produce transition between the magnetic energy levels.

Nucleus with net spin ($I = 0$) will not produce NMR spectra and are NMR inactive.

Rules for determining net spin (I)

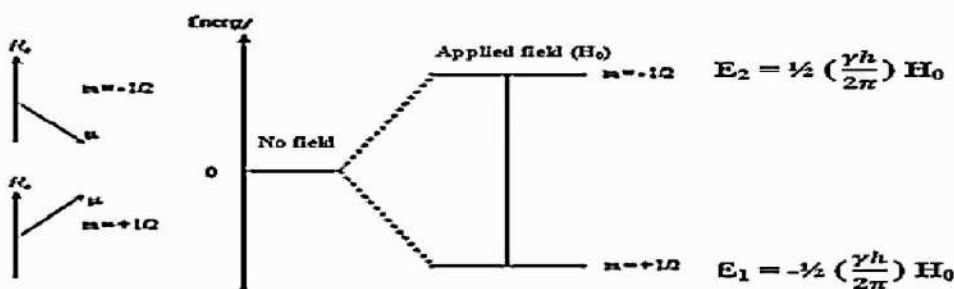
- If the number of protons & number of neutrons, both are even, then $I = \text{Zero}$. (${}_{6}\text{C}^{12}$, ${}_{8}\text{O}^{16}$)
- If the number of protons & number of neutrons, both are odd, then I is an integer such as 1, 2, 3 etc. (${}_{7}\text{N}^{14}$, ${}_{1}\text{H}^2$)
- If the sum of the number of protons and number of neutrons is an odd number, then I has half integral values such as $\frac{1}{2}$, $\frac{3}{2}$, $\frac{5}{2}$, etc. (${}_{1}\text{H}^1$, ${}_{6}\text{C}^{13}$, ${}_{9}\text{F}^{19}$, ${}_{15}\text{P}^{31}$ etc, $I = \frac{1}{2}$)

Instrumentation of NMR spectrometer



According to quantum mechanics, a nucleus with net spin(I) has $(2I+1)$ orientations are possible. In the absence of magnetic field, these orientations are of equal energy. But if a magnetic field is applied, these orientations are splitted into energy levels. Each energy level is characterized by its own specific magnetic quantum number (m)

Nucleus with net spin only produce NMR spectrum, eg; H^1 (two orientations are possible. But in the absence of magnetic field, these two orientations have equal energy. In the presence of magnetic field, energy levels split into two. Each one is having its own specific magnetic quantum number.



The energies E_1 & E_2 corresponds to the two states $m = +1/2$ and $m = -1/2$

$$E_1 = -\frac{1}{2} \left(\frac{\gamma h}{2\pi} \right) H_0 \quad \text{and} \quad E_2 = \frac{1}{2} \left(\frac{\gamma h}{2\pi} \right) H_0, \text{ where } H_0 \text{ is the applied field strength, } \gamma$$

is the gyro magnetic constant.

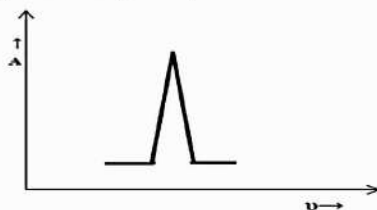
When the nucleus absorbs energy it get promoted from lower energy level E_1 to the next higher energy level E_2 , then the change in energy (ΔE)

$$\Delta E = E_2 - E_1 = \frac{1}{2} \left(\frac{\gamma h}{2\pi} \right) H_0 - \left\{ -\frac{1}{2} \left(\frac{\gamma h}{2\pi} \right) H_0 \right\} = \left(\frac{\gamma h}{2\pi} \right) H_0 = h\nu$$

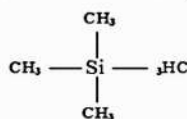
$$\nu = \left(\frac{\gamma}{2\pi} \right) H_0 \quad \text{or} \quad \nu \propto H_0 \quad \boxed{\nu \propto H_0}$$

Thus frequency emitted or absorbed by the nucleus in moving from one energy level to another is directly proportional to the applied field strength.

When the nucleus having net spin is placed in a magnetic field (H_0), then the nucleus absorbs energy get excited. Thereafter it loses energy and returns to the ground state. Again it absorbs energy get excited and then returns to the ground state. This process continuous. This state of the nucleus is called resonance. This motion of the nucleus is just like a spinning top. This motion of the nucleus is called precessional motion and the frequency required for the nucleus to perform precessional motion is called precessional frequency (resonance frequency) (Larmor frequency) . As the field strength increases, precessional frequency increases and this causes transition between the magnetic energy levels and the energy absorbed in this process produces a signal at the detector which is amplified and recorded as a band in the NMR spectrum. NMR spectrum is obtained by plotting absorbance against frequency.



It is not possible to find out the absolute value of resonance frequency. To solve this problem, resonance frequency of nucleus in a sample is measured relative to that of a reference compound. Usually used reference compound is TMS (Tetra methyl silane).



TMS is the most ideal reference compound in NMR because of its characteristics.

- i) All the 12 protons in the TMS are equivalent. Hence it produces a single absorption line.
- ii) It is chemically inert.

iii) It is soluble in most of the organic solvents.

iv) It is highly volatile and can be easily removed from the system

In the NMR spectra, we get a reference peak corresponding to TMS. The position of peaks in the NMR spectra is measured relative to that of reference compound and is expressed in terms of chemical shift (δ)

Shift in position of NMR signals due to shielding and de-shielding of protons by the circulation of electrons is called **chemical shift**.

Chemical shift can be calculated by the expression,

$$\text{Chemical shift, } \delta = \frac{\nu_{\text{sample}} - \nu_{\text{TMS}}}{\nu_0} \times 10^6 \text{ ppm}$$

ν_0 – operating frequency

ν_{sample} – frequency of sample

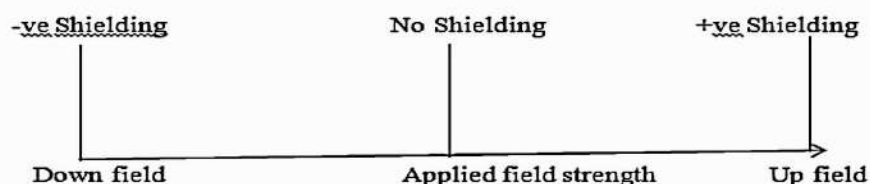
ν_{TMS} – frequency of reference (TMS)

Generally chemical shift value is in between 0 and 10 ppm. There are two scales are used for the measurement of chemical shift. They are δ - scale & τ - scale. These two scales are related to each other by the expression,

$$\tau = 10 - \delta$$

In τ – scale, signal for TMS is obtained at 10ppm. But in δ – scale, TMS signal is obtained at 0 ppm.

When a molecule is placed in a magnetic field, the electrons are forced to circulate about its own protons or nearby protons and this circulation produce an induced magnetic field. The rotation of electrons about its own protons produces an induced magnetic field, which opposes the applied field. Thus the field felt by the proton is diminished and the proton is said to be shielded. Shielding shift the absorption upfield. If the protons are rotated about nearby protons, then the induced magnetic field either opposes or reinforces the applied field. If the induced magnetic field opposes the applied field, proton is said to be shielded. If the induced magnetic field reinforces the applied field, then the proton feels higher field strength and the proton is said to be de-shielded. De-shielding shifts the absorption downfield. Chemical shift for different kinds of protons are measured relative to that of the reference peak (TMS signal). The NMR signals for different types of protons in a molecule appear at different field strengths with respect to TMS signal. This difference in absorption position of protons with respect to TMS signal is called chemical shift.



- Calculate the frequency of operation of NMR instrument, if particular proton of δ value 4.2 shows a difference in frequency 1260 Hz from the TMS.

$$\text{Chemical shift, } \delta = \frac{\nu_{\text{Sample}} - \nu_{\text{TMS}}}{\nu_{\text{Instrument}}} \times 10^6$$

$$4.2 = \frac{1260}{\nu_0} \times 10^6$$

$$\nu_0 = \frac{1260}{4.2} \times 10^6$$

$$= 300 \times 10^6 \text{ Hz} = 300 \text{ MHz}$$

- CHCl_3 protons show a shift in frequency of 728 Hz from TMS signal in a 100MHz NMR instrument. How much would be the shift in frequency for the same proton from TMS in a 300MHz NMR instrument?

$$\text{Chemical shift, } \delta = \frac{\nu_{\text{Sample}} - \nu_{\text{TMS}}}{\nu_{\text{Instrument}}} \times 10^6 = \frac{\Delta\nu}{\nu_{\text{Instrument}}}$$

Chemical shift, δ is constant

$$\Delta\nu \propto \nu$$

$$\frac{\Delta\nu_1}{\Delta\nu_2} = \frac{\nu_1}{\nu_2}$$

$$\frac{728}{\Delta\nu_2} = \frac{100}{300}$$

$$\Delta\nu_2 = \frac{728 \times 300}{100} = 2184 \text{ Hz}$$

- If gyromagnetic ratio of ^{13}C is $\frac{1}{4}$ of that of ^1H . What is the frequency must be irradiated to take ^{13}C NMR spectrum if same instrument take ^1H NMR spectrum at 300MHz.

$$\nu = \left(\frac{\gamma}{2\pi}\right) H_0, \text{ Here field strength } H_0 \text{ is constant.}$$

$$\frac{\nu_1}{\nu_2} = \frac{\gamma_1}{\gamma_2}$$

$$\frac{300}{\nu_2} = \frac{1}{1/4}$$

$$\nu_2 = \frac{300}{4} = 75 \text{ MHz}$$

Factors affecting chemical shift

i) Electronegativity

If the electronegativity of substituents attached to the protons increases, then electron density around the protons decreases and the protons feels higher field strength & the protons are said to be de-shielded. In the case of methyl halides, protons of CH_3F are least shielded (most de-shielded) and those of CH_3I (2.2ppm) are most shielded (least de-shielded).

Compounds	CH_3F	$\text{CH}_3\text{-O-CH}_3$	$(\text{CH}_3)_3\text{N}$	$\text{CH}_3\text{-CH}_3$
δ of CH_3 protons	4.3ppm	3.2ppm	2.2ppm	0.9ppm

ii) Cumulative effects of electronegative substituents

If the number of electronegative substituents attached to the protons increases, then the protons feels higher field strength and the proton is said to be de-shielded. For example consider the chemical shifts for various chlorinated methane derivatives,

Compounds	CHCl_3	CH_2Cl_2	CH_3Cl
δ of CH_3 protons	7.3ppm	5.3ppm	3.1ppm

iii) Distance from the electronegative atom

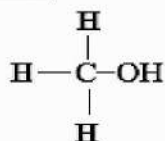
If the distance from the electronegative atom substituted in the hydrocarbon chain increases, electron density around protons increases and shielding increases so chemical shift value decreases.

Compound	$\text{H}_3\text{C} - \text{CH}_2 - \text{CH}_2\text{Cl}$		
Chemical shift (δ)(ppm)	1	1.4	3.4

iii) De-shielding

In de-shielding, induced magnetic field reinforces the applied magnetic field. Therefore de-shielding increases the chemical shift (δ) values. In the case of aromatic protons and olefinic protons δ value is high due to the de-shielding effect.

Low resolution NMR Spectrum of $\text{CH}_3\text{-OH}$



In methanol ($\text{CH}_3\text{-OH}$) there are three identical CH bonds and one OH bond are present. The chemical environment of CH bonds and one OH bond are different. Since oxygen is more electronegative than carbon. So electron density around -OH proton is lesser than that around CH_3 - protons. As a result, CH_3 - protons are more shielded than -OH proton. That means shielding constant (σ) is greater for CH_3 - protons.

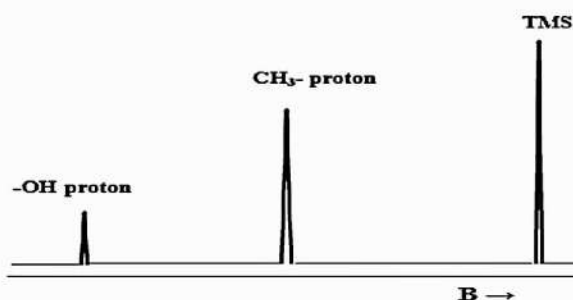
$$\sigma_{\text{CH}_3} > \sigma_{\text{OH}}$$

Shielded proton feels lower field strength. So observed magnetic field (B) is greater for -OH proton.

$$B_{\text{OH}} > B_{\text{CH}_3}$$

That means actual field felt by the CH_3 - protons is lesser than that felt by -OH proton. Hence on increasing the external magnetic field, -OH proton will come into resonance earlier than CH_3 - protons. As a result NMR signal for -OH proton will be observed at a lower field strength and that of CH_3 - protons will be observed at higher field strength.

The area under each peak is directly proportional to the number of protons. Thus the area under the signal of CH_3 - protons will be three times larger than that under -OH proton.



High Resolution NMR Spectrum

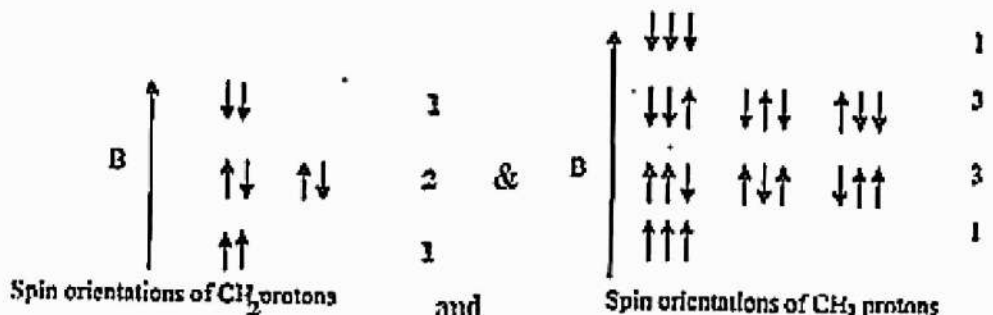
If we take the high resolution NMR Spectrum of molecule, we can see a multiplet instead of a single peak. It is due to a phenomenon called spin-spin splitting.

Spin -spin splitting (spin-spin coupling)

The interaction between spins of neighbouring nuclei in a molecule can cause splitting of lines in the NMR spectrum. This is called spin -spin splitting (spin-spin coupling)

In order to explain spin -spin splitting (spin-spin coupling), let us consider the high resolution spectrum of $\text{CH}_3\text{-CH}_2\text{-Br}$. This compound contains two types of protons, so two signals are expected in the low resolution NMR spectrum. But in high resolution NMR spectrum,

we do not get singlet for each type of proton, instead a group of peaks (multiplet) are observed. For CH_3 - protons, singlet will split into a triplet with intensity ratio 1:2:1 and for CH_2 < protons, singlet will split into a quartet with intensity ratio 1:3:3:1. This can be explained by considering the spin orientation of each type of protons.



The spin of CH_2 < protons can couple with adjacent CH_3 - protons in three different ways relative to the external field. Hence the field felt by the CH_3 - protons can be modified in three different ways. That means NMR signal due to CH_3 - protons will split into three (triplet).

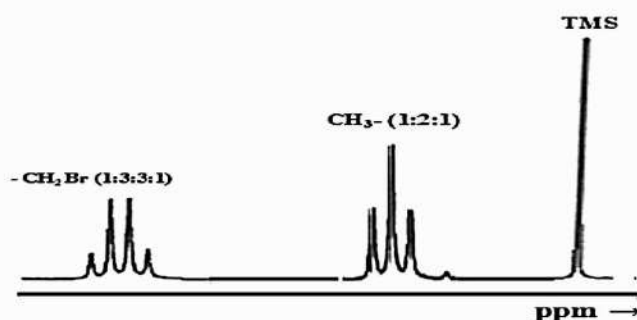
Similarly the spin of CH_3 - protons can couple with adjacent CH_2 < protons in four different ways. Hence the field felt by the CH_2 < protons can be modified in four different ways. That means NMR signal due to CH_2 < protons will split into four (quartet).

Area under the broad NMR and the multiplet remains the same. Spin – spin coupling is independent of the applied field strength. The spacing between peaks of multiplet is the measure of spin – spin coupling and is called spin – spin coupling constant (J).

We can easily determine the relative intensity of multiplet using Pascal's triangle method.

	1	1				
		1	2	1		
		1	3	3	1	
		1	4	6	4	1

Pascal's Triangle



Applications of NMR spectroscopy

- i) Structural elucidation of many organic and inorganic compounds.
- ii) NMR spectroscopy is used to study keto-enol tautomerism.
- iii) It is used in the study of isotopes.
- iv) MRI technique is based on the principle of NMR.

Magnetic Resonance Imaging (MRI)

MRI is the medical technique used in radiology to get the detailed pictures of internal body parts. MRI uses a very strong magnetic field, radio frequency wave and a computer to produce the detailed pictures of body parts such as soft tissues, bones etc. These images can be examined in the computer monitor, transmitted electronically, printed or copied to a CD.

Principle:

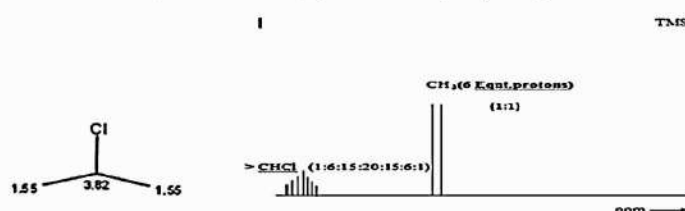
It is the medical version of NMR. This method uses magnetic properties of hydrogen present in the body cells and its interaction with external magnetic field to produce highly detailed pictures of internal body parts. In order to perform MRI scanning, a very strong magnetic field of 0.5 – 1.5T is required

Applications

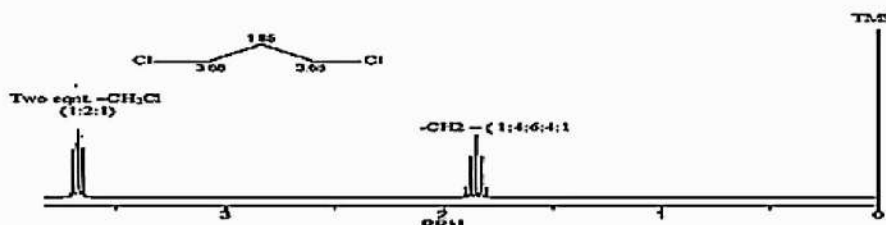
- Physicians use MRI for the treatment of diseases like tumors of abdomen, liver cirrhosis, heart problems etc.
- Measuring physiological functions like neuromuscular skeletal functions.
- Magnetic resonance angiography is used for getting pictures of arteries.

NMR Spectra of compounds

1. Predict NMR spectrum of $\text{CH}_3\text{-CHCl-CH}_3$ (2-chloro propane)

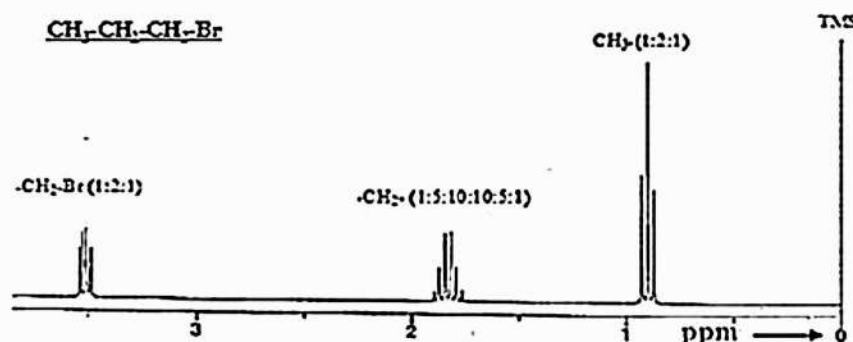


2. Write splitting pattern in the NMR spectrum of $\text{CH}_2\text{Cl-CH}_2\text{-CH}_2\text{Cl}$ (1, 3- dichloro propane)



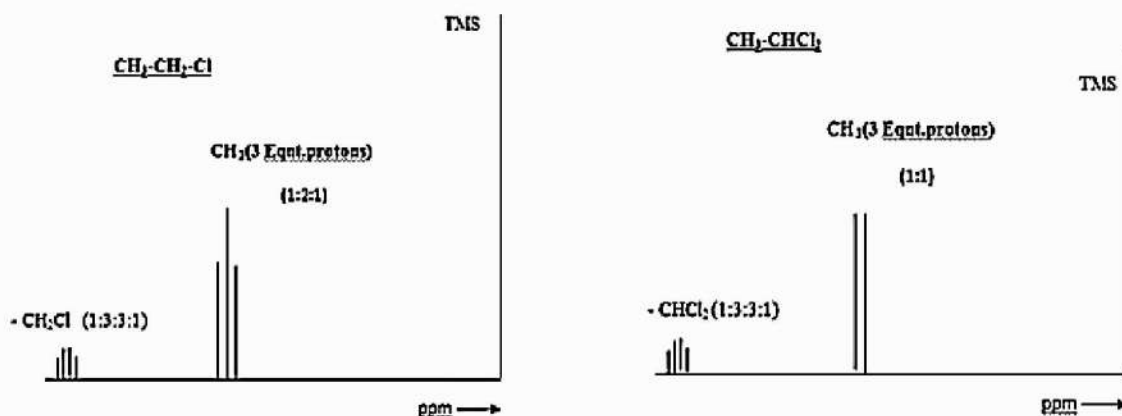
3. Give number of signals, peak ratio and multiplicity of different sets of protons in the nmr spectrum of 1-bromopropane.

In 1-bromopropane, three types of protons are present. So three signals are expected. The Br attached CH_2 - has lesser electron density, so signal is obtained far away from TMS. (i.e., at higher δ value)

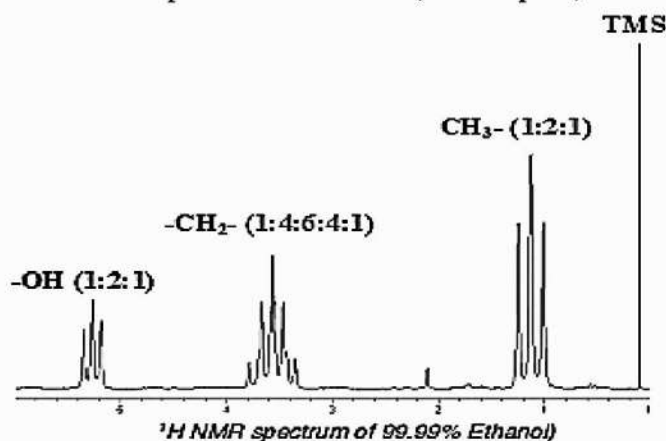


4. How can you distinguish NMR spectrum of $\text{CH}_3\text{CH}_2\text{Cl}$ and CH_3CHCl_2 applying the concept of spin – spin splitting

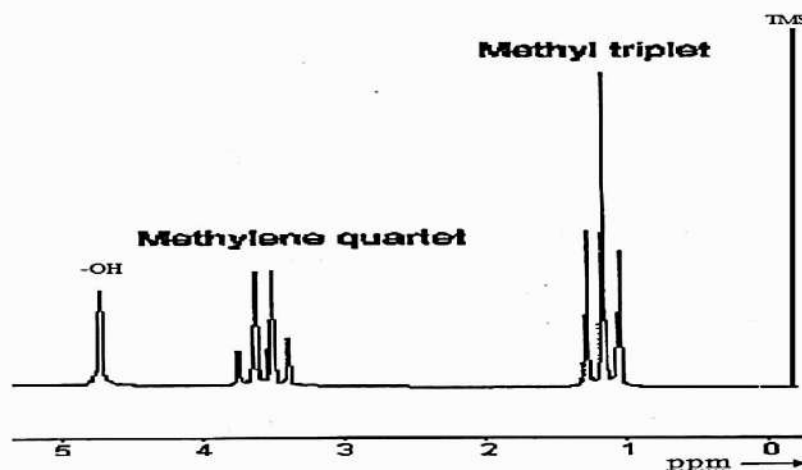
NMR spectrum of both the compounds has two peaks. In $\text{CH}_3\text{-CH}_2\text{Cl}$, the $\text{-CH}_2\text{Cl}$ is attached to the more electronegative Cl atom and is less shielded, so its signal is obtained away from TMS signal. But $\text{CH}_3\text{-}$ is more shielded, so its signal is obtained near to TMS. But in high resolution spectra each singlet is splitted into a multiplet due to spin - spin splitting. In $\text{CH}_3\text{-CH}_2\text{Cl}$, the $\text{CH}_3\text{-}$ signal is splitted into triplet with intensity ratio 1:2:1, whereas in $\text{CH}_3\text{-CHCl}_2$, the $\text{CH}_3\text{-}$ signal is splitted into doublet with intensity ratio 1:1. But in both cases $\text{-CH}_2\text{Cl}$ & -CHCl_2 , we get a quartet with intensity ratio (1:3:3:1).



5. Draw the high resolution nmr spectrum of ethanol (99.99% pure)



6. Draw the high resolution NMR spectrum for ethanol containing impurities such as water, acetic acid etc.



MODULE III INSTRUMENTAL METHODS AND NANOMATERIALS

Thermal Methods of Analysis

Thermal method of analysis is the measurement of physical property of a substance or its reaction product as a function of temperature as the substance is subjected to controlled temperature programme. Two important thermal methods are

1. TGA
2. DTA

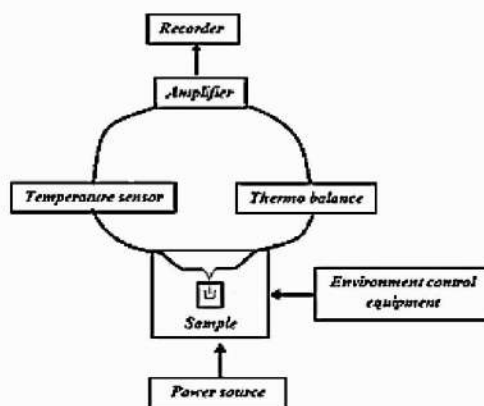
Thermo Gravimetric Analysis (TGA)

TGA is a thermal method of analysis in which the mass of the sample is measured as a function of temperature when the temperature of the sample is increased linearly from room temperature to 1200°C.

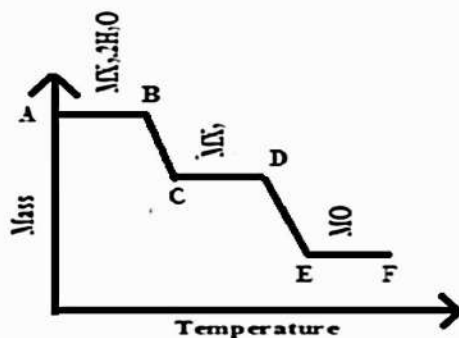
A sample on heating mass change occurs due to the physical and chemical changes undergone by the substance.

This method gives an idea about quantitative as well as qualitative picture of the sample under investigation. On heating mass of the sample changes due to physical changes like vaporisation of moisture volatile component or due to the partial or complete loss of water of crystallisation. It is also due to chemical changes like decomposition, dissociation of substance, oxidation, reduction and combination with atmospheric gases.

TGA Apparatus



Principle and method:

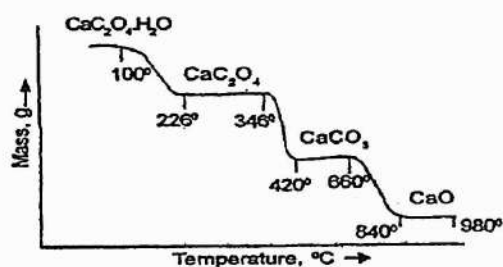


In order to explain the principle and method of TGA, let us consider the thermo gram of the compound $\text{MX}_2 \cdot 2\text{H}_2\text{O}$.

From the figure it is clear that from A to B, this compound is stable and there is no weight change. At B the compound begins to loss its weight and the process is completed at C. This is due to the evolution of 2 moles of water per each mole of the compound produces anhydrous sample. From C to D, the compound is stable. So we get a horizontal weight level at this region. At D, the compound again begins to lose weight due to the decomposition of MX_2 . From E to F, again we get a horizontal weight level. This shows the stability of MO. From the various regions of the curve, the thermal stability of initial compound, intermediate compound and the final product can be obtained. It also gives an idea about the stoichiometry of the compound at any given temperature.

Applications:

1. Qualitative Analysis



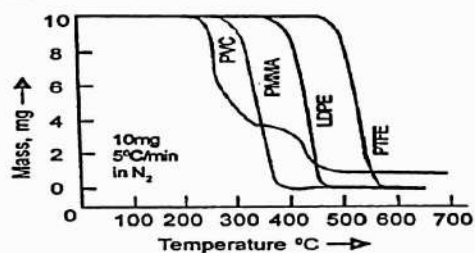
T.G. of calcium oxalate ($\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$)

In order to explain the qualitative analysis, let us consider the thermogram of $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$.

$\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$ is stable upto 100°C . So we get a horizontal region in this temperature region. On increasing the temperature above 100°C it loses the two mols of water per each mole of the compound producing anhydrous CaC_2O_4 . So the horizontal weight level changes. Anhydrous CaC_2O_4 is stable from 226°C - 346°C . So again we get a horizontal weight level. Above 346°C evolution of CO takes place producing CaCO_3 . CaCO_3 is stable from 420°C - 660°C . So horizontal weight level obtained in this temperature region. Above 660°C decomposition of CaCO_3 takes place producing CaO and the process is completed at 840°C . CaO is stable from 840°C - 980°C . So we get a horizontal weight level in this temperature region.

