NEHRU COLLEGE OF ENGINEERING AND RESEARCH CENTRE
(NAAC Accredited)
(Approved by AICTE, Affiliated to APJ Abdul Kalam Technological University, Kerala)

DEPARTMENT OF COMPUTER SCIENCE AND 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.

ABOUT DEPARTMENT

- Established in: 2002
- Course offered : B.Tech in Computer Science and Engineering
  M.Tech in Computer Science and Engineering
  M.Tech in Cyber Security
- Approved by AICTE New Delhi and Accredited by NAAC
- Affiliated to the University of A P J Abdul Kalam Technological University.

DEPARTMENT VISION

Producing Highly Competent, Innovative and Ethical Computer Science and Engineering Professionals to facilitate continuous technological advancement.

DEPARTMENT MISSION

1. To Impart Quality Education by creative Teaching Learning Process
2. To Promote cutting-edge Research and Development Process to solve real world problems with emerging technologies.
3. To Inculcate Entrepreneurship Skills among Students.
4. To cultivate Moral and Ethical Values in their Profession.
5.

PROGRAMME EDUCATIONAL OBJECTIVES

PEO1: Graduates will be able to Work and Contribute in the domains of Computer Science and Engineering through lifelong learning.

PEO2: Graduates will be able to Analyse, design and development of novel Software Packages, Web Services, System Tools and Components as per needs and specifications.

PEO3: Graduates will be able to demonstrate their ability to adapt to a rapidly changing environment by learning and applying new technologies.

PEO4: Graduates will be able to adopt ethical attitudes, exhibit effective communication skills, Teamworkand leadership qualities.

PROGRAM OUTCOMES (POS)

Engineering Graduates will be able to:

1. **Engineering knowledge**: Apply the knowledge of mathematics, science, engineering fundamentals, and an engineering specialization to the solution of complex engineering problems.
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.
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.
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.
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.
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.
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.
8. **Ethics**: Apply ethical principles and commit to professional ethics and responsibilities and norms of the engineering practice.
9. **Individual and team work**: Function effectively as an individual, and as a member or leader in diverse teams, and in multidisciplinary settings.
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.

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.
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.

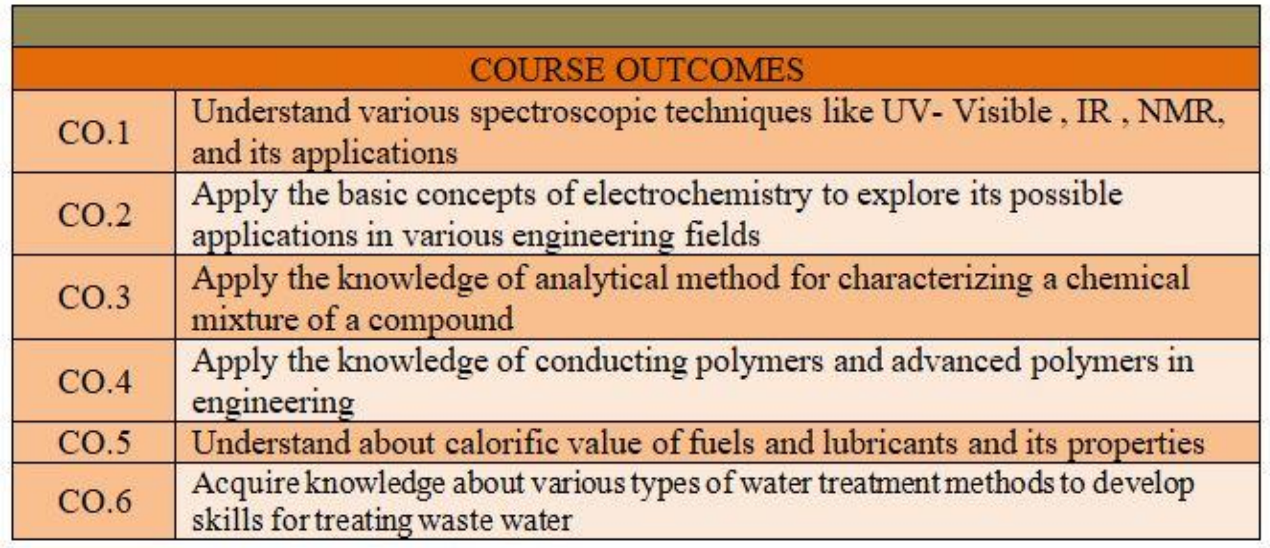
PROGRAM SPECIFIC OUTCOMES (PSO)

PSO1: Ability to Formulate and Simulate Innovative Ideas to provide software solutions for Real-time Problems and to investigate for its future scope.

PSO2: Ability to learn and apply various methodologies for facilitating development of high quality System Software Tools and Efficient Web Design Models with a focus on performance optimization.

PSO3: Ability to inculcate the Knowledge for developing Codes and integrating hardware/software products in the domains of Big Data Analytics, Web Applications and Mobile Apps to create innovative career path and for the socially relevant issues.

COURSE OUTCOME



COURSE OUTCOMES	
CO.1	Understand various spectroscopic techniques like UV- Visible , IR , NMR, and its applications
CO.2	Apply the basic concepts of electrochemistry to explore its possible applications in various engineering fields
CO.3	Apply the knowledge of analytical method for characterizing a chemical mixture of a compound
CO.4	Apply the knowledge of conducting polymers and advanced polymers in engineering
CO.5	Understand about calorific value of fuels and lubricants and its properties
CO.6	Acquire knowledge about various types of water treatment methods to develop skills for treating waste water

CO VS PO’S AND PSO’S MAPPING

CO	PO1	PO2	PO3	PO4	PO5	PO6	PO7	PO8	PO9	PO10	PO11	PO12	PS01	PSO2
CO 1	3	**2**	**-**	**3**	**-**	**3**	**-**	**-**	**-**	**-**	**-**	**2**	**-**	**-**
CO 2	**3**	**3**	**3**	**-**	**-**	**2**	**-**	**-**	**-**	**-**	**-**	**2**	**-**	**-**
CO 3	**2**	**-**	**2**	**3**	**-**	**-**	**-**	**-**	**-**	**-**	**-**	**2**	**-**	**2**
CO 4	**2**	**-**	**-**	**-**	**-**	**3**	**3**	**-**	**-**	**-**	**-**	**2**	**2**	**-**
CO 5	**3**	**3**	**3**	**2**	**-**	**3**	**3**	**2**	**-**	**-**	**-**	**3**	**-**	**-**
CO 6	**3**	**1**	**3**	**3**	**2**	**3**	**3**	**3**	**-**	**-**	**-**	**3**	**-**	**-**
CO	**2.70**	**2.25**	**2.75**	**2.75**	**2**	**2.8**	**3**	**2.5**	**0**	**0**	**0**	**2.3**	**2**	**2**

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

SYLLABUS

Course No.	Course Name	L-T-P-Credits	Year of Introduction
CY100	ENGINEERING CHEMISTRY	3-1-0-4	2015

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:

- 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 (worked out examples)	1	15%
	UV-visible spectroscopy - Principle, Instrumentation and applications	2	
	IR spectroscopy- Principle and applications	2	
	^{1}H NMR spectroscopy - Principle, chemical shift - spin - spin splitting and applications including MRI	4	
II	Electrochemistry: Different types of electrodes (general) – SHE, Calomel electrode, Glass electrode and determination of E^0 using SHE & Calomel	2	15%

	electrode		
	Electrochemical series and its applications.	1	
	Nernst equation for an electrode- 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 - Dulongs 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			

QUESTION BANK

MODULE- I(SPECTROSCOPY)

1. Which of the following nuclei can give NMR spectrum? Give reason.
   a) $_{1}H^{1}$ b) $_{6}C^{12}$ c) $_{9}F^{19}$ d)$_{8}O^{16}$ (2)
2. The vibrational frequency of HCl molecule is 2886 cm^{-1}.Calculate the force constant of the molecule. Reduced mass of HCl is $1.63X\ 10^{-27}$ Kg. (3)
3. How can you distinguish NMR spectrum of CH_3CH_2Cl and CH_3CHCl_2.Apply the concept of spin spin splitting. (3)
4. Which of the following molecules show UV Visible absorption? Give reason.
   a)ethane b)butadiene c)benzene d)phenol (3)
5. What is a Spectrometer? Write the principle components of UV Visible spectrometer.(4)
6. Predict NMR spectrum of $CH_3CHClCH_3$.(3)
7. Write the theory of vibrational spectroscopy. (2)
8. Sketch the various modes of vibrations possible for CO_2. Which are IR active .Write the reason for your answer. (5)
9. Chemical shift value of methyl chloride is lower compared to that of methyl fluoride?(2)
10. List all the electronic transitions possible for CH_3Cl and HCHO. (3)
11. Predict the splitting pattern in the NMR spectra of $CH_3CH_2COOCH_3$ and CH_3CHCl_2. (5)
12. The fundamental vibrational frequency of CO ($^{12}C\ ^{16}O$)is 2140cm^{-1} .Without calculating force constant , find the fundamental frequency of $^{13}C\ ^{17}O$ in cm^{-1}. (5)
13. Which among the following molecules will give $n \rightarrow \pi^*$ transition.
    C_2H_6 , CH_3CHO ,$C_6H_5CONH_2$, C_2H_5OH ,C_2H_4 . Rationalize your answer. (5)
14. Briefly explain chemical shift and factors affecting it .(5)
15. Which of the following molecules can give IR absorption ? Give reason.
    a) O_2 b) HCl c)N_2 d) CO_2 (2)
16. The fundamental vibrational frequency of CO is 2140 cm^{-1} .Calculate the force constant of the bonds if reduced mass of CO is $1.14X10^{-26}$ Kg. (3)
17. Explain spin spin splitting .Write the splitting pattern in the NMR spectrum of $CH_2ClCH2CH2Cl$.(4)
18. Explain the various modes of vibrations possible for H_2O which of them are IR active .Give reasons. (3)
19. 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 dm^2mol^{-1}. (3)

MODULE II

ELECTROCHEMISTRY

1. Define standard electrode potential?
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?
6. Explain Standard Hydrogen Electrode? Write down its merits and limitations?
7. Explain Saturated Calomel Electrode?
8. What are the advantages of Potentiometric titration?
9. Explain fuel cell with an example?
10. Explain Lithium ion cell?
11. What do you mean by glass electrode? How can we determine the P^H of a solution? Explain its merits and limitation?
12. What do you mean by electrochemical series? What are its application?
13. What is Nernst equation? Derive Nernst equation and write its application?
14. Explain Acid – Base titration and Redox titration by Potentiometric method?

MODULE III

INSTRUMENTAL METHODS

1. What do you mean by R_f value?
2. Give any two applications of TLC
3. What do you mean by elution?
4. What do you mean by cell constant? How is it determined?
5. Define specific conductance .How is it expressed?
6. What are the requirements of a good adsorbent in chromatography?
7. How the TLC plate is prepared and developed in TLC.
8. Give any three applications of DTA.
9. What do you mean by cell constant? How is it determined?
10. Differentiate retention time and retention factor.
11. Give the applications of TGA.
12. Briefly explain the columns and detectors used in HPLC
13. Explain the basic principle of thermogravimetry.How is this technique useful in analysis.
14. Briefly explain Differential Thermal analysis.
15. Gas Chromatography is the most efficient and convenient tool in recent days. Comment.
16. What do you mean by conductivity? How is it experimentally determined?

17. How TGA and DTA differ from each other.
18. Write short note on column chromatography.
19. How HPLC becomes a superior analytical tool? Explain.

MODULE 4
(CHEMISTRY OF ENGG MATERIALS)

1. Describe the term copolymerization with an example.
2. Name the monomers used in the manufacture of following polymers. (a)SBR (b) Kevlar.
3. What is OLED.Mention its applications
4. Give any four uses of nanotubes.
5. Give any two chemical methods of preparation of nanoparticles
6. Write any four properties of fullerenes.
7. What are the important properties of nanotubes?
8. Write briefly on Buckminster fullerene.
9. Give the name of two engineering plastics, their structure and uses.
10. What are conducting polymers? Write the structure of two conducting polymers.
11. What are silicon rubbers? What are their special properties and uses?
12. Write a note on biological nanomaterials.
13. Give the preparation and properties of (a) SBR (b) ABS.
14. Describe the preparation and any two uses of any two advanced polymers.
15. Give the method of preparation, properties and uses of (a) Kevlar (b) polybutadiene.
16. Give the classification of conducting polymers and write the mechanism of conduction in them.
17. Describe the preparation, structure and uses of polypyrrole.
18. What are carbon nanotubes? How are they classified? State their two applications

MODULE 5

(FUELS AND LUBRICANTS)

EACH QUESTION CARRIES 2 MARKS EACH

1. .Distinguish between gross and net calorific values of fuel?
2. Write the composition and uses of natural gas
3. Distinguish between solid, liquid and gaseous fuels.
4. Distinguish between octane number and cetane number
5. Define the term calorific value. How is it expressed?
6. Give any four functions of lubricants

7. Differentiate between vegetable oil and mineral lubricants
8. What is biodiesel? Give its environmental advantages

EACH QUESTION CARRIES 3 MARKS EACH

1. Give two examples of solid lubricants. Compare their structure
2. What are greases? Write a brief note on their classification?
3. Write a note on biodiesel
4. What do you meant by oiliness of a lubricant? How can it be improved?
5. Give the structure of graphite and explain how it acts as a lubricant.
6. What is grease? How is it made?
7. How viscosity index is calculated for unknown oil?
8. Discuss any three types of greases.

EACH QUESTION CARRIES 10MARKS EACH

1. Define calorific value of a fuel. How calorific value of a fuel can be determined by Bomb calorimeter?

2. i)calculate the gross and net calorific value of a coal sample having the following composition=82%,H=8% , O=5% and ash=3.6 % .

ii) Explain the importance of octane number and cetane number

3. Write any four desirable properties of lubricants and indicate their significance

4. Write short notes on i) octane number ii) cetane number iii) biodiesel

5. Write short notes on i) Solid lubricants ii) Liquid lubricants ii) Liquid lubricants.

MODULE VI(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 10MARKS 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

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.

$$\text{Log}\,\frac{I0}{It}\ \alpha\ c$$

$$\text{Log}\,\frac{I0}{It} = kc$$

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.

$$\log\frac{I0}{It}\ \alpha\ t$$

$$\log\frac{I0}{It} = kt$$

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.

$$\log\frac{I0}{It}\ \alpha\ ct$$

$$\log\frac{I0}{It} = \varepsilon ct$$

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.

$$A = \log\frac{I0}{It}$$

Transmittance (T)

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

$$T = \frac{It}{I0}$$

$$\log\frac{1}{T} = \varepsilon ct$$

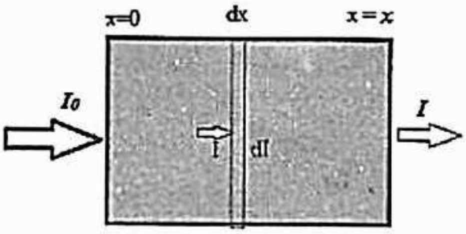
$$-\log T = \varepsilon ct$$

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, 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

$$-\int_{I0}^{It}\frac{dI}{I} = KC\int_0^t dt$$

$$-\ln\frac{It}{I0} = KCt$$

$$\boxed{\ln\frac{I0}{It} = KCt}$$

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

$$2.303\log\frac{I0}{It} = KCt \qquad \log\frac{I0}{It} = \frac{K}{2.303}Ct$$

$$\boxed{A = \log\frac{I0}{It} = \varepsilon Ct}$$

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 A^0. If the path length of light through the sample is doubled and the concentration is made half, what will be the value of absorbance?

$$\mathbf{A = \varepsilon ct}$$

$$\frac{A1}{A2} = \frac{C1t1}{c2t2} = \frac{c1t1}{\frac{c1}{2}2t1} = \mathbf{1,\ absorbance\ remains\ same}$$

- 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.

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

$$\frac{A1}{A2} = \frac{C1}{C2}$$

$$\frac{0.045}{0.022} = \frac{0.04}{C2}$$

$$C2 = 0.0195M$$

- The percentage transmittance of a 0.01m dye solution in ethanol is 20% in a 2cm cell for light of wave length 5000A^0. Find the absorbance and molar absorption coefficient.

$$A = \log\frac{I0}{It} = \varepsilon Ct$$

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

$$\varepsilon = \frac{A}{Ct} = \frac{0.6989}{0.01X2} = 34.945\ M^{-1}cm^{-1}$$

- 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.

$$-\log T = \varepsilon Ct, \text{ where } \varepsilon \ \& \ t \text{ are constants.}$$

$$\frac{\log T1}{\log T2} = \frac{C1}{C2}$$

$$\frac{\log 0.2}{\log 0.4} = \frac{50}{C2}$$

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

- 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 $12000 dm^2 mol^{-1}$.

$$A = \log\frac{I0}{It} = \varepsilon ct = 0.6986$$

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

$$c = \frac{A}{\varepsilon t} = \frac{0.6986}{12000 \text{ X } 0.25} = 2.3296 \text{ X } 10^{-4} \text{ mol dm}^{-3}$$

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 E1, the excess energy can be emitted in the form of radiation of definite frequency (ν).

$$\Delta E = E_2 - E_1$$

$$h\nu = E_2 - E_1$$

$$\nu = \frac{E2-E1}{h}$$

where 'h' is the Plank'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 A°.

$$1\text{nm} = 10^{-9} \text{ meter}$$
$$1\text{A}° = 10^{-12} \text{ meter}$$

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 Hertz = 1 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 $3 \times 10^8 \text{ ms}^{-1}$

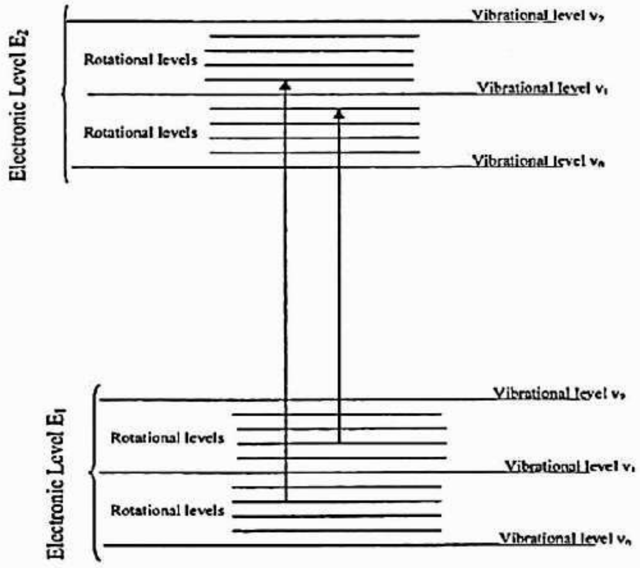
4. Wave number ($\bar{\upsilon}$)

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

$$\bar{\upsilon} = {}^{1}/_{\lambda}$$

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 = $E_{ele} + E_{vib} + E_{rot}$

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.

$E_{ele} - E^1_{ele} > E_{vib} - E^1_{vib} > E_{rot} - E^1_{rot}$

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.

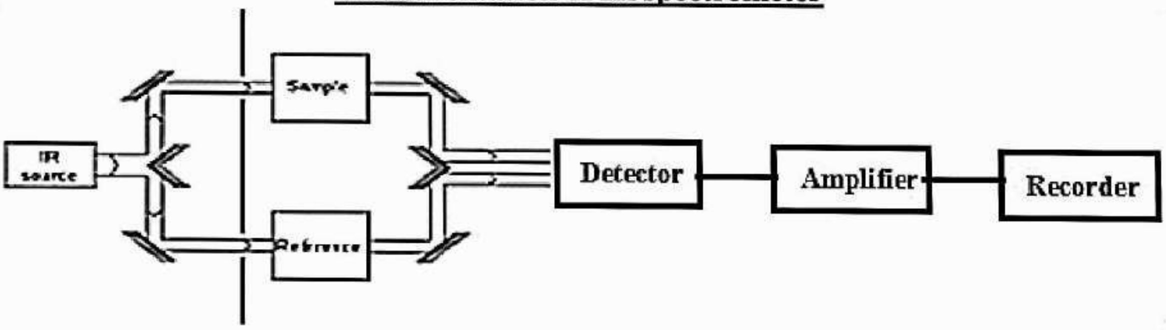
Vibrational Spectra (IR Spectra)

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

$$E_{vib} = (v + {}^1/_2)\, h\omega$$

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.

$$\text{Reduced mass } (\mu) = \frac{m1m2}{m1+m2}$$

When the molecule is in the vibrational ground level (v =0), $E_{vib} = {}^1/_2\, h\omega$. 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).

Energy change during vibrational transition (ΔE_{vib}) = $\mathbf{E}_{v} - \mathbf{E}_{v1}$

$$= (v + {}^{1}/_{2})\, h\omega - (v^{1} + {}^{1}/_{2})\, h\omega$$

$$= (v - v^{1})\, h\omega = \Delta v h\omega$$

The selection rule for vibrational spectrum is $\boxed{\Delta v = \pm 1}$

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

Spectrum can be explained in terms of wave number.

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

According to ***Hooke's law***, $\boxed{\bar{\upsilon} = \frac{1}{2\pi c}\sqrt{\frac{k}{\mu}}}$

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

Thus the frequency or wave number of absorbed line depends on

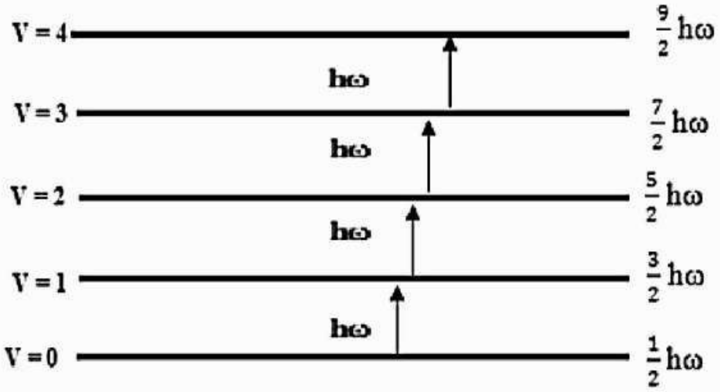
- Force constant(k)
- Reduced mass(μ)

Stretching frequency for C≡C, C=C, C–C bond are in the following order etc.

$$\boxed{C{\equiv}C > C{=}C > C{-}C}$$

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

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



Different vibrational transitions are possible between the vibrational energy levels, but all the vibrational energy levels are equally spaced with a spacing of ***'hω'***. 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 → 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 ΔV = +2, then the most probable transition is **0 → 2 transition** and the resultant lines are called **first overtones**. They have lesser intensity than the fundamental lines. If ΔV = +3, then the most probable transition is **<u>0 → 3 transition</u>** and the resultant lines are called **<u>second overtones</u>**. 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)

$$\bar{\upsilon} = 3050\text{cm-1} = 3050\text{X}100\ \text{m}^{-1}$$

$$\mu = \frac{\text{mim2}}{\text{m1+m2}}\ \text{X 1u} = \frac{1\text{X}35}{1+35}\text{X } 1.67 \text{ X } 10^{-27} \text{ kg} = 1.63\text{X}10^{-27} \text{ Kg.}$$

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

$$= \mathbf{532.8Nm^{-1}}$$

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

$$\bar{\upsilon} = \frac{1}{2\prod c}\sqrt{\frac{k}{\mu}}$$

$$\mu = \frac{mim2}{m1+m2}\text{ X 1U} = \frac{12\ X16}{12+16}\text{ X } 1.67 \text{ X } 10^{-27}\text{kg}$$

$$k = 4\pi^2C^2\bar{\upsilon}^2\mu$$

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

- The vibrational frequency of HCl molecule is 2886cm^{-1}.Calculate the force constant of the molecule. Reduced mass of HCl is 1.63X10^{-27} Kg.

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

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

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

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

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

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

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

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

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

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

- Calculate the force constant of HF molecule, if it shows IR absorption at4138 cm^{-1}. Given that atomic masses of hydrogen and flourine are 1u and 19u respectively. What would be the wave number if hydrogen atoms are replaced by deuterium atoms?

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

$$\mu = \frac{mim2}{m1+m2}\text{ X 1U} = \frac{1\ X19}{1+19}\text{ X } 1.66 \text{ X } 10^{-27}\text{kg} = 1.577 \text{ X } 10^{-27}\text{kg}$$

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

When deuterium is substituted for hydrogen, k remains constant.

$$\bar{\upsilon}^2 \propto {}^{1}/_{\mu}$$

$$\frac{\bar{\upsilon}1^2}{\bar{\upsilon}2^2} = \frac{\mu 2}{\mu 1}$$

$$\frac{4138^2}{\bar{\upsilon}2^2} = \frac{\frac{2X19}{2+19}}{\frac{1X19}{1+19}}$$

$$\bar{\upsilon}_2 = 2998\ \mathrm{cm}^{-1}$$

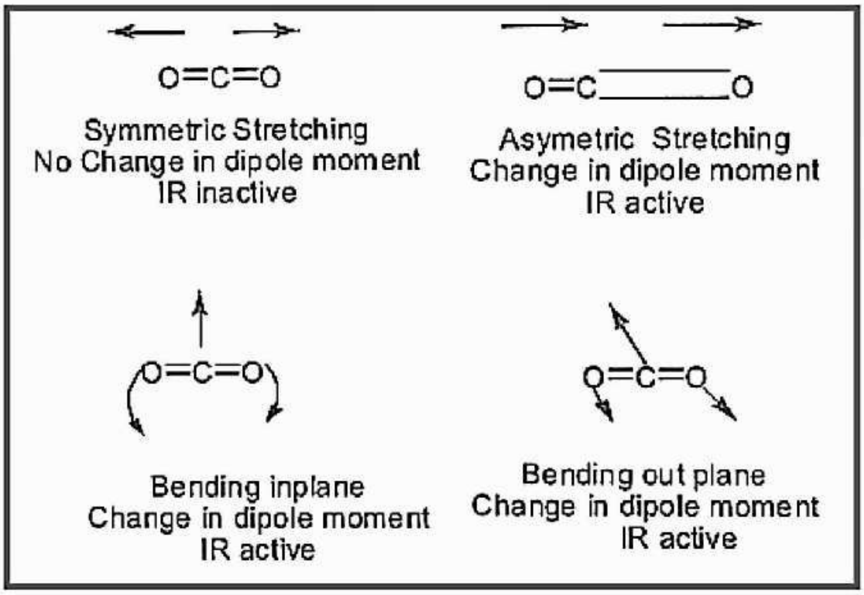
IR Spectrum of polyatomic molecules

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:

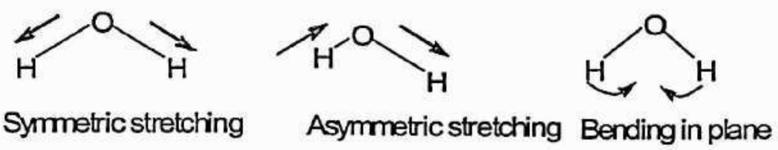


Asymmetric stretching and bending modes of vibration of O=C=O molecule results in the variations of dipole moment. Hence these vibrational modes are IR active.

H_2O is a non –linear molecule.

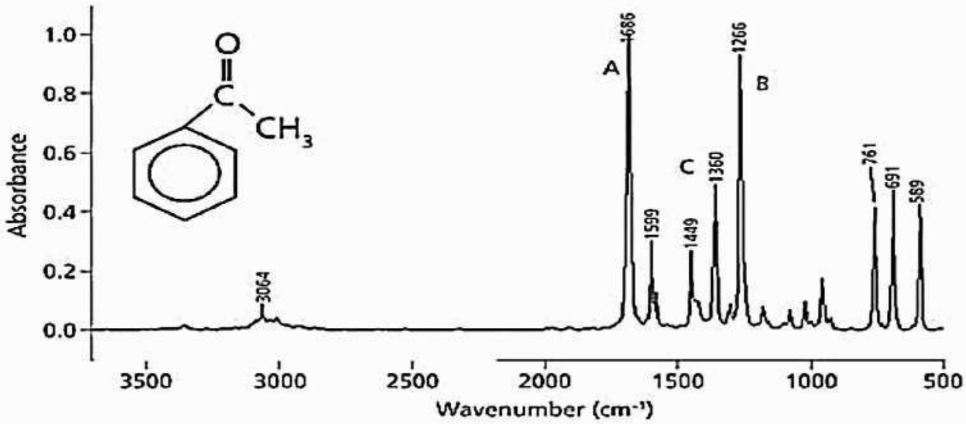
So number of vibrational modes = 3n -6 =3X3 – 6 =3.

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

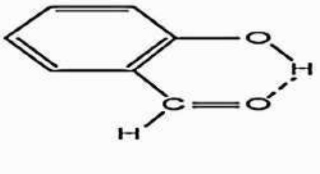
In order to explain the features of IR spectrum, let us consider the IR spectrum of aceto phenone. Spectrum can be divided into two regions. First region lies in between 1600 – 4000 cm^{1}. This region is called functional group region, since the vibrational modes of most of the functional groups occur 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.



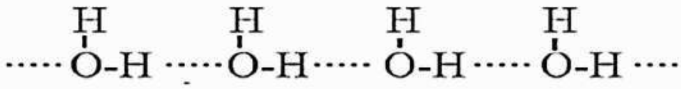
Applications of IR spectroscopy;

- 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.

Intramolecular H-bonding

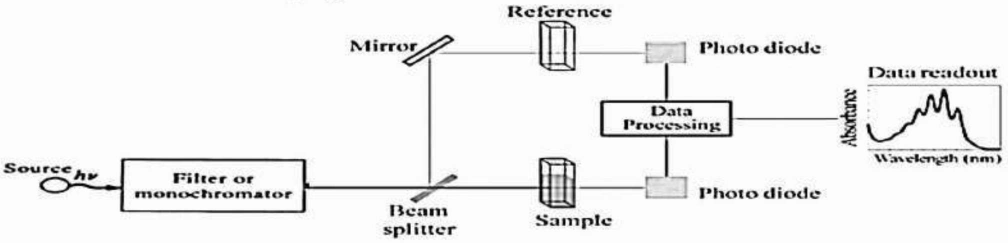


Intermolecular H-bonding



Electronic (UV –Visible) Spectroscopy

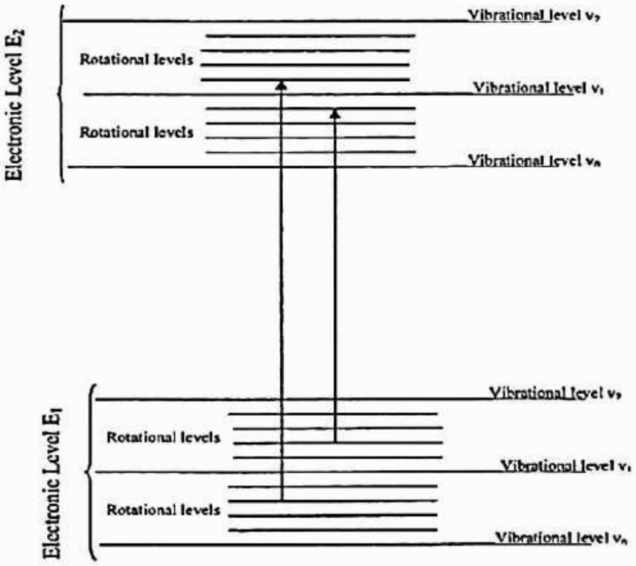
Instrumentation of UV –Visible) Spectrometer



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 $(\Delta E) = (E - E^1)$

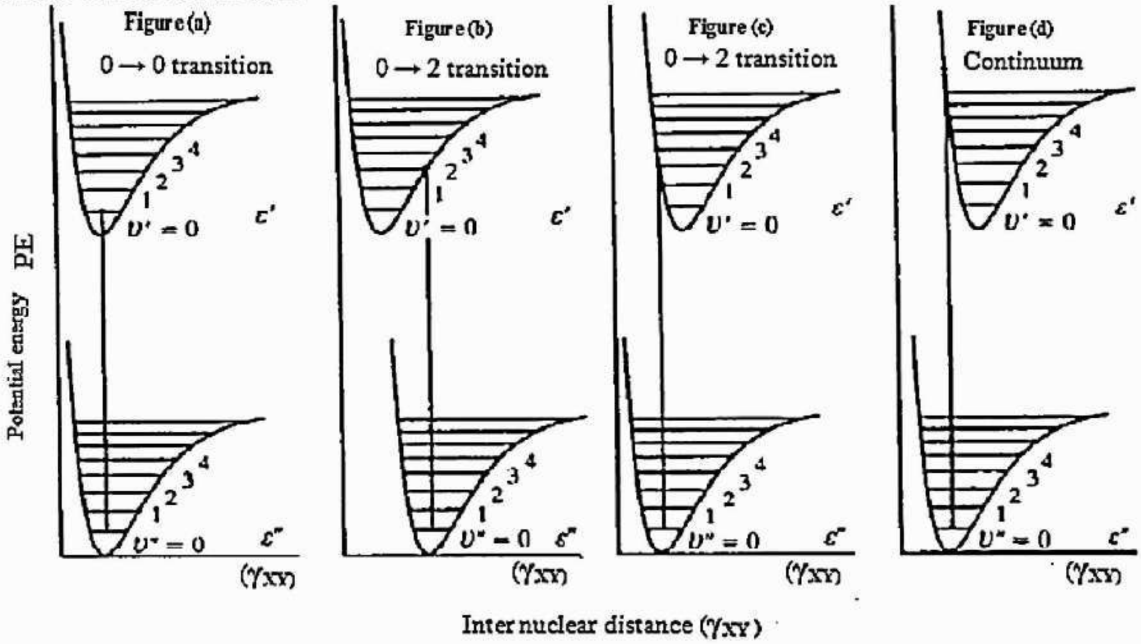
$$= (E_{(ele)} + E_{(vib)} + E_{(rot)}) - (E^1_{(ele)} + E^1_{(vib)} + E^1_{(rot)})$$

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 → 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 → 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 → 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 ≡ C —, —N≡ 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

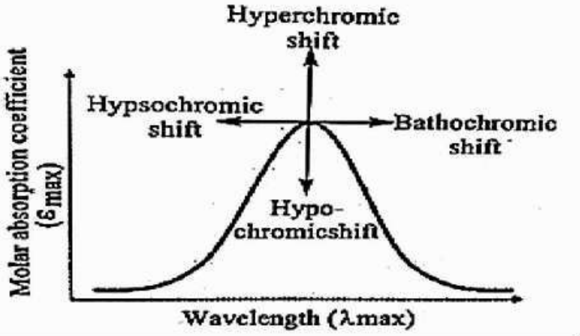
   Eg. Ethylene, acetylene etc.