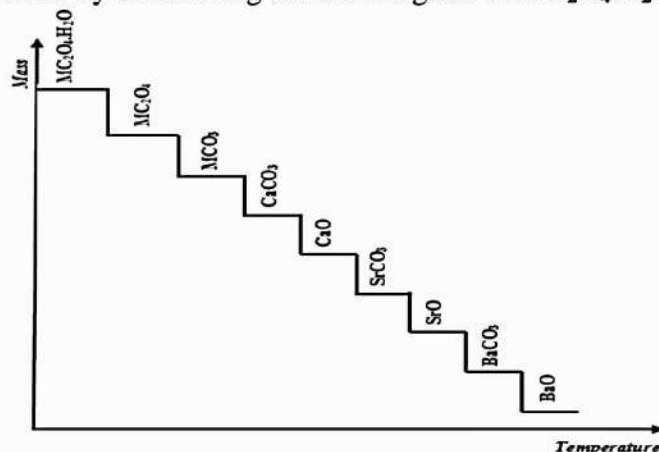
2. Study of polymers

Thermo grams provide ready information about the decomposition pattern of various polymers. Decomposition pattern is the characteristics of each type of polymer. So TGA helps for the identification of polymers.



3. Quantitative analysis – Analysis of binary mixtures

TGA is used for the quantitative analysis of a mixture of calcium, strontium and barium ions. This can be explained by considering the thermo gram of $MC_2O_4 \cdot H_2O$.



Limitations of TGA:

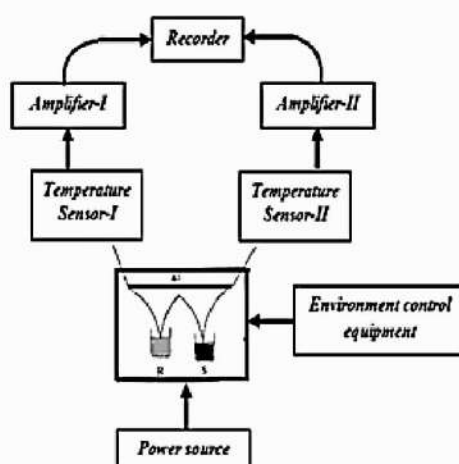
- TGA will not give any information about phase transition of crystalline substance. Since these transitions do not involve weight change.
- It will not give any information about melting point, boiling point and transition temperature of crystalline substances.

Differential Thermal Analysis (DTA)

DTA is a thermal method of analysis in which difference in temperature between the sample and inert reference compound is measured as a function of sample temperature as the sample and the reference compound are heated uniformly in a constant rate. Usually used reference compounds are alumina and silicon carbide.

In DTA, difference in temperature between the sample and the reference compound is monitored continuously and is plotted against sample temperature to obtain differential thermo gram.

DTA Apparatus

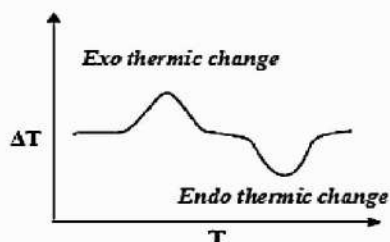


Principle and method:

In DTA, peaks are obtained due to the physical and chemical changes undergone by the substance on heating. Physical changes are endothermic or exothermic. Physical changes like

fusion, evaporation, sublimation, absorption, desorption etc. are endothermic. But adsorption and crystallisation are exothermic physical changes. Chemical changes are also endothermic or exothermic. Reduction in inert atmosphere, dehydration and decomposition are usual endothermic chemical changes. Oxidation in air, polymerisation are exothermic chemical changes.

DTA THERMOGRAM



Upward peak or maxima corresponds to exothermic change, whereas downward peak or minima correspond to endothermic change.

Peak areas in differential thermo grams depend upon the mass of the sample (m), enthalpy change (ΔH) of the physical or chemical changes and certain geometric and conductivity factors.

Peak Area (A) = $-kGm\Delta H$

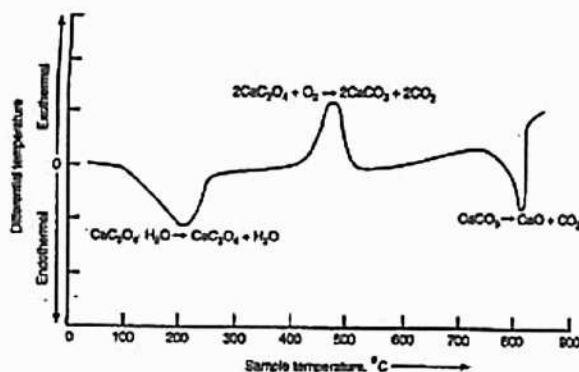
A is the peak area, G is the calibration factor which depends upon the sample geometry and k is a constant related to the thermal conductivity of the sample.

Applications:

1. Study and characterization of polymers

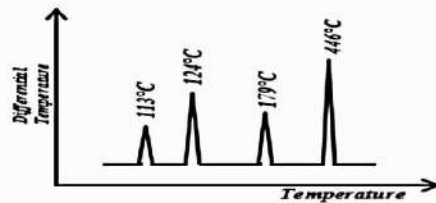
Thermal transitions of polymer occur over an extended range of temperature since polymers are mixtures of different homologues. Each peak corresponds to the melting point of the components present.

2. Study of the thermal behaviour of inorganic species



In the DTA of hydrated calcium oxalate, first peak (minima) corresponds to the dehydration of hydrated calcium oxalate. It is endothermic change. Second peak (maxima) corresponds to the oxidation of anhydrous oxalate. Oxidation is an exothermic change. Second minima correspond to the decomposition of CaCO_3 . Decomposition is endothermic change.

3. Study of phase transition



In the differential thermo gram of sulphur, a peak at 113°C represents solid phase transition from rhombic sulphur to monoclinic sulphur. Peak at 124°C represents the melting point of sulphur. Peak at 179°C represents the presence of liquid sulphur. Peak at 446°C represents the boiling point of sulphur.

Merits of DTA:

- It can be used for studying phase transition which cannot be studied using TGA.
- It gives information about melting point, transition temperature etc. of crystalline substance, whereas TGA cannot give these data.

• Differentiate between TGA thermo gram and DTA thermo gram graphically

TGA Thermo gram	DTA Thermo gram
1. TGA thermo gram is the plot of mass (m) against temperature (T)	1. DTA thermo gram is the plot of difference in temperature between the sample and the reference compound (ΔT) against temperature (T).
2. <div style="text-align: center;"> <p style="text-align: center;">TGA THERMOGRAM</p> </div>	2. <div style="text-align: center;"> <p style="text-align: center;">DTA THERMOGRAM</p> </div>
3. <div style="text-align: center;"> <p style="text-align: center;">T.G. of calcium oxalate ($\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$)</p> </div>	3. <div style="text-align: center;"> <p style="text-align: center;">DTA of Calcium Oxalate ($\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$)</p> </div>
4. TGA cannot be used for phase transition study.	4. DTA can be used for phase transition study.

Distinguish between TGA & DTA.

TGA	DTA
1) TGA is a thermal method of analysis in which mass of the sample is measured as a function of temperature as the temperature of the sample is increased linearly from room temperature to 1200°C.	1) DTA is a thermal method of analysis in which difference in temperature between the sample and inert reference compound is measured as a function of sample temperature as the sample and reference are heated uniformly in a constant manner.
2) In TGA, mass of the substance is recorded continuously as a function of temperature.	2) In DTA, temperature of the sample and the inert reference compound is measured as a function of temperature
3) TGA is used to study physical and chemical changes that is followed by mass changes	3) DTA is used to study physical and chemical changes that occurs with or without mass change

Chromatography

The term chromatography means colour writing. This was introduced by the scientist Mikhail Tswette. He employed it for the separation of plant pigments such as chlorophyll and xanthophyll by passing the solution of these substances through a glass column packed with finely divided CaCO_3 . The separated components appeared as coloured bands in the column. So he chose the name chromatography. This method is generally used for the separation of complex mixtures which cannot be separated by other methods. It is also useful for the separation and purification of organic compounds when they are available in very smaller quantity.

General principle of chromatography

It is based on the principle of selective distribution of mixture of compounds between two phases, viz stationary phase and mobile phase.

Stationary phase is the fixed phase. For example, a column of adsorbent, paper, a thin film of liquid supported on an inert solid, a thin layer of adsorbent coated over a glass plate can be used as stationary phase.

Stationary phase is a solid or a liquid. If the stationary phase is a solid, then the principle adsorption and such type of chromatography is called adsorption chromatography. Example column chromatography.

If the stationary phase is a liquid, then the principle partition and such type of chromatography is called partition chromatography. Example Gas liquid chromatography.

Mobile phase is the moving phase. It can be a liquid or gas. The components to be separated are carried by the mobile phase through the stationary phase.

Classification of chromatography based on mechanism of separation,

a) Adsorption chromatography:

In this chromatography stationary phase is solid and mobile phase is a liquid or gas. Here separation occurs due to the difference in the adsorption coefficients of the components.

b) Partition chromatography:

In this chromatography stationary phase is a liquid supported on inert solid and mobile phase is a liquid or gas. Here separation occurs due to the difference in the partition coefficients of the components.

c) Ion exchange chromatography:

In this chromatography stationary phase is an ion exchanger and the separation of the mixture is based on ion exchange principle and applicable for ionic species.

Classification of chromatography based on the mobile phase,

a) Liquid chromatography:

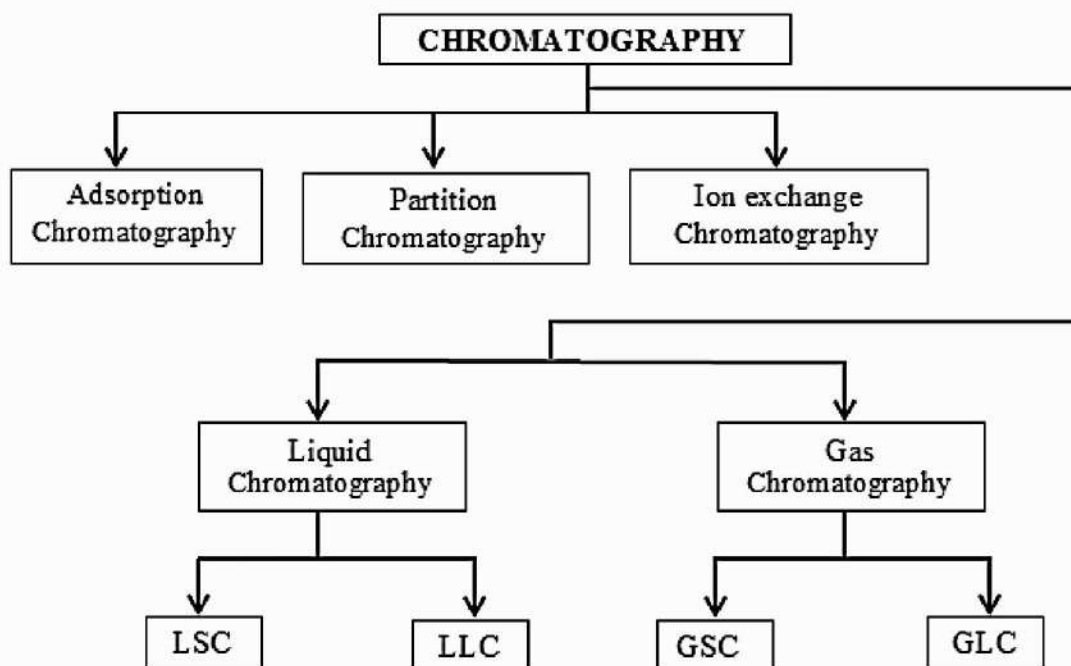
If the mobile phase is liquid and the stationary phase is solid, then the chromatography is called LSC (Liquid Solid Chromatography)

If the mobile phase is liquid and the stationary phase is liquid supported on solid, then the chromatography is called LLC (Liquid Liquid Chromatography)

b) Gas chromatography:

If the mobile phase is gas and the stationary phase is solid, then the chromatography is called GSC (Gas Solid Chromatography)

If the mobile phase is gas and the stationary phase is liquid, then the chromatography is called GLC (Gas Liquid Chromatography)



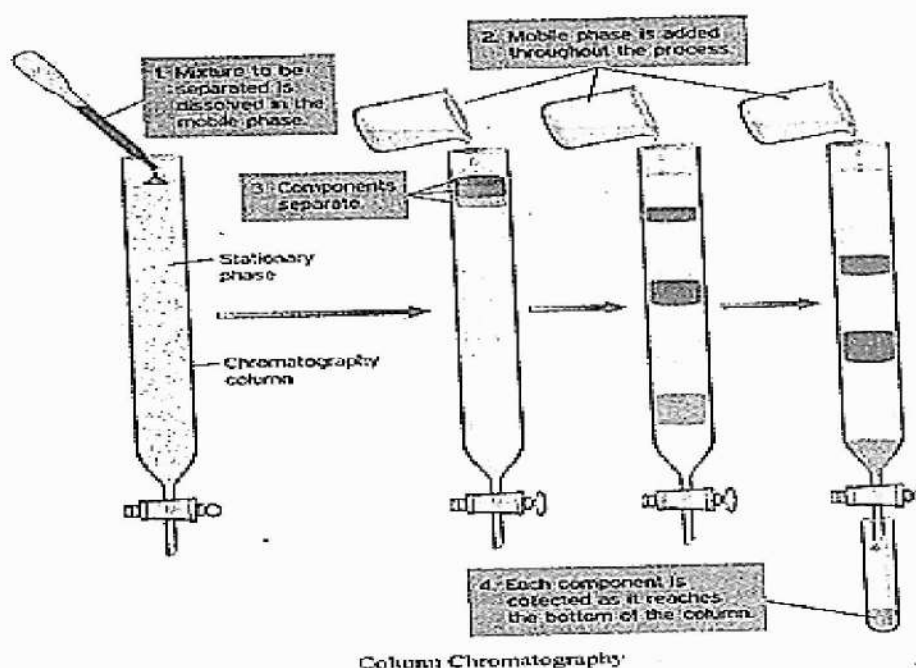
Column chromatography.

In column chromatography stationary phase is held in a narrow tube and is packed with solid adsorbents like Al_2O_3 , silica gel, MgO etc. This can function as the stationary phase. The mixture to be separated is dissolved in a suitable solvent will constitute the mobile phase. Mobile phase is forcefully passed through the stationary phase under pressure or by gravity. Then the most readily adsorbed components get retained at the top, whereas the less readily adsorbed components penetrate various distances down the column depending on the degree to which they

get adsorbed. As a result components in the mixture are separated as a series of rings or bands in the column. If the components are coloured then the bands obtained are also coloured. Such coloured banded column of adsorbent is called **chromatogram**. If the components are colourless, then a colour developing reagent is sprayed on the chromatogram to make the separated components coloured and visible. This process is called development of chromatogram

. The process of recovery of components from the chromatogram is called elution. Different methods are employed for this purpose.

- Column of adsorbent is pushed out of the tube and is then cut at the boundaries using a knife. Every zone can then be extracted with suitable solvent.
- Column of adsorbent is washed with more and more solvent which separate out the components one by one.



Applications:

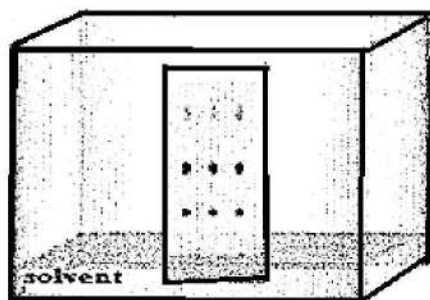
- This method is used for the separation of organic compounds from plant pigments.
- It is also used for the separation and purification of natural compounds like alkaloids, glycosides etc.
- It is also used for large scale separation and purification of pharmaceuticals.

Thin Layer Chromatography (TLC)

Thin layer chromatography was developed by Izmailov and Shraiber. It is better than column chromatography. This method is used for determining the number of components in a mixture. This method will give an idea about the identity of components in the mixture. This will give an idea about the purity of compounds.

In TLC, a glass plate coated with adsorbent (Silica gel, alumina) is used as the stationary phase. The adsorbent is made as a slurry or paste with water and is spread over the glass plate. These coated glass plates are dried and activated by heating in an oven at 120°C. The mixture to be separated is applied at one end of the glass plate. The glass plate is then placed in the

development tank at an angle of 45° and the bottom of the tank is filled with solvent (nearly 1mm). When the solvent moves upwards, it carries the components in the mixture to different heights. Thus components in the mixture get separated. This process takes about 20- 40 minutes.

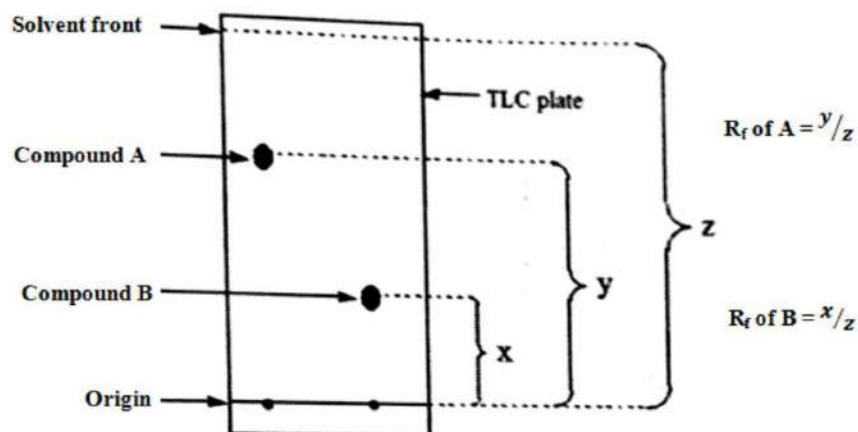


Then the glass plate is taken out of the development tank and the solvent front is marked. It is then allowed to dry. If the components in the mixture are coloured then they can be visually detected as coloured spots in the glass plate. If the separated components are colourless, then they can be visualized in the following manner.

- Using UV-lamp
- Using colour developing reagents such as KMnO_4
- Using 2,4-dinitro phenyl hydrazine reagent to detect carbonyl compounds
- Iodine vapours are also used

In this way position of all the components in the mixture are located and they can be identified by knowing their R_F values. R_F value (Retention factor or ratio of fronts) is the ratio of distance travelled by the sample component to that of the solvent front. It is the characteristics of each component and is specific for each component.

$$R_F \text{ value} = \frac{\text{distance travelled by the component}}{\text{distance travelled by the solvent front}}$$



Hence we can identify the components in a mixture.

Applications:

- It is used for finding the purity of compounds.
- To determine appropriate solvent for column chromatographic separation.
- It is used for the identification of a compound.
- It is used for monitoring column chromatographic separation.

Advantages:

- It requires simple equipment.
- Speed of separation is high.
- Very sharp and sensitive separation.

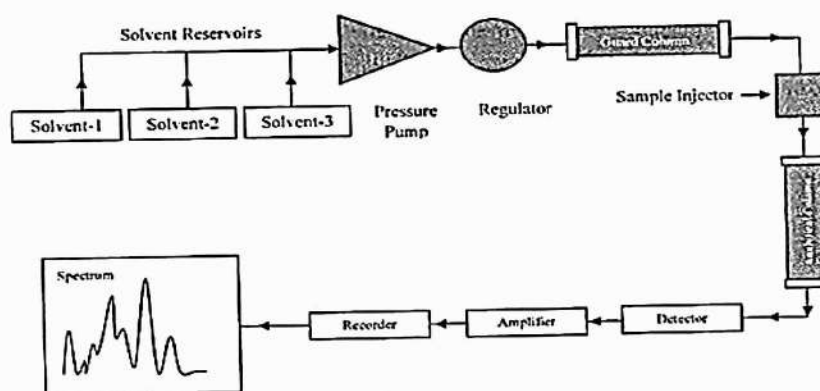
High Pressure Liquid Chromatography (HPLC)

HPLC is widely used for analytical separation because of its high sensitivity, accurate quantitative determination and its ability to separate non – volatile species.

HPLC Apparatus

- Solvent delivery system
- Sample injection system
- Chromatographic column
- Detector
- Recorder

Instrumentation:



Working

In HPLC solvents are introduced from two or more reservoirs into the mixing chamber at rates that vary continuously with time. The solvents used here are filtered through a Millipore filter under vacuum to remove the dissolved gases and suspended matter. Solvent is then pumped through the column at the same time a dilute solution of the sample under analysis is also introduced into the column by a sample injection system. As the solution flows through the column, some more solvent is introduced into it. Generally narrow column of 10–30 cm length are used. Usually columns are made up of heavy glass or stainless steel to withstand high pressure. The efficiency of HPLC columns improves significantly as the particle size is reduced. Hence HPLC columns are packed with particles having narrow particle size. Pumping pressures of several thousand pounds per square inch (psi) is required. HPLC systems usually make use of pump working at a pressure of 6000 psi so that flow ranging from 0.1 -10 ml/minute can be obtained. Three types of pumps are used. They are pneumatic (constant pressure) pump, displacement pump and reciprocating pump.

Column packing material:

Packing in HPLC column consists of small rigid particles having narrow particle size. A solid glass bead of 30-50µm in diameter can be coated with a thin layer of porous material. These coated glass beads are called pellicular beads. The porous layer serves as the solid

stationary phase. The porous layer is chemically bonded to the solid glass bead. So that it is not washed away by the mobile phase under high pressure.

Solvents:

Successful separation can be achieved by matching the polarities of sample and the packing material. But the solvent has a very different polarity. Lower the viscosity of the solvent, greater the chromatographic affinity.

Guard column:

It helps to remove the particulate and contaminants from the solvent.

Detector:

Bulk property detector and solute property detector are used as detectors. Bulk property detectors respond to the bulk properties like refractive index, dielectric constant, density etc., of the mobile phase. When a particular molecular species is separated out, these properties will change and the detector gives the signal. Solute property detectors respond to the solute properties like UV absorbance, fluorescence of the solute molecules. For example paracetamol can be detected using UV detector since it gives absorption at 255 nm due to the presence of benzene ring in the molecule. Every separated component at the detector produces electrical signals.

Recorder:

The signals from the detector can be recorded as different peaks. The area under each peak represents the amount of components present in the sample.

Applications:

- Used in pharmaceutical biological study.
- Used in the analysis of water soluble and fat soluble vitamins.
- Used in the analysis and separation of amino acids & proteins.
- Used in the separation of lipids & steroids.

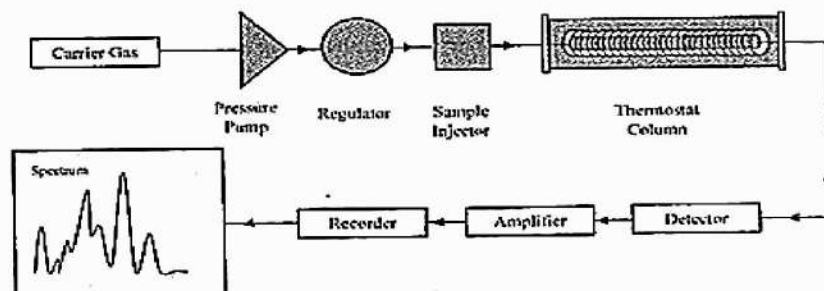
Gas chromatography (GC)

Gas chromatography is based on the principle of selective distribution components of mixture between two phases, viz stationary phase and mobile phase. In gas chromatography separation occurs between gas mixture and the stationary phase. ***Mobile phase is a mixture of vaporized sample and inert carrier gas.*** Usually used carrier gas is nitrogen. Sometimes Ar, He, H₂ can also be used as the carrier gas depending on the nature of mixture. Stationary phase may be a solid or liquid. So there are two types of gas chromatography

- 1) Gas Solid Chromatography (GSC)
- 2) Gas liquid Chromatography (GLC)

In GSC, stationary phase consists of silica, alumina etc. and the principle is adsorption. In GLC, a thin film of high boiling liquid paraffin or poly ethylene glycol coated on an inert solid material like celite or kieselghur is used as the stationary phase. Here the principle is partition.

Instrumentation Gas Chromatography Apparatus



Schematic representation of Gas chromatograph

Working:

In gas chromatography a mixture of vaporized sample and inert carrier gas (mobile phase) is passed through the stationary phase. Stationary phase is held in a narrow column. As the mixture of gases pass through the column, separation of components occurs via adsorption or partition on the basis of the physical state of the stationary phase. In GSC separation of components occurs on the basis of the degree to which they get adsorbed. In GLC, separation of components occurs on the basis of the difference in the partition coefficients. Since the partition coefficients of individual components in the mixture are different. So they are carried along the column at different rates. The components which leave the column passes through the detector and recorder. The detector produces electrical signals and the recorder converts it as a trace on a paper. The resultant trace is a plot of signal intensity against time and is called chromatogram. By GC even 10^{-12} g quantity of mixtures can be separated and identified. Hence it is an important analytical technique.

Detectors used in GC:

i) Flame Ionization detector (FID)

FID is one of the most widely used detector for GC.

Advantages:

High sensitivity, low noise, easy to use.

Disadvantage:

It causes the destruction of the sample.

ii) Thermal Conductivity Detector (TCD)

It works on the principle that presence of analyte molecule in the gas stream will produce a change in thermal conductivity.

Advantages:

Simple to use, non – destructive in nature and it gives respond to both organic and inorganic matter.

Disadvantage:

Low sensitivity

Some other detectors like *thermionic detector (TID)*, *atomic emission detector (AED)* and *electron capture detector (ECD)* are also used.

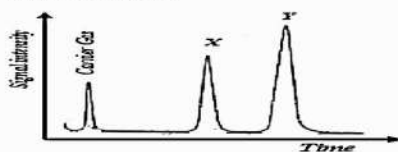


Figure shows the chromatogram of mixture of two gases X & Y. First peak always represents the carrier gas and other two peaks represent the pure components X & Y. Each component can be identified by actual isolation time or retention time. It is the time required for the components to

emerge from the column. This can be compared with the retention time of known samples under identical conditions.

Applications:

- Used for qualitative analysis
- Used to test the purity of compounds. The presence of impurities will be revealed by the appearance of extra peaks.
- Widely used for study of air pollution.
- By GC ethyl alcohol content in the blood can be determined with high degree of accuracy.
- Banned drugs used by athletes can be detected by taking the GC of blood or urine sample.

Comparison of GSC & GLC.

Point of differences	GSC	GLC
Stationary phase	Solid	Liquid
Mobile phase	Gas	Gas
Principle	Adsorption	Partition
Packing of the column	Granular powder of adsorbent is packed in the column	Both packed and capillary column can be used
Length of the column	0.7 – 2m	3 – 300m
Thermal stability of stationary phase	Good stability	Less stable above 300°C
Reactions in the column	Packing may catalyze chemical change	Packing does not catalyze
Application	Useful for the separation of permanent gases and low boiling substances	Useful for the separation of volatile high boiling substances

Nanomaterials

Materials having the dimension of the order of billionth of a meter or nano meter are called **nanomaterials**.

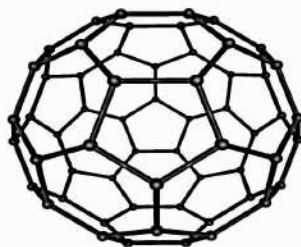
Classification:

- 1. Nano crystalline materials**
- 2. Fullerenes**
- 3. Dendrimer**
- 4. Polyhedral silsesqui oxane**
- 5. Nano intermediates**
- 6. Nano composites**
- 7. Biological nanomaterials**

Nano crystalline materials:

These are aggregates containing a few hundred to several thousands of atoms which are joined to form crystalline form of matter. Resultant crystalline form of matter is called clusture. So these nanomaterials are called nano crystals. They can be used for getting semiconductor crystals. Their diameter is nearly 1nm. They are used for making very strong and long lasting metallic parts. On mixing nano crystals with plastic we get nano composites.

Fullerenes:



These are the molecular form of very pure carbon. They are discovered in 1995. They possess cage like structure of carbon atoms. Most abundant fullerene is buckminsterfullerene (buckminsterfullerene, C_{60}). They possess spherical structure of 60 carbon atoms. Fullerenes contain twelve five membered rings and twenty six membered rings and possess a perfect icosahedral geometry. This geometry is similar to that of a soccer football. In fullerene, each carbon atom is bonded to three other carbon atoms and is SP^2 hybridized.

Uses:

- They are used in drug delivery system.
- They are used in electronic circuits.
- They are used as lubricant in ball bearings.

Dendrimer:

These are organic nano particles. These are highly branched tree like organic polymers. These are obtained from monomers which are added in discrete steps to get tree like appearance. Highly controlled step wise reactions and purifications are required at each step to control the size, structure and functionality of dendrimer.

Eg. PAMAM Dendrimer (Poly Amido Amine)

Polyhedral silsesquioxane:

These are inorganic organic hybrid nano particles. They possess unique set of physical and chemical properties such as high solubility, thermal stability, dielectric constant, permeability and optical transparency. The stoichiometry of the compound is $RSiO_{1.5}$. That means every silicon atom is bound to an average of one and half oxygen (Silsesquiox) and to a hydrocarbon group (ane). Hence the name polyhedral silsesquioxane.

Nano intermediates:

They include nano structured films, dispersions, high surface area materials, supra molecular compounds etc. They are used in solar cells, sensors, battery etc.