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

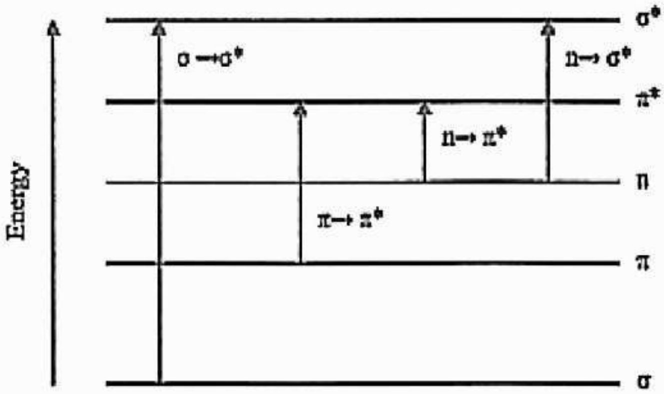
Shift in which there is an increase in intensity of absorption band is called hyper chromic shift.

Hypo chromic shift

Shift in which there is an 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 $\sigma - \sigma^*$, $\boldsymbol{\pi} - \boldsymbol{\pi}^*$, $n - \boldsymbol{\pi}^*$ & $n - \sigma^*$ 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 $CH_2=CH_2$ 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 – **π^*** transition

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

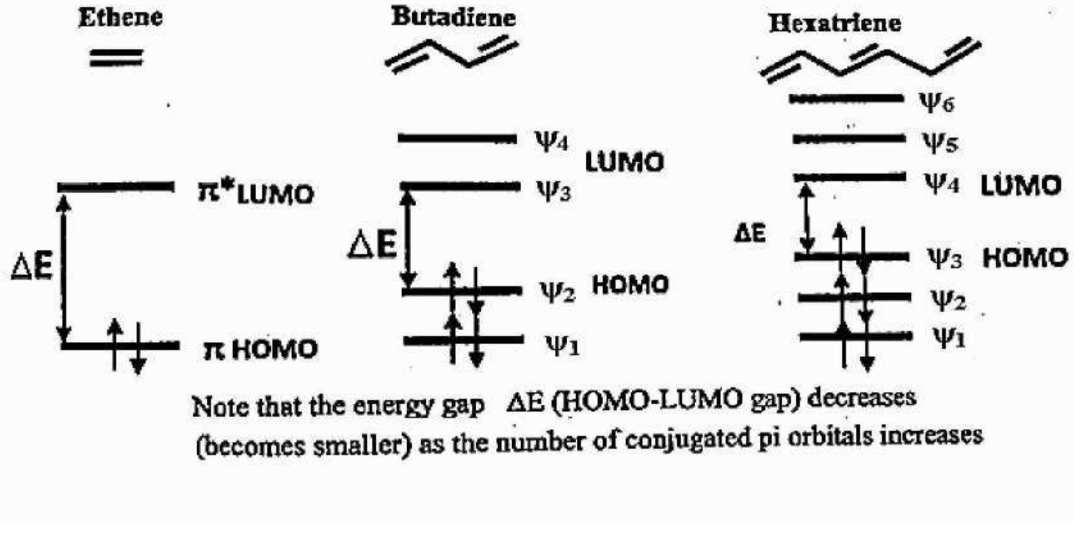
4) n – σ^* transition

Saturated compounds containing atoms such as O, N, S, X etc, containing lone pair of electrons produces absorption band due to n – σ^* transition and the absorption bands are observed in the near UV region. Generally absorption takes place below 200nm. (eg., CH_3OH, CH3NH$_2$& (CH3)$_2$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

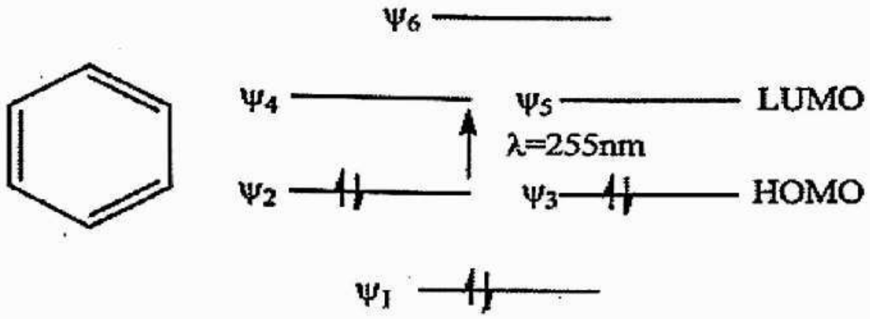


Note that the energy gap ΔE (HOMO-LUMO gap) decreases (becomes smaller) as the number of conjugated pi orbitals increases

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 $HCl, HBr, HF, H_2O, CO_2, NH_3, CO, CH_3Cl$

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.

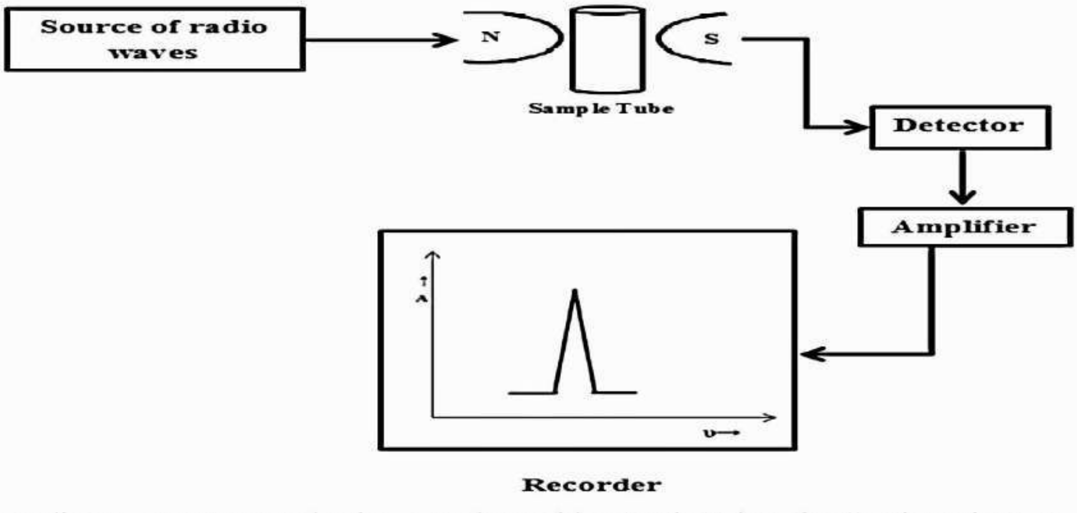
Rules for determining net spin (I)

i) If the number of protons & number of neutrons, both are even, then I = Zero. ($_6C^{12}$, $_8O^{16}$)

ii) If the number of protons & number of neutrons, both are odd, then I is an integer such as 1, 2, 3 etc. ($_7N^{14}$, $_1H^2$)

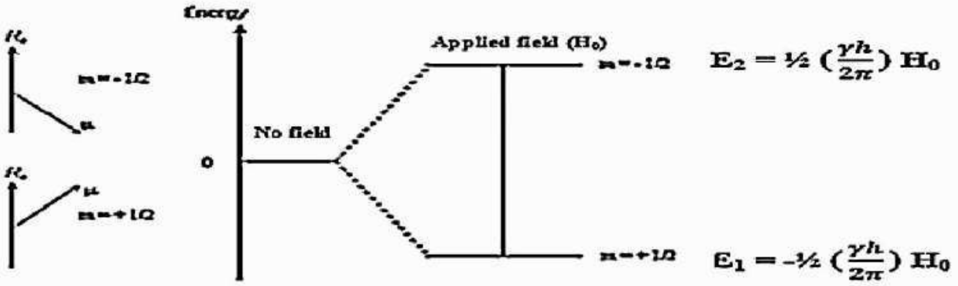
iii) If the sum of the number of protons and number of neutrons is an odd number, then I has half integral values such as $\frac{1}{2}, \frac{3}{2}, \frac{5}{2}$, etc.($_1H^1$, $_6C^{13}$, $_9F^{19}$, $_{15}P^{31}$etc, $I = \frac{1}{2}$)

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 E1 & E2 corresponds to the two states **m** = +½ and **m** = -½

$\mathbf{E_1} = -½ (\frac{\gamma h}{2\pi})$ **H_0** and**E_2** = ½ $(\frac{\gamma h}{2\pi})$ **H_0**, where **Ho** is the applied field strength, γ is the gyro magnetic constant.

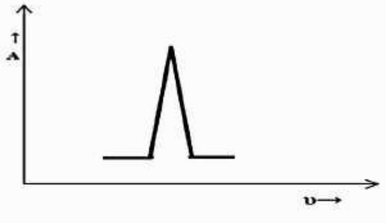
When the nucleus absorbs energy it get promoted from lower energy level E_1 to the next higher energy level E_2, then the change in energy(ΔE)

$$\Delta E = E_2 - E_1 = ½ (\frac{\gamma h}{2\pi}) H_0 - \{-½ (\frac{\gamma h}{2\pi}) H_0\} = (\frac{\gamma h}{2\pi}) H_0 = h\upsilon$$

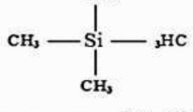
$$\upsilon = (\frac{\gamma}{2\pi}) H_0 \quad \text{or} \quad \upsilon \infty H_0 \qquad \boxed{\upsilon \infty H_0}$$

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,

$$\textbf{Chemical shift,}\boldsymbol{\delta} = \frac{\upsilon\text{sample}-\upsilon\text{TMS}}{\upsilon 0} \text{X } 10^{6}\text{ppm}$$

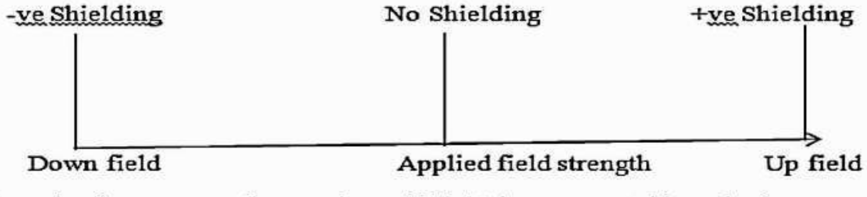
υ_o –operating frequency
υ_{sample}– frequency of sample
υ_{TMS} – frequency of reference (TMS)

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,

$$\boxed{\tau = 10 - \delta}$$

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.

$$\textbf{Chemical shift, }\boldsymbol{\delta} = \frac{v_{Sample}-v_{TMS}}{v_{Instrument}} \text{ X } 10^{6}$$

$$\mathbf{4.2} = \frac{\mathbf{1260}}{v0} \text{ X } 10^{6}$$

$$V_0 = \frac{\mathbf{1260}}{\mathbf{4.2}} \text{ X } 10^{6}$$

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

- $CHCl_3$ 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?

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

Chemical shift, **δ** is constant

$$\Delta\nu \propto \boldsymbol{\nu}$$

$$\frac{\Delta\nu 1}{\Delta\nu 2} = \frac{\nu 1}{\nu 2}$$

$$\frac{728}{\Delta\nu 2} = \frac{100}{300}$$

$$\Delta\nu 2 = \frac{728 \text{ X } 300}{100} = 2184 \text{ Hz}$$

- 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.

$$\upsilon = \left(\frac{\gamma}{2\pi}\right) \text{H}_0, \text{ Here field strength } \text{H}_0 \text{ is constant.}$$

$$\frac{\nu 1}{\nu 2} = \frac{\gamma 1}{\gamma 2}$$

$$\frac{300}{\nu 2} = \frac{1}{1/4}$$

$$\nu 2 = \frac{300}{4} = 75 \text{ MHz}$$

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	CH_3-O-CH_3	$(CH_3)_3N$	CH_3-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

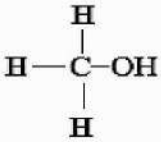
If the distance from the electronegative atom substituted in the hydrocarbon chain increases, electron density around protons increases and shielding increases so chemical shift value decreases.

Compound	$H_3C - CH_2 - CH_2Cl$
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 CH_3-OH



$$H-\overset{\overset{H}{|}}{\underset{\underset{H}{|}}{C}}-OH$$

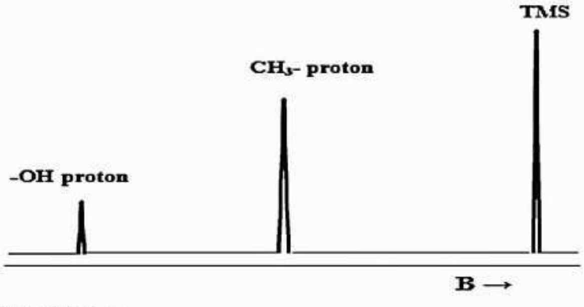
In methanol (CH_3-OH) there are three identical CH bonds and one OH bond are present. The chemical environment of CH bonds and one OH bond are different. Since oxygen is more electronegative than carbon. So electron density around -OH proton is lesser than that around CH_3- protons. As a result, CH_3-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

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

$$\boxed{B_{OH} > B_{CH3}}$$

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 comes 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.



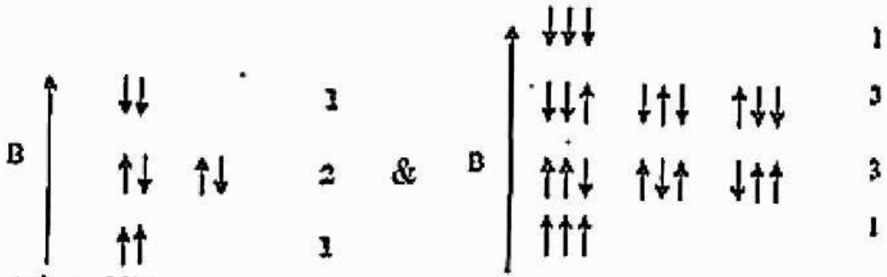
High Resolution NMR Spectrum

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 CH_3-CH_2-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.



Spin orientations of CH_2 protons and Spin orientations of CH_3 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.

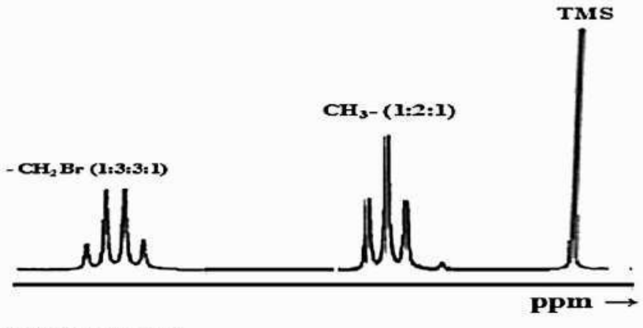
1 1

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:

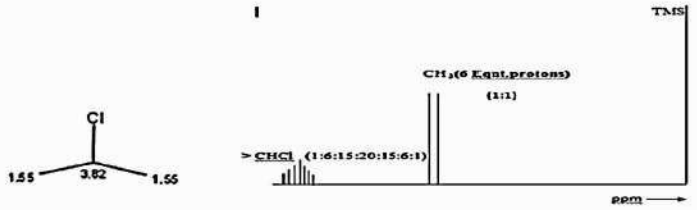
It is the medical version of NMR. This method uses magnetic properties of hydrogen present in the body cells and its interaction with external magnetic field to produce highly detailed pictures of internal body parts. In order to perform MRI scanning, a very strong magnetic field of 0.5 – 1.5T is required

Applications

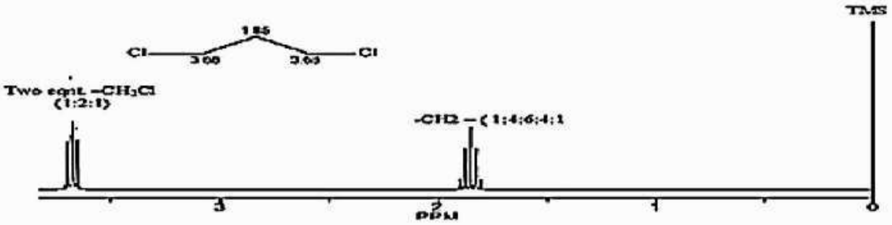
- Physicians use MRI for the treatment of diseases like tumors of abdomen, liver cirrhosis, heart problems etc.
- Measuring physiological functions like neuromuscular skeletal functions.
- Magnetic resonance angiography is used for getting pictures of arteries.

NMR Spectra of compounds

1. Predict NMR spectrum of CH_3-CHCl-CH_3(2–chloro propane)

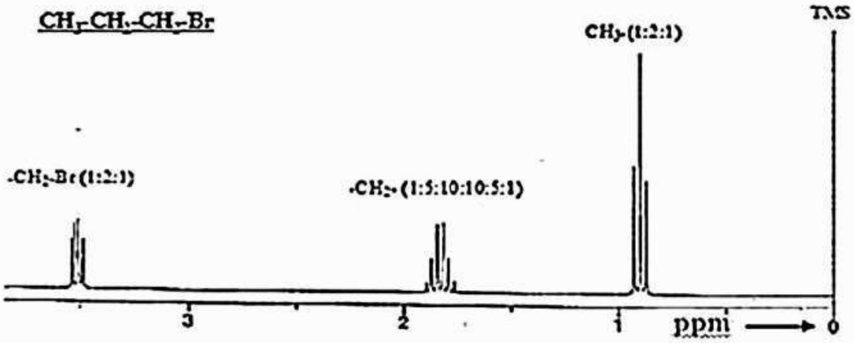


2. Write splitting pattern in the NMR spectrum of CH_2Cl-CH_2-CH_2Cl (1, 3- dichloro propane)



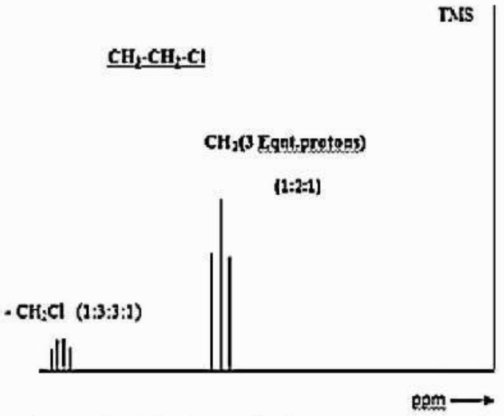
3. Give number of signals, peak ratio and multiplicity of different sets of protons in the nmr spectrum of 1-bromopropane.