Nano composites:

On mixing solid nano particles with plastic resin we get nano composites. They possess more strength. They are lighter and stiffer than thermoplastics. They are less brittle. They possess excellent corrosion resistance. Hence they are used as an anticorrosive material.

Biological nano materials:

These are nano materials of biological origin.

Properties of biological nano materials:

- Self assembly property
- Specific molecular recognition

Eg. DNA nano particles, nano structured peptides

Self assembled nano particles can be used to release compounds under specific conditions and are used in drug delivery systems.

(*Self assembly is a phenomenon where the components of the system assemble themselves spontaneously via an interaction to form larger functional unit.*)

(* **Molecular Recognition** is the specific interaction between two or more molecules through non covalent bond.*)

Classification based on dimension

This is the classification based on the number of dimensions which are not confined to the nanoscale range(<100 nm).

1. Zero dimension (0-D)

Here all the three dimensions are in the nanometric range. Eg. Nano particles

2. One dimension (1-D)

Here one of the dimensions is outside the nanometric range and the other two are within the range. Eg. Nano wires, fibres and tubes.

3. Two dimension (2-D)

Here two of the dimensions is outside the nanometric range and one is within the range. Eg. Nano films, layers and coatings

4. Three dimension (3-D)

Here all the dimensions are outside the nano metric range and one is within the range. Eg. Bundles of nano wires and tubes, multilayers.

Nanotubes

CNT is a tiny hollow cylinder with outside diameter of a nanometer. These are formed spontaneously from carbon atoms. CNT's are sheets of graphene rolled to make a tube. Graphene is one atom thick planar sheets of SP^2 hybridized carbon atoms as in graphite. On aligning in specific manner, their atoms can conduct electricity as effectively as copper. On aligning in a slightly different manner they become electrical semiconductor. They are stronger than steel.

Classification of nano tubes:

On the basis of alignment of carbon atoms, nanotubes are three types.

1. Arm chair nanotube
2. Zig-zag nanotube
3. Chiral nanotube

- **Arm chair nanotube:**

If the line of hexagons is parallel to the axis of the nanotube, then the resultant nanotube is called arm chair nanotube.

- **Zig-zag nanotube:**

If the line hexagon is arranged in a zig-zag manner, then the resultant nanotube is called zig-zag nanotube.

- **Chiral nanotube:**

Line of hexagon exhibit a twist or spiral around the axis of the nanotube which is called chirality. Hence the name chiral nanotube.

On the basis of number of cylindrical structures, nanotubes are of two types.

1. SWCN (Single Walled Carbon Nanotubes)
2. MWCN (Multi Walled Carbon Nanotubes)

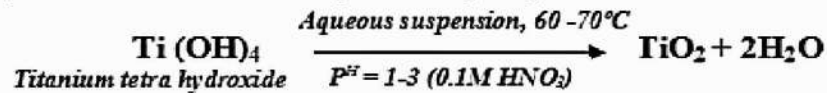
- **SWCN:**

They contain only one nanotube cylinder.

- **MWCN:**

They contain more than one nanotube cylinders.

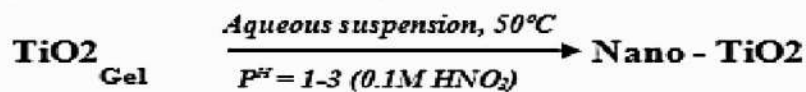
Titanium tetra hydroxide sol will undergo poly condensation by peptisation at a temperature of 60 - 70°C for a period of 18 – 20 hours to produce a precipitate.



Resultant TiO₂ precipitate possesses three dimensional network structure. The precipitate is then washed with ethanol and dried under vacuum conditions for three hours at a temperature of 100°C to get TiO₂ gel(Liquid in solid).

STEP III:

In this step TiO₂ gel is annealed to get Nano crystalline TiO₂.



Scanning Electron Microscopy (SEM)

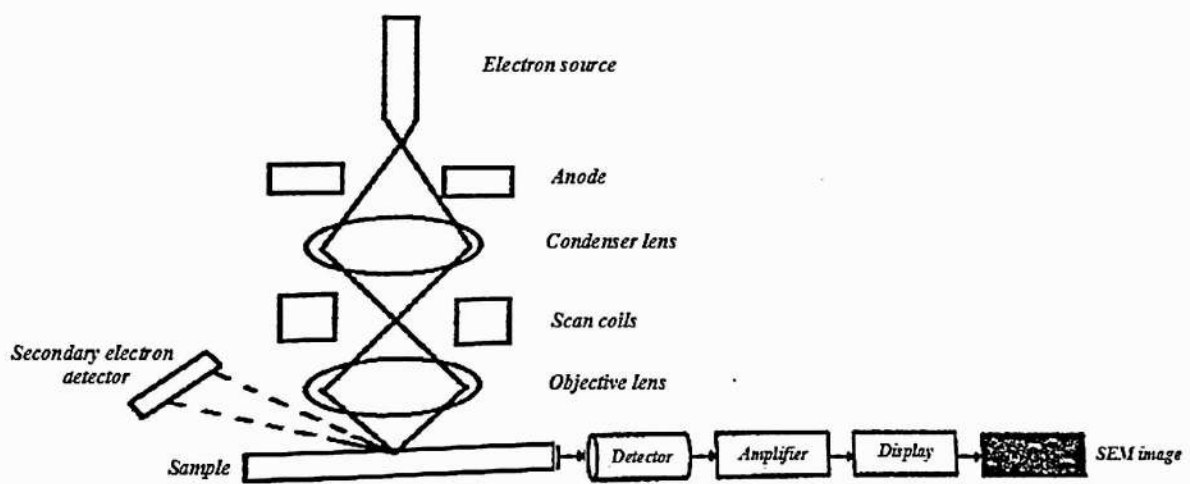
SEM is an important surface characterisation technique used in nanotechnology. It is a type of electron microscope that produces images of a sample by scanning the surface with a focused beam of electrons. This can provide information about topography (surface features), morphology (shape and size of the particles), composition and crystallographic information.

Principle

SEM scans a focused electron beam over a surface to create an image. The electrons in the beam interact with the sample, producing various signals that can give information about the surface topography and composition. Electrons from the top of the column is accelerated down and passed through a combination of lenses to produce a focused beam of electrons which hits the surface of the sample. As a result of the electron sample interaction, signals are produced. These signals are then detected by appropriate detectors. Thus high resolution three dimensional images are produced.

Instrumentation

SEM provides detailed surface information by tracing a sample with an electron beam. This process begins with an electron gun (electron source) generating a beam of energetic electrons down the column and are then passed through a series of electromagnetic lenses. Usually used electron gun is a tungsten wire. Condenser lens compresses the electrons to a narrow beam and the objective lens focuses the electron beam to the sample chamber. This chamber holds the sample under vacuum to eliminate interference of unwanted particles. When the electrons come in contact with the sample, energetic electrons are released from the surface of the sample. Finally detectors will detect signals from the sample. The signals usually include secondary electrons (SE), back scattered electrons (BSE) and X-rays. BSE are incidental electrons reflected backwards. This comes from the deeper regions of the sample. SE originates from the surface of the sample. Therefore BSE and SE provide different types of information. X-rays emitted from beneath the sample surface can provide element and mineral information. SEM produces black and white three dimensional images. A display monitor can be used for the display of images.



Applications

- In morphological and topographical analysis of materials.
- Forensic investigations utilize SEM to uncover the evidence.
- SEM is used study bacteria and viruses.
- In microchip design and production.

Disadvantages

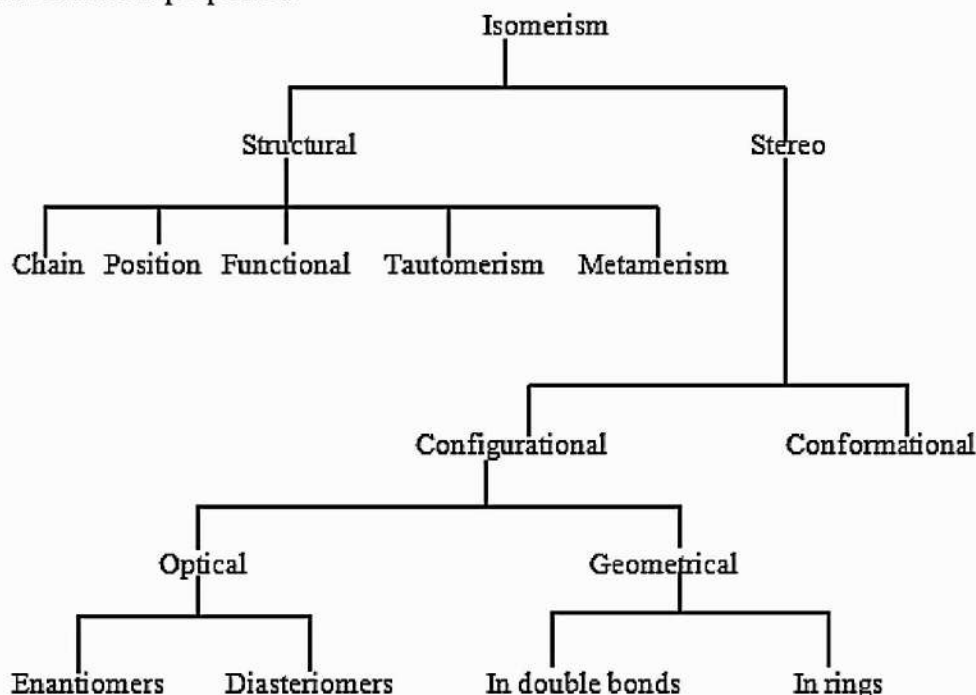
- SEM is very expensive.
- Special training is required to operate SEM.
- Small risk of radiation exposure.

MODULE IV

Stereochemistry and Polymer Chemistry

Stereochemistry:

Stereochemistry is the branch of chemistry which deals with the spatial arrangement of atoms or groups in a molecule. Organic compounds with same molecular formula but different structures are called isomers. This phenomenon is called isomerism. Isomers differ in their physical and chemical properties.

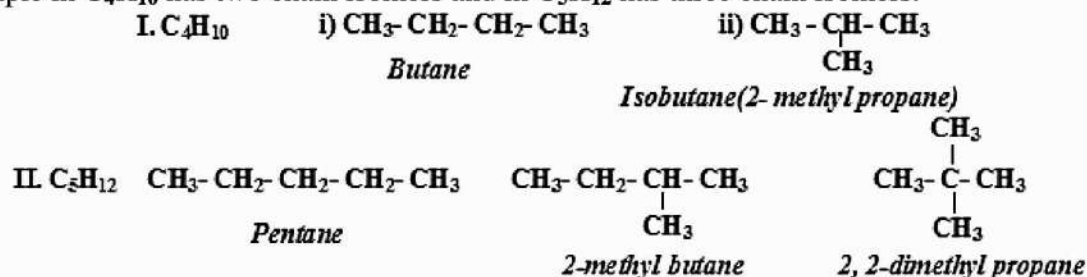


Structural isomerism

Isomerism arises due to the difference in the arrangement of atoms within the molecule and is independent of the position of atoms in the space around the molecule. Structural isomerism is of different types.

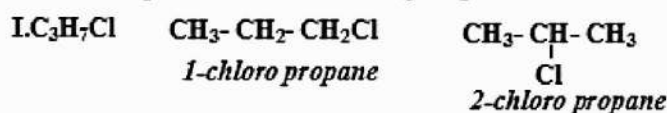
1. Chain (nuclear) isomerism:

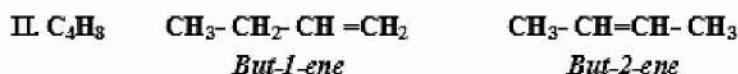
It arises due to the different arrangement of carbon atoms in a carbon chain or skeleton, for example in C_4H_{10} has two chain isomers and in C_5H_{12} has three chain isomers.



2. Position isomerism

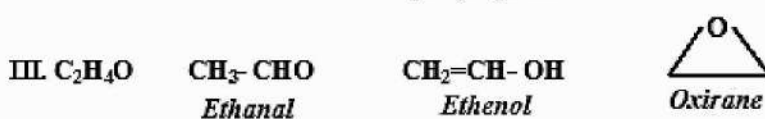
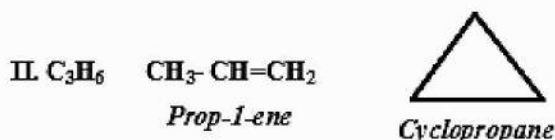
It arises due to the different position of atoms or groups in a carbon chain.





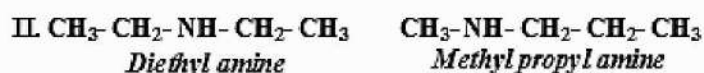
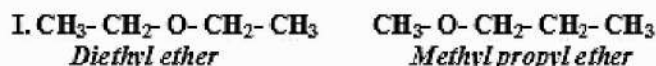
3. Functional isomerism

It arises due to the difference in the functional groups attached to the carbon chain.



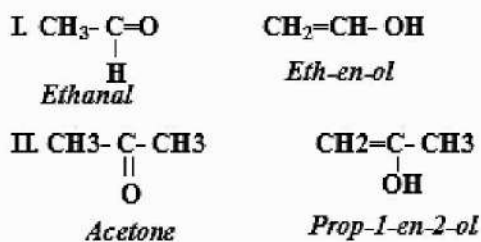
4. Metamerism

It arises due to the unequal distribution of carbon atoms on either side of the functional group.



5. Tautomerism

It is a type of functional isomerism. When two isomers are mutually interconvertible and exist in dynamic equilibrium, they are called tautomers and this phenomenon is called tautomerism.



II. Stereo isomerism:

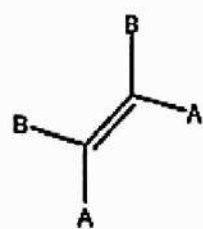
Isomerism arises due to the difference in the spatial arrangement of atoms is called stereo isomerism. This can be divided into conformational isomerism and configurational isomerism. In conformational isomerism, the isomers go on changing into another rapidly due to the rotation about single covalent bonds and cannot be separated. In configurational isomerism, the isomers do not change into one another automatically. These isomers can be interconverted only by breaking and remaking of covalent bonds. Configurational isomerism can be divided into geometrical isomerism and optical isomerism.

1. Geometrical isomerism:

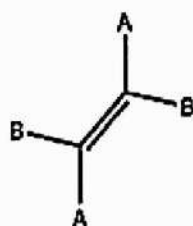
Isomerism arises due to the different spatial arrangement of atoms or groups around a double bond or ring structure is called geometrical isomerism.

a) Geometrical isomerism in double bonds:

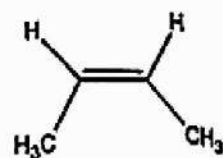
When carbon atoms are joined by a double bond, free rotation about the bond is restricted and the two substituents on each carbon atom are different, geometrical isomerism arises.



Cis- form



Trans-form



(cis)-but-2-ene

Examples

No	Compound	Cis-Isomer	Trans-Isomer
1	1,2-Dichloroethane		
2	Maleic & Fumaric Acids	<p>Maleic Acid</p>	<p>Fumaric Acid</p>
3	2-Butene		
4	Crotonic & Isocrotonic acid	<p>Crotonic acid</p>	<p>Isocrotonic acid</p>

b) Geometrical isomerism in cyclic structures:

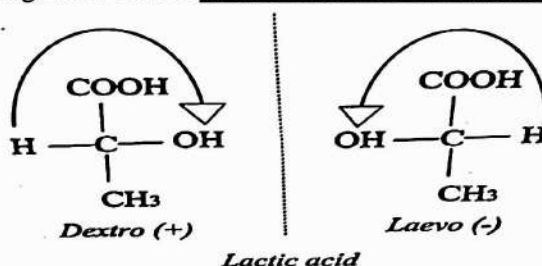
Geometrical isomerism arises in cyclic structures or ring compounds due to the restricted free rotation of carbon atoms about their axis.

Examples

No	Compound	Cis-Isomer	Trans-Isomer
1	1,2-Dimethyl cyclopropane		
2	Cyclobutane dicarboxylic acid		
3	1,4-Dimethyl cyclohexane		

Optical isomerism (Enantiomerism)

Substances which have the ability to rotate the plane polarized light towards right or left are called optically active substances. This phenomenon of rotating plane polarized light is called optical activity. Substances which rotate the plane polarized light clockwise is called dextrorotatory and is indicated as d or + whereas substances which rotate the plane polarized light anticlockwise is called laevorotatory and is indicated as l or -. The d and l isomers have same degree of rotation but opposite sign. Optically active isomers of a compound forms non-super imposable mirror images are called **enantiomers or enantiomorphs**. Example, Lactic acid



Conditions for optical isomerism

- ❖ Molecule should possess chiral carbon atom.
- ❖ Molecule should not super impose on its mirror image.
- ❖ Molecule should not have plane of symmetry.

If a molecule possess plane of symmetry its mirror image will be superimposable and optically inactive. All planar molecules are optically inactive since they possess plane of symmetry. For example, a man standing in front of a mirror with his both hands down has a plane of symmetry and the mirror image is superimposable. If he raises right hand while keeping left hand down, he

does not possess plane of symmetry. The mirror image has left hand up and right hand down, the mirror image will not be superimposable.

Stereoisomers

Chiral and Achiral Molecules:

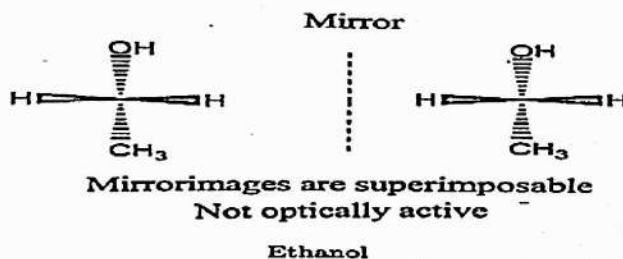
- Some molecules are like hands. Left and right hands are mirror images, but they are not identical, or superimposable.



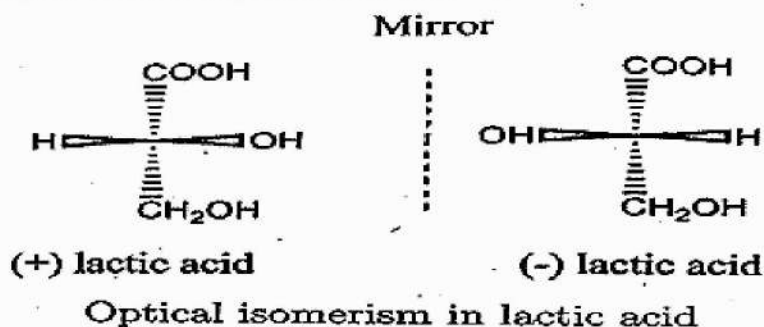
• A molecule (or object) that is *not* superimposable on its mirror image is said to be *chiral*.

30

If two groups around a carbon atom are the same, the mirror image is superimposable and the molecule is not optically active example ethanol.

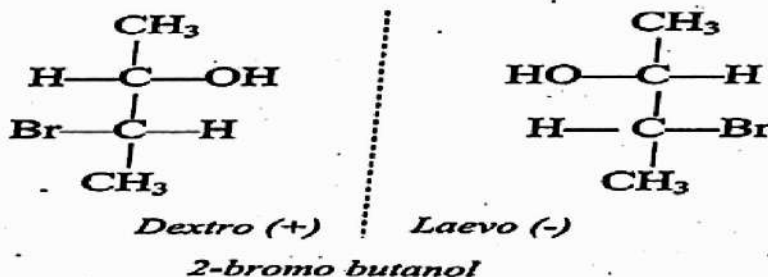


If a molecule possesses one chiral carbon atom it has $2^1 = 2$ optical isomers. They are related to each other as mirror images. Example lactic acid. (+) lactic acid is having specific rotation $+2.67^\circ$ whereas its mirror image (-) lactic acid is having specific rotation -2.67° . Lactic acid present in sour milk is (+) lactic acid. Equimolar mixture of + and - forms of an optically active substance is called racemic mixture. It is having net optical rotation zero and is optically inactive due to external compensation. It is represented as dl or \pm .



Properties of enantiomers:

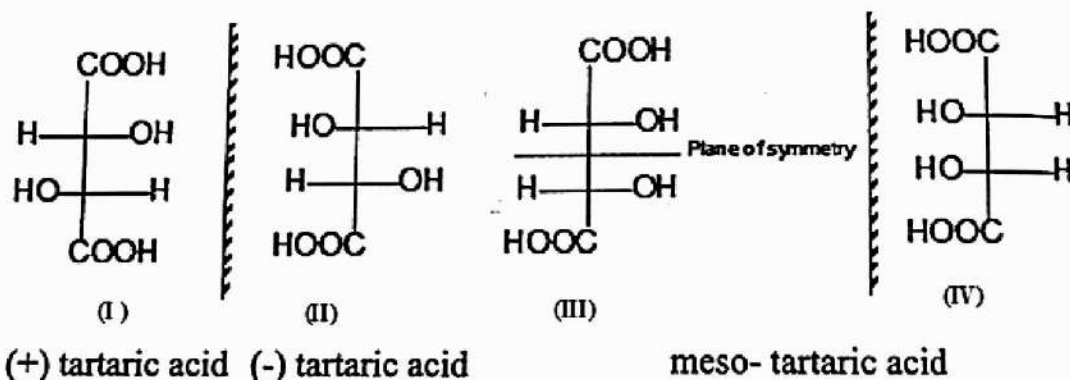
Optically active non-super imposable mirror images of a compound are called enantiomers.



- They have identical properties in all respects except in their interaction with plane polarized light.
- They have identical chemical properties, but differ in their reactivity with optically active reagents.
- They have different biological properties.

Diastereomers:

The stereoisomers which are non-superimposable and are not related as object and mirror images are called diastereoisomers. Due to the difference in the free energy they have different physical and chemical reactivity. Since they differ in physical and chemical properties, they can be separated by crystallization or chromatography.



(I) & (II) are being mirror images of each other, are enantiomers. But (III) & (IV) are not mirror images of each other are termed as diastereoisomers.

Comparison of enantiomers & diastereomers

Enantiomers	Diastereomers
Have identical physical properties	Have different physical properties
Have identical chemical properties	Have similar but not identical chemical properties
Cannot be separated by physical methods	Can be easily separated by physical methods such as chromatography, fractional distillation etc.
Originates from chirality.	May result from chirality or from cis-trans isomerism.
Cis-trans isomers are not enantiomers	Cis-trans isomers are always diastereomers.

Molecules having two asymmetric carbon atoms with different terminal groups:

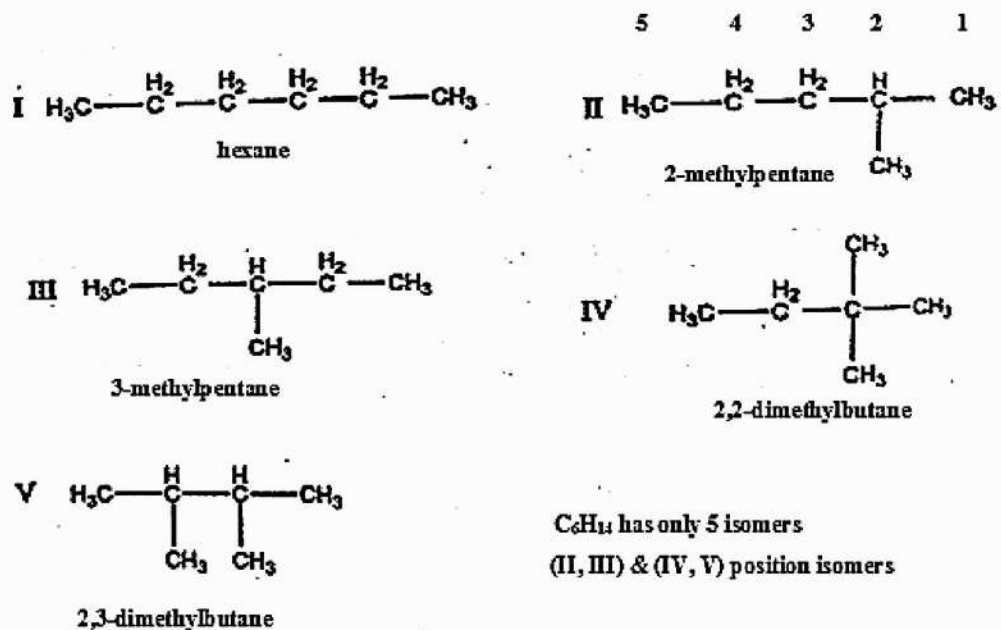
Example, 2, 3-dihydroxy butanoic acid, $\text{CH}_3\text{-*CH(OH)-*CH(OH)-COOH}$, here carbon atoms marked with * are asymmetric. If there are two asymmetric carbon atoms, $2^2 = 4$ optical isomers are possible. They are

In $\text{CH}_3-\text{*CH}(\text{NH}_2)-\text{CHO}$, here all the four groups around the marked carbon atoms are different.

In butanol, $\text{CH}_3-\text{CH}_2-\text{*CH}(\text{OH})-\text{CH}_3$, here also all the four groups around the marked carbon atoms are different.

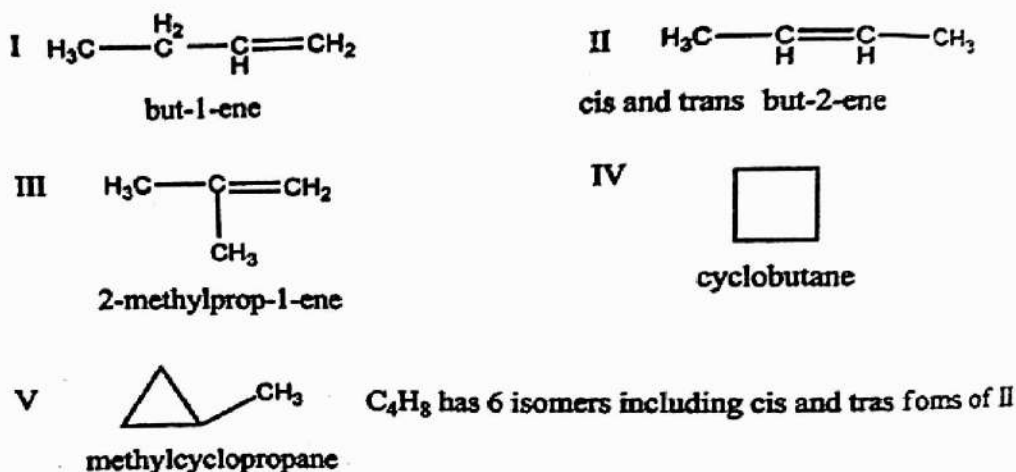
So (b) & (c) are optically active.

3. How many isomers are possible for C_6H_{14} ?



Isomers of C_6H_{14}

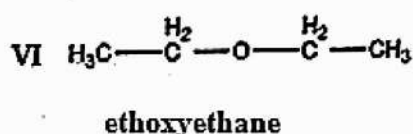
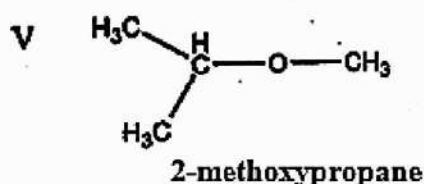
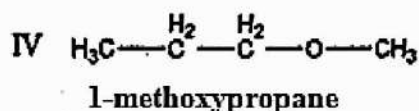
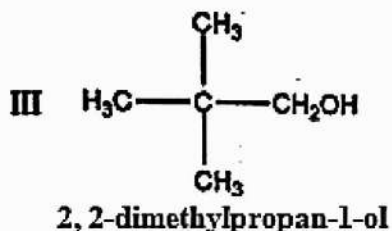
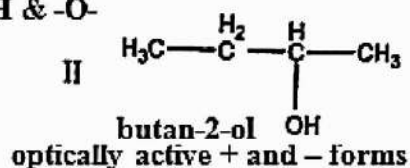
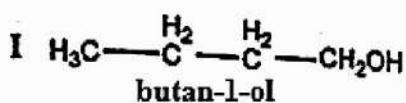
4. How many isomers are possible for C_4H_8 ?



Isomers of C_4H_8

5. How many isomers are possible for $\text{C}_4\text{H}_{10}\text{O}$?

The possible functional groups are -OH & -O-



$\text{C}_4\text{H}_{10}\text{O}$ has seven isomers including optically active forms

6. Which of the following compounds are optically active?

(Cis) 1, 2-dimethyl cyclopropane, (Trans) 1, 2-dimethyl cyclopropane, (Cis) 1, 3-dimethyl butane, (Trans) 1, 2-dimethyl butane, (Cis) 1, 2-dimethyl cyclohexane, (Trans) 1, 2-dimethyl cyclohexane

(Trans) 1, 2-dimethyl cyclopropane & (Trans) 1, 2-dimethyl cyclohexane are optically active.

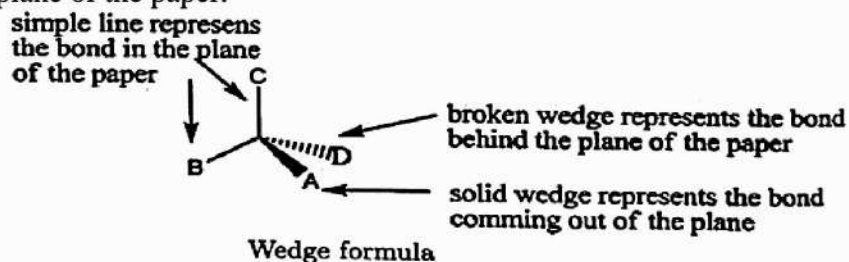
Three dimensional representations of organic molecules

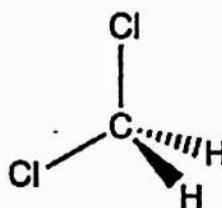
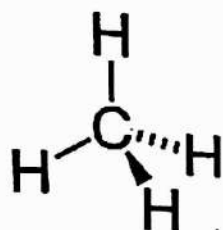
Three dimensional representations of structures are important in stereochemistry. The SP^3 hybridized C-atom has tetrahedral structure with a bond angle of 109.5° . Wedge formula, Fischer projection formula, Saw-Horse formula, Newman projection formula etc are used to represent 3D structures.

Wedge formula

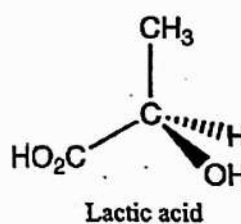
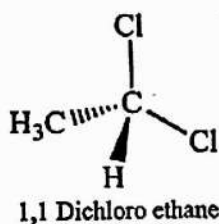
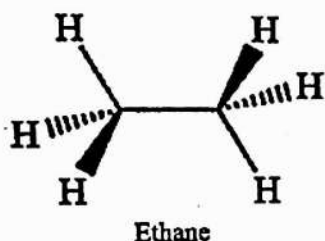
Wedge formulas are the most popular representations used to represent 3D shape and are suitable showing the structures of SP^3 hybridized (tetrahedral) atoms. A Wedge formula represents a molecule in which three types of lines are used to represent 3D structure.

- Solid lines to represent bonds which are in the plane of the paper.
- Dashed lines to represent bonds that extend away from the viewer or the bonds behind the plane of the paper.
- Wedge (dark thick) lines to represent bonds oriented facing the viewer (bonds coming out of the plane of the paper).





Wedge Projection of Methane and dichloromethane molecules

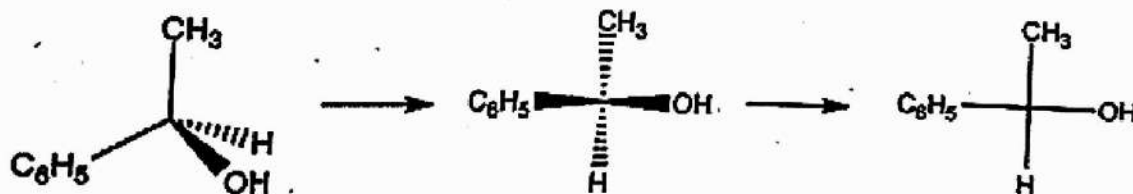


Fischer projection

In Fischer projection the asymmetric carbon atom is taken at the center with bonds attached to this are represented by crossed horizontal and vertical lines. The horizontal bonds represent the groups which are oriented towards us. The vertical bonds represent the groups which are oriented away from us. Carbon -1(C_1) of the compound can be written vertically at the top. Molecules with multiple chiral centers are written in an eclipsed conformation. Fischer projections are 2D representations of a 3D molecule.

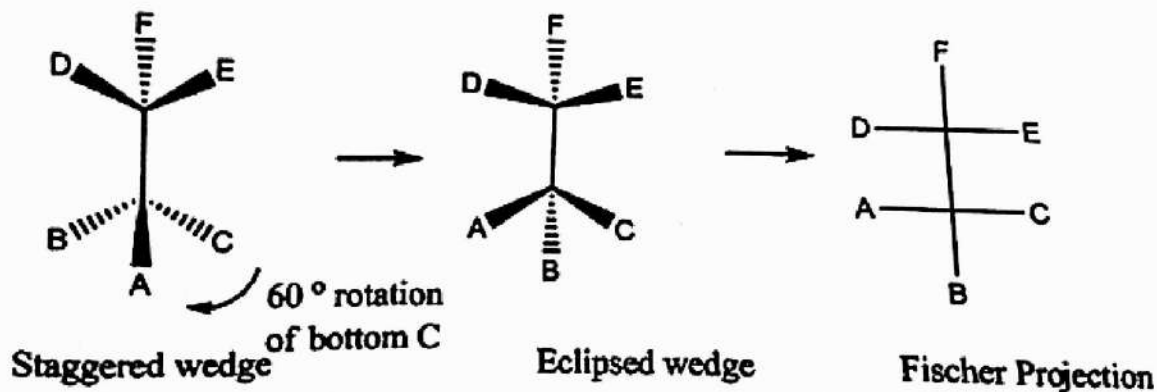
Conversion of wedge formula into Fischer projection formula

In Fischer projection formula thick bond and any of the bonds in the plane are brought to horizontal direction.



Conversion of wedge formula into Fischer projection formula

Conversion of wedge formula of substituted ethane to Fischer projection

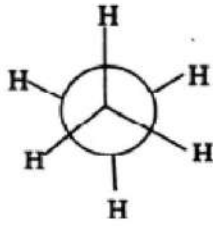
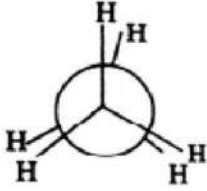
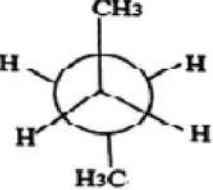
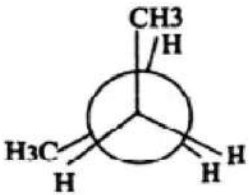


Conversion of wedge formula into Fischer projection formula

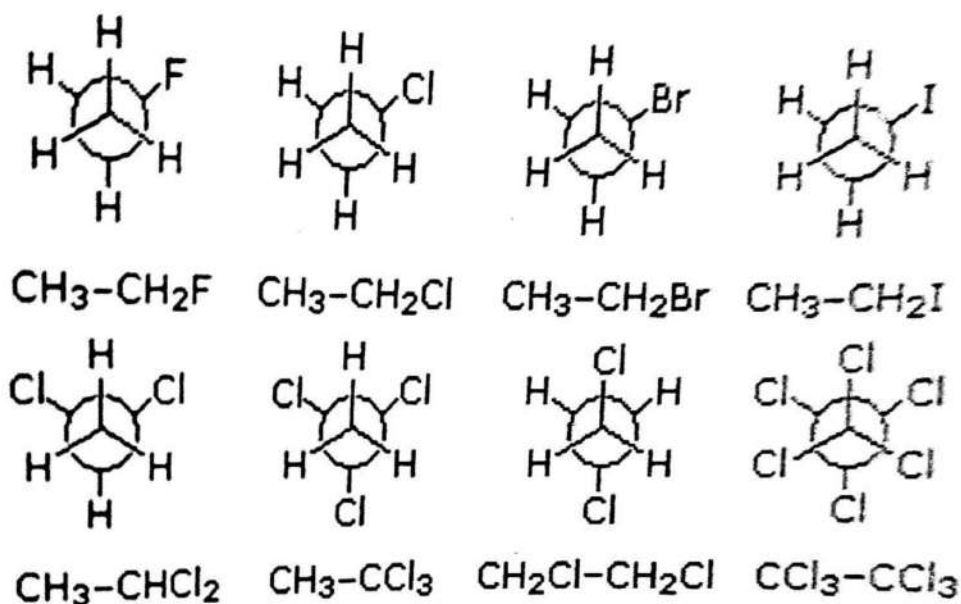
Wedge formula for substituted ethane can be drawn either in staggered conformation or eclipsed conformation. But Fischer projection formula can represent only eclipsed conformation of ethane. Thus in order to convert staggered wedge formula to Fischer projection formula, first transform staggered wedge formula to eclipsed wedge formula and then to Fischer projection formula. The same is shown above.

Newman projection formula

Newman projection formula is used only for substituted ethane and not for substituted methane. Both eclipsed and staggered conformations of ethane can be represented by using this formula. In this formula, the bonds originating from the center of a circle represent the front carbon atom (orienting towards us) and the bonds originating from the circumference of a circle represent the back carbon atom.

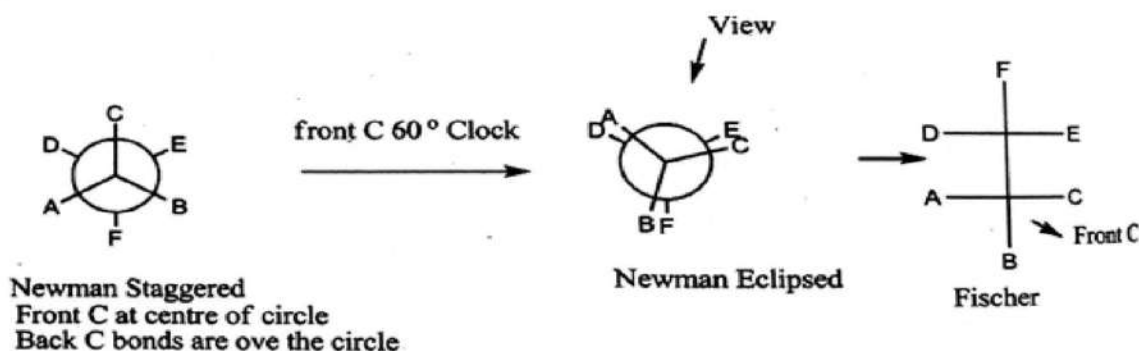
<i>Molecule</i>	<i>Staggered form</i>	<i>Eclipsed form</i>
<i>Ethane</i>		
<i>Butane</i>		

New man projection formulas of some compounds



Conversion of Newman formula of substituted ethane to Fischer projection

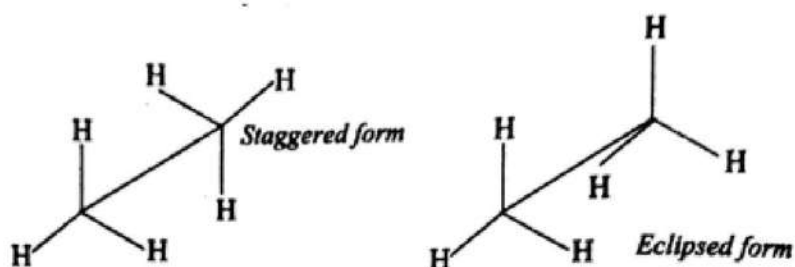
Newman formula of substituted ethane can be drawn either in staggered conformation or eclipsed conformation. But Fischer projection formula can represent only eclipsed conformation of ethane. Thus in order to convert staggered Newman formula into Fischer projection formula, first transform staggered Newman formula to eclipsed Newman formula and then to Fischer projection formula.



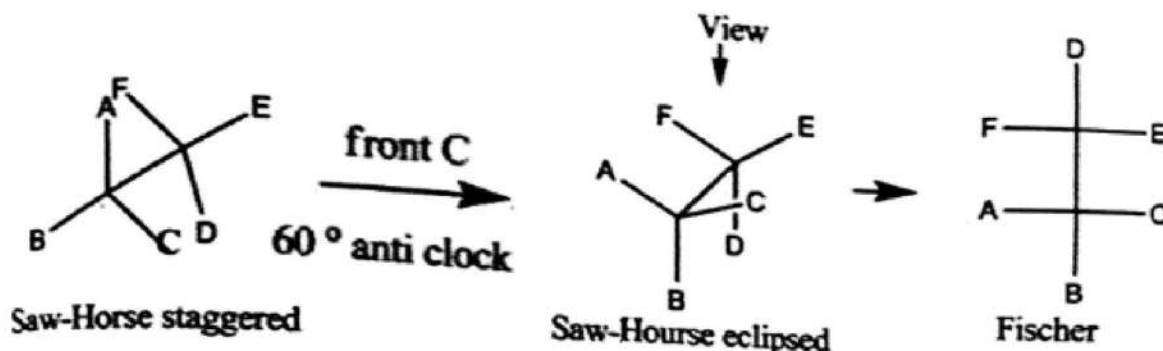
Conversion of Newman formula into Fischer projection formula

Saw horse formula

Saw horse formula represent either eclipsed or staggered conformations of ethane. In this formula, the Carbon atom oriented downwards represent front C- atom.

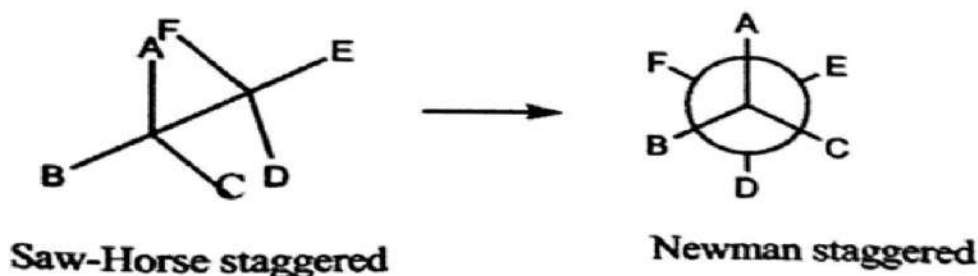


Conversion of Sawhorse formula of substituted ethane to Fischer projection formula



Saw Horse formula of substituted ethane can be drawn either in staggered conformation or in eclipsed conformation. But Fischer projection formula can represent only eclipsed conformation of ethane. Thus in order to convert staggered Saw-Horse formula into Fischer projection formula, first transform staggered Saw-Horse formula into eclipsed Saw-Horse formula and then to Fischer projection formula and the scheme is given above.

Conversion of Sawhorse formula of substituted ethane to Newman formula



E and Z notation of geometrical isomers

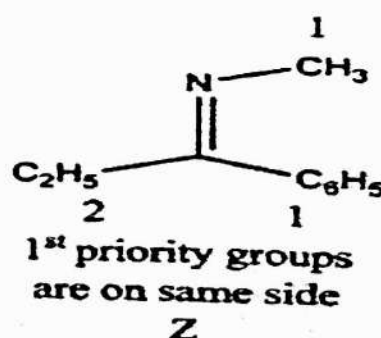
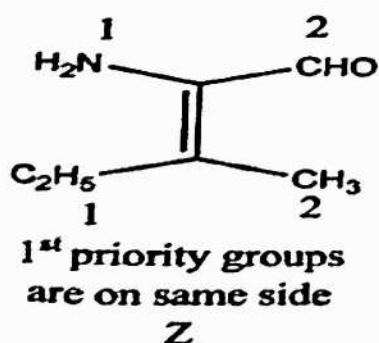
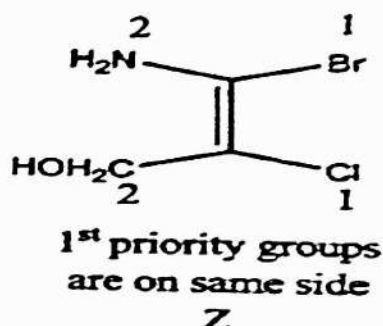
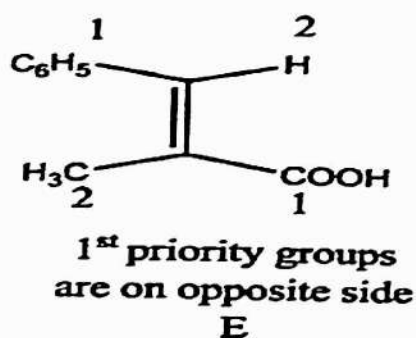
The term cis-trans are being widely used to describe geometrical isomers. But, in compounds where all the four atoms or groups attached to C-atoms of double bond are different, then cis-trans cannot be effective. Such geometrical isomers are designated by E & Z nomenclature. The terms E & Z have been derived from the German words entgegen (meaning opposite) and zusammen (meaning follow together)

A set of rules are used for assigning E & Z nomenclature

1. Assign priority number 1 or 2 to groups on each Carbon atoms of the double bond.
2. Compare the priority of the group or atom at one Carbon relative to the other.
3. The configuration is represented as Z, if both the first priority groups are on opposite sides of the double bond. If the high priority groups are on the opposite sides of the double bond, then the configuration is E.

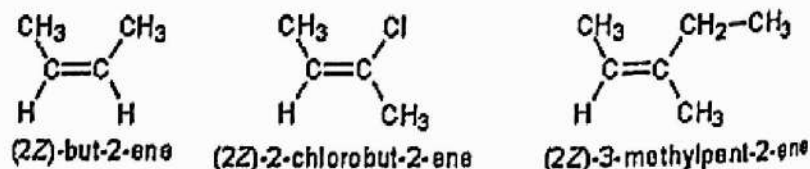
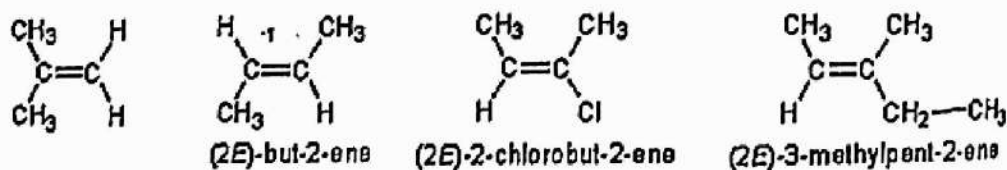
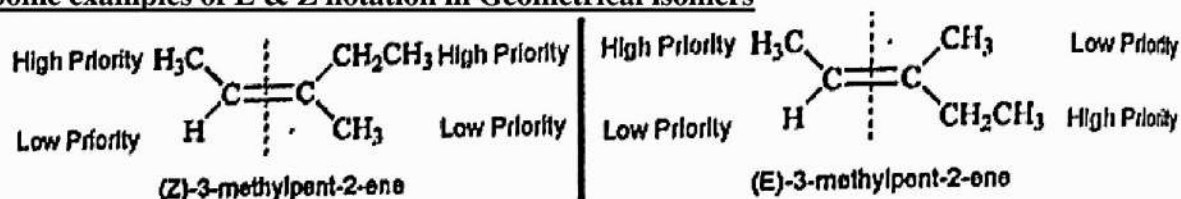
Atoms or groups are assigned priority by the following rules,

- a. A group gets first priority or high priority, if its atomic number is high.
- b. When the first atoms attached to the double bond have the same atomic number (i.e., have the same priority), the second atoms are considered. Then priority is given to the group with second atom of higher atomic number.



E-Z notations

Some examples of E & Z notation in Geometrical isomers

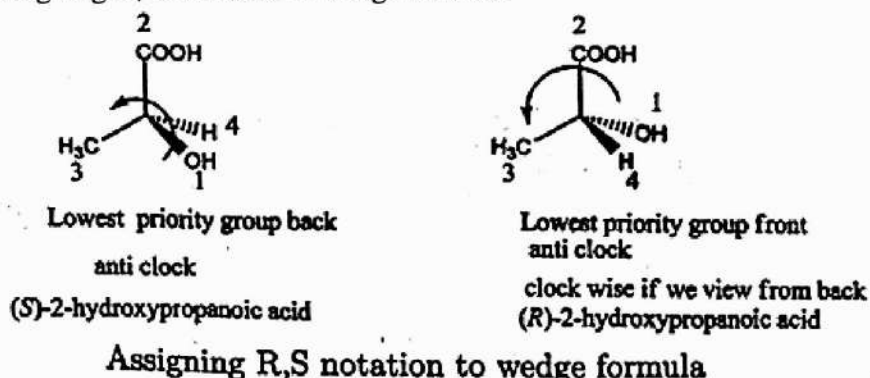


R & S configuration (absolute)(Cahn, Ingold and Prelog system) for optical isomers

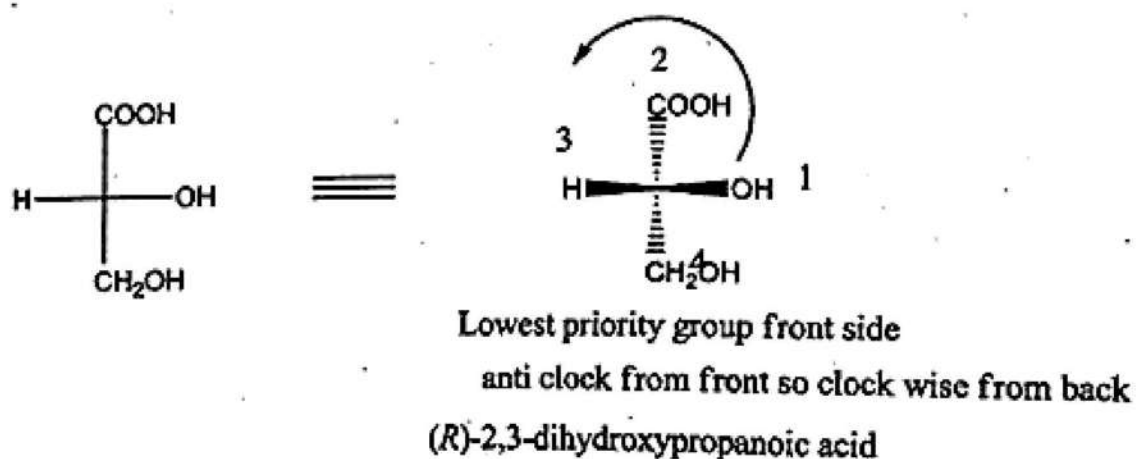
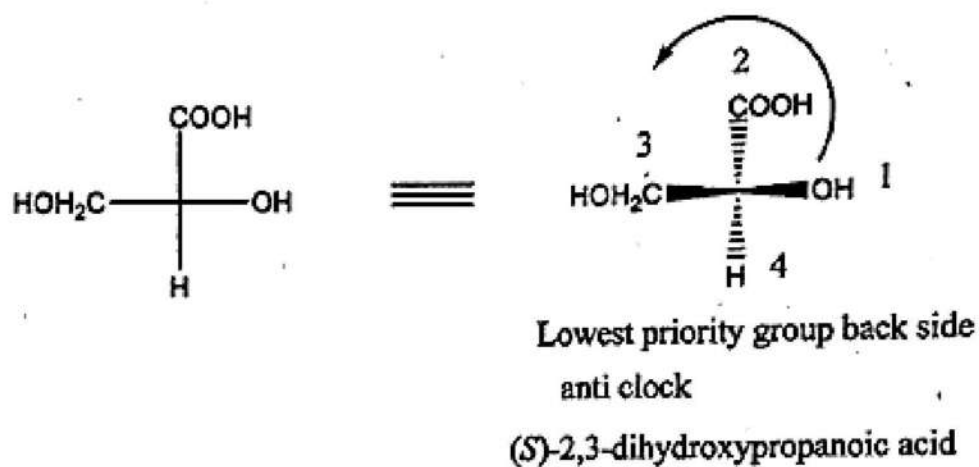
R, S notation is the 3D arrangement of group or atoms in an asymmetric molecule. This system was suggested by Cahn, Ingold and Prelog. This system is based upon the nature of group attached to the asymmetric center and the priority is assigned to them. Here the absolute configuration is given by a prefix R (from Greek word rectus, meaning right handed) or prefix S (from the Greek word sinister, meaning left handed depending upon the sequence of groups. The following rules are used for assigning R, S nomenclature.

- The order of priority is determined on the basis of atomic numbers of atoms attached directly to the chiral Carbon. The greater the atomic number, the higher is the priority. For example if $-H$, $-OH$, $-CH_3$ and $-Br$ are the groups attached to the chiral Carbon, then Br (At. No. 35) will have highest priority, followed by $-OH$ group (At. No. of O is 16) then $-CH_3$ (At. No. of C is 6) and finally hydrogen (At. No. of H is 1). So the order of priority will be $Br > O > C > H$.
- If two isotopes of same element are present, then heavier isotope has higher priority, that is $D > H$ and $^{13}C > ^{12}C$.
- If the two atoms directly linked to the chiral C are identical, then atomic numbers of the next atoms are used for assigning priority. For example when $-COOH$ & $-CHO$ are present, then $-COOH$ has higher priority.
- A doubly or triply bonded atom present in a group attached to the chiral carbon is considered equivalent to two or three singly bonded atoms in determining the priority. For example bonds like $-C=O$, $>C=C<$, are treated as two oxygen attachment and two carbon attachment.
- A molecule is viewed in such a way that the lowest priority group is away from us and if we look for the priority order, the sequence is clockwise or right handed direction, then the notation R is given and the sequence is anticlockwise or left handed direction, then the notation S is given.
- If the lowest priority group given in the structure is towards us, then take the opposite rotation of what we obtained from front side, so that the lowest priority group is made away from us.

Problem 1: Assigning R, S notation to wedge formula

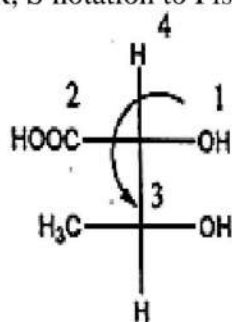


Problem 2: Assigning R, S notation to Fischer formula

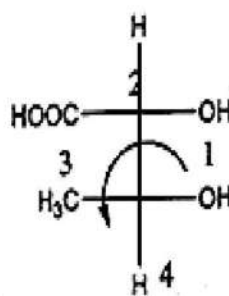


Assigning R,S notation to Fischer formula

Problem 3: Assigning R, S notation to Fischer projection formula for two chiral carbon molecule



Carbon -2
H-atoms is on vertical line
Lowest priority group is away
anticlock -notation -S

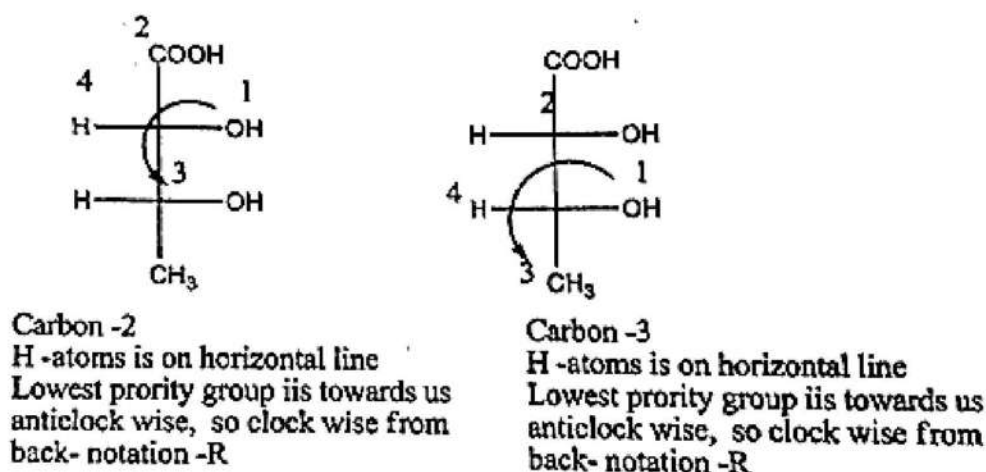


Carbon -3
H-atoms is on vertical line
Lowest priority group is away
anticlock -notation -S

2(*S*),3(*S*)-dihydroxybutanoic acid

Assigning R,S notation to Fischer projection formula for two chiral Carbon

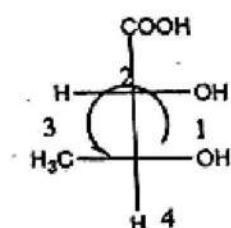
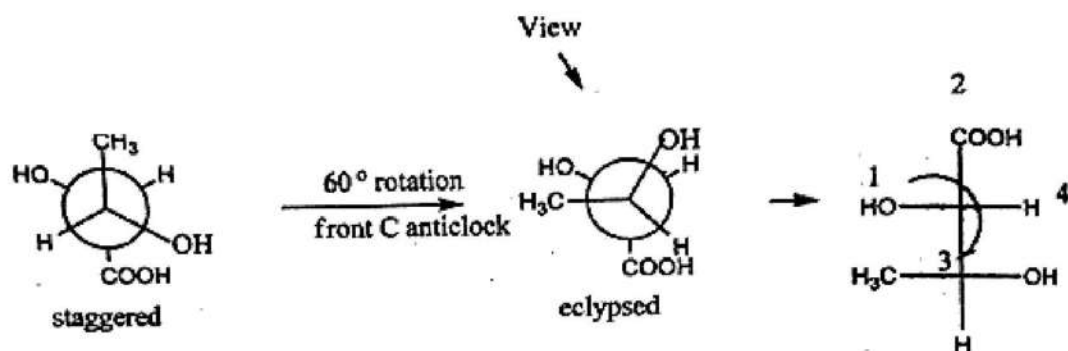
Problem 4: Assigning R, S notation to Fischer projection formula for two chiral carbon molecule



2(R),3(R)-dihydroxybutanoic acid

Assigning R,S notation to Fischer projection formula for two chiral Carbon molecule

Problem 5: Assigning R, S notation to Newman projection formula for two chiral carbon molecule



Carbon -3
H-atoms is on vertical line
Lowest priority group is away from us
anticlock notation -S

Carbon -2
H-atoms is on horizontal line
Lowest priority group is towards us
clock so anti clock from back
notation -S

2(S)3(S)-dihydroxybutanoic acid

Assigning R,S notation to Newman projection formula

Conformational analysis

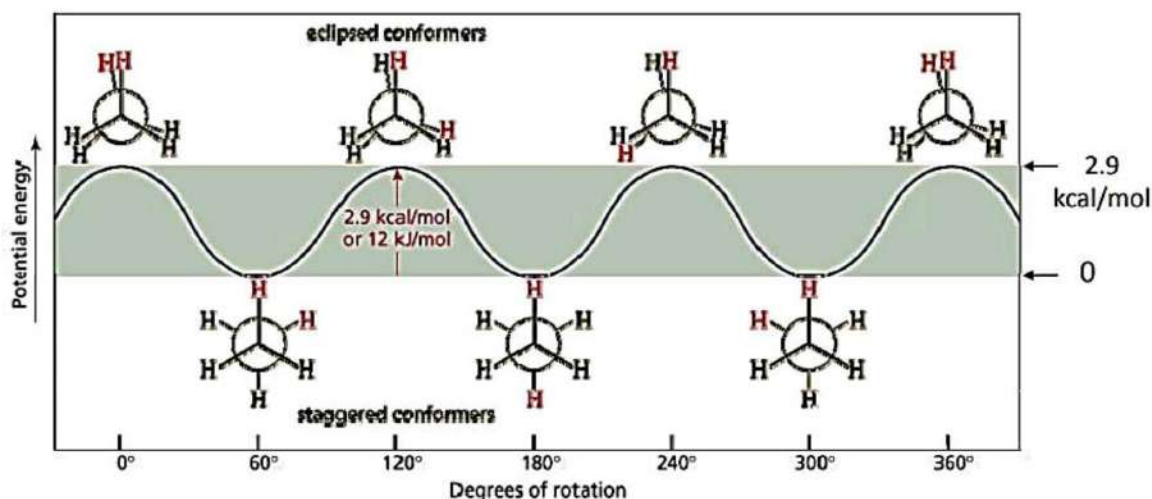
The different spacial arrangement of atoms due to the rotation of groups about a C- C σ bond is called conformational isomers or rotational isomers. The energy difference between two extreme conformations is very small, thus rapid inter conversions takes place at room temperature. It is

not possible to separate one conformer from other, low energy conformer is more populated than high energy conformer at room temperature.