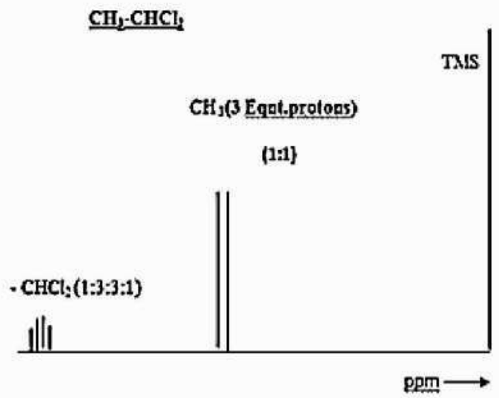
In 1-bromopropane, three types of protons are present. So three signals are expected. The Br attached CH_2- has lesser electron density, so signal is obtained far away from TMS. (i.e, at higher δ value)



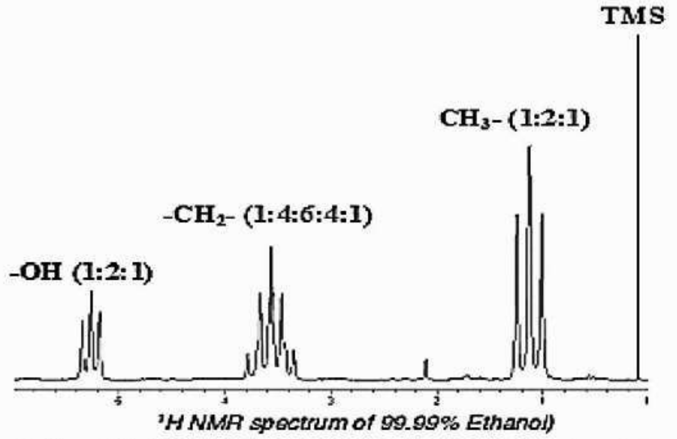
4. How can you distinguish NMR spectrum of $CH_3CH_2Cl$and CH_3CHCl_2applying the concept of spin – spin splitting

NMR spectrum of both the compounds has two peaks. In CH_3-CH_2Cl, the -CH_2Cl is attached to the more electronegative Cl atom and is less shielded, so its signal is obtained away from TMS signal. But CH_3- 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 CH_3-CH_2Cl, the CH_3- signal is splitted into triplet with intensity ratio 1:2:1, whereas in CH_3-$CHCl_2$, the CH_3- signal is splitted into doublet with intensity ratio 1:1. But in both cases -CH_2Cl & -$CHCl_2$, we get a quartet with intensity ratio (1:3:3:1).



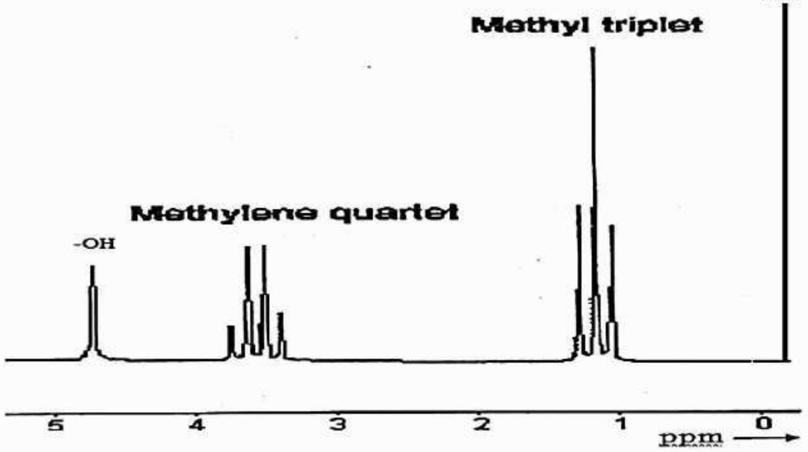


5. Draw the high resolution nmr spectrum of ethanol (99.99%pure)



¹H NMR spectrum of 99.99% Ethanol)

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



MODULE II

ELECTROCHEMISTRY

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
• It is used for the conversion of electrical energy to chemical energy.	• It is used for the conversion of chemical energy to electrical energy.
• It requires EMF.	• It produces EMF.
• Anode is +ve and cathode is –ve.	• Anode is –ve and cathode is +ve.
• Discharges of ions occur at both the electrodes.	• Discharges of ions occur only at cathode.
• Non-spontaneous reaction occurs.	• Spontaneous reaction occurs.
• These are irreversible.	• These may be reversible.

Comparison of electrolytic cell & galvanic cell

Electrolytic cell	Electro chemical cell
• Oxidation takes place at the anode and reduction at the cathode.	• Oxidation takes place at the anode and reduction at the cathode.
• Flow of electrons from anode to cathode.	• Flow of electrons from anode to cathode.
• Electrons leave the cell at anode and enter the cell at 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.

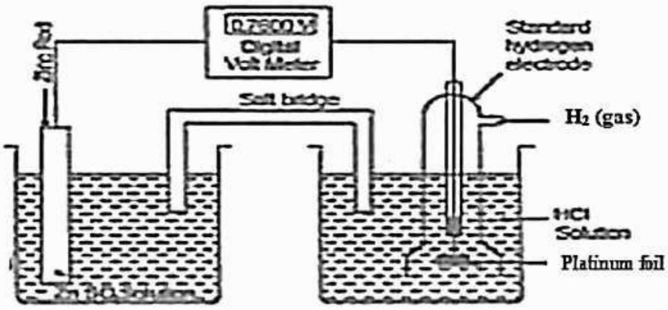
Reduction potential

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 $ZnSO_4$ 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,

$$\mathbf{Zn/Zn^{2+}//H+_{(1M)}/H2_{(1atm)}/Pt}$$

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

$$= E^0_{\text{SHE}} - E^0_{\text{Zn/Zn2+}}$$

$$0.76\text{ V} = 0 - E^0_{\text{Zn/Zn2+}}$$

$$(E^0_{\text{Zn/Zn2+}} = -0.76\text{V})$$

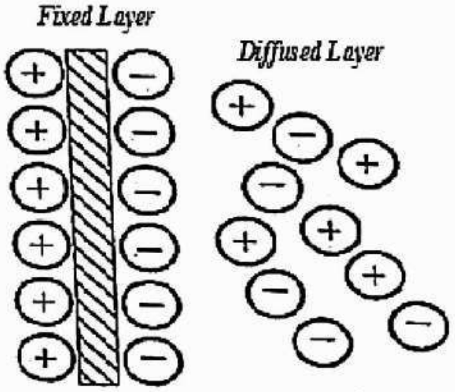
Helmholtz electrical double layer

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

$$\Phi = \frac{\sigma a}{\varepsilon 0 \varepsilon}$$

Where '**σ**' is the charge density, i.e. $Charge/_{Unit\ area}$

'**a**' is the distance between the layers of positive and negative charges.
'Ɛ' is the dielectric constant of the medium and Ɛ₀ 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)

Potassium (K)
Calcium (Ca)
Sodium (Na)
Magnesium (Mg)
Aluminium (Al)
Zinc (Zn)
Iron (Fe)
Nickel (Ni)
Tin (Sn)
Leads (Pb)
Hydrogen (H)
Copper (Cu)
Mercury (Hg)
Silver (Ag)
Platinum (Pt)
Gold (Au)
Fluorine (F)

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:

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

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, Ecell should be positive for spontaneous reaction. Ecell 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.

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.

Then electrical energy = nFE = - ΔG

$$\Delta G = -nFE$$

Criteria for spontaneity in terms of cell emf

Case 1: If $\Delta G < 0$ or ΔG is –ve, then Ecell > 0 or Ecell is +ve and the reaction will be spontaneous.

Case 2: If $\Delta G = 0$, then Ecell = 0 and the reaction will be in equilibrium.

Case 3: If $\Delta G > 0$ or ΔG is +ve, then Ecell < 0 or Ecell 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.

$$M^{n+} + ne^- \rightarrow M$$

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

$$\Delta G = \Delta G^0 + RT \ln K \qquad (1)$$

Where ΔG is the free energy change, ΔG^0 is the standard free energy change, R is the universal gas constant, K is the equilibrium constant and T is the temperature in Kelvin.

$$K = \frac{[M]}{[M+]}$$

According to Gibbs-Helmholtz suggestion,

$$\Delta G = -nFE \ \& \ \Delta G^0 = -nFE^0 \qquad (2)$$

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 = 8.314J/K, T = 298K & F = 96500C, 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,

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

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 $E^0_{(cell)}$ 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_0cell= 1.1V.

$$\text{Log } K = \frac{n\text{Eocell}}{0.0591} = \frac{2 \ X \ 1.1}{0.0591} = 37.22$$

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

- Calculate the standard emf of $H_2 - O_2$ fuel cell. (E^0values for hydrogen and oxygen half cells are -0.40V & 0.83V respectively.

$$E^0_{\mathbf{cell}} = E^0_{\mathbf{Cathode}} - E^0_{\mathbf{Anode}} = E^0_{\mathbf{O2}} - E^0_{\mathbf{H2}} = 0.83 - (-0.40) = 1.23V$$

- 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.

$$\text{Log } K = \frac{n\text{Eocell}}{0.0591} = \frac{2x0.295}{0.0591} = 10$$

$$K = 10^{10}$$

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

$$E_{cell} = E^{o}_{cell} + \frac{0.0591}{2}\log\frac{[Cu2+]}{[Ni2+]}$$

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

$$0.601 = 0.59 + 0.0295 \log \frac{0.75}{[Ni2+]}$$

$$\frac{0.011}{0.0295} = \log \frac{0.75}{[Ni2+]}$$

$$\frac{0.75}{[Ni2+]} = 2.356.$$

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

- Calculate the emf of the cell Zn/Zn^{2+} (0.01M)//Cu^{2+} (0.1M)/Cu. Write its half-cell reactions isE^{0}_{Zn} is -0.76V and E^{0}_{Cu} is +0.34V.

The cell reaction is

$$Zn_{(s)} + Cu^{2+}_{(aq)} \rightarrow Zn^{2+}_{(aq)} + Cu_{(s)}$$

Nernst equation for this cell reaction is

$$E\ cell = E0\ cell + \frac{0.0591}{2}\log\frac{[Cu2+]}{[Zn2+]}$$

But $E^{0}_{cell} = E^{0}_{R} - E^{0}_{L} = 0.34 + 0.76 = 1.1V$

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

- Calculate the equilibrium constant of the reaction, $Cu + 2Ag^{+} \rightarrow Cu^{2+} + 2Ag$ (E_0 $Ag(s)/Ag^{+}$ is 0.80V & E_0 $Cu^{2+}/Cu(s)$ is 0.34V.)

Eocell= E_0 $Ag(s)/Ag^{+}$ - E_0 $Cu^{2+}/Cu(s)$ = 0.80 – 0.34 = 0.46

$$\text{Log } K = \frac{n\text{Eocell}}{0.0591} = \frac{2 X 0.46}{0.0591} = 15.57$$

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

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

$Zn|Zn^{2+}_{(a = 0.0004)} || Cd^{2+}_{(a = 0.2)} |Cd$; ($E^{0}_{Cd2+/Cd}$ =-0.403V & $E^{0}_{Zn2+/Zn}$ =-0.76V)

$$E^{0}_{cell} = E^{0}_{cathode} - E^{0}_{anode} = E^{0}_{Cd2+/Cd} - E^{0}_{Zn2+/Zn} = -0.403 + 0.76 = 0.357V$$

$$E_{cell} = E^{0}_{cell} + \frac{0.0591}{2}\log\frac{[Cd2+]}{Zn2+} = 0.357 + \frac{0.0591}{2}\log\frac{[0.2]}{0.0004} = 0.4367V$$

- Find the single electrode potential for copper metal in contact with0.1M Cu^{2+} solution at 298K. $E^{0}_{Cu2+/Cu} = 0.34V$

$$E_{Cu} = E^{0}_{Cu} + \frac{0.0591}{2}\log[Cu^{2+}] = 0.34 + \frac{0.0591}{2}\log[0.1] = 0.31045V$$

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

E^{o}_{cell} = $E_{cathode} - E_{anode}$ = - 0.25 - (- 0.76) = + 0.51 V

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

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

ΔG^{o} = - (2X 96500 X 0.51) = - 98430 Joules

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

ΔG = -nFE = -2X96500X1.5 = 289500J

Therefore electric energy available for 10g Zn $= \frac{289500X\ 10}{65.5} = 44198$ 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.

Zn/Zn^{2+}, Cu/Cu^{2+}

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

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

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.

Hydrogen electrode ($Pt/H_2/H^+$)

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.

$Hg/Hg_2Cl_2/KCl$

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

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.

$Pt|Fe^{2+}|Fe^{3+}$, $Pt|Ce^{4+}|Ce^{3+}$.

$$E_{cell} = E^0_{cell} + 0.0591 \log \frac{[Fe3+]}{[Fe2+]}$$

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

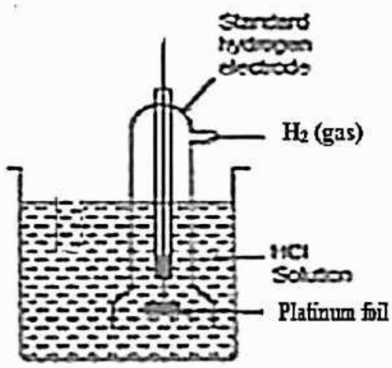
Reference electrodes are of two types. They are

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

$Pt, H_{2\,(g)\,1atm} / H^+_{(1M)}$

Cell reaction:

$\frac{1}{2} H_2 \rightarrow H^+ + 1e^-$

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

$H^+_{(1M)} / H_{2\,(g)\,1atm}, Pt$

Cell reaction:

$H^+ + 1e^- \rightarrow \frac{1}{2} H_2$

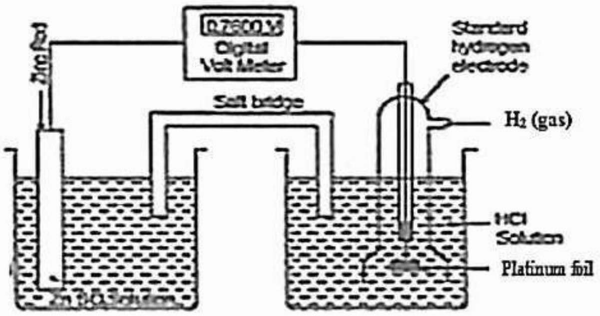
Uses:

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,

$Zn_{(S)} / Zn^{2+}\,(1M) // H^+(1M)/Pt, H_2\,(g)\,1atm$



$$E^0\,Cell = E^0_{cathode} - E^0_{anode}$$
$$= E^0_{SHE} - E^0_{Zn/Zn2+}$$
$$0.76\,V = 0 - E^0_{Zn/Zn2+}$$

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

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

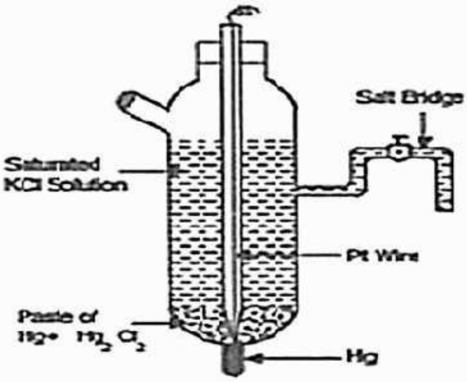
Draw backs of SHE

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, **$Pt,Hg_{(l)}| Hg_2Cl_{2(s)}|KCl(sat)$**

$$E_{cal} = E^0_{cal} - \frac{2.303RT}{2F} \log [Cl^-]^2 = E^0_{cal} - \frac{2.303RT}{F} \log[Cl^-] = E^0_{cal} - \frac{0.0591}{1} \log[Cl^-]$$

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

Oxidation

$$2Hg_{(l)} \rightarrow 2Hg^+ + 2e^-$$
$$2Hg^+ + 2Cl^- \rightarrow Hg_2Cl_2$$

Overall oxidation reaction

$$2Hg_{(l)} + 2Cl^- \rightarrow Hg_2Cl_2 + 2e^-$$

Reduction

$$Hg_2Cl_2 \rightarrow 2Hg^+ + 2Cl^-$$
$$2Hg^+ + 2e^- \rightarrow 2Hg$$

Overall reduction reaction

$$Hg_2Cl_2 + 2e^- \rightarrow 2Hg_{(l)} + 2Cl^-$$

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.

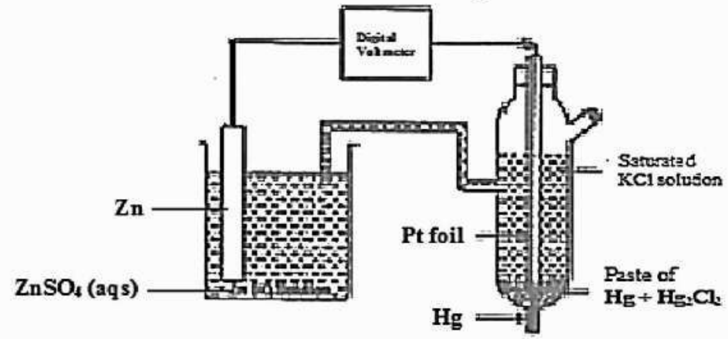
Potential of calomel electrode depends on the concentration of KCl solution.