Conformations of ethane

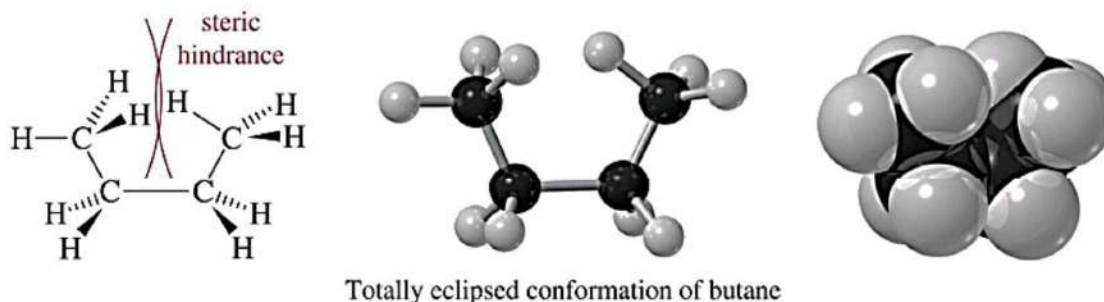
For ethane, we get various conformations due to the number of rotations of $-\text{CH}_3$ group about the C-C σ bond. The staggered conformation is the most stable conformation. Since it has the lowest PE. This conformation allows the maximum possible separation of electron pairs of the six carbon-hydrogen bonds and therefore it has the lowest energy. The least stable conformation of ethane is the eclipsed conformation. In this conformation, hydrogen atoms attached to each carbon atom are directly opposite to each other. This conformation requires the maximum repulsive interaction between electron pairs of the six carbon-hydrogen bonds and therefore it has the highest PE. We can represent the conformational analysis graphically by plotting PE as a function of rotation about the C-C bond. In ethane, the difference in energy between the staggered and eclipsed conformation is 12KJ/mol.

Conformations of Ethane



Conformations of butane

Butane has steric and torsional strain in its eclipsed conformation



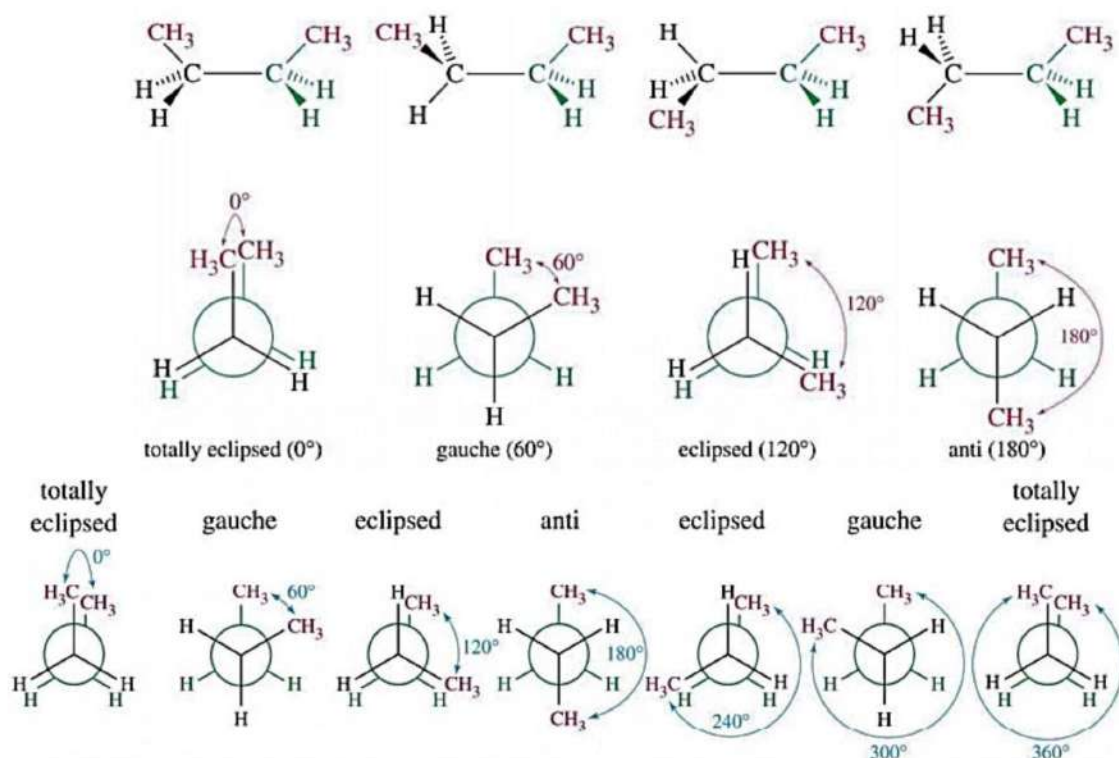
If one $\text{CH}_3\text{-CH}_2\text{-}$ group is kept stationary, and the other $\text{CH}_3\text{-CH}_2\text{-}$ group is allowed to rotate through 360° in six steps (60° each time), then the following conformations are obtained. In the conformational isomerism of butane, it is observed that,

- The fully staggered form in which the methyl groups are far apart with a dihedral angle of 180° is having the lowest PE and is the most stable conformation. It is called anti conformation.

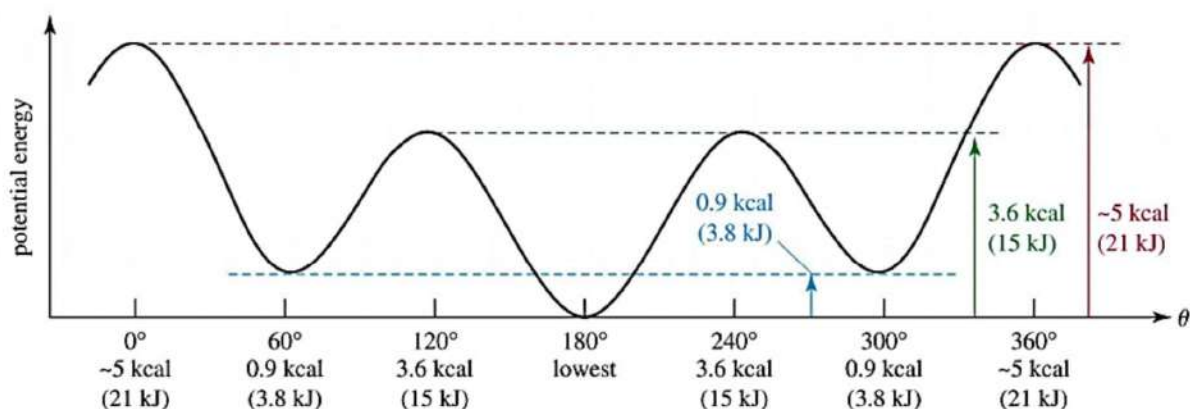
- The conformation in which the methyl groups are only 60° apart (nearly staggered) with slightly higher energy than fully staggered form and is called Gauche conformation.
- Eclipsed conformation is having the highest energy and is the less stable conformer.

In general full staggered anti conformation has the lowest energy and the highest population. The nearly staggered gauche conformation has an appreciable population than eclipsed conformation

Conformations of Butane



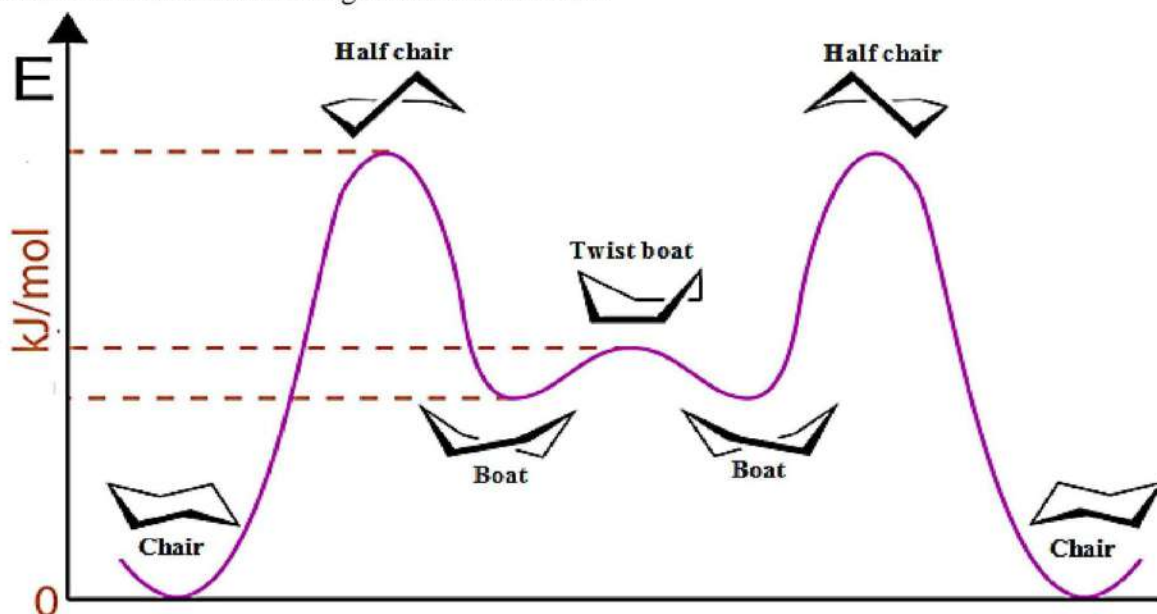
Conformational Analysis of Butane



Conformational analysis of cyclohexane

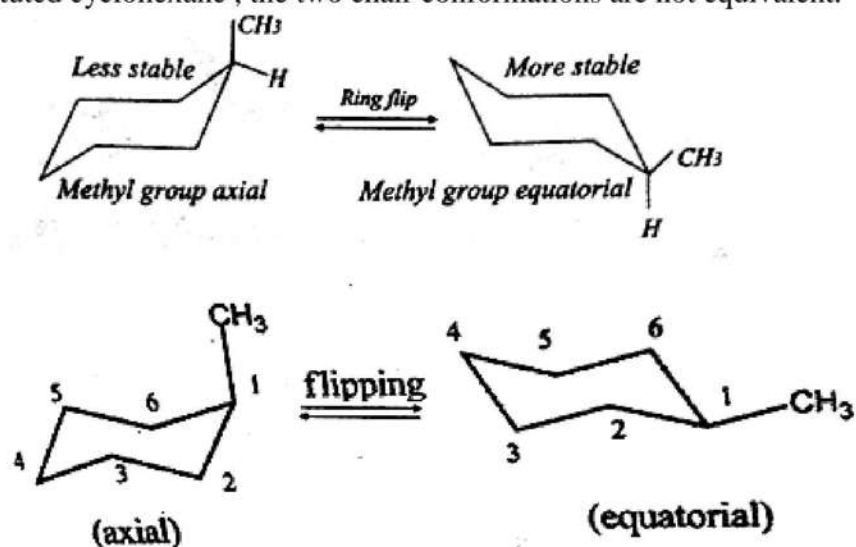
Cyclohexane is a saturated compound with all carbon atoms are sp^3 hybridized and is tetrahedral, ideal bond angle is 109.5° . But the planarity of the ring would force the carbons to have bond angles of 120° , which makes it unstable. Cyclohexane has two stable forms, boat and chair form. Both the conformations are free from angle strain. In chair form all the C-H bonds on adjacent carbon atoms are in fully staggered position which minimizes strain makes it most

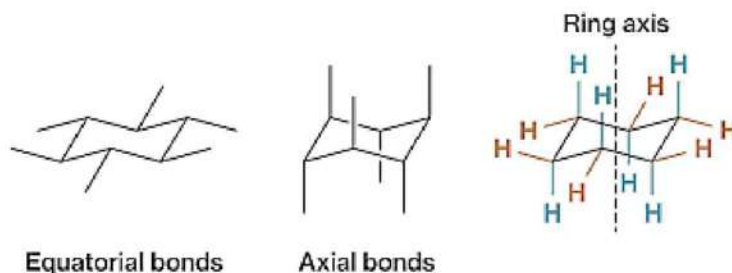
stable. A half chair conformation is also possible, but due to angle strain and ring strain, it is the most unfavorable condition. Its energy is 10Kcal/mol above the chair conformation. In the boat form conformation, total strain is larger than chair form and the boat form is also less stable than chair form. The chair form is rigid and resists distortion and when it is changed into boat form some angular deformation occurs. Its energy is 6.5Kcal/mol above the chair conformation. Twist boat conformation is also possible. Its energy is 5.5Kcal/mol above the chair conformation. The conformations involve following order of stability: chair > twist boat > boat > half-chair. All relative conformational energies are shown below



Conformational analysis of monosubstituted cyclohexane

In monosubstituted cyclohexane, the two chair conformations are not equivalent.





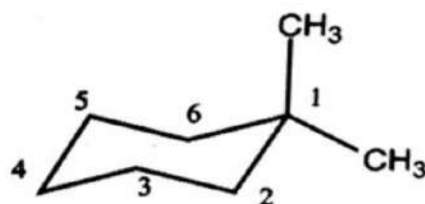
Due to ring flipping, mono substituted methyl cyclohexane is a mixture of chair conformation with an equatorial methyl group and a chair conformation with an axial methyl group. Methyl group is less crowded when it is equatorial than when it is axial. The conformation with axial methyl group has 7KJ/mol energy greater than those with axial methyl group. So at room temperature 95% of the molecules of methyl cyclohexane are in the chair conformation that has an equatorial methyl group. But we cannot separate the two conformations of methyl cyclohexane because they rapidly interconvert by ring flipping

Conformational analysis of di-substituted cyclohexane

In di-substituted cyclohexane, there are four possible position isomers, namely (1,1), (1,2), (1,3) and (1,4).

1) 1, 1-dimethyl cyclohexane

In this compound the two methyl groups are substituted at axial or equatorial position C1. On flipping axial bonds are converted as equatorial bonds and vice versa, thus only one conformer exists.



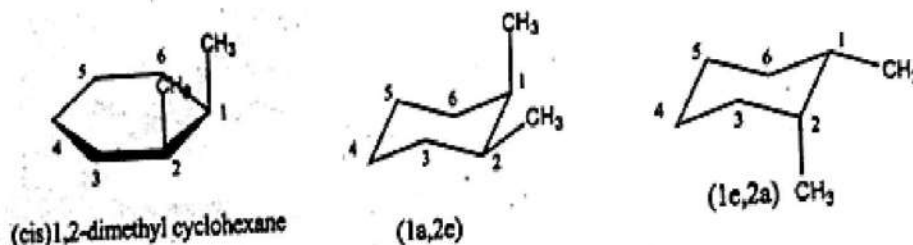
Conformations of 1,1-dimethyl cyclohexane

2). 1, 2-dimethyl cyclohexane

This compound has two geometrical isomers cis and trans. They will not interconvert each other by flipping.

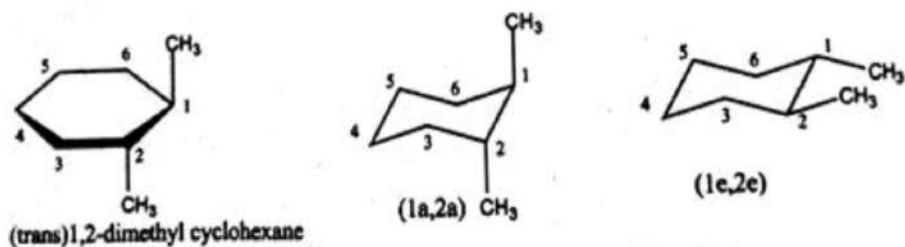
a). (Cis) 1, 2-dimethyl cyclohexane

This compound has two conformers (1a, 2e) and (1e, 2a). Both are equally stable since they have equal number of gauche interactions.



b). (Trans) 1, 2-dimethyl cyclohexane

This compound has two conformers (1a, 2a) and (1e, 2e). They interconvert each other by flipping. (1a, 2a) has four Gauche interactions with the ring CH₂ groups whereas (1e, 2e) has only one Gauche interaction. Thus (1e, 2e) conformer is more stable in (trans) 1, 2-dimethyl cyclohexane.

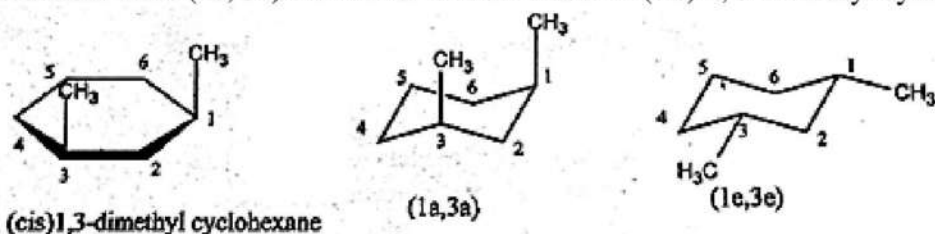


3). 1, 3-dimethyl cyclohexane

This compound has two geometrical isomers cis and trans. They will not interconvert each other by flipping.

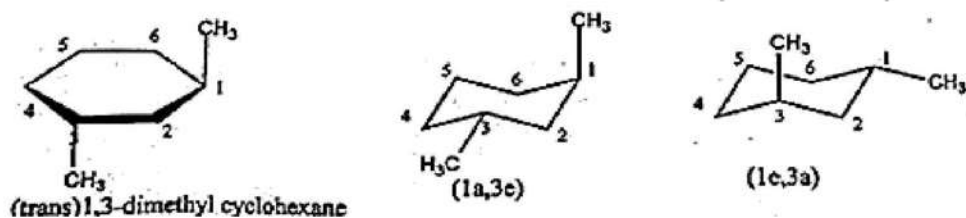
a). (Cis) 1, 3-dimethyl cyclohexane

This compound has two conformers (1a, 3a) and (1e, 3e). They interconvert each other by flipping. (1a, 3a) has two Gauche interactions with the ring CH₂ groups whereas (1e, 3e) has no Gauche interaction. Thus (1e, 3e) conformer is more stable in (cis) 1, 3-dimethyl cyclohexane.



b). (Trans) 1, 3-dimethyl cyclohexane

This compound has two conformers (1a, 3e) and (1e, 3a). Both are equally stable since they have equal number of gauche interactions. They interconvert each other by flipping. Both are equally stable since they have equal number of gauche interactions.

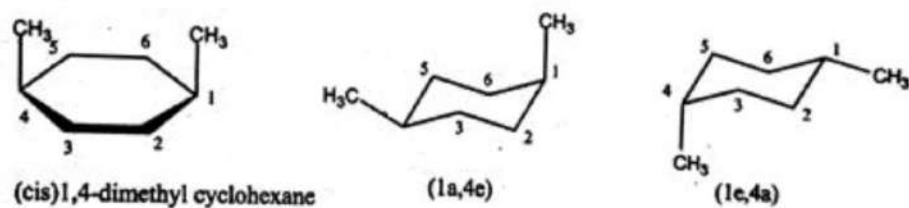


4). 1, 4-dimethyl cyclohexane

This compound has two geometrical isomers cis and trans. They will not interconvert each other by flipping.

a). (Cis) 1, 4-dimethyl cyclohexane

This compound has two conformers (1a, 4e) and (1e, 4a). Both are equally stable since they have equal number of gauche interactions.



b). (Trans) 1, 3-dimethyl cyclohexane

This compound has two conformers (1a, 4a) and (1e, 4e). They interconvert each other by flipping. In (1a, 4a) has four Gauche interactions with the ring CH₂ groups whereas (1e, 3e) has

aniline can be increased by protonation. At room temperature its conductivity is 1000 Scm^{-1} . It is soluble in organic solvents.

Properties:

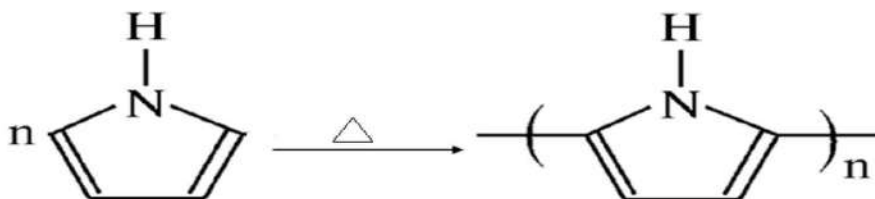
- It is highly flexible
- Possess high strength.
- Low cost material.
- It is stable both in air and water.
- Possess excellent anti-corrosion property.

Applications:

- 1) Used in LED, since the colour changes with the application of particular voltage and chemicals..
- 2) Used as electromagnetic shield and IR absorber.
- 3) Used for making rechargeable batteries.
- 4) Used as a corrosion resistive material.

Poly pyrrole:

Poly pyrrole is a conducting polymer obtained by the polymerization of pyrrole under the influence of free radical, anionic or cationic initiator.



Poly pyrrole is a conjugated polymer. The conductivity of poly pyrrole is due to the electronic transfer along the conjugated π system.

Properties:

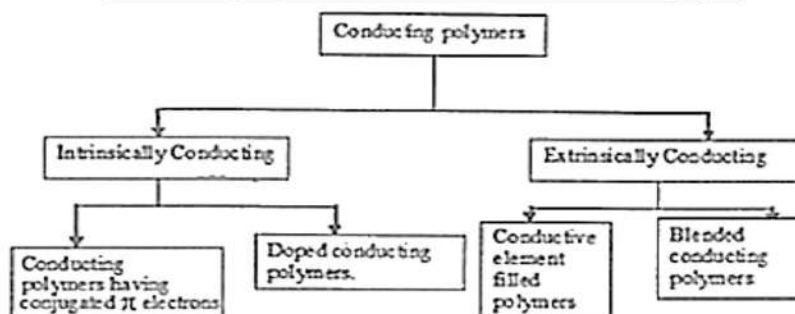
- It has excellent thermal, chemical and mechanical properties.
- It can be processed into any desired shape.
- It has good environmental stability.
- Electrical resistance decreases with increase in temperature. Hence conductivity increases.

Applications:

1. Used for making rechargeable batteries.
2. Used for making chemical carrying pipes.
3. Used as a very good electrical conductor.
4. It can be used as a tissue (cell) support substrate.

Classification of Conducting Polymers:

Conducting polymers can be classified into following types



Polymers which can conduct electricity are called conducting polymers. Polymers are usually pure conductors of electricity due to the absence of free electrons. In the case of polymers band gap is very large (1.5 – 4 eV). But by the careful design of the chemical structure of polymeric back-bone, it is possible to reduce the band gap as low as possible (0.5 – 1eV). Conducting polymers are classified into

1) Intrinsically conducting polymers

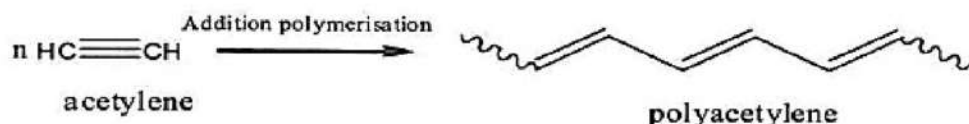
2) Extrinsically conducting polymers

1) Intrinsically conducting polymers

These are conducting polymers which have extensive conjugation in the polymeric back-bone which is responsible for conductance. These are again classified into

a) Conducting polymers containing conjugated π electrons:

These conducting polymers contain conjugated π electrons along the polymeric chain. The orbitals of conjugated π electrons overlap over the entire polymeric back-bone, resulting in the formation of valence band and conduction band, which extends over the entire polymeric back-bone. These bands are separated by a very small band gap. Thus electrical conduction would occur when electrons from valence band are excited to conduction band either thermally or photolytically. Eg. Poly acetylene



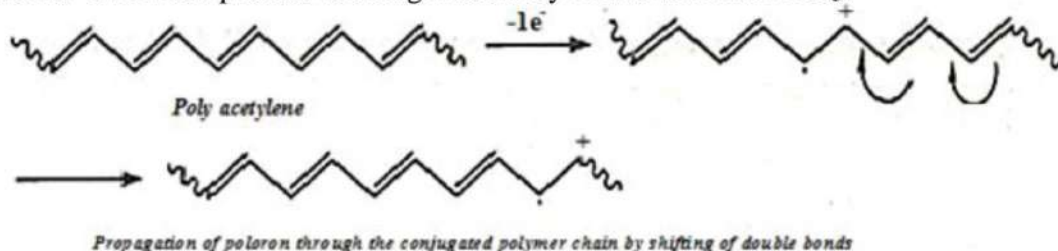
b) Doped conducting polymers:

Conductivity of intrinsically conducting polymers can be increased by creating a positive charge or negative charge by oxidation or reduction. This process is called doping. Conducting polymers obtained by this process is called doped conducting polymers. Doping is of two types.

p – doping & n - doping

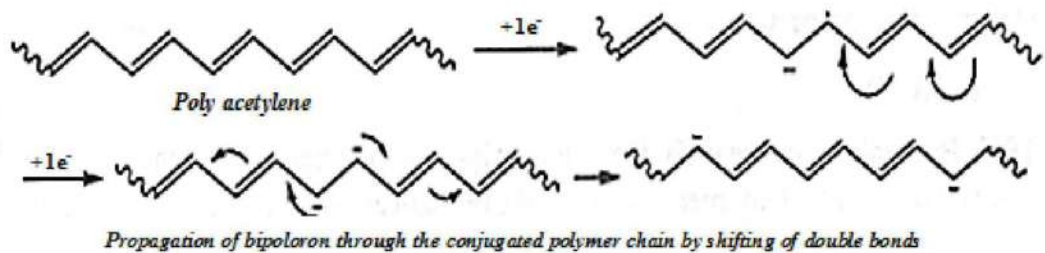
Mechanism of conduction by p – Doping:

p – Doping is done by oxidation process. In this process some electrons of the π -bonds of the conjugated double bonds are removed and holes are created which can move along the polymer and the polymer becomes electrically conductive. The radical cation produced is called polaron. The polarons are mobile and can move along the polymer chain by the rearrangement of double and single bonds. Oxidation process is brought about by Lewis acid like FeCl_3 .



Mechanism of conduction by n – Doping:

n – Doping is done by reduction process. In this process some electrons are introduced into the polymer having conjugated double bonds. Reduction can be done by using Lewis base like sodium naphthalide. This will lead to the formation of polaron and bipolaron in two steps.



2) Extrinsicly conducting polymers:

These are conducting polymers whose conductivity is due to the presence of externally added ingredients in them. These are also classified into two.

a) Conducting element filled conducting polymers.

These are polymers which are filled with conducting elements such as carbon black, metallic fibers, metal oxides etc. Here the polymers act as a binder to hold the conducting elements together. These polymers are low cost, light weight, mechanically durable and strong and can be easily processed into different shapes and sizes.

b) Blended conducting polymers

These are polymers obtained by blending conducting polymers with conventional polymers. They possess better physical, chemical and mechanical properties.

Distinguish between p-Doping & n-Doping

p-Doping	n-Doping
<ul style="list-style-type: none"> • Done by Oxidation • Positive charge is created during the process. • Polorons are produced. • Single step process. • Lewis acid like FeCl_3 is used as the reagent. 	<ul style="list-style-type: none"> • Done by reduction • Negative charge is created during the process. • Polorons and bipolarons are produced. • Two step process. • Lewis base like sodium naphthalide is used as reagent.

OLED (Organic Light Emitting Diode)

OLED is an advanced form of LED and is made up of conducting polymer like polyaniline. Its thickness is 200 times smaller than human hair.

Parts of OLED:

1. Substrate:
2. Anode
3. Hole Transport Layer (HTL)
4. Electron Transport Layer (ETL)
5. Cathode

Substrate:

A clear plastic or glass that supports OLED is called substrate.