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 Zn^{2+}/Zn (-0.76V). Therefore reduction reaction takes place at SCE.



$$Hg_2Cl_2 + 2e^- \rightarrow 2Hg + 2Cl^-$$

$$Zn \rightarrow Zn^{2+} + 2e^-$$

The resultant cell can be represented as

$$Zn/Zn^{2+}//KCl_{(sat)}/Hg_2Cl_{2(s)}/Hg_{(l)}/Pt$$

$$E_{cell} = E_R - E_L = E_{cal} - E_{Zn/Zn2+} = 0.2422 - E_{Zn/Zn2+}$$

$$E_{Zn/Zn2+} = 0.2422 - E_{cell}$$

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

Advantages of Calomel electrode

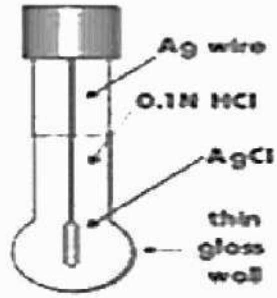
1. It is very easy to set up.
2. Its emf will not change with chemical reaction.

Glass electrode

Glass electrode is a secondary reference electrode. Corning 015glass 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% SiO_2, 6% CaO & 22% Na_2O.

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.



Ag,AgCl(s)/HCl(0.1N)/Glass//

Glass electrode works on the principle that potential difference between thesurface 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.

$$H^+_{(solution)} + Na^+Gl^- \rightarrow Na^+_{(solution)} + H^+Gl^-$$

$$E_G = E^0_G + 0.0591 \log [H^+] = E^0_G - 0.0591\, P^H$$

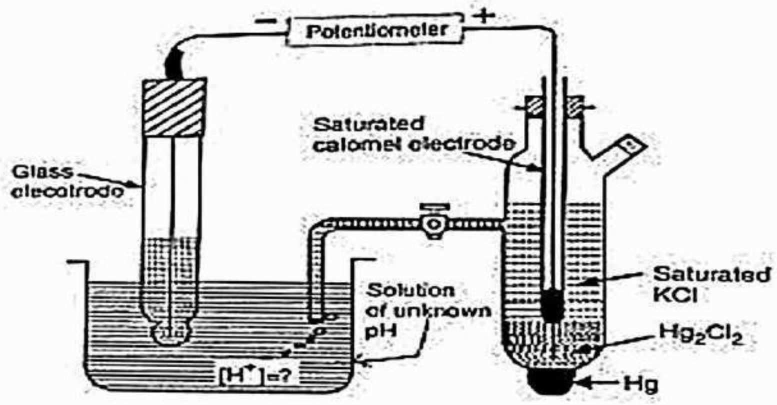
The potential of glass electrode varies with concentration of H^+ ions. E^0_G is constant and it depends on the nature of the glass and also the P^H of the solution taken inside the glass bulb.

E^0_G= 0.6990 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, $Ag,AgCl_{(S)}$/0.1N HCl/Glass/Solution of Unknown P^H// $KCl_{(sat)}/Hg_2Cl_{2(s)}/Hg_{(l)}/Pt$



$$\begin{aligned} E_{cell} &= E_R - E_L = E_{SCE} - E_G \\ &= 0.2422 - (E^0_G - 0.0591\, P^H) \\ &= 0.2422 - E^0_G + 0.0591\, P^H \end{aligned}$$

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

$$0.0591\, P^H = E_{cell} + E^0_G - 0.2422$$

$$P^H = \frac{E_{Cell} + E^0G - 0.2422}{0.0591}$$

Advantages of glass electrode

1. It is very simple to operate.

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

Draw backs of glass electrode

1. It cannot be used as a reference electrode for solutions having $\mathbf{P^H}$ 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^{0}C. Given that E_{SCE}= **0.2422V.**

$$\mathbf{E_{cell} = E_{cal} - E_{H2} = 0.2422 + 0.0591\ P^H = 0.523V}$$

$$\mathbf{P^H = \frac{0523-0.2422}{0.0591} = 4.75}$$

- Potential of H_2 electrode set up in acid solution of unknown strength is 0.295 volts at 25^{0}C when coupled with SHE. Find the P^H of the solution.

$$E_{H2} = E^0_{H2} + 0.0591 \log [H+] = -0.0591P^H$$

$$E_{Cell} = E_{Cathode} - E_{Anode} = E_{SHE} - E_{H2} = 0 + 0.0591\ P^H = 0.0591P^H$$

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

- Find out the PH 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 $E°_{Glass}$ = 0.57V.

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

Primary and secondary cells

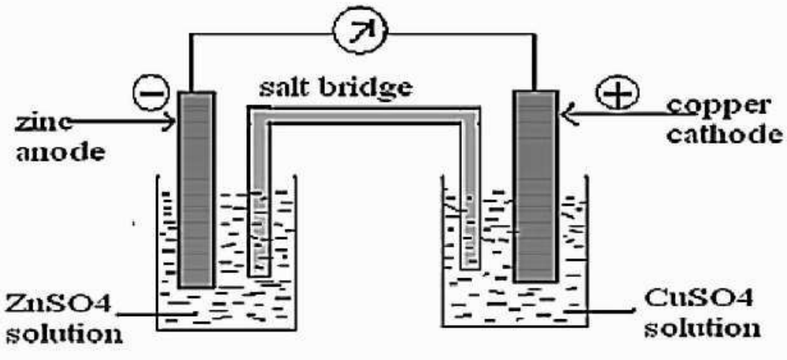
Cells which becomes dead over a period of time, because the chemical reaction occurs only once. After that the cell becomes exhausted or discharged.They cannot be recharged or reused again.

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 inZ$CuSO_4$ 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

$$Zn_{(s)}/Zn^{2+}(aqs)//Cu^{2+}(aqs)/Cu_{(s)}$$

Oxidation: $Zn \rightarrow Zn^{2+} + 2e^-$
Reduction: $Cu^{2+} + 2e^- \rightarrow Cu$
Over all reaction: $Zn + Cu^{2+} \rightarrow Zn + Cu$

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

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

Nernst equation is given as, $E_{cell} = E^o_{cell} + \frac{2.303RT}{nF}\log\frac{[Cu2+]}{[Zn2+]}$

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

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

Case III, When $[Cu^{2+}] > [Zn^{2+}]$, logarithmic term becomes positive. Then $E_{cell} > E^o_{cell}$ & 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, KNO_3, K_2SO_4, NH_4NO_3 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 H_2 electrode, $E_{H2} = E^0_{H2} + 0.0591 \log [H+] = -0.0591P^H$

At $P^H = 0$, $E_{H2} = -0.0591P^H = 0.0591 \times 0 = 0$ V

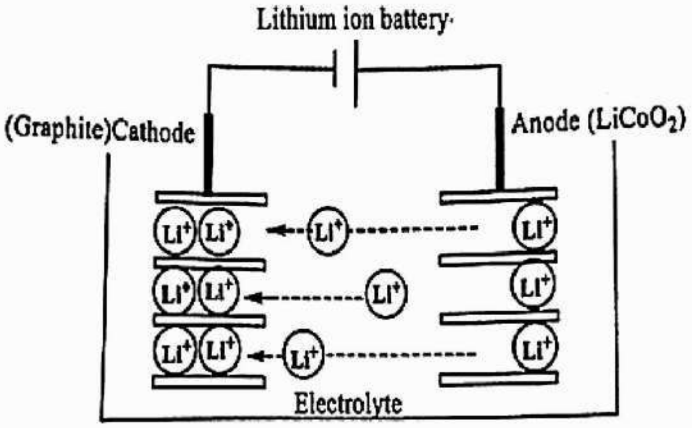
At $P^H = 7$, $E_{H2} = -0.0591P^H = 0.0591 \times 7 = 0.4137$V

At $P^H = 14$, $E_{H2} = -0.0591P^H = 0.0591 \times 14 = 0.8274$ 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.

Anodic reaction;

$$LiMO_2 \underset{Discharging}{\overset{Charging}{\rightleftharpoons}} Li_{(1-x)}MO_2 + xLi^+ + xe^-$$

Cathodic reaction;

$$C_G + xLi^+ + xe^- \underset{Discharging}{\overset{Charging}{\rightleftharpoons}} Li_xC_G$$

Overall reaction;

$$LiMO_2 + C_G' \underset{Discharging}{\overset{Charging}{\rightleftharpoons}} Li_{(1-x)}MO_2 + Li_xC_G$$

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; **$Li_xC_G|LiX$ in PC-EC$|Li_{(1-x)}MO_2$**

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

$$Ce^{4+} + e^- \rightarrow Ce^{3+}$$

$$Fe^{2+} \rightarrow Fe^{3+} + e^-$$

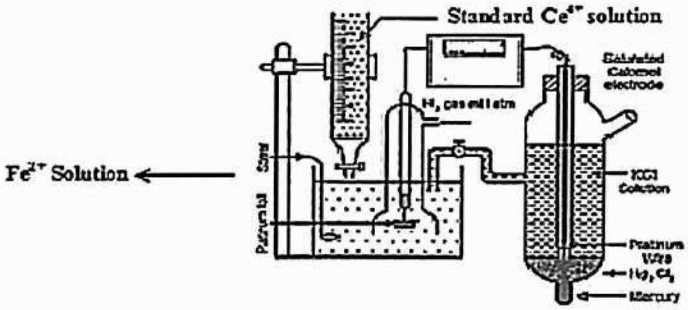
Over all reaction;

$$Ce^{4+} + Fe^{2+} \rightarrow Ce^{3+} + Fe^{3+}$$

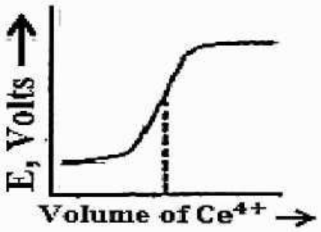
The potential of indicator electrode is

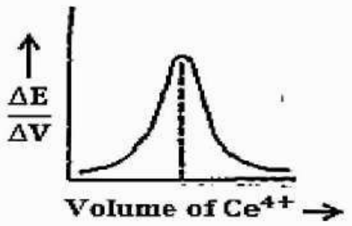
$$E = E_0 + \frac{0.0591}{n}\log\frac{[oxidised\ state]}{[reduced\ state]} = E_0 + \frac{0.0591}{1}\log\frac{[Fe^{3+}]}{[Fe^{2+}]}$$

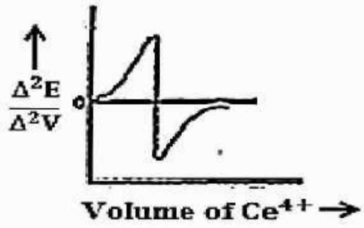
20 ml ferrous sulphate solution is mixed with 20ml 4N H_2SO_4 in a beaker. A platinum electrode is then inserted into it. It is then coupled with SCE. The electrodes are then connected using a potentiometer. Then standard ceric ammonium sulphate solution is added from the burette. After each addition 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 Fe^{2+}. Near the end point potential changes sharply. After the end point emf changes very slowly.



Emf is then plotted against volume of Ce^{4+} solution, we get an 'S' shaped curve. More and most accurate results are obtained by plotting $\frac{\Delta E}{\Delta V}$ against volume of Ce^{4+} solution and $\frac{\Delta^2 E}{\Delta^2 V}$ against volume of Ce^{4+} 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.

$I \infty V$

$V = IR$

Resistance:

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

$R \infty l$ and $R \infty \frac{1}{A}$

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

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}

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

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 $Scm^{-1}mol^{-1}$.

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

Equivalent conductance:

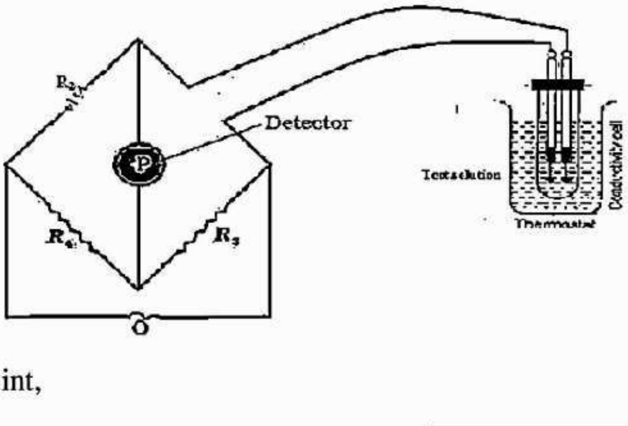
Equivalent conductance is the conductance of a solution containing 1gram equivalent of an electrolyte which is placed between two electrodes which are separated by unit distance. It is denoted by the letter λ. Its unit is $Scm^{-1}equi^{-1}$.

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

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

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

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,

$$\boxed{\frac{Rsolution}{R2} = \frac{R3}{R4}} \qquad \boxed{R\ solution = \frac{R2R3}{R4}}$$

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 X$\frac{l}{A}$, 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.

$$\boxed{\textbf{K = C X Cell constant}}$$

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

PROBLEMS

1. The specific conductivity of $^{N}/_{50}$ KCl solution at 25^0C is $0.0002765 ohm^{-1}cm^{-1}$. If the resistance of the cell containing this solution is 500Ω, what is its cell constant?

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

Cell constant = K X R = 0.0002765 X 500 =0.13825cm-1

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

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

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

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 75k Ω and 300k Ω respectively at 298K in the same conductivity cell. Specific conductance of KCl is $0.012Scm^{-1}$.

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

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

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

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

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

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 Ω^{-1} cm^{-1}.

$K_{KCl} = C_{KCl}$ X Cell constant

$$\text{Cell constant} = \frac{K\ KCl}{C\ KCl} = \frac{0.01288}{1200\ X\ 10^{-6}} = 10.73\ cm^{-1}$$

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

MODULE III
INSTRUMENTAL METHODS

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

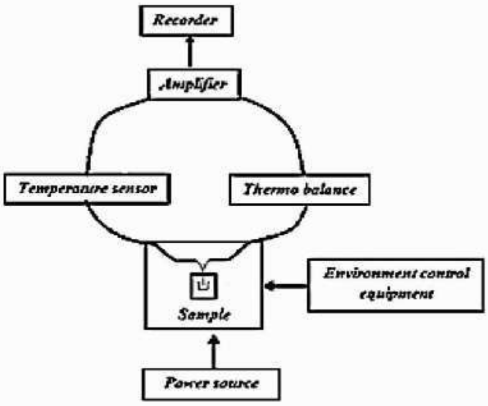
Thermo Gravimetric Analysis (TGA)

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.

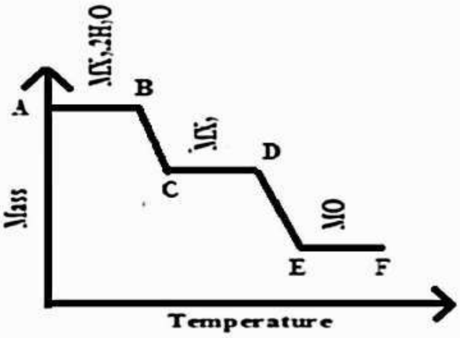
A sample on heating mass change occurs due to the physical and chemical changes undergone by the substance.

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:



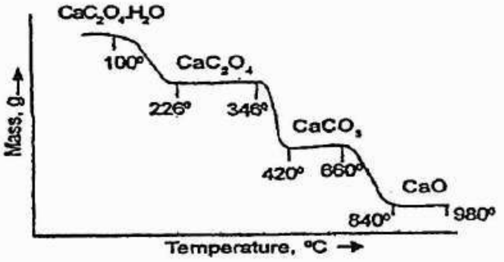
In order to explain the principle and method of TGA, let us consider the thermo gram of the compound $MX_2.2H_2O$.

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



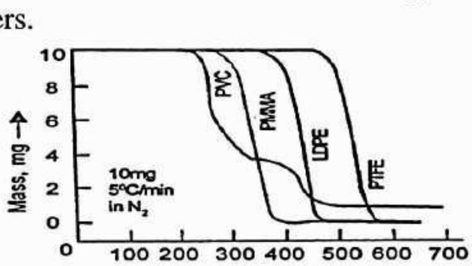
T.G. of calcium oxalate ($CaC_2O_4.H_2O$)

In order to explain the qualitative analysis, let us consider the thermogram of $CaC_2O_4.H_2O$.

$CaC_2O_4.H_2O$ is stable upto 100°C. So we get a horozontal region in this temperature region. On inceasing the temperature above 100°C it loses the two mols of water per each mole of the compound producing anhydrousCaC_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.

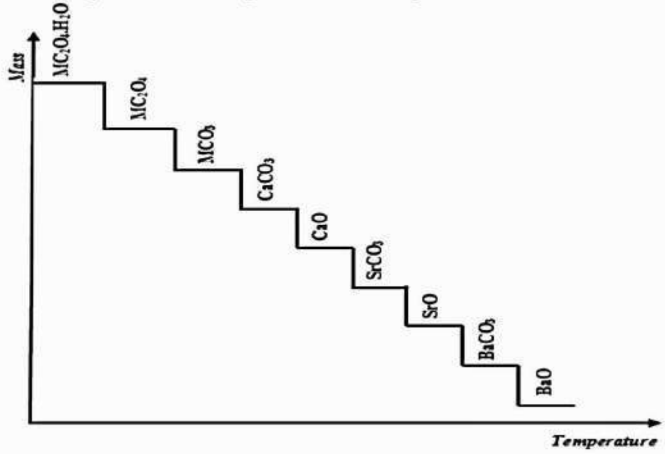
2. Study of polymers

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 $MC_2O_4.H_2O$.



Limitations of TGA:

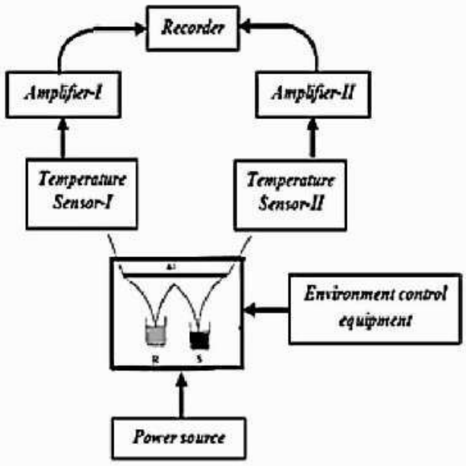
- TGA will not give any information about phase transition of crystalline substance. Since these transitions do not involve weight change.
- It will not give any information about melting point, boiling point and transition temperature of crystalline substances.

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.

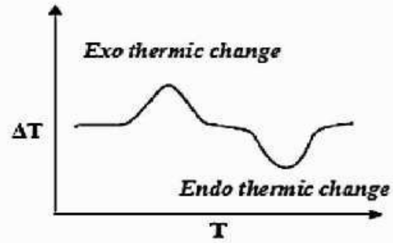
DTA Apparatus



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) = $-kGm\Delta H$

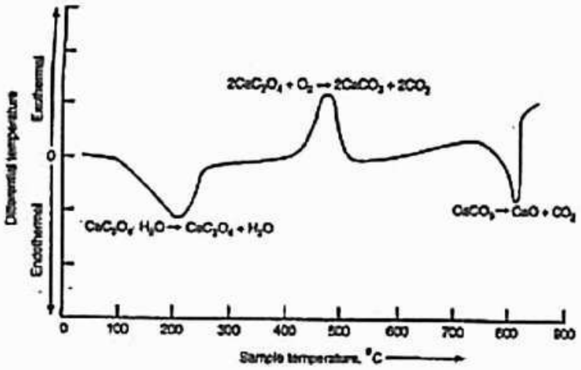
A is the peak area, G is the calibration factor which depends upon the sample geometry and k is a constant related to the thermal conductivity of the sample.

Applications:

1. Study and characterization of polymers

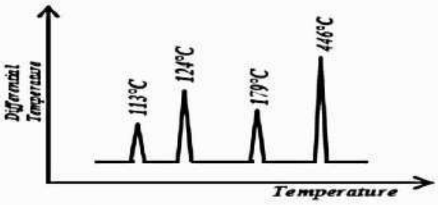
Thermal transitions of polymer occur over an extended range of temperature since polymers are mixtures of different homologues. Each peak corresponds to the melting point of the components present.

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

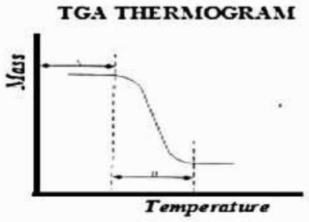
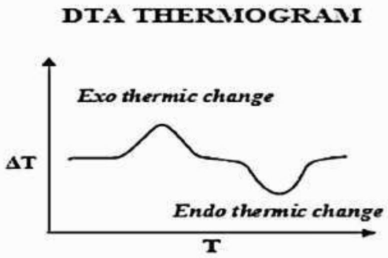
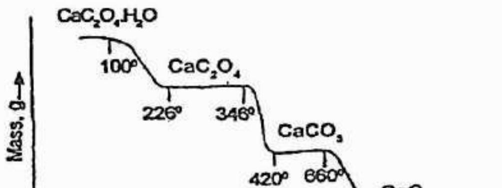
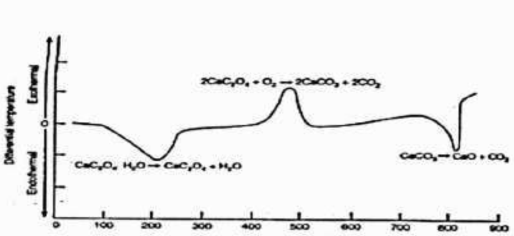


In the differential thermo gram of sulphur, a peak at 113°C represents solid phase transition from rhombic sulphur to monoclinic sulphur. Peak at 124°C represents the melting point of sulphur. Peak at 179°C represents the presence of liquid sulphur. Peak at 446°C represents the boiling point of sulphur.

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. 	2. 
3.  T.G. of calcium oxalate ($CaC_2O_4.H_2O$)	3.  DTA of Calcium Oxalate ($CaC_2O_4.H_2O$).
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 clour writing. This was introduced by the scientist Mikhail Tswette. He employed itfor 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 seperated components appeared as coloured bands in the column. So he choose th name chromatography.This method is generally used for the seperation of complex mixtures which cannot be seperated by other methods. It is also useful for the seperation 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 exmple, 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 chromatoraphy.

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

Mobile phase is the moving phase. It can be a liqid or gas. The components to be seperatedis 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:

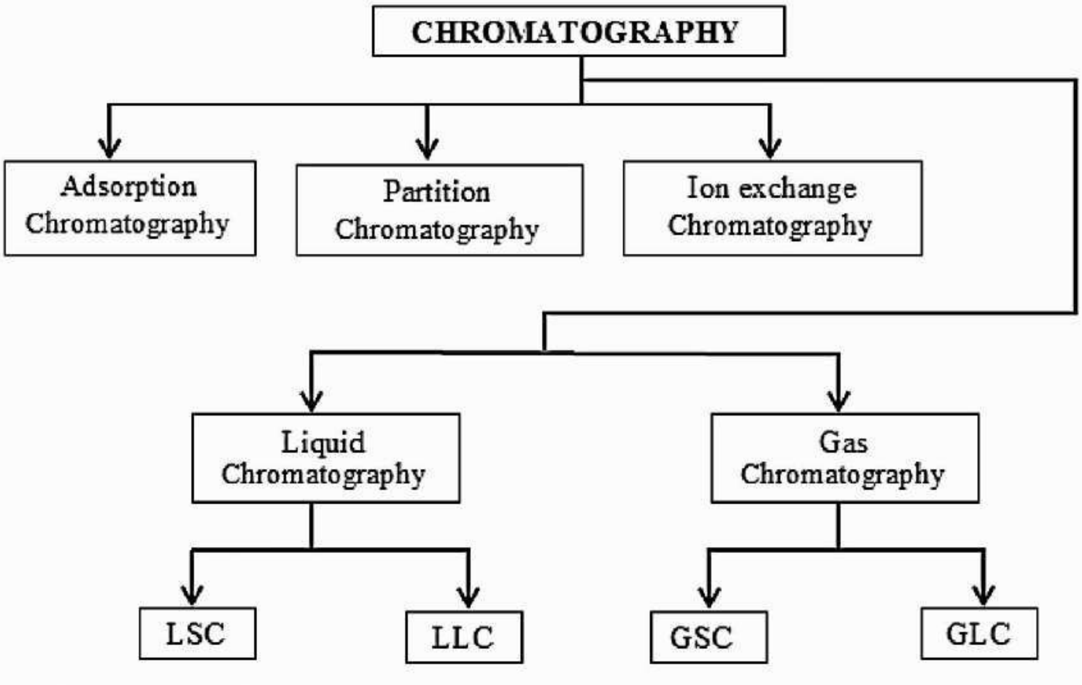
If the mobile phase is liquid and the stationary phase is solid, then the chromatography is called LSC (Liquid Solid Chromatography)

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)

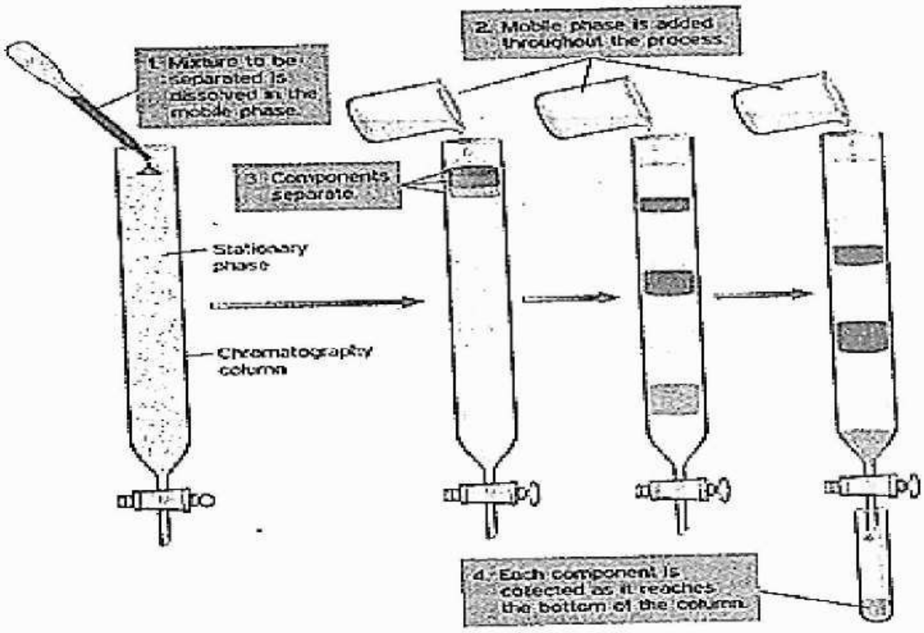


Column chromatography.

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.



Column Chromatography

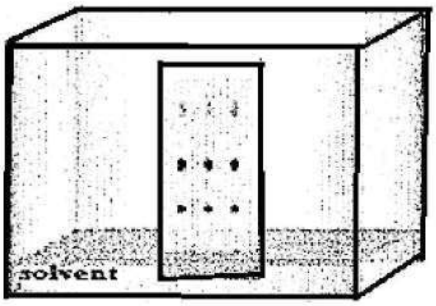
Applications:

- 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.

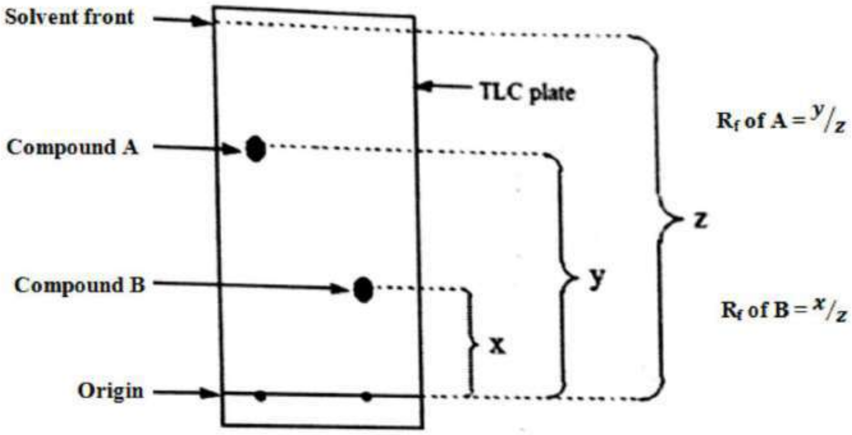


Then the glass plate is taken out of the development tank and the solvent front is marked. It is then allowed to dry. If the components in the mixture are coloured then they can be visually detected as coloured spots in the glass plate. If the separated components are colourless, then they can be visualized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

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



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.

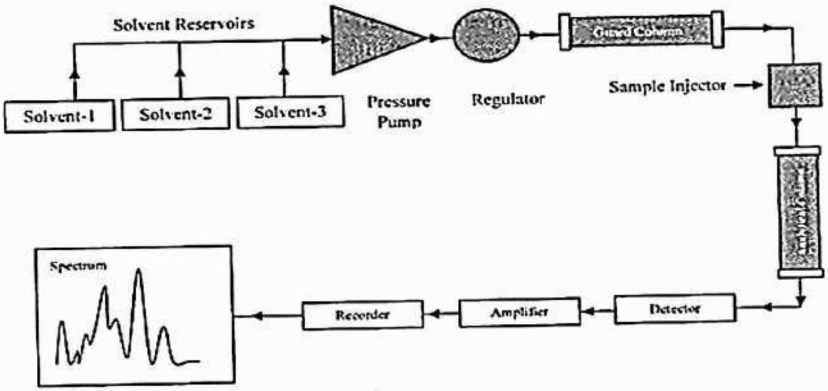
High Pressure Liquid Chromatography (HPLC)

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

i) Solvent delivery system
ii) Sample injection system
iii) Chromatographic column
iv) Detector
v) 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 pellicellar 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.

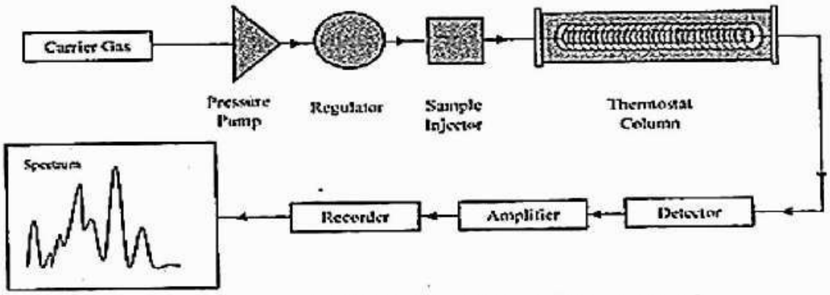
Gas chromatography (GC)

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, H_2 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 leave 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.

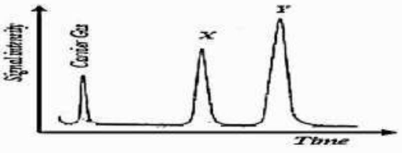


Figure shows the chromatogram of mixture of two gases X & Y. First peak always represents the carrier gas and other two peaks represent the pure components X & Y. Each component can be identified by actual isolation time or retention time. It is the time required for the components to emerge from the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

MODULE IV

POLYMER & NANOTECHNOLOGY

Co- polymers

Polymers which are formed by the polymerization of two or more different monomers are called co-polymers. (Eg. BS, ABS co-polymers)

Types of co-polymers

1. Random co-polymer:

If the monomeric units are arranged in a random fashion, then the co-polymer is known as random co-polymer.

·····A – B – B – B – A – A – B – A – B – A – A – A – B·····

2. Alternating co-polymer

If the monomers are arranged in a regular alternating fashion, then it is called alternating co-polymer.

·····A – B – A – B – A – B – A – B – A – B – A – B – A – B·····

3. Block co-polymer

Co-polymer which can be formed with a long chain of homo polymer followed by a block of another homo polymer chain, then it is called block co-polymer.

·····A – A – A – A – A – B – B – B – B – B·····

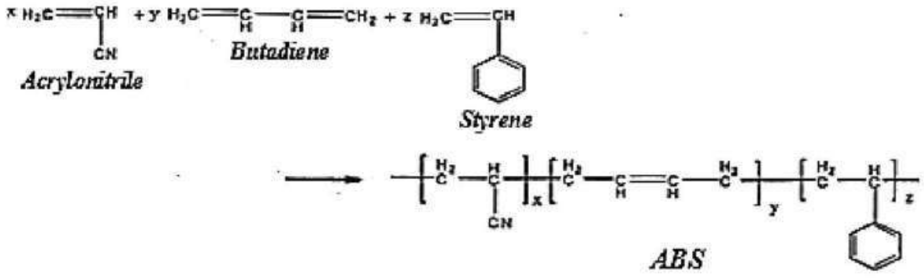
4. Graft co-polymer

Co-polymers can be formed with homo polymers remaining grafted to the main chain of homo polymer at intervals, and then it is called graft co-polymer.

ABS (Acrylonitrile Butadiene Styrene)

Preparation:

It is obtained by dissolving poly butadiene in liquid acrylonitrile and styrene in presence of free radical initiator.



Properties:

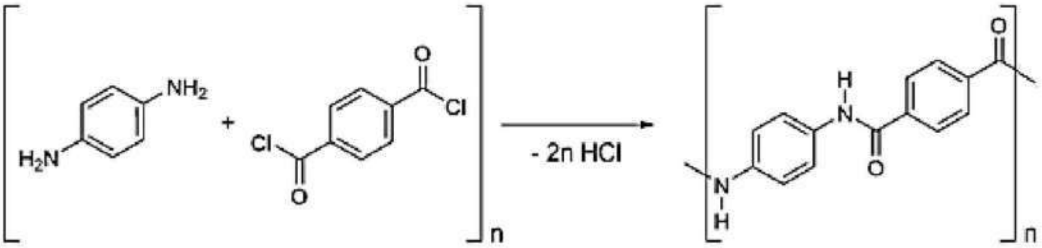
- Very hard, rigid and tough material.
- Resistive to impact, stretch, bent etc.
- Possess high tensile strength.
- Possess stiffness.
- Possess chemical resistance and heat resistance.
- Ductile in nature.

Uses:

- Used for making automobile parts.
- Used for making building materials.
- Used for making house wares such as refrigerator parts, parts of micro wave oven, coffee maker etc.

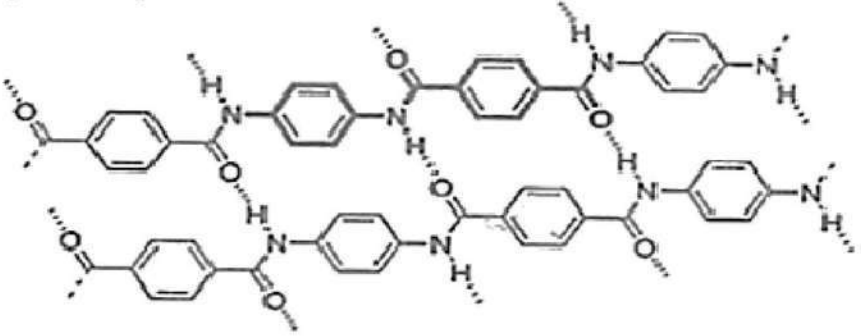
KEVLAR (PPTA)

KEVLAR is poly para-phenylene terephthalamide. It is obtained by the condensation polymerization of para phenylene diamine and terephthaloyl chloride.