Anode:

When current passes through the OLED, it removes electrons and adds holes. Usually used anode is ITO (Indium Titanium Oxide)

HTL:

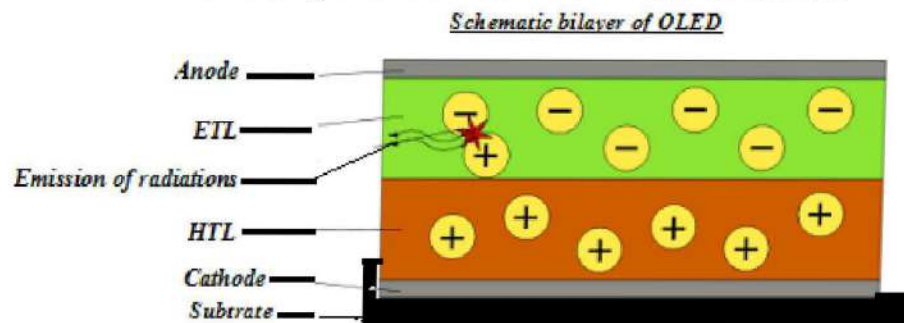
It is the conducting layer made of conducting polymer like polyaniline. It helps for the transport of holes from the anode through the OLED.

ETL:

It is the emissive layer made of polyfluorene. Light is produced in the ETL. It helps for the transport of electrons from the cathode through the OLED.

Cathode:

It ejects electrons when current flows through the OLED. Al or Ca is used as cathode.

**Working of OLED:**

When a voltage is applied across the OLED, a current of electrons flows from cathode to anode. During this current flow electron hole capture each other by electrostatic force of attraction. Recombination of electrons with holes produces light. The wave length of light produced depends on the band gap of the conducting polymer.

Properties:

- It is considered as a cold lighting source. Since no heat is generated during its working.
- Its power consumption is very less.
- It is flexible, very thin and small.
- It generates good quality light.
- More efficient than incandescent lamps and halogen lamps.

Applications:

1. They are used for making screens of smart watches, mobile phones, laptops and televisions.
2. They can be used for getting ambient lighting sources.

Limitation:

- Life time of the organic polymer is limited.

Advantages

- Manufacture OLED is highly economical and efficient.
- No backlight is produced by the device and its power consumption is very less.
- Its response time is less than 0.01 minutes.

Module V

Water Technology and Sewage Water Treatment

About 75% earth's crust is water. Water is essential for living beings as well as for industries. It is used as an engineering material, as a coolant in power plants and also used for power generation purpose. But only 1% of earth's water resources are available for ready use. Hence it is urgently required to treat the water most carefully and economically. Such type of all treatments comes under the heading water technology.

Hardness of water

The property of water which prevents lather formation with soap solution is called hardness of water. It is due to the presence of dissolved salts of Ca, Mg and some other heavy metals. On the basis of hardness, water is of two types;

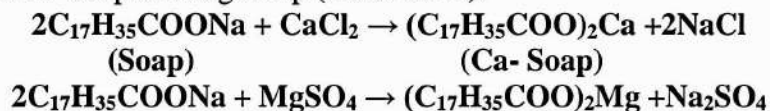
1. Soft water
2. Hard water

Soft water:

Water which can form ready and permanent lather with soap solution is called soft water.

Hard water:

Water which cannot form ready and permanent lather with soap solution is called hard water. Soap is sodium or potassium salts of higher fatty acid which when treated with hard water produces insoluble Ca-Soap and Mg-Soap (white scum).

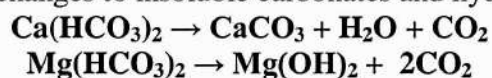


Hardness is of two types.

1. Temporary (Carbonate) hardness
2. Permanent (Non-carbonate) hardness

Temporary (Carbonate) hardness:

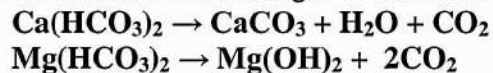
Hardness which will remain for a shorter period and can be easily removed by boiling is called temporary (Carbonate) hardness. It is due to the presence of bicarbonates of Ca & Mg. On boiling, soluble bicarbonate changes to insoluble carbonates and hydroxides.



Removal of temporary hardness

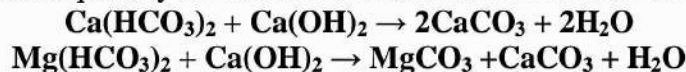
1. Boiling

On boiling, soluble bicarbonate changes to insoluble carbonates and hydroxides.



2. Clark's process

In this method, calculated quantity of lime is added to convert it as insoluble carbonate.



Permanent (Non-carbonate) hardness:

Hardness due to the presence of chlorides and sulphates of Ca, Mg, Al, Fe, etc. are called permanent hardness.

Removal of Permanent (Non-carbonate) hardness:

1. Lime soda process
2. Zeolite process
3. Ion exchange process

Degree of hardness

Hardness is expressed in terms of degree of hardness. Degree of hardness is expressed in terms of CaCO₃ equivalent hardness. The concentration of hardness producing ions and non-hardness producing ions are expressed in terms of equivalent amount of CaCO₃ and is called CaCO₃ equivalent hardness. The choice of CaCO₃ in particular due to,

1. Molecular weight is 100.
2. Equivalent weight is 50.
3. It is the most insoluble precipitate in most of the water treatment processes.

$$\text{CaCO}_3 \text{ equivalent hardness} = \frac{\text{Mass of HPS} \times \text{Equivalent weight of CaCO}_3}{\text{Equivalent weight of HPS}}$$

Where HPS is hardness producing substance.

The same formula can be modified by replacing the equivalent weight by molecular weight.

$$\text{CaCO}_3 \text{ equivalent hardness} = \frac{\text{Mass of HPS} \times \text{Molecular weight of CaCO}_3}{\text{Molecular weight of HPS}}$$

Let X be the mass of HPS, then $\text{CaCO}_3 \text{ equivalent hardness} = \frac{X \times 100}{M \text{ HPS}}$

Units of hardness

The important units of hardness are

1. Ppm
2. Mg/L
3. Degree French (°F)
4. Degree Clark (°Cl)
5. Equivalents per million (epm)

Ppm:

It is the number of parts of CaCO₃ equivalent hardness present per million parts of water.

$$1 \text{ ppm} = \frac{1}{10^6}$$

$$10^6 \text{ ppm} = 1$$

Mg/L:

It is the number of milligrams of CaCO₃ equivalent hardness present per litre of water.

$$1 \text{ mg/L} = \frac{1}{10^6} = 1 \text{ ppm}$$

$$10^6 \text{ mg/L} = 1$$

Degree French:

It is the number of parts of CaCO₃ equivalent hardness present per 10⁵ parts of water.

$$1^\circ \text{F} = \frac{1}{10^5}$$

$$10^5 \text{ }^\circ \text{F} = 1$$

Degree Clark:

It is the number of parts of CaCO₃ equivalent hardness present per 70000 parts of water.

$$1^\circ \text{Cl} = \frac{1}{70000}$$

Equivalents per million:

It is the number of equivalents of CaCO₃ equivalent hardness present per million parts of water.

$$1 \text{ epm} = \frac{50}{10^6}$$

$$\frac{10^6}{50} \text{ epm} = 1$$

Inter conversion of various units of hardness

$$70000^\circ \text{Cl} = 1$$

$$10^6 \text{ Ppm} = 10^6 \text{ mg/L} = 10^5 \text{ }^\circ \text{F} = 70000^\circ \text{Cl} = \frac{10^6}{50} \text{ epm} = 1$$

$$1 \text{ ppm} = 1 \text{ mg/L} = 0.1^\circ \text{F} = 0.07^\circ \text{Cl} = 0.02 \text{ epm}$$

Disadvantages of hard water

- It doesn't form lather with soap solution. Instead it produces sticky precipitates of Ca-Soap and Mg-Soap. This will lead to the wastage of soap.
- Hard water used in boilers cause problems such as boiler corrosion, scales and sludges in boilers, priming and foaming, caustic embrittlement, etc.
- Water containing chlorides and sulphates if used for concrete mixing affect the hydration of cement and the final strength of hardened cement.
- The boiling point of hard water is high. So it leads to the wastage of fuel.
- Tea and coffee prepared in hard water have an unpleasant taste.
- Hard water cannot be used in dyeing industry. Since it cannot produce the exact shades of colours due to the adherence of Ca-Soap and Mg-Soap.
- It cannot be used in sugar industry. Since it causes difficulties in the crystallization of sugar and makes the sugar deliquescent.
- It cannot be used in paper industry, because it will affect the smoothness, glossiness, colour, etc. of the paper.

1. Calculate the hardness of water sample containing the following salts/litre. CaSO_4 – 16.2mg/L, $\text{Mg}(\text{HCO}_3)_2$ – 1.4mg/L, MgCl_2 – 9.5mg/L.

Constituents	Quantity	M_{HPS}	CaCO_3 equivalent hardness = Quantity $\times \frac{100}{M_{\text{HPS}}}$
CaSO_4	16.2mg/L	136	$16.2 \times \frac{100}{136} = 11.9$ ppm
$\text{Mg}(\text{HCO}_3)_2$	1.4mg/L	146	$1.4 \times \frac{100}{146} = 0.97$ ppm
MgCl_2	9.5mg/L	95	$9.5 \times \frac{100}{95} = 10$ ppm

$$\text{Total hardness} = 11.9 + 0.97 + 10 = 22.87 \text{ ppm}$$

$$\text{Temporary hardness} = 0.97 \text{ ppm}$$

$$\text{Permanent hardness} = \text{Total hardness} - \text{Temporary hardness} = 22.87 - 0.97 = 21.9 \text{ ppm}$$

2. A sample of water on analysis gives the following results: $\text{Ca}^{2+} = 30\text{mg/L}$, $\text{Mg}^{2+} = 18\text{mg/L}$, $\text{HCO}_3^- = 244\text{mg/L}$, $\text{Na}^+ = 11.5\text{mg/L}$. Calculate the temporary and permanent hardness of water sample.

Constituents	Quantity (mg/L)	M_{HPS}	CaCO_3 equivalent hardness = Quantity $\times \frac{100}{M_{\text{HPS}}}$
Ca^{2+}	30	40	$30 \times \frac{100}{40} = 75$
Mg^{2+}	18	24	$18 \times \frac{100}{24} = 75$
HCO_3^-	122	61	$122 \times \frac{100}{2 \times 61} = 100$
Na^+	11.5	-	-

$$\text{Total hardness} = 75 + 75 = 150 \text{ ppm}$$

$$\text{Temporary hardness} = 100 \text{ ppm}$$

$$\text{Permanent hardness} = \text{Total hardness} - \text{Temporary hardness} = 150 - 100 = 50 \text{ ppm}$$

3. A water sample is having 400 ppm permanent hardness and 100 ppm temporary hardness. If 42 mg/L NaHCO_3 is added to this water, calculate the new temporary and permanent hardness.

$$\text{Total hardness} = 400 + 100 = 500 \text{ mg/L}$$

Temporary hardness of water sample increases with the addition of 42 mg/L NaHCO_3 .

$$\text{Increase in temporary hardness} = \frac{42 \times 100}{2 \times 84} = 25 \text{ ppm}$$

$$\text{New temporary hardness} = 100 + 25 = 125 \text{ mg/L}$$

$$\text{New permanent hardness} = \text{Total hardness} - \text{New temporary hardness} = 500 - 125 = 375 \text{ mg/L}$$

4. A water sample contains $(\text{HCO}_3)_2$ – 36.5 ppm, $\text{Ca}(\text{HCO}_3)_2$ – 40.5 ppm, MgSO_4 – 30.0 ppm, CaSO_4 – 34.0 ppm, CaCl_2 – 27.75 ppm, NaCl – 10 ppm. Calculate the temporary and permanent hardness of water sample.

Constituents	Quantity (ppm)	M_{HPS}	CaCO_3 equivalent hardness = Quantity $\times \frac{100}{M_{\text{HPS}}}$
$\text{Ca}(\text{HCO}_3)_2$	40.5	162	$40.5 \times \frac{100}{162} = 25$ ppm
$\text{Mg}(\text{HCO}_3)_2$	36.5	146	$36.5 \times \frac{100}{146} = 25$ ppm
MgSO_4	30.3	120	$30.0 \times \frac{100}{120} = 25$ ppm
CaSO_4	34.0	136	$34.0 \times \frac{100}{136} = 25$ ppm
CaCl_2	27.75	111	$27.75 \times \frac{100}{111} = 25$ ppm
NaCl	10	-	-

$$\text{Temporary hardness} = \text{Hardness due to } \text{Ca}(\text{HCO}_3)_2 + \text{Hardness due to } \text{Mg}(\text{HCO}_3)_2 \\ = 25 + 25 = 50 \text{ ppm}$$

$$\text{Permanent hardness} = \text{Hardness due to } \text{MgSO}_4 + \text{Hardness due to } \text{CaSO}_4 + \text{Hardness} \\ \text{due to } \text{CaCl}_2 = 25 + 25 + 25 = 75 \text{ ppm}$$

5. A sample of water on analysis gives the following results: $\text{Ca}^{2+} = 400\text{mg/L}$, $\text{Mg}^{2+} = 240\text{mg/L}$, $\text{HCO}_3^- = 244\text{mg/L}$, $\text{Na}^+ = 92\text{mg/L}$. Calculate the temporary and permanent hardness of water sample.

Constituents	Quantity (ppm)	M_{HPS}	CaCO_3 equivalent hardness = Quantity $\times \frac{100}{M_{\text{HPS}}}$
Ca^{2+}	400	40	$400 \times \frac{100}{40} = 1000$
Mg^{2+}	240	24	$240 \times \frac{100}{24} = 1000$
HCO_3^-	244	61	$244 \times \frac{100}{2 \times 61} = 200$
Na^+	92	-	-

$$\text{Total hardness} = 1000 + 1000 = 2000 \text{ ppm}$$

$$\text{Temporary hardness} = 200 \text{ ppm}$$

$$\text{Permanent hardness} = 2000 - 200 = 1800 \text{ ppm}$$

6. A water sample contains $\text{Mg}(\text{HCO}_3)_2$ – 43.8mg/L, $\text{Ca}(\text{HCO}_3)_2$ – 48.6 ppm, MgSO_4 – 24.0 ppm, CaSO_4 – 27.2mg/L, NaHCO_3 – 16.8mg/L. Calculate the temporary and permanent hardness of water sample.

Constituents	Quantity (mg/L)	M_{HPS}	CaCO_3 equivalent hardness = Quantity $\times \frac{100}{M_{\text{HPS}}}$
$\text{Ca}(\text{HCO}_3)_2$	48.6	162	$48.6 \times \frac{100}{162} = 30$ ppm
$\text{Mg}(\text{HCO}_3)_2$	43.8	146	$43.8 \times \frac{100}{146} = 30$ ppm
MgSO_4	24.0	120	$24.0 \times \frac{100}{120} = 20$ ppm
CaSO_4	27.2	136	$27.2 \times \frac{100}{136} = 20$ ppm
NaHCO_3	16.8	84	$16.8 \times \frac{100}{2 \times 84} = 10$ ppm

$$\text{Total hardness} = 30+30+20+20 = 100 \text{ ppm}$$

$$\text{Temporary hardness} = 30+30+10 = 70 \text{ ppm}$$

$$\text{Permanent hardness} = 100 - 70 = 30\text{ppm}$$

7. A sample of water on analysis gives the following results: $\text{Ca}^{2+} = 320\text{mg/L}$, $\text{Mg}^{2+} = 72\text{mg/L}$, $\text{HCO}_3^- = 610\text{mg/L}$, $\text{Na}^+ = 23\text{mg/L}$. Calculate the temporary and permanent hardness of water sample.

Constituents	Quantity (mg/L)	M_{HPS}	CaCO_3 equivalent hardness = Quantity $\times \frac{100}{M_{\text{HPS}}}$
Ca^{2+}	320	40	$320 \times \frac{100}{40} = 800$
Mg^{2+}	72	24	$72 \times \frac{100}{24} = 300$
HCO_3^-	610	61	$610 \times \frac{100}{2 \times 61} = 500$
Na^+	23	-	-

$$\text{Total hardness} = 800 + 300 = 1100 \text{ ppm}$$

$$\text{Temporary hardness} = 500 \text{ ppm}$$

$$\text{Permanent hardness} = \text{Total hardness} - \text{Temporary hardness} = 1100 - 500 = 600 \text{ ppm}$$

8. Calculate the hardness of 0.1M CaCl_2 solution.

$$\begin{aligned} \text{Hardness} &= \text{Normality} \times \text{Eqnt Wt}_{\text{CaCO}_3} \times 1000 \\ &= 0.1 \times 2 \times 50 \times 1000 = 10000 \text{ ppm} \end{aligned}$$

9. Calculate the hardness of 0.4 N Ca^{2+} solution.

$$\begin{aligned} \text{Hardness} &= \text{Normality} \times \text{Eqnt Wt}_{\text{CaCO}_3} \times 1000 \\ &= 0.4 \times 50 \times 1000 = 20000 \text{ ppm} \end{aligned}$$

10. A sample of water is found to contain $\text{Mg}(\text{HCO}_3)_2 - 7.3\text{mg/L}$, $\text{Ca}(\text{HCO}_3)_2 - 16.2 \text{ mg/L}$, $\text{MgCl}_2 - 9.5 \text{ ppm}$ and $\text{CaSO}_4 - 13.6\text{mg/L}$. Calculate the temporary and permanent hardness of water sample. What happens to the temporary and permanent hardness of water sample if 10.6mg/L Na_2CO_3 is added?

Constituents	Quantity (mg/L)	M_{HPS}	CaCO_3 equivalent hardness = Quantity $\times \frac{100}{M_{\text{HPS}}}$
$\text{Ca}(\text{HCO}_3)_2$	16.2	162	$16.2 \times \frac{100}{162} = 10 \text{ ppm}$
$\text{Mg}(\text{HCO}_3)_2$	7.3	146	$7.3 \times \frac{100}{146} = 5 \text{ ppm}$
MgCl_2	9.5	95	$9.5 \times \frac{100}{95} = 10 \text{ ppm}$
CaSO_4	13.6	136	$13.6 \times \frac{100}{136} = 10 \text{ ppm}$
Na_2CO_3	10.6	106	$10.6 \times \frac{100}{106} = 10 \text{ ppm}$

$$\text{Total hardness} = 10+5+10+10 = 35 \text{ ppm}$$

$$\text{Temporary hardness} = 10+5 = 15 \text{ ppm}$$

$$\text{Permanent hardness} = 35 - 15 = 20 \text{ ppm}$$

If 10.6mg/L Na_2CO_3 is added to water, it removes permanent Ca^{2+} as CaCO_3 and Mg^{2+} cannot be removed.

CaCO_3 equivalent hardness of $\text{Na}_2\text{CO}_3 = 10 \text{ ppm}$. Thus 10 ppm permanent Ca is removed as CaCO_3 .

$$\text{New total hardness} = 35 - 10 = 25 \text{ ppm}$$

$$\text{Temporary hardness} = 15 \text{ ppm}$$

$$\text{New permanent hardness} = 25 - 15 = 10 \text{ ppm}$$

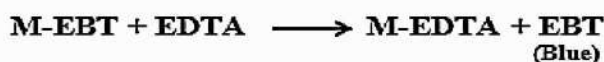
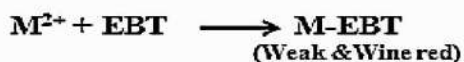
Estimation of hardness by EDTA process

It is a complexometric method used for the determination of hardness of water sample. In this method, EDTA is used as titrant and EBT (Erio-chrome Black-T) is the titrant. It is blue in

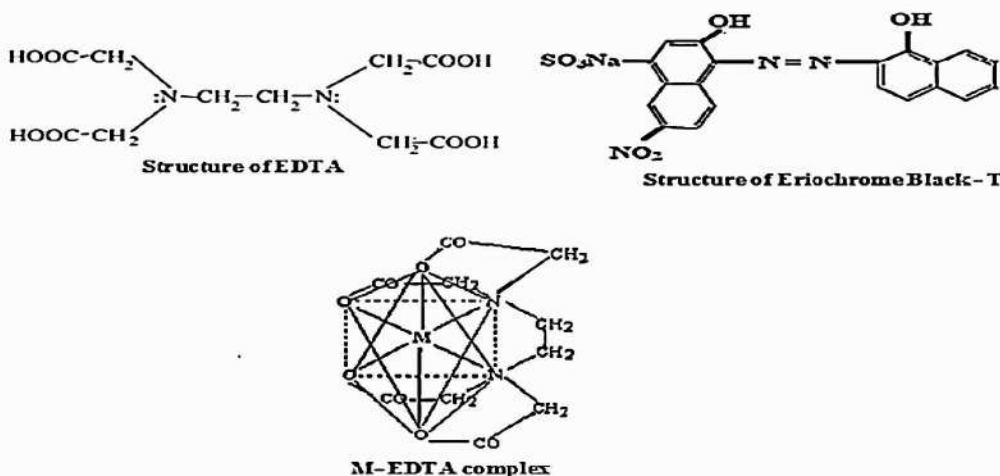
colour. It works effectively at the P^H of 10. So a buffer solution is required to maintain the P^H at 10. Usually used buffer is ammonium chloride- ammonium hydroxide buffer.

Principle and method of EDTA process:

At a P^H of 10, the Ca^{2+} & Mg^{2+} ions present in water forms a weak wine red coloured complex with EBT. When EDTA is added to this, weak EBT can be replaced by strong EDTA to form metal- EDTA complex. At the same time, wine red colour changes to blue due to the regeneration of EBT.



The PH is maintained around 10 using NH_4Cl and NH_4OH buffer, since indicator effective only at this PH. Initially M-EBT complex is formed, which is unstable. Then the addition of EDTA replaces EBT from the M-EBT complex produces M-EDTA complex and the colour changes from wine red to blue.



Procedure:

I. Preparation of solutions

a) Standard Hard Water (SHW)

Dissolve 1g pure dry $CaCO_3$ in minimum quantity dil.HCl and evaporate to dryness. The residue obtained is dissolved in distilled water and is made up to 1 litre. Each ml of this solution is equivalent to 1mg $CaCO_3$ equivalent hardness.

b) EDTA solution

Dissolve 4g EDTA crystals and 0.1g $MgCl_2$ in 1 litre distilled water.

c) EBT indicator

Dissolve 0.5g EBT powder in 100 ml alcohol.

d) Buffer solution

67.5g NH_4Cl is added to 570 ml of liquor NH_3 and is diluted to 1 litre using distilled water.

II. Standardisation of EDTA

50 ml SHW is mixed with 10 ml buffer solution and add 3-4 drops of EBT indicator. It is then titrated against EDTA till the wine red colour changes to blue.

Let the volume of EDTA consumed be V_1 ml & N_1 be its normality.

50 ml SHW = V_1 ml EDTA

(Each ml SHW contains 1mg $CaCO_3$ equivalent hardness.)

V_1 ml EDTA = 50mg $CaCO_3$ equivalent hardness

$$1 \text{ ml EDTA } (N_1) = \frac{50}{V_1} \text{ mg CaCO}_3 \text{ equivalent hardness}$$

III. Determination of Total hardness

50 ml Unknown Hard Water (UHW) is mixed with 10 ml buffer solution and add 3-4 drops of EBT indicator. It is then titrated against standardized EDTA till the wine red colour changes to blue.

Let the volume of EDTA consumed be V_2 ml.

N_2 be the normality of UHW.

$$50 \text{ ml UHW} = V_2 \text{ ml EDTA}$$

$$V_{\text{UHW}} \times N_{\text{UHW}} = V_{\text{EDTA}} \times N_{\text{EDTA}}$$

$$50 \times N_2 = V_2 \times \frac{50}{V_1}$$

$$1 \text{ ml UHW } (N_2) = \frac{V_2}{V_1}$$

$$1 \text{ litre of UHW} = \frac{V_2}{V_1} \times 1000 \text{ mg CaCO}_3 \text{ equivalent hardness}$$

$$\text{Total hardness} = \frac{V_2}{V_1} \times 1000 \text{ mg/L or ppm}$$

IV. Determination of permanent hardness

250 ml UHW is boiled to 50 ml. During boiling, soluble bicarbonates changes to insoluble CaCO_3 & Mg(OH)_2 . These are precipitates are filtered off and the filtrate is collected and is made upto 250 ml. It contains only permanent hardness causing ingredients.

50 ml of this Boiled Hard Water (BHW) is mixed with 10 ml buffer solution and add 3-4 drops of EBT indicator. It is then titrated against standardized EDTA till the wine red colour changes to blue.

Let the volume of EDTA consumed be V_3 ml.

N_3 be the normality of BHW.

$$50 \text{ ml UHW} = V_3 \text{ ml EDTA}$$

$$V_{\text{BHW}} \times N_{\text{BHW}} = V_{\text{EDTA}} \times N_{\text{EDTA}}$$

$$50 \times N_3 = V_3 \times \frac{50}{V_1}$$

$$1 \text{ ml BHW } (N_3) = \frac{V_3}{V_1}$$

$$1 \text{ litre of BHW} = \frac{V_3}{V_1} \times 1000 \text{ mg CaCO}_3 \text{ equivalent hardness}$$

$$\text{Permanent hardness} = \frac{V_3}{V_1} \times 1000 \text{ mg/L or ppm}$$

V. Determination of temporary hardness

Temporary hardness = Total hardness – Permanent hardness

$$= \left\{ \frac{V_2}{V_1} \times 1000 - \frac{V_3}{V_1} \times 1000 \right\} \text{ mg/L or ppm}$$

$$= \frac{V_2 - V_3}{V_1} \times 1000 \text{ mg/L or ppm}$$

Advantages of EDTA process

- It is more accurate.
- It is more convenient.
- It is a rapid procedure.

1. Calculate the hardness of 0.1M CaCl_2 solution.

$$\begin{aligned} \text{Hardness} &= \text{Normality} \times \text{Eqnt. Wt. CaCO}_3 \times 1000 = \text{Molarity} \times 2 \times \text{Eqnt. Wt. CaCO}_3 \times 1000 \\ &= 0.1 \times 2 \times 50 \times 1000 = 10000 \text{ ppm} \end{aligned}$$

2. Calculate the hardness of 0.4 N Ca^{2+} solution.

$$\begin{aligned} \text{Hardness} &= \text{Normality} \times \text{Eqnt. Wt. CaCO}_3 \times 1000 \\ &= 0.4 \times 50 \times 1000 = 20000 \text{ ppm} \end{aligned}$$

3. A standard hard water containing 15g CaCO₃ per litre. 20ml of this required 25ml EDTA solution. 100ml of sample of water required 18ml EDTA solution. The same sample after boiling required 12ml EDTA solution. Calculate the temporary hardness.

Step I: Preparation of SHW

1 litre SHW = 15g CaCO₃
 1000 ml SHW = 15000mg CaCO₃
 1 ml SHW = 15mg CaCO₃
 Normality of SHW = 15mg CaCO₃

Step II: Standardisation of EDTA

20 ml SHW = 25 ml EDTA
 $V_{SHW} \times N_{SHW} = V_{EDTA} \times N_{EDTA}$
 $20 \times 15 = 25 \times N_{EDTA}$
 $N_{EDTA} = \frac{20 \times 15}{25} = 12\text{mg CaCO}_3$

Step III: Estimation of total hardness

100 ml UHW = 18 ml EDTA
 $V_{UHW} \times N_{UHW} = V_{EDTA} \times N_{EDTA}$
 $100 \times N_{UHW} = 18 \times 12$
 $N_{UHW} = \frac{18 \times 12}{100} = 2.16\text{mg}$
 Total Hardness = 2.16 X 1000 = 2160 ppm

Step IV: Determination of permanent hardness

100 ml BHW = 12 ml EDTA
 $V_{BHW} \times N_{BHW} = V_{EDTA} \times N_{EDTA}$
 $100 \times N_{BHW} = 12 \times 12$
 $N_{BHW} = \frac{12 \times 12}{100} = 1.44\text{mg}$
 Permanent Hardness = 1.44 X 1000 = 1440 ppm

Step V: Determination of temporary hardness

Temporary hardness = Total hardness - Permanent hardness = 2160 – 1440 = 720 ppm

4. A standard hard water was prepared by dissolving 1g CaCO₃ in dil. HCl. It is then evaporated and made up to 1 litre using distilled water. 50ml of this required 48ml EDTA solution. 50ml of test hard water required 15ml EDTA solution. 50 ml of the same test water sample after boiling and filtration required 10ml EDTA solution. Calculate the total, permanent and temporary hardness.