Structure of KEVLAR

It possesses planar sheet like structure.



Three types of bonding are possible in Kevlar.

1. Covalent bonding

It is the strongest bonding in Kevlar.

2. Vander Waals forces of interaction

These are weak bondings. Different chains in the Kevlar structure are held together by Vander Waals forces of interaction.

3. Hydrogen bonding

Hydrogen bondings are possible between amide linkages.

Due to the difference in the strength of covalent and Vander waals forces, Kevlar possesses anisotropy.

Properties:

- It is five times stronger than steel.
- Possess high tensile strength and chemical resistance.
- Extremely light weight material.
- Possess heat resistance.

Uses:

- For making bullet proof vests
- For making industrial gloves, helmets, body pads etc.
- For making sports equipments.
- For making industrial hoses.

Conducting Polymers

Recently synthesized organic polymers are called organo electronic compounds. They can function as conductor or super conductor. Polymers are usually poor conductors of electricity, because of the absence of free electrons.

Polymers which can conduct electricity is called **conducting polymers**.

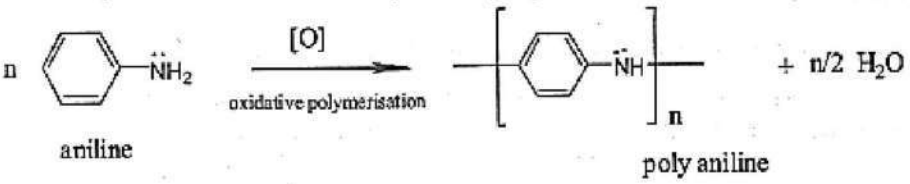
Eg.Polyacetylene, polyaniline, polypyrrole etc.

The first widely studied is polyacetylene. Its conductivity can be increased by a factor of 10^{12} by doping it with an electron donor like alkaline earth metal ion or an electron acceptor like I_2 or AsF_5.

Conductivity increases with decrease in band gap because in that case small amount of energy is required to promote an electron from valence band to the conduction band. In the case of polymeric insulators band gap is very large(1.5-4eV) which obstruct the flow of electrons. 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)

Poly aniline:

Poly aniline is a conducting polymer obtained by the oxidative polymerization of aniline. It is also obtained by the self-stabilized dispersion polymerization of aniline



The conductivity of poly aniline is due to the transfer of electrons along the conjugated system, which is due to the presence of lone pair of electrons on nitrogen. Conductivity of poly aniline can be increased by protonation. At room temperature its conductivity is 1000Scm-1.It is soluble organic solvents.

Properties:

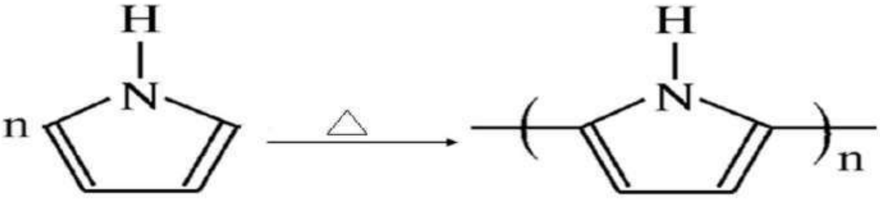
- It is highly flexible
- Possess high strength.
- Low cost material.
- It is stable both in air and water.
- Possess excellent anti-corrosion property.

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 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:

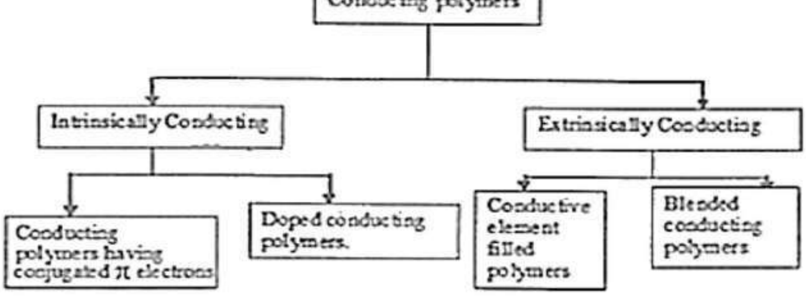
- It has excellent thermal, chemical and mechanical properties.
- It can be processed into any desired shape.
- It has good environmental stability.
- Electrical resistance decreases with increase in temperature. Hence conductivity increases.

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

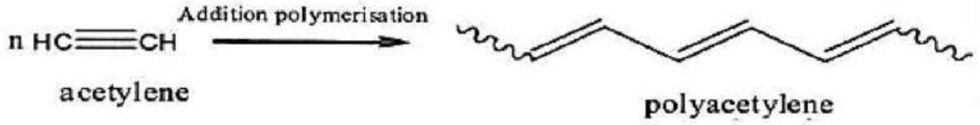
1) Intrinsically conducting polymers
2) Extrinsically conducting polymers

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

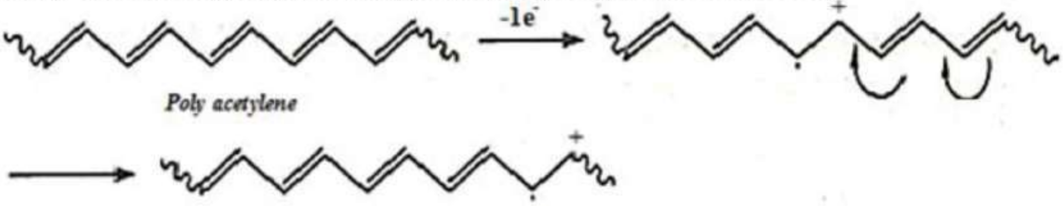


b) Doped conducting polymers:

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:

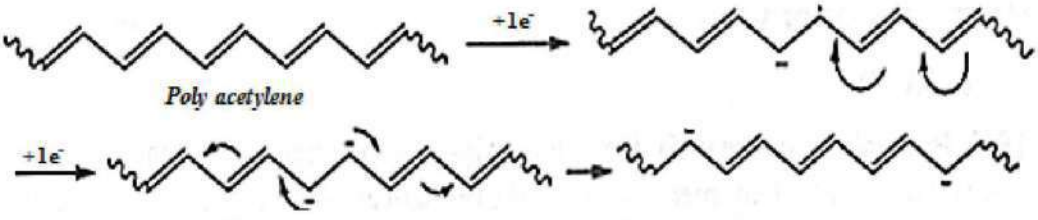
p – Doping is done by oxidation process. In this process some electrons of the π-bonds of the conjugated double bonds are removed and holes are created which can move along the polymer and the polymer becomes electrically conductive. The radical cation produced is called poloron. The polorons are mobile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



Propagation of poloron through the conjugated polymer chain by shifting of double bonds

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 poloron and bipoloron in two steps.



Propagation of bipoloron through the conjugated polymer chain by shifting of double bonds

2) Extrinsically 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
• 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.	• Done by reduction • Negative charge is created during the process. • Polorons and bipolorons 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.

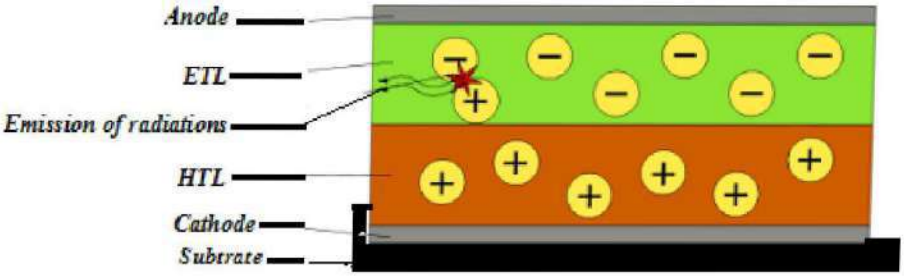
ETL:

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.

Schematic bilayer of OLED



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.

NANO TECHNOLOGY

Nanomaterials

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

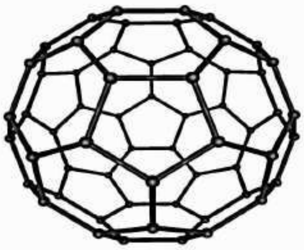
Classification:

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 buck minister fullerene (buckymann, 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 silsequioxane:

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 (Silsequiox) and to a hydrocarbon group (ane). Hence the name polyhedral silsequioxane.

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 plastc 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, multinanolayers.

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)

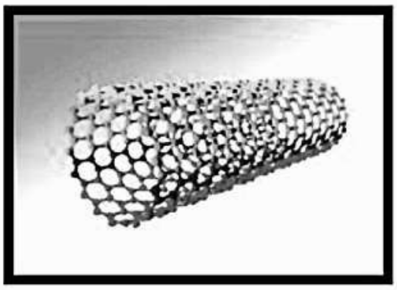
- **SWCN:**

They contain only one nanotube cylinder.

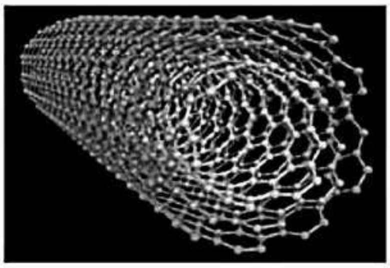
- **MWCN:**

They contain more than one nanotube cylinders.

SWCN



MWCN



Properties:

- Young's modulus is 10 times more than that of steel.
- They possess excellent magneto resistance.
- They are very stiff, hard to bend. Once they are bent, they are very resilient.
- Their thermal conductivity is more than diamond and is very high.
- They are very good conductors of electricity.

Uses of nanotubes:

- They can be used as mechanical reinforcement material.
- It can be used a catalyst in many reactions.
- Lithium which is a charge carrier in some of the batteries can be stored inside the nanotube.
- They can be used in field effect transistors.
- They can be used as paper batteries.
- They can be used in solar cells.

Synthesis of nano materials:

1. Reduction :

a) Chemical Reduction:

Molybdenum nano particles can be obtained by reducing molybdenum chloride in toluene using tri ethyl boro hydride.

$MoCl_3 + 3NaB\,(C_2H_5)_3H \rightarrow Mo + 3NaCl + B\,(C_2H_5)_3 + {}^{3}/_{2}H_2$

Tri ethyl lithium boro hydride, sodium boro hydride can also be used as reducing agents.

b) Electro reduction:

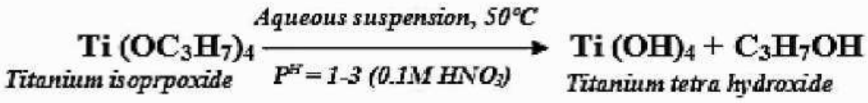
Copper nanoparticles can be prepared by this method. The electro reduction process chamber consists of a copper plating bath containing homogeneous acidified $CuSO_4$ solution. The nano particles formed as spongy layers of ball structures at the cathode. These spongy layers of Cu can be easily separated to give fine nano particles.

2. Hydrolysis: Sol- Gel Method or Chemical Solution Deposition

This method is used for the synthesis of nano crystalline titanium powder.

STEP I:

Nano crystalline TiO_2 powder is prepared by the hydrolysis of titanium isopropoxide to get a sol(Solid in liquid).



$$\underset{\text{Titanium isoprpoxide}}{Ti\,(OC_3H_7)_4} \xrightarrow[P^{H} = 1\text{-}3\ (0.1M\ HNO_3)]{\text{Aqueous suspension, } 50^\circ C} \underset{\text{Titanium tetra hydroxide}}{Ti\,(OH)_4 + C_3H_7OH}$$

STEP II:

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.

$$\underset{\textit{Titanium tetra hydroxide}}{Ti(OH)_4} \xrightarrow[P^H = 1\text{-}3\ (0.1M\ HNO_3)]{\textit{Aqueous suspension, } 60\text{-}70^\circ C} TiO_2 + 2H_2O$$

Resultant TiO_2 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 TiO_2 gel(Liquid in solid).

STEP III:

In this step TiO_2 gel is annealed to get Nano crystalline TiO_2.

$$TiO2_{\text{Gel}} \xrightarrow[P^H = 1\text{-}3\ (0.1M\ HNO_3)]{\textit{Aqueous suspension, } 50^\circ C} \text{Nano - TiO2}$$

Scanning Electron Microscopy (SEM)

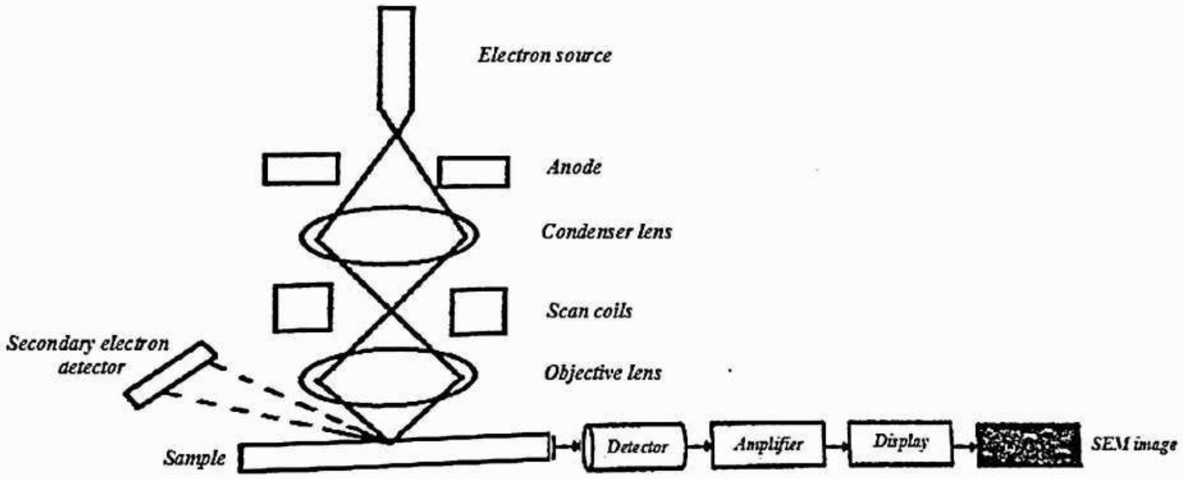
SEM is an important surface characterisation technique used in nanotechnology. It is a type of electron microscope that produces images of a sample by scanning the surface with a focused beam of electrons. This can provide information about topography (surface features), morphology (shape and size of 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 – 5

INTRODUCTION

Fuel is a combustible substance containing carbon as the major constituent which on proper burning gives large amount of heat that can be used economically for domestic and industrial purposes. In other words any source of heat energy is termed as fuel. e.g., wood, coal, charcoal, kerosene, petrol, producer gas etc.

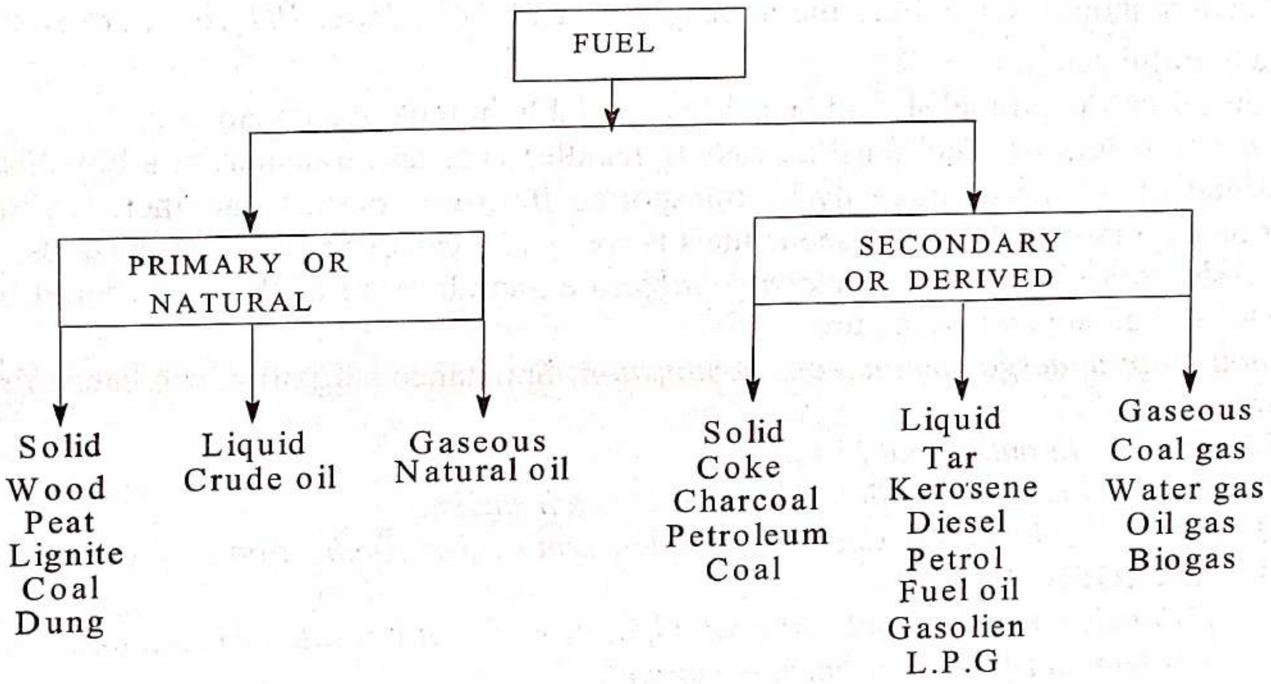
During the process of combustion of a fuel like coal, the atoms of carbon, hydrogen etc. combine with oxygen simultaneously liberating heat at a rapid rate. The energy is liberated due to rearrangement of valence electrons in these atoms resulting formation of compounds [CO_2, H_2O etc.]. The products have comparatively less energy. So the energy released during the process of combustion is the difference of energy of reactants and that of products.

$$Fuel + O_2 \xrightarrow{\qquad} \text{Pr}oducts + Heat$$

However, combustion is not necessary for a fuel to give out energy. According to the modern concept of fuel, any chemical or reactant which produces energy in a form that can be used for production of power is called fuel. A typical example of this is fuel cell.