Step I: Preparation of SHW

1 litre SHW = 1g CaCO₃
 1000 ml SHW = 1000mg CaCO₃
 1 ml SHW = 1mg CaCO₃
 Normality of SHW = 1mg CaCO₃

Step II: Standardisation of EDTA

50 ml SHW = 48 ml EDTA
 $V_{SHW} \times N_{SHW} = V_{EDTA} \times N_{EDTA}$
 $50 \times 1 = 48 \times N_{EDTA}$
 $N_{EDTA} = \frac{50 \times 1}{48} = 1.04\text{mg CaCO}_3$

Step III: Estimation of total hardness

50 ml UHW = 15 ml EDTA
 $V_{UHW} \times N_{UHW} = V_{EDTA} \times N_{EDTA}$
 $50 \times N_{UHW} = 15 \times 1.04$
 $N_{UHW} = \frac{15 \times 1.04}{50} = 0.312\text{mg}$
 Total Hardness = 0.312 X 1000 = 312 ppm

Step IV: Determination of permanent hardness

$$50 \text{ ml BHW} = 10 \text{ ml EDTA}$$

$$V_{\text{BHW}} \times N_{\text{BHW}} = V_{\text{EDTA}} \times N_{\text{EDTA}}$$

$$50 \times N_{\text{BHW}} = 10 \times 1.04$$

$$N_{\text{BHW}} = \frac{10 \times 1.04}{50} = 0.208 \text{ mg}$$

$$\text{Permanent Hardness} = 0.208 \times 1000 = 208 \text{ ppm}$$

Step V: Determination of temporary hardness

$$\text{Temporary hardness} = \text{Total hardness} - \text{Permanent hardness} = 312 - 208 = 104 \text{ ppm}$$

5. 2.8g CaCO₃ was dissolved in dil. HCl and made upto 1 litre using distilled water. 100ml of this required 28ml EDTA solution. 100ml of test hard water required 35ml EDTA solution. 100 ml of the same test water sample after boiling and filtration when titrated against EDTA required 10ml EDTA solution. Calculate the total, permanent and temporary hardness.

Step I: Preparation of SHW

$$1 \text{ litre SHW} = 2.8 \text{ g CaCO}_3$$

$$1000 \text{ ml SHW} = 2800 \text{ mg CaCO}_3$$

$$1 \text{ ml SHW} = 2.8 \text{ mg CaCO}_3$$

$$\text{Normality of SHW} = 2.8 \text{ mg CaCO}_3$$

Step II: Standardisation of EDTA

$$100 \text{ ml SHW} = 28 \text{ ml EDTA}$$

$$V_{\text{SHW}} \times N_{\text{SHW}} = V_{\text{EDTA}} \times N_{\text{EDTA}}$$

$$100 \times 2.8 = 28 \times N_{\text{EDTA}}$$

$$N_{\text{EDTA}} = \frac{100 \times 2.8}{28} = 10 \text{ mg CaCO}_3$$

Step III: Estimation of total hardness

$$100 \text{ ml UHW} = 35 \text{ ml EDTA}$$

$$V_{\text{UHW}} \times N_{\text{UHW}} = V_{\text{EDTA}} \times N_{\text{EDTA}}$$

$$100 \times N_{\text{UHW}} = 35 \times 10$$

$$N_{\text{UHW}} = \frac{35 \times 10}{100} = 3.5 \text{ mg}$$

$$\text{Total Hardness} = 3.5 \times 1000 = 3500 \text{ ppm}$$

Step IV: Determination of permanent hardness

$$100 \text{ ml BHW} = 10 \text{ ml EDTA}$$

$$V_{\text{BHW}} \times N_{\text{BHW}} = V_{\text{EDTA}} \times N_{\text{EDTA}}$$

$$100 \times N_{\text{BHW}} = 10 \times 10$$

$$N_{\text{BHW}} = \frac{10 \times 10}{100} = 1 \text{ mg}$$

$$\text{Permanent Hardness} = 1 \times 1000 = 1000 \text{ ppm}$$

Step V: Determination of temporary hardness

$$\text{Temporary hardness} = \text{Total hardness} - \text{Permanent hardness} = 3500 - 1000 = 2500 \text{ ppm}$$

6. 0.30g CaCO₃ was dissolved in dil. HCl and made upto 1 litre using distilled water. 100ml of this required 30ml EDTA solution. 100ml of test hard water required 33ml EDTA solution. 100 ml of the same test water sample after boiling and filtration when titrated against EDTA required 10ml EDTA solution. Calculate the total, permanent and temporary hardness.

Step I: Preparation of SHW

$$1 \text{ litre SHW} = 0.30 \text{ g CaCO}_3$$

$$1000 \text{ ml SHW} = 300 \text{ mg CaCO}_3$$

$$1 \text{ ml SHW} = 0.3 \text{ mg CaCO}_3$$

$$\text{Normality of SHW} = 0.3 \text{ mg CaCO}_3$$

Step II: Standardisation of EDTA

$$100 \text{ ml SHW} = 30 \text{ ml EDTA}$$

$$V_{SHW} \times N_{SHW} = V_{EDTA} \times N_{EDTA}$$

$$100 \times 0.3 = 30 \times N_{EDTA}$$

$$N_{EDTA} = \frac{100 \times 0.3}{30} = 1 \text{ mg CaCO}_3$$

Step III: Estimation of total hardness

$$100 \text{ ml UHW} = 33 \text{ ml EDTA}$$

$$V_{UHW} \times N_{UHW} = V_{EDTA} \times N_{EDTA}$$

$$100 \times N_{UHW} = 33 \times 1$$

$$N_{UHW} = \frac{33 \times 1}{100} = 0.33 \text{ mg}$$

$$\text{Total Hardness} = 0.33 \times 1000 = 330 \text{ ppm}$$

Step IV: Determination of permanent hardness

$$100 \text{ ml BHW} = 10 \text{ ml EDTA}$$

$$V_{BHW} \times N_{BHW} = V_{EDTA} \times N_{EDTA}$$

$$100 \times N_{BHW} = 10 \times 1$$

$$N_{BHW} = \frac{10 \times 1}{100} = 0.1 \text{ mg}$$

$$\text{Permanent Hardness} = 0.1 \times 1000 = 100 \text{ ppm}$$

Step V: Determination of temporary hardness

$$\text{Temporary hardness} = \text{Total hardness} - \text{Permanent hardness} = 330 - 100 = 230 \text{ ppm}$$

7. In an EDTA experiment, the following values are obtained. Calculate the different types of hardness.

i) 20ml standard hard water (10g CaCO₃ per litre) = 25ml EDTA solution

ii) 50ml hard water sample = 25ml EDTA solution

iii) 50ml boiled hard water sample = 14ml EDTA solution

Step I: Preparation of SHW

$$1 \text{ litre SHW} = 10 \text{ g CaCO}_3$$

$$1000 \text{ ml SHW} = 10000 \text{ mg CaCO}_3$$

$$1 \text{ ml SHW} = 10 \text{ mg CaCO}_3$$

$$\text{Normality of SHW} = 10 \text{ mg CaCO}_3$$

Step II: Standardisation of EDTA

$$20 \text{ ml SHW} = 25 \text{ ml EDTA}$$

$$V_{SHW} \times N_{SHW} = V_{EDTA} \times N_{EDTA}$$

$$20 \times 10 = 25 \times N_{EDTA}$$

$$N_{EDTA} = \frac{20 \times 10}{25} = 8 \text{ mg CaCO}_3$$

Step III: Estimation of total hardness

$$50 \text{ ml UHW} = 25 \text{ ml EDTA}$$

$$V_{UHW} \times N_{UHW} = V_{EDTA} \times N_{EDTA}$$

$$50 \times N_{UHW} = 25 \times 8$$

$$N_{UHW} = \frac{25 \times 8}{50} = 4 \text{ mg}$$

$$\text{Total Hardness} = 4 \times 1000 = 4000 \text{ ppm}$$

Step IV: Determination of permanent hardness

$$50 \text{ ml BHW} = 14 \text{ ml EDTA}$$

$$V_{BHW} \times N_{BHW} = V_{EDTA} \times N_{EDTA}$$

$$50 \times N_{BHW} = 14 \times 8$$

$$N_{BHW} = \frac{14 \times 8}{50} = 2.24 \text{ mg}$$

$$\text{Permanent Hardness} = 2.24 \times 1000 = 2240 \text{ ppm}$$

Step V: Determination of temporary hardness

$$\text{Temporary hardness} = \text{Total hardness} - \text{Permanent hardness} = 4000 - 2240 = 1760 \text{ ppm}$$

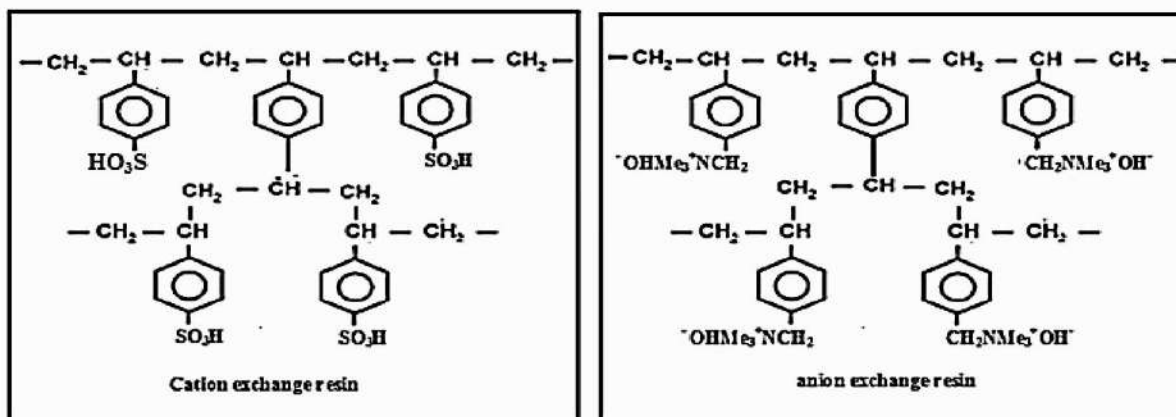
Water softening processes

The process by which hard water can be converted as soft water is called water softening process. One of the very important types of water softening process is called ion exchange process.

Ion exchange process : Ion exchange resins are insoluble cross linked long chain organic polymers having micro porous structure, where the functional group attached to the chain are responsible for their ion exchange capacity. Cation exchange resin (RH^+) contains acidic functional groups like $-\text{COOH}$, $-\text{SO}_3\text{H}$, etc. Anion exchange resin (ROH^-) contains basic functional groups like $-\text{OH}$, $-\text{NH}_2$, etc. Amberlite IR - 120, Dowex - 50 are commercially available cation exchange resins. Amberlite IR - 400, Dowex - 3 are commercially available anion exchange resins.

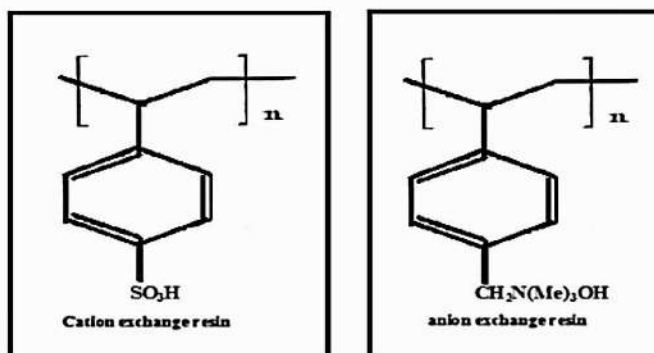
Cation exchange resins are basically styrene-divinyl benzene copolymers, which on sulphonation attain the capability to exchange its H^+ ions with cations of water.

Anion exchange resins are basically styrene-divinyl benzene or amine formaldehyde copolymers containing quaternary ammonium group, which on treatment with NaOH attain the capability to exchange its OH^- ions with cations of water.



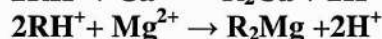
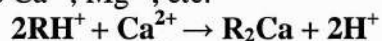
OR

Simply we can draw the structure of cation exchange resin and anion exchange resin in the following manner.

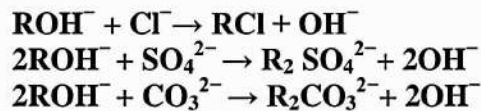


Procedure:

Initially hard water is allowed to pass through cation exchange resin column to remove all the cations like Ca^{2+} , Mg^{2+} , etc.



Then the hard water is allowed to pass through anion exchange resin column to remove all the anions like SO_4^{2-} , Cl^- , etc.

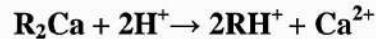


The H^+ ions and OH^- ions produced from cation and anion exchange resin column combine to form water.

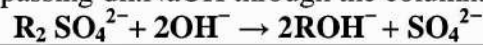


Water thus coming out of the exchanger will be free from both cations and anions. Hence it is called deionised water or demineralised water.

When the exchanger becomes exhausted, i.e. its capacity to exchange H^+ ions and OH^- ions is lost, it is regenerated. Cation exchangers are regenerated by passing dil.HCl or dil. H_2SO_4 through the column.



Anion exchangers are regenerated by passing dil.NaOH through the column.



In the deionization process, water is first passed through the cation exchanger and then through anion exchanger, Why?

When hard water is first passed through anion exchanger anions like Cl^- or SO_4^{2-} are replaced by OH^- of anion exchanger. Thus Ca^{2+} and Mg^{2+} ions of hard water produces $\text{Ca}(\text{OH})_2$ and $\text{Mg}(\text{OH})_2$ precipitates. These precipitates will lead to clogging. Thus in the deionization process, water is first passed through the cation exchanger and then through anion exchanger

Advantages:

1. Even highly acidic alkaline water can be softened by this method.
2. Gives water of very low hardness (2 ppm).
3. Water obtained by this method can be used even in high pressure boilers because of its low hardness.
4. No sludge is formed.

Disadvantages:

1. Equipment and chemicals used are costly.
2. Turbid water cannot be treated by this method.

Drinking water (Municipal water) (Potable water)

Water safe to drink is called drinking water (Municipal water) (Potable water).

Specifications of drinking water

- It must be very clear, odourless, and pleasant in taste.
- It must be soft, total hardness should not exceed 300 ppm and pH should come within 6.5-8.5.
- It must be cool and free from dissolved toxic gases like H_2S .
- It should not contain harmful minerals like Pb, As, Cr, Mn, etc.
- TDS (Total Dissolved Solids) should not exceed 500 ppm.
- It should not contain any disease causing microorganisms.

Natural water from rivers, canals may not meet all the required specifications of drinking water. So it needs purification.

Methods are used for the purification of drinking water:

I. Removal of suspended impurities:

a) Screening:

In this method, water is passed through bar screens having large number of holes which removes floating matter.

b) Sedimentation:

In this method, water is taken big tanks (sedimentation tanks) for about 2-6 hours. At that time, suspended particles settle down by the force of gravity. The clear supernatant water can then be pumped out.

If the water to be purified contains fine clay particles and colloidal matter, then simple sedimentation fails. In that case, preferred method is **sedimentation with coagulation**. Usually used coagulants are alums ($K_2SO_4Al_2(SO_4)_3 \cdot 24H_2O$), $FeSO_4$, $NaAlO_2$, etc. These coagulants when added to water produce insoluble, gelatinous, flocculant precipitates, which descends through water entrap fine colloidal impurities in water forming bigger flocs that settle down easily.

c) Filtration:

In this method, water is passed through bed of fine sand and other proper sized granular materials to remove colloidal matter, bacteria, microorganisms, etc. Sand filter consists of a thick top layer of fine sand, a middle coarse particle layer and a bottom gravel layer. As water percolates through the sand filter, most of the impurities get retained in the pores of filter. So after a long time of filtration, due to clogging of filter bed with impurities, rate of filtration may become slow. In that situation, filtration is stopped and a 2-3cm portion of the top sand layer is scrapped off and is replaced with clean sand. Scrapped sand layer can be reused after washing with water and drying.

II. Removal of microorganisms (Disinfection methods)

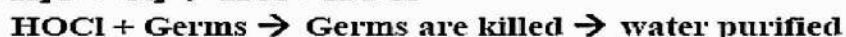
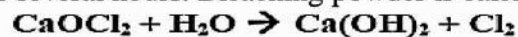
The process of removing bacteria and microorganisms from water are called disinfection. The chemicals used for this purpose is called disinfectants. Disinfection can be done by the following methods.

1. Boiling:

In this method water is boiled for a period of 10 minutes to remove the disease causing bacteria and microorganisms.

2. Addition of bleaching powder:

Bleaching powder is added at a rate of 1kg per 1000 kilo litres of water and allowed to stand undisturbed for several hours. Bleaching powder is calcium oxy chloride.



The hypochlorous acid produces is a powerful germicide. It reacts with enzymes in the cells of microorganisms, deactivating them and killing them.

Disadvantages:

- It increases the Ca content in the water and makes the water harder.
- Excess of bleaching powder produces an unpleasant taste to water.

3. Chlorination:

Chlorine is added to water either in the gaseous form or concentrated solution form produces HOCl. Chlorinator is the apparatus used for chlorination, which uses liquid chlorine.



Advantages:

- It is very effective and economical.
- Storage is easy.
- It can be used at low and high temperatures.
- No salt impurities in the treated water.

Disadvantages:

- Excess of chlorine, produces an unpleasant taste and odour to water.
- It causes irritation to mucous membrane.
- It is not an effective disinfectant above 6.5 P^H.

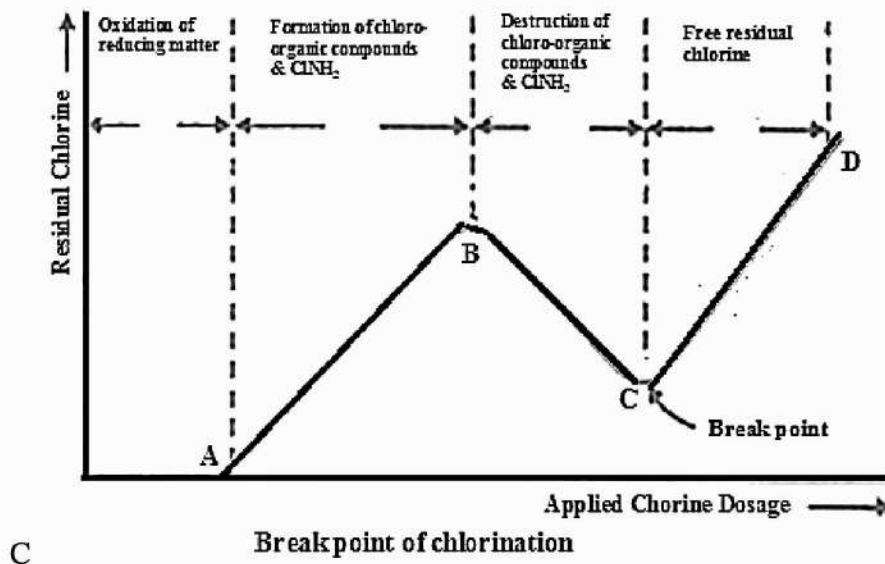
Break point of chlorination:

Break point of chlorination is defined as the addition of sufficient amount of chlorine to kill the microorganisms and to destroy them completely by the oxidation of reducing matter, organic matter, and free ammonia and leave behind free residual chlorine to continue the further disinfection.

If we plot, residual chlorine against applied chlorine, we get a curve. The dip in the curve 'C' shows the break point.

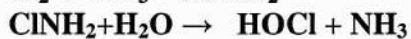
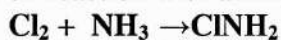
At the break point all the colour, odour, taste disappears and all the disease causing microorganisms get killed. It completely oxidises the organic compounds, ammonia and reducing compounds. After the break point, any further addition of chlorine appears to be present as free residual chlorine which will continue the further disinfection.

The amount of free chlorine required for continuing further disinfection is 0.1-0.2 ppm. If over chlorination occurs, excess chlorine can be removed by passing the water through molecular sieve or by stirring it with activated carbon followed by filtration. Excess chlorine can be removed by adding dechlorinating agents like SO_2 , Na_2SO_3 , sodium thiosulphate, etc.



4. Addition of ClNH_2

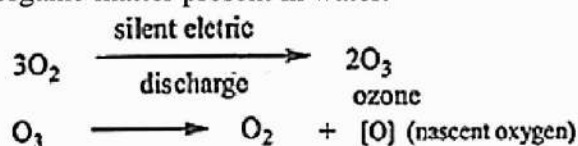
Chlorine on reaction with ammonia produces ClNH_2 .



ClNH_2 is a better disinfectant than chlorine, since its residuals remain in water for a longer period and will continue the disinfection. Its excess does not produce any irritating odour. Its presence imparts good taste to water.

5. Using ozone

Ozone is an excellent disinfectant and it is used in the gaseous form. Ozone is produced by passing silent electric discharge through cold and dry oxygen. Ozone thus produced is unstable and breaks down liberating nascent oxygen, which is a powerful oxidizing agent. It destroys all the bacteria and oxidises organic matter present in water.



Advantages

- Simultaneous removal of colour, odour, taste without leaving any residual in water.

- Its excess does not cause any harm to water as nascent oxygen is unstable and can be easily converted as molecular oxygen.

Disadvantages

- This method is costly.
- Microbial growth may again start in the treated water as it contains no residuals. In order to prevent this; add a small amount of Cl_2 after ozonation.

Small scale disinfection

1. Disinfection by UV light

Disinfection can be brought about by exposing water to UV light. A quartz tube containing Hg-lamp is used as a source of UV light.

Advantages

- No chemicals are used in this treatment.
- No taste or odour is imparted to water.
- It is mainly employed in swimming pools as disinfection using chemicals may cause harmful effects to the skin of the people swimming.

Disadvantages

- It requires costly equipment.
- Technical skill is required for this method.

2. Disinfection by sunlight

Sunlight can destroy microorganisms without imparting any colour, odour, and taste to water. But it has the disadvantage that it cannot penetrate into the depth of the water.

3. Disinfection by KMnO_4

KMnO_4 is a powerful oxidizing agent. It provides nascent oxygen, which will oxidise organic matter in the water.

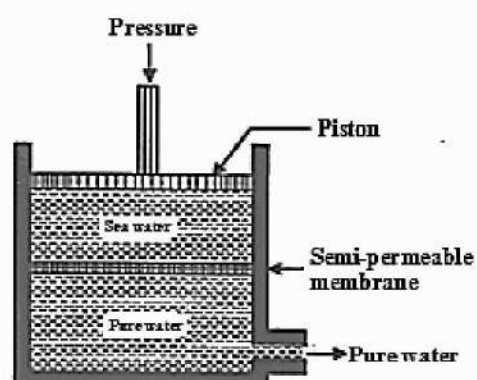
Brackish water treatment

Water containing high concentration of dissolved salt with a brackish taste is called brackish water. Eg: Brine

Brackish water is unfit for drinking. Hence it needs desalination. Reverse osmosis is the best method used for the desalination of brackish water.

Reverse osmosis

When two solutions of unequal concentrations are separated by a semipermeable membrane, then the solvent flows from dilute to the concentrated solution due to osmosis. But if the hydrostatic pressure is greater than the osmotic pressure, then the solvent flows through the semipermeable membrane in a direction opposite to that of natural osmosis i.e. from concentrated to the dilute solution. This is called reverse osmosis. Usually a pressure of 15-40 kgm^{-2} is required. Membranes made up of cellulose acetate or polymethacrylate can be used as the semipermeable membrane.



Sea water can be purified by this method. The apparatus used for this process contains two chambers separated by semipermeable membrane. Sea water to be purified is taken in one of the chambers. If a pressure of $15\text{-}40\text{kgm}^{-2}$ is applied on the sea water side to force the pure water alone present in it through the semipermeable membrane to leave behind the dissolved solids. Hence we get the pure water from the other chamber.

Advantages

- It is simple, low cost and is the best method to convert sea water to fresh water.
- It helps for the removal of ionic matter, non-ionic matter, colloidal matter and high molecular weight organic matter.
- Colloidal silica which cannot be removed by demineralization can be removed effectively by this method.
- Life time of semipermeable membrane is quite high and is about 2 years.
- Semipermeable membrane can be replaced within a few minutes. Thus providing nearly uninterrupted water supply.

Disadvantage

- High pressure has to be maintained throughout the process which is very difficult.

Sewage (Waste water)

Sewage is the liquid waste which includes human waste, house hold waste, industrial waste, etc. It contains 99.99% of water and 0.01% of organic matter, inorganic matter, suspended impurity, colloidal impurity, etc. Sewage contains both aerobic and anaerobic bacteria that bring out the oxidation of organic compounds in it. Aerobic oxidation is the oxidation of organic matter in the sewage by aerobic bacteria in the presence of excess oxygen. Anaerobic oxidation is the oxidation of organic matter in the sewage by anaerobic bacteria in the presence of limited quantity oxygen.

Distinguish between aerobic and anaerobic oxidation

Aerobic oxidation	Anaerobic oxidation
<ul style="list-style-type: none"> • It occurs in presence of excess oxygen. • Oxidation by aerobic bacteria. • The products of oxidation are CO_2, nitrates, phosphates, sulphates. • The products are non-offensive smelling. • During decomposition, carbohydrates are converted as CO_2 and water. • Energy released is more and rate of decomposition is slow. • No bio-gas fuel is produced. 	<ul style="list-style-type: none"> • It occurs in presence of limited quantity oxygen. • Oxidation by anaerobic bacteria. • The products of oxidation are acetic acid, methane, H_2S, NH_3, phosphine. • The products are offensive smelling. • During decomposition, carbohydrates are converted as CO_2 and methane. • Energy released is less and rate of decomposition is fast. • Bio-gas fuel like methane is produced.

Dissolved oxygen (DO)

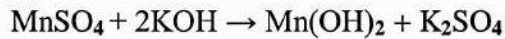
Dissolved oxygen is defined as the free oxygen present in water or any other liquid. It is the parameter used to assess water quality. Low dissolved oxygen content can cause harm to aquatic life and it also affect the water quality.

Factors that governs the amount of dissolved oxygen in water

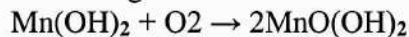
- Dissolved oxygen varies with water temperature. Pure water at 30°C contains 7.8 ppm dissolved oxygen, whereas that at 20°C contains 9.2 ppm dissolved oxygen. That means cold water is having greater dissolved oxygen than hot water.
- Dissolved oxygen in water gets affected by the presence of oxidisable impurities or pollutants like starch, cellulose, etc.
- Dissolved oxygen also varies with altitude. At higher altitudes, lesser the atmospheric pressure and hence lesser will be the DO.

Experimental determination of DO by Winkler's titration method

Take a 125 mL glass bottle having air tight stopper. Fill the bottle completely with water without bubbling. 1 mL $MnSO_4$ solution and 1 mL alkaline KI solution are introduced into the solution using a graduated pipette. Close the lid of the bottle without leaving any air bubble and shaken vigorously and allowed to stand for about 15 minutes. The precipitate formed gets settled at the bottom.



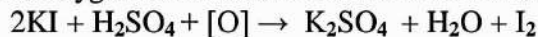
The DO present in the sample oxidizes some of the Mn^{2+} to Mn^{4+} , which is precipitated as brown hydrated manganese dioxide.



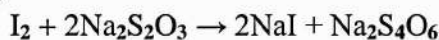
Add 2 mL 1:1 H_2SO_4 from the top using graduated pipette. Close the lid and shaken well till all the precipitate get dissolved.



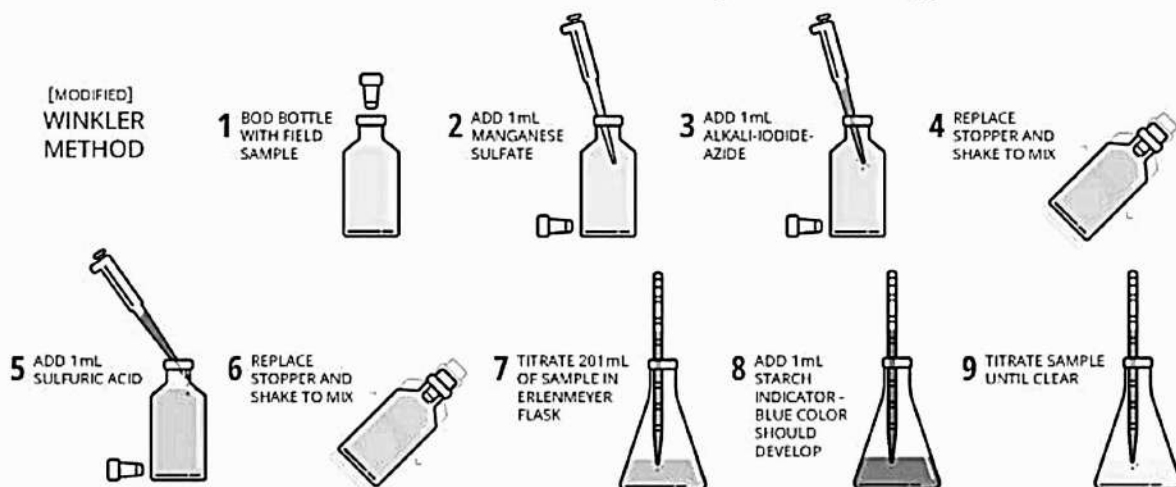
The nascent oxygen reacts with KI in the solution in presence of H_2SO_4 to liberate iodine.



The solution is then transferred to a 250 mL conical flask and titrated against standard thiosulphate solution taken in the burette using starch as indicator. Thus the liberated iodine is estimated.



1ml of 0.01N $Na_2S_2O_3$ solution = 0.1mg Dissolved Oxygen



BOD & COD

The extent of water pollution is assessed in terms of BOD & COD. It indicates the extent of treatment required for sewage water to make it safe for discharge into rivers.

Biological Dissolved Oxygen (BOD)

It is defined as the total amount of oxygen required for the complete oxidation of biologically active organic matter under aerobic conditions by bacteria and microorganisms at 20°C for a period of 5 days or 27°C for a period of 3 days.

Significance of BOD

- Larger the concentration of organic matter, greater will be the BOD.
- Larger the BOD, greater will be the pollution.
- BOD helps for finding the degree of pollution. It also helps for pollution study.

Disadvantage

- The results are obtained only after 5 days.

Experimental determination of BOD of water sample

A known volume of sewage is diluted with fresh water whose DO content is predetermined. Then it is kept in a closed vessel at 20°C for a period of 5 days or 27°C for a period of 3 days in an incubator. After this time period, the dissolved oxygen content in the water sample is measured. From the difference in the dissolved oxygen content, it is possible to calculate the BOD of the sample.

$$\text{BOD} = \frac{(D_1 - D_2) \text{ Volume of the sample after dilution}}{\text{Volume of the sample before dilution}}$$

Where D_1 is the DO of the sample in mg/l at the beginning of the experiment & D_2 is the DO of the sample in mg/l after 5 days

Chemical Oxygen Amount (COD)

It is the amount of oxygen required for the complete oxidation of biologically active and biologically inert materials present in sewage water using strong oxidizing agent like acidified $\text{K}_2\text{Cr}_2\text{O}_7$ for a period of 3 hours. Only less time is required for the determination of COD. COD is always greater than BOD, since it causes the oxidation of both biologically active and biologically inert material.

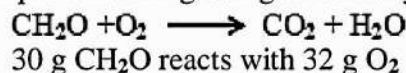
Experimental determination of COD of water sample

A known volume of sewage is mixed with a fixed volume of $\text{K}_2\text{Cr}_2\text{O}_7$ solution and dil. sulphuric acid and is refluxed for about 2-3 hours in presence of small amount of Ag_2SO_4 catalyst. The solution is then cooled and titrated with standard ferrous ammonium sulphates solution. Thus the unreacted $\text{K}_2\text{Cr}_2\text{O}_7$ in the solution can be determined. A blank experiment is conducted with pure water. From the difference between the titre values of the blank and the test solution, COD can be calculated.

$$\text{COD} = \frac{(V_1 - V_2) \times N \times 8}{V_e} \times 1000$$

Where V_1 & V_2 are the volumes of Mohr salt used by the blank and test samples respectively. V_e is the volume of effluent sample taken for test and N is the normality of Mohr's salt solution.

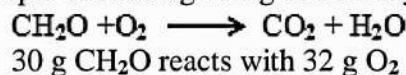
1. Find the BOD of the water sample containing 60mg of carbohydrate (CH_2O) per litre.



Therefore, 60 mg carbohydrate requires $60 \times \frac{32}{30} = 64$ mg oxygen

Thus the BOD of the water sample = 64mg/L = 64 ppm

2. Find the BOD of the water sample containing 75mg of carbohydrate (CH_2O) per litre.



Therefore, 75 mg carbohydrate requires $75 \times \frac{32}{30} = 80$ mg oxygen

Thus the BOD of the water sample = 64mg/L = 80 ppm

3. 100ml of water sample after reaction with fixed amount of acidified $K_2Cr_2O_7$ consumes 15ml, 0.1N Ferrous solution. For blank titration the ferrous solution consumed is 25ml. Find the COD of water sample.

$$COD = \frac{(V_1 - V_2) \times N \times 8}{V_e} \times 1000$$

$$COD = \frac{(25 - 15) \times 0.1 \times 8}{100} \times 1000 = 80 \text{ ppm}$$

4. 100 mL sewage water is diluted to 500 mL with dilution water; the initial dissolved oxygen was 7.5 ppm. The dissolved oxygen level after 5 days of incubation was 3.5 ppm. Find the BOD of the sewage.

$$BOD = \frac{(D_1 - D_2) \text{ Volume of the sample after dilution}}{\text{Volume of the sample before dilution}}$$

$$BOD = \frac{(7.5 - 3.5) 500}{100} = 20 \text{ ppm}$$

Sewage treatment

Sewage treatment is carried out using an artificial process called sewerage. It occurs via different steps. They are

1. Primary treatment
2. Secondary treatment
3. Tertiary treatment

1. Primary treatment

In this process, large solids and inorganic matter, which are suspended in the sewage, are removed. This can be done by

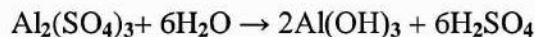
- a) Screening
- b) Sedimentation

Screening

In this process, sewage is passed through bar screen or mesh screen which removes the suspended impurities.

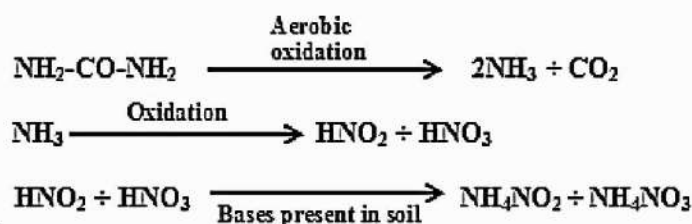
Sedimentation

Majority of suspended impurities present in the sewage can be removed by this process. In this process, sewage is taken in sedimentation tank. Along with sewage, some coagulants like alums, $Al_2(SO_4)_3$, $NaAlO_2$, etc. are added before sedimentation. Coagulants form gelatinous precipitate, which can entrap small sized organic matter to form bigger precipitate. Then settling occurs rapidly.



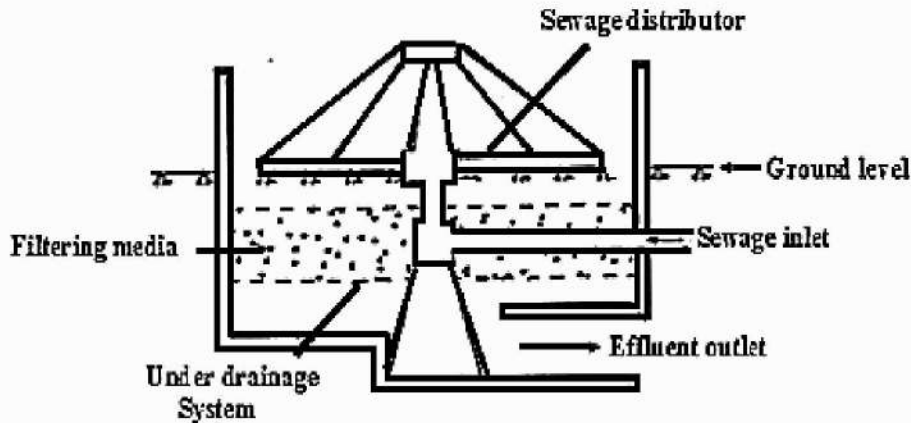
2. Secondary treatment or biological treatment

Secondary treatment is the biological treatment. In this process, aerobic oxidation of sewage occurs. During this process, carbon and nitrogen in the sewage get oxidised to CO_2 and NH_3 . Ammonia on further oxidation produces nitrites and nitrates.



a. Trickling filter process

It is a type of biological treatment carried out using a special type of filter called trickling filter.



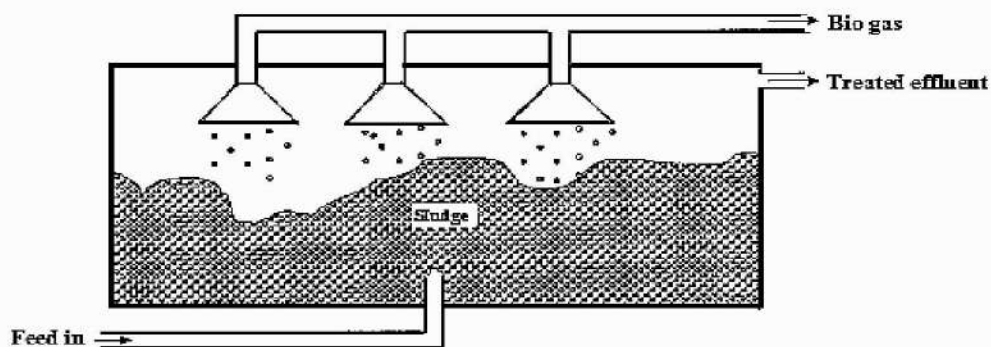
Trickling Filter

It is rectangular in shape with 2m depth. It is filled with crushed rocks, broken bricks, etc. on that microbial growth occurs and fitted with rotating distributor. Sewage trickles through the filter with the help of rotating distributor. Then it moves down through the filtering medium. During this movement, microorganisms start consuming organic matter in the sewage. A more or less clear effluent is collected through the under drainage system.

b. Activated sludge process

It is also a biological treatment. In this process, aerobic oxidation of sewage is carried out in the presence of activated sludge. Activated sludge is the sludge taken from previous oxidation process.

c. Upflow Anaerobic Sludge Blanket (UASB) (USAB) process



USAB reactor

It is an anaerobic treatment. In this process, effluent is fed from the bottom of the reactor and it moves upwards through the sludge blanket. Sludge blanket is composed of biological granules containing large number of bacteria. As the waste comes in contact biological granules, anaerobic oxidation takes place producing gases like methane.

The gases with biological granules move towards the upper region of the reactor, where the gases only set free and the granules come back to the sludge blanket. Gases are collected at the gas collector dome at the top of the reactor. The Upflow velocities are 0.6-0.9m/hour.

3. Tertiary treatment

This is the advanced phase of sewage treatment. By this process, nitrogen and phosphorous content in the effluent get reduced. Three important processes employed for this purpose are

a) Precipitation

In this process, effluent obtained after the secondary treatment is treated with CaO, so that phosphorous get precipitated as $\text{Ca}_3(\text{PO}_4)_2$.

b) Nitrogen stripping

By this process, ammonia gas can be removed by passing the effluent through a series of baffle plates. Since ammonia is having lower density than air.

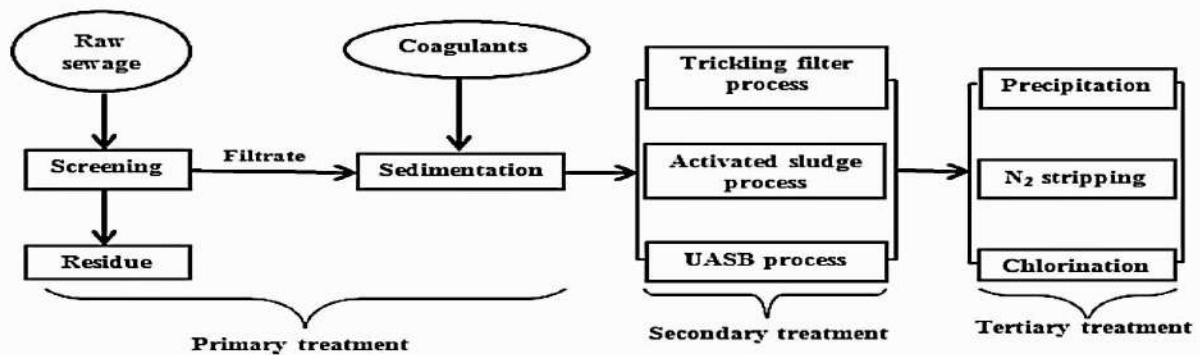
c) Chlorination

Disinfection of effluent is done by treating it with chlorine.



The hypochlorous acid produces is a powerful germicide. It reacts with enzymes in the cells of microorganisms, deactivating them and killing them.

Flow diagram of sewage(Wastewater) treatment



Problems

1. Calculate the hardness of water sample containing the following salts/litre. CaSO_4 – 16.2mg/L, $\text{Mg}(\text{HCO}_3)_2$ – 1.4mg/L, MgCl_2 – 9.5mg/L.

Constituents	Quantity	M _{HPS}	CaCO_3 equivalent hardness = Quantity X $\frac{100}{\text{MHPS}}$
CaSO_4	16.2mg/L	136	$16.2 \times \frac{100}{136} = 11.9$ ppm
$\text{Mg}(\text{HCO}_3)_2$	1.4mg/L	146	$1.42 \times \frac{100}{146} = 0.97$ ppm
MgCl_2	9.5mg/L	95	$9.5 \times \frac{100}{95} = 10$ ppm

$$\text{Total hardness} = 11.9 + 0.97 + 10 = 22.87 \text{ ppm}$$

$$\text{Temporary hardness} = 0.97 \text{ ppm}$$

$$\text{Permanent hardness} = \text{Total hardness} - \text{Temporary hardness} = 22.87 - 0.97 = 21.9 \text{ ppm}$$

2. A sample of water on analysis gives the following results: $\text{Ca}^{2+} = 30\text{mg/L}$, $\text{Mg}^{2+} = 18\text{mg/L}$, $\text{HCO}_3^- = 244\text{mg/L}$, $\text{Na}^+ = 11.5\text{mg/L}$. Calculate the temporary and permanent hardness of water sample.

Constituents	Quantity (mg/L)	M _{HPS}	CaCO_3 equivalent hardness = Quantity X $\frac{100}{\text{MHPS}}$
Ca^{2+}	30	40	$30 \times \frac{100}{40} = 75$
Mg^{2+}	18	24	$18 \times \frac{100}{24} = 75$

HCO ₃ ⁻	122	61	$122 \times \frac{100}{2 \times 61} = 100$
Na ⁺	11.5	-	-

Total hardness = 75 + 75 = 150 ppm

Temporary hardness = 100 ppm

Permanent hardness = Total hardness - Temporary hardness = 150 - 100 = 50 ppm

3. A water sample is having 400 ppm permanent hardness and 100 ppm temporary hardness. If 42 mg/L NaHCO₃ is added to this water, calculate the new temporary and permanent hardness.

Total hardness = 400 + 100 = 500 mg/L

Temporary hardness of water sample increases with the addition of 42 mg/L NaHCO₃.

Increase in temporary hardness = $\frac{42 \times 100}{2 \times 84} = 25$ ppm

New temporary hardness = 100 + 25 = 125 mg/L

New permanent hardness = Total hardness - New temporary hardness = 500 - 125 = 375 mg/L

4. A water sample contains Mg(HCO₃)₂ - 36.5 ppm, Ca(HCO₃)₂ - 40.5 ppm, MgSO₄ - 30.0 ppm, CaSO₄ - 34.0 ppm, CaCl₂ - 27.75 ppm, NaCl - 10 ppm. Calculate the temporary and permanent hardness of water sample.

Constituents	Quantity (ppm)	M _{HPS}	CaCO ₃ equivalent hardness = Quantity X $\frac{100}{MHPS}$
Ca(HCO ₃) ₂	40.5	162	$40.5 \times \frac{100}{162} = 25$ ppm
Mg(HCO ₃) ₂	36.5	146	$36.5 \times \frac{100}{146} = 25$ ppm
MgSO ₄	30.3	120	$30.0 \times \frac{100}{120} = 25$ ppm
CaSO ₄	34.0	136	$34.0 \times \frac{100}{136} = 25$ ppm
CaCl ₂	27.75	111	$27.75 \times \frac{100}{111} = 25$ ppm
NaCl	10	-	-

Temporary hardness = Hardness due to Ca(HCO₃)₂ + Hardness due to Mg(HCO₃)₂
= 25 + 25 = 50 ppm

Permanent hardness = Hardness due to MgSO₄ + Hardness due to CaSO₄ + Hardness due to CaCl₂ = 25 + 25 + 25 = 75 ppm

5. A sample of water on analysis gives the following results: Ca²⁺ = 400 mg/L, Mg²⁺ = 240 mg/L, HCO₃⁻ = 244 mg/L, Na⁺ = 92 mg/L. Calculate the temporary and permanent hardness of water sample.

Constituents	Quantity (ppm)	M _{HPS}	CaCO ₃ equivalent hardness = Quantity X $\frac{100}{MHPS}$
Ca ²⁺	400	40	$400 \times \frac{100}{40} = 1000$
Mg ²⁺	240	24	$240 \times \frac{100}{24} = 1000$
HCO ₃ ⁻	244	61	$244 \times \frac{100}{2 \times 61} = 200$
Na ⁺	92	-	-

Total hardness = 1000 + 1000 = 2000 ppm

Temporary hardness = 200 ppm

Permanent hardness = 2000 - 200 = 1800 ppm

6. A water sample contains Mg(HCO₃)₂ - 43.8 mg/L, Ca(HCO₃)₂ - 48.6 ppm, MgSO₄ - 24.0 ppm, CaSO₄ - 27.2 mg/L, NaHCO₃ - 16.8 mg/L. Calculate the temporary and permanent hardness of water sample.

Constituents	Quantity (mg/L)	M _{HPS}	CaCO ₃ equivalent hardness = Quantity X $\frac{100}{MHPS}$
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Ca(HCO ₃) ₂	48.6	162	$48.6 \times \frac{100}{162} = 30 \text{ ppm}$
Mg(HCO ₃) ₂	43.8	146	$43.8 \times \frac{100}{146} = 30 \text{ ppm}$
MgSO ₄	24.0	120	$24.0 \times \frac{100}{120} = 20 \text{ ppm}$
CaSO ₄	27.2	136	$27.2 \times \frac{100}{136} = 20 \text{ ppm}$
NaHCO ₃	16.8	84	$16.8 \times \frac{100}{2 \times 84} = 10 \text{ ppm}$

Total hardness = 30+30+20+20 = 100 ppm

Temporary hardness = 30+30+10 = 70 ppm

Permanent hardness = 100 – 70 = 30ppm

7. A sample of water on analysis gives the following results: Ca²⁺ = 320mg/L, Mg²⁺ = 72mg/L, HCO₃⁻ = 610mg/L, Na⁺ = 23mg/L. Calculate the temporary and permanent hardness of water sample.

Constituents	Quantity (mg/L)	M _{HPS}	CaCO ₃ equivalent hardness = Quantity X $\frac{100}{M_{HPS}}$
Ca ²⁺	320	40	$320 \times \frac{100}{40} = 800$
Mg ²⁺	72	24	$72 \times \frac{100}{24} = 300$
HCO ₃ ⁻	610	61	$610 \times \frac{100}{2 \times 61} = 500$
Na ⁺	23	-	-

Total hardness = 800 + 300 = 1100 ppm

Temporary hardness = 500 ppm

Permanent hardness = Total hardness - Temporary hardness = 1100 – 500 = 600 ppm

8. Calculate the hardness of 0.1M CaCl₂ solution.

$$\begin{aligned} \text{Hardness} &= \text{Molarity} \times M_{\text{CaCO}_3} \times 1000 \\ &= 0.1 \times 100 \times 1000 = 10000 \text{ ppm} \end{aligned}$$

9. Calculate the hardness of 0.4 N Ca²⁺ solution.

$$\begin{aligned} \text{Hardness} &= \text{Normality} \times \text{Eqnt. Wt.}_{\text{CaCO}_3} \times 1000 \\ &= 0.4 \times 50 \times 1000 = 20000 \text{ ppm} \end{aligned}$$

10. A standard hard water containing 15g CaCO₃ per litre. 20ml of this required 25ml EDTA solution. 100ml of sample of water required 18ml EDTA solution. The same sample of water, after boiling required 12ml EDTA solution. Calculate the temporary hardness.

Step I: Preparation of SHW

$$1 \text{ litre SHW} = 15\text{g CaCO}_3$$

$$1000 \text{ ml SHW} = 15000\text{mg CaCO}_3$$

$$1 \text{ ml SHW} = 15\text{mg CaCO}_3$$

$$\text{Normality of SHW} = 15\text{mg CaCO}_3$$

Step II: Standardisation of EDTA

$$20 \text{ ml SHW} = 25 \text{ ml EDTA}$$

$$V_{\text{SHW}} \times N_{\text{SHW}} = V_{\text{EDTA}} \times N_{\text{EDTA}}$$

$$20 \times 15 = 25 \times N_{\text{EDTA}}$$

$$N_{\text{EDTA}} = \frac{20 \times 15}{25} = 12\text{mg CaCO}_3$$

Step III: Estimation of total hardness

$$100 \text{ ml UHW} = 18 \text{ ml EDTA}$$

$$V_{\text{UHW}} \times N_{\text{UHW}} = V_{\text{EDTA}} \times N_{\text{EDTA}}$$

$$100 \times N_{\text{UHW}} = 18 \times 12$$

$$N_{\text{UHW}} = \frac{18 \times 12}{100} = 2.16\text{mg}$$

$$\text{Total Hardness} = 2.16 \times 1000 = 2160 \text{ ppm}$$

Step IV: Determination of permanent hardness

$$100 \text{ ml BHW} = 12 \text{ ml EDTA}$$

$$V_{\text{BHW}} \times N_{\text{BHW}} = V_{\text{EDTA}} \times N_{\text{EDTA}}$$

$$100 \times N_{\text{BHW}} = 12 \times 12$$

$$N_{\text{BHW}} = \frac{12 \times 12}{100} = 1.44 \text{ mg}$$

$$\text{Permanent Hardness} = 1.44 \times 1000 = 1440 \text{ ppm}$$

Step V: Determination of temporary hardness

$$\text{Temporary hardness} = \text{Total hardness} - \text{Permanent hardness} = 2160 - 1440 = 720 \text{ ppm}$$

11. A standard hard water was prepared by dissolving 1g CaCO₃ in dil. HCl. It is then evaporated and made up to 1 litre using distilled water. 50ml of this required 48ml EDTA solution. 50ml of test hard water required 15ml EDTA solution. 50 ml of the same test water sample after boiling and filtration required 10ml EDTA solution. Calculate the total, permanent and temporary hardness.

Step I: Preparation of SHW

$$1 \text{ litre SHW} = 1 \text{ g CaCO}_3$$

$$1000 \text{ ml SHW} = 1000 \text{ mg CaCO}_3$$

$$1 \text{ ml SHW} = 1 \text{ mg CaCO}_3$$

$$\text{Normality of SHW} = 1 \text{ mg CaCO}_3$$

Step II: Standardisation of EDTA

$$50 \text{ ml SHW} = 48 \text{ ml EDTA}$$

$$V_{\text{SHW}} \times N_{\text{SHW}} = V_{\text{EDTA}} \times N_{\text{EDTA}}$$

$$50 \times 1 = 48 \times N_{\text{EDTA}}$$

$$N_{\text{EDTA}} = \frac{50 \times 1}{48} = 1.04 \text{ mg CaCO}_3$$

Step III: Estimation of total hardness

$$50 \text{ ml UHW} = 15 \text{ ml EDTA}$$

$$V_{\text{UHW}} \times N_{\text{UHW}} = V_{\text{EDTA}} \times N_{\text{EDTA}}$$

$$50 \times N_{\text{UHW}} = 15 \times 1.04$$

$$N_{\text{UHW}} = \frac{15 \times 1.04}{50} = 0.312 \text{ mg}$$

$$\text{Total Hardness} = 0.312 \times 1000 = 312 \text{ ppm}$$

Step IV: Determination of permanent hardness

$$50 \text{ ml BHW} = 10 \text{ ml EDTA}$$

$$V_{\text{BHW}} \times N_{\text{BHW}} = V_{\text{EDTA}} \times N_{\text{EDTA}}$$

$$50 \times N_{\text{BHW}} = 10 \times 1.04$$

$$N_{\text{BHW}} = \frac{10 \times 1.04}{50} = 0.208 \text{ mg}$$

$$\text{Permanent Hardness} = 0.208 \times 1000 = 208 \text{ ppm}$$

Step V: Determination of temporary hardness

$$\text{Temporary hardness} = \text{Total hardness} - \text{Permanent hardness} = 312 - 208 = 104 \text{ ppm}$$

12. 2.8g CaCO₃ was dissolved in dil. HCl and made up to 1 litre using distilled water. 100ml of this required 28ml EDTA solution. 100ml of test hard water required 35ml EDTA solution. 100 ml of the same test water sample after boiling and filtration when titrated against EDTA required 10ml EDTA solution. Calculate the total, permanent and temporary hardness.

Step I: Preparation of SHW

$$1 \text{ litre SHW} = 2.8 \text{ g CaCO}_3$$

$$1000 \text{ ml SHW} = 2800 \text{ mg CaCO}_3$$

$$1 \text{ ml SHW} = 2.8 \text{ mg CaCO}_3$$

$$\text{Normality of SHW} = 2.8 \text{ mg CaCO}_3$$

Step II: Standardisation of EDTA

$$100 \text{ ml SHW} = 28 \text{ ml EDTA}$$

$$V_{SHW} \times N_{SHW} = V_{EDTA} \times N_{EDTA}$$

$$100 \times 2.8 = 28 \times N_{EDTA}$$

$$N_{EDTA} = \frac{100 \times 2.8}{28} = 10 \text{mg CaCO}_3$$

Step III: Estimation of total hardness

$$100 \text{ ml UHW} = 35 \text{ ml EDTA}$$

$$V_{UHW} \times N_{UHW} = V_{EDTA} \times N_{EDTA}$$

$$100 \times N_{UHW} = 35 \times 10$$

$$N_{UHW} = \frac{35 \times 10}{100} = 3.5 \text{mg}$$

$$\text{Total Hardness} = 3.5 \times 1000 = 3500 \text{ ppm}$$

Step IV: Determination of permanent hardness

$$100 \text{ ml BHW} = 10 \text{ ml EDTA}$$

$$V_{BHW} \times N_{BHW} = V_{EDTA} \times N_{EDTA}$$

$$100 \times N_{BHW} = 10 \times 10$$

$$N_{BHW} = \frac{10 \times 10}{100} = 1 \text{mg}$$

$$\text{Permanent Hardness} = 1 \times 1000 = 1000 \text{ ppm}$$

Step V: Determination of temporary hardness

$$\text{Temporary hardness} = \text{Total hardness} - \text{Permanent hardness} = 3500 - 1000 = 2500 \text{ ppm}$$

13. 0.30g CaCO₃ was dissolved in dil. HCl and made upto 1 litre using distilled water. 100ml of this required 30ml EDTA solution. 100ml of test hard water required 33ml EDTA solution. 100 ml of the same test water sample after boiling and filtration when titrated against EDTA required 10ml EDTA solution. Calculate the total, permanent and temporary hardness.

Step I: Preparation of SHW

$$1 \text{ litre SHW} = 0.30 \text{g CaCO}_3$$

$$1000 \text{ ml SHW} = 300 \text{mg CaCO}_3$$

$$1 \text{ ml SHW} = 0.3 \text{mg CaCO}_3$$

$$\text{Normality of SHW} = 0.3 \text{mg CaCO}_3$$

Step II: Standardisation of EDTA

$$100 \text{ ml SHW} = 30 \text{ ml EDTA}$$

$$V_{SHW} \times N_{SHW} = V_{EDTA} \times N_{EDTA}$$

$$100 \times 0.3 = 30 \times N_{EDTA}$$

$$N_{EDTA} = \frac{100 \times 0.3}{30} = 1 \text{mg CaCO}_3$$

Step III: Estimation of total hardness

$$100 \text{ ml UHW} = 33 \text{ ml EDTA}$$

$$V_{UHW} \times N_{UHW} = V_{EDTA} \times N_{EDTA}$$

$$100 \times N_{UHW} = 33 \times 1$$

$$N_{UHW} = \frac{33 \times 1}{100} = 0.33 \text{mg}$$

$$\text{Total Hardness} = 0.33 \times 1000 = 330 \text{ ppm}$$

Step IV: Determination of permanent hardness

$$100 \text{ ml BHW} = 10 \text{ ml EDTA}$$

$$V_{BHW} \times N_{BHW} = V_{EDTA} \times N_{EDTA}$$

$$100 \times N_{BHW} = 10 \times 1$$

$$N_{BHW} = \frac{10 \times 1}{100} = 0.1 \text{mg}$$

$$\text{Permanent Hardness} = 0.1 \times 1000 = 100 \text{ ppm}$$

Step V: Determination of temporary hardness

$$\text{Temporary hardness} = \text{Total hardness} - \text{Permanent hardness} = 330 - 100 = 230 \text{ ppm}$$

14. A sample of water is found to contain Mg(HCO₃)₂ – 7.3mg/L, Ca(HCO₃)₂ – 16.2 mg/L, MgCl₂ – 9.5 ppm and CaSO₄ – 13.6mg/L. Calculate the temporary and permanent hardness of

water sample. What happens to the temporary and permanent hardness of water sample if 10.6mg/L Na₂CO₃ is added?

Constituents	Quantity (mg/L)	M _{HPS}	CaCO ₃ equivalent hardness = Quantity X $\frac{100}{M_{HPS}}$
Ca(HCO ₃) ₂	16.2	162	$16.2 \times \frac{100}{162} = 10 \text{ ppm}$
Mg(HCO ₃) ₂	7.3	146	$7.3 \times \frac{100}{146} = 5 \text{ ppm}$
MgCl ₂	9.5	95	$9.5 \times \frac{100}{95} = 10 \text{ ppm}$
CaSO ₄	13.6	136	$13.6 \times \frac{100}{136} = 10 \text{ ppm}$
Na ₂ CO ₃	10.6	106	$10.6 \times \frac{100}{106} = 10 \text{ ppm}$

$$\text{Total hardness} = 10+5+10+10 = 35 \text{ ppm}$$

$$\text{Temporary hardness} = 10+5 = 15 \text{ ppm}$$

$$\text{Permanent hardness} = 35 - 15 = 20 \text{ ppm}$$

If 10.6mg/L Na₂CO₃ is added to water, it removes permanent Ca²⁺ as CaCO₃ and Mg²⁺ cannot be removed.

$$\text{CaCO}_3 \text{ equivalent hardness of Na}_2\text{CO}_3 = 10 \text{ ppm}$$

Thus 10 ppm permanent Ca is removed as CaCO₃.

$$\text{New total hardness} = 35 - 10 = 25 \text{ ppm}$$

$$\text{Temporary hardness} = 15 \text{ ppm}$$

$$\text{New permanent hardness} = 25 - 15 = 10 \text{ ppm}$$