CLASSIFICATION OF FUEL

The fossil fuels have been classified according to their: (a) occurrence, and (b) the state of aggregation. According to occurrence fuel is of natural (primary) or derived (secondary) type and according to state of aggregation the fuels are classified as solid, liquid and gaseous fuels.



CHARACTERISTICS OF A GOOD FUEL

(a) *High calorific value*: A fuel should possess high calorific value, since the amount of heat liberated and temperature attained thereby depends upon the calorific value of fuel.

(b) *Moderate ignition temperature*: Ignition temperature is the lowest temperature to which the fuel must be preheated so that it starts burning smoothly. Low ignition temperature is dangerous for storage and transport of fuel, since it can cause fire hazards. On the other hand, high ignition temperature cause difficulty in the ignition of the fuel, but the fuel is safe during storage, handling and transport. Hence, an ideal fuel should have moderate ignition temperature.

(c) *Low moisture content*: The moisture content of the fuel reduces the heating value and involves in a loss of money, because it is paid for at the same rate as the fuel. Hence, fuel should have low moisture content.

(d) *Low non-combustible matter content*: After combustion, the non-combustible matter remains, generally, in the form of ash or clinker. The non-combustible matter also reduces the heating value, besides additional cost of storage, handling and disposal of the waste products produced. Each percent of non-combustible matter in fuel means a heat loss of about 1.5%. Hence, a fuel should have low content of non-combustible matter.

(e) *Moderate velocity of combustion*: If the rate of combustion is low, then the required high temperature may not be possible, because a part of the heat liberated may get radiated, instead of raising the temperature. On the other hand, too high combustion rates are also not required.

(f) *Products of combustion should not be harmful*: Fuel, on burning, should not give out objectionable and harmful gases. In other words, the gaseous products of combustion should not pollute the atmosphere. CO, SO_2, H_2S, PH_3, etc., are some of the harmful gases.

(g) *Low cost*: A good fuel should be readily available in bulk at a cheap rate.

(h) *Easy to transport*: Fuel must be easy to handle, store and transport at a low cost. Solid and liquid fuels can easily be transported from one place to another. On the other hand, transportation of gaseous fuels is costly and can even cause fire hazards.

(i) *Combustion should be easily controllable*: i.e., combustion of the fuel should be easy to start or stop, when required.

(j) *Should not undergo spontaneous combustion*: Spontaneous ignition can cause fire hazards.

(k) *Storage cost in bulk should be low.*

(l) *Should burn in air with efficiency, without much smoke.*

(m) *In case of solid fuel, the size should be uniform so that combustion is regular.*

CALORIFIC VALUE

Calorific value of a fuel is the total quantity of heat liberated when a unit mass (or volume) of the fuel is burnt completely.

(a) Higher or Gross Calorific Value: Hydrogen is found to be present in almost all fuels and when the calorific value of fuel is determined experimentally, hydrogen is converted into steam. If the product of combustion are condensed to room temperature (i.e., 25°C or 77°F), the latent heat of condensation of steam is also included in the measured heat. *The total value calculated is known as higher or gross calorific value [HCV] and may be defined as the total amount of heat liberated when one unit of the fuel is burnt completely and the combustion products are cooled to room temperature.*

(b) Lower or net calorific value: In actual use of any fuel, the water vapour and moisture, etc., are not condensed and escape as such along with hot combustion gases. Hence, a lesser amount of heat is available. So, *net or lower calorific value [LCV] is the heat produced, when unit mass/ volume of the fuel is burnt completely and the products are permitted to escape.*

Thus, Net or lower calorific value[LCV] = HCV - Latent heat of water vapour formed

Now since one part by mass of hydrogen gives nine parts by mass of water, the equation becomes:

Net or lower calorific value[LCV] = HCV - Mass of $H_2 \times 9 \times$ Latent heat of steam

The latent heat of steam is 587 kcl/kg or 1060 B.Th.U/Ib of water vapour formed at room temperature (i.e., 25°C)

Units of calorific value: The calorific value is, generally, expressed in calorie/gram (cal/g) or kilocalorie/kg (kcal/kg) or British thermal unit (B.Th.U/lb) in case of solid or liquid fuel. In case of gaseous fuels, the units used are kilocalorie/cubic metre (kcal/m^3) or B.Th.U./cubic feet (B.Th.U./ft^3).

THEORITICAL CALCULATION OF CALORIFIC VALUE OF A FUEL

The calorific value of fuel can be approximately calculated by noting the amounts of constituents of the fuel. The higher calorific value of some combustible constituents of fuel are given Table.5A.1.

Table 5A.1: Calorific value of fuel constituents

Constituents	HCV(kcal/kg)
H	34,500
C	8,080
S	2,240

The oxygen (if present) in the fuel is assumed to be present in combined form with hydrogen i.e., in the form of fixed hydrogen (H_2O).

Amount of hydrogen -

available for combustion = $Total\ mass\ of\ hydrogen\ in\ fuel - Fixed\ hydrogen$

$= Total\ mass\ of\ hydrogen\ \ in\ fuel - (1/8)\ mass\ of\ oxygen\ in\ fuel$

[∴ 8 parts of oxygen combine with one part of hydrogen to form H_2O]

Dulong's formula for calorific value from the chemical composition of fuel is,

$$HCV = \frac{1}{100}\left[8{,}080\,C + 34{,}500\left\{H - \frac{O}{8}\right\} + 2{,}240\,S\right] kcal/kg$$

Where, C, H, O and S are the percentages of carbon, hydrogen, oxygen and sulphur in the fuel respectively.

Oxygen is assumed to be present in combination with hydrogen as water.

$$LCV = \left[HCV - \frac{9}{100}H \times 587\right] kcal/kg$$

$$\therefore\ LCV = [HCV - 0.09H \times 587]\,kcal/kg$$

As 1 part of H by mass gives 9 parts of H_2O

$$2H_2 + O_2 \longrightarrow 2H_2O$$

$$By\,Wt. \quad 4 \qquad\qquad 36$$

Latent heat of steam $= 587\,kcal/kg$

SOLVED EXERCISES USING DULONG'S FORMULA

Exercise 1. Calculate the gross and net calorific value of coal having the following composition: $C = 85\%,\ H = 8\%,\ S = 1\%,\ N = 2\%,\ ash = 4\%$, latent heat of steam $= 587\,cal/g.$

Solution: Gross calorific value (GCV):

$$GCV = \frac{1}{100}\left[8{,}080\,C + 34{,}500\left(H - \frac{O}{8}\right) + 2{,}240\,S\right] kcal/kg$$

$$= \frac{1}{100}\left[8{,}080 \times 85 + 34{,}500\left(H - \frac{0}{8}\right) + 2{,}240 \times 1\right] kcal/kg$$

$$= \frac{1}{100}[686{,}800 + 276{,}000 + 2{,}240]\,kcal/kg$$

$$= \frac{1}{100}[965{,}040]\,kcal/kg = 9{,}650.4\,kcal/kg$$

Net calorific value (NCV) $= (GCV - 0.09\,H \times 587)\,kcal/kg$

$$= (9{,}650.4 - 0.09 \times 8 \times 587)\,kcal/kg.$$

Exercise 2. A coal has the following composition by weight: $C = 90\%,\ O = 3.0\%$, $S = 0.5\%,\ N = 0.5\%,\ ash = 2.5\%$. Net calorific value of the coal was found to be 8,490.5kcal/kg. Calculate the percentage of hydrogen and higher calorific value of coal.

Solution: HCV) $= (HCV + 0.09\,H \times 587)\,kcal/kg$

$$= (8{,}490.5 + 0.09\,H \times 587)\,kcal/kg$$

$$= (8{,}490.5 + 52.8)\,kcal/kg \ ----------(i)$$

$$HCV = \frac{1}{100}\left[8{,}080\ C + 34{,}500\left(H - \frac{O}{8}\right) + 2{,}240\ S\right] kcal\ /\ kg$$

$$= \frac{1}{100}\left[8{,}080 \times 90 + 34{,}500\left(H - \frac{3.0}{8}\right) + 2{,}240 \times 0.5\right] kcal\ /\ kg$$

$$= [7{,}272 + 345\ H - 129.4 + 11.2]\, kcal\ /\ kg$$

$$= [7{,}754.8 + 345\ H]\, kcal\ /\ kg \qquad ----------(ii)$$

From (i) and (ii), we get:

$$7{,}754.8 + 345\,H = 8{,}490.5 + 52.8H$$

$$292.2\,H = 8{,}490.5 - 7{,}154.8 = 1{,}335.7$$

$$Percentage\ of\ H = \frac{1{,}335.7}{292.2} = 4.575\% ------------(iii)$$

$$HCV = (8{,}490.5 + 52.8 \times 4.575)\, kcal\,/\,kg \qquad [From\,(i)\,and\,(iii)]$$

$$\therefore \quad = (8{,}490.5 + 241.3)\, kcal\,/\,kg = 8{,}731.8\, kcal\,/\,kg$$

Exercise 3. 0.72g of a fuel containing 80% carbon, when burnt in a bomb calorimeter, increased the temperature of water from 27.3 – 29.1°C. If the calorimeter contains 250g of water and its water equivalent is 150 g, calculate the HCV of the fuel. Give your answer in kJ/kg.

Solution: Here $x = 0.72g,\ W = 250g,\ w = 150g,\ t_1 = 27.3\ °C,\ t_2 = 29.1\ °C.$

$$HCV\ \ of\ \ fuel\,(L) = \frac{(W + w)(t_2 - t_1)}{x}\, kcal\,/\,kg$$

$$= \frac{(250 + 150)(29.1 - 27.3)}{0.72}\, kcal\,/\,kg = 1{,}000 \times 4.2\, kJ\,/\,kg = 4{,}200\ kJ\,/\,kg$$

Exercise 4. When 0.84g of sample of fuel was completely burnt in excess of oxygen, the increase in temperature of water in a calorimeter containing 1060 g of water was 2.5°C. Calculate the HCV of fuel, if water equivalent of calorimeter is 135g.

Solution: Here $x = 0.84g,\ W = 1060g,\ w = 135g,\ t_2 - t_1 = 2.5\ °C.$

$$HCV\ \ of\ \ fuel\,(L) = \frac{(W + w)(t_2 - t_1)}{x}\, kcal\,/\,kg$$

$$= \frac{(1060 + 135)2.5}{0.84}\, kcal\,/\,kg = 3556.55\, kcal\,/\,kg.$$

Exercise 5. A sample of coal contains: $C = 93\%,\ H = 6\%$ and $ash = 1\%$. The following data were obtained when the above coal was tested in bomb calorimeter: (i) Weight of coal burnt = 0.92g, (ii) Weight of water taken = 550g, (iii) Water equivalent of bomb calorimeter = 2,200g, (iv)Rise in temperature = 2.42°C, (v) Fuse wire correction = 10cal, (vi) Acid correction = 50 cal. Calculate gross and net calorific value of the coal, assuming the latent heat of condensation of steam as 580cal/kg.

Solution: Weight of coal sample (x) = 0.92g, weight of water (W) = 550g, water equivalent of calorimeter (w) = 2,200g, temperature rise $(t_2 - t_1)$ = 2.42°C, acid correction = 50 cal, fuse wire correction = 10 cal., latent heat of steam = 580 cal/g, percentage of hydrogen = 6%.

$$GCV\ of\ fuel\ = \frac{(W + w)(t_2 - t_1) - [Acid + Fuse\ correction]}{x}$$

$$= \frac{(550 + 2{,}200)2.42 - [50 + 10]}{0.92} = 7{,}168.5\,cal/g.$$

$$NCV = [GCV - 0.09\,H \times Latent\ heat\ of\ steam]$$

$$= [7{,}168.5 - 0.09 \times 6 \times 580]\,cal/g = 6{,}855.3\,cal/g$$

Exercise 6. The following data were obtained in a Boy's gas calorimeter experiment. Volume of gas used = 0.1m^3 at STP, weight of water heated = 25kg, temperature of the inlet water = 20°C, temperature of the outlet water = 33°C, weight of steam condensed = 0.025kg. Calculate HCV and LCV per m^3 at STP. Take the heat liberated in condensing water vapour and cooling the condensate as 580 kcal/kg.

Solution: $V = 0.1\text{m}^3$, W=25kg, t_1 =20°C, t_2 =33°C, m = 0.025kg.

$$HCV\,(L)\frac{W(t_2 - t_1)}{V} = \frac{25(33 - 20)}{0.1} = 3{,}250\,kcal/m^3$$

$$LCV = HCV - \left(W'/V\right) \times 580$$

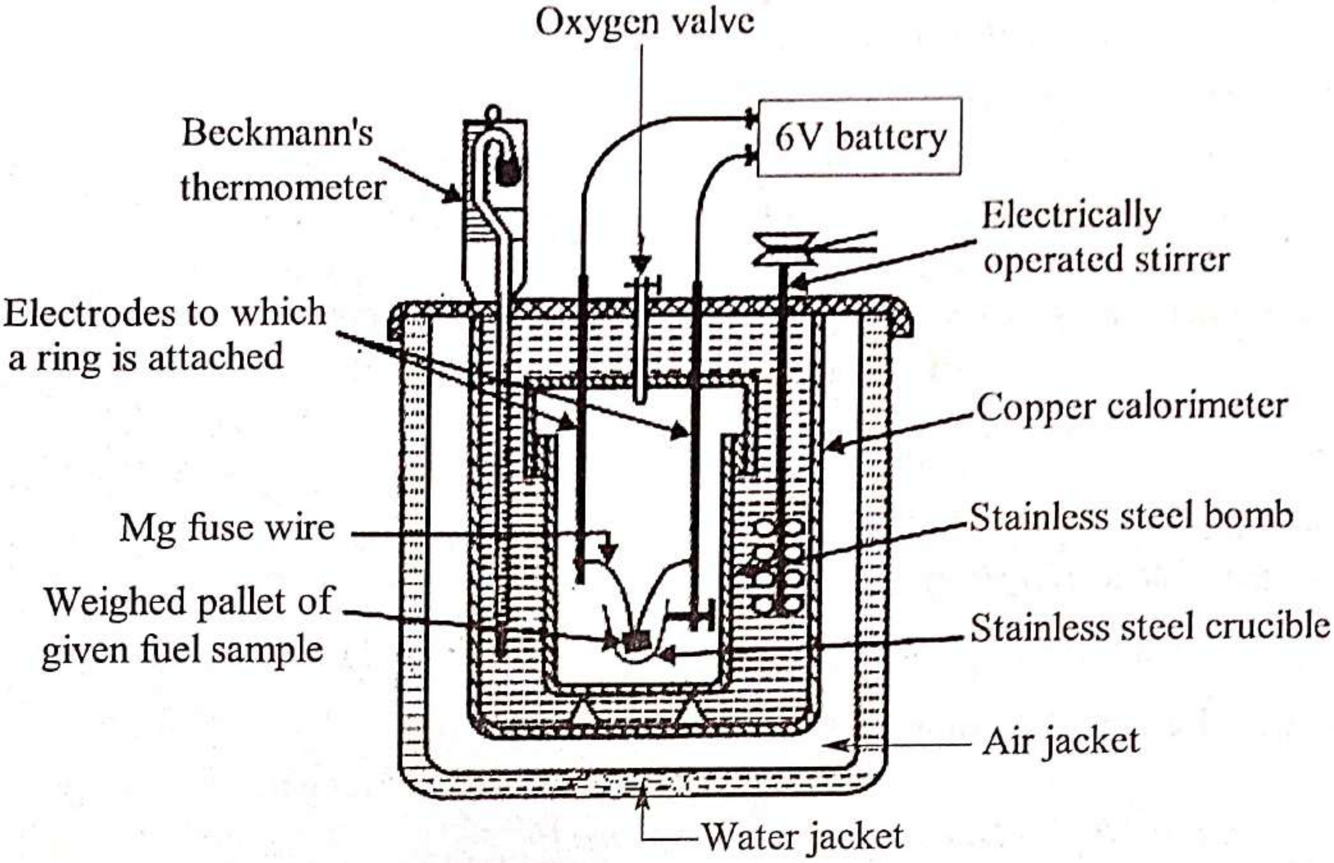
$$= 3{,}250 - \frac{0.025}{0.1} \times 580 = 3{,}105\,kcal/m^3$$

DETERMINATION OF CALORIFIC VALUE

1. Bomb calorimeter:

Bomb calorimeter is used for determining the calorific value of solid and liquid fuels.

Construction: A simple sketch of bomb calorimeter is shown in Fig.5A.1. It consists of strong cylindrical stainless steel bomb in which the combustion of fuel is carried out. The bomb has a lid, which can be screwed to the body of bomb so as to make a perfect gas tight seal. The lid is provided with two stainless steel electrodes and an oxygen inlet valve. To one of the electrodes, a small ring is attached. In this ring, a nickel or stainless steel crucible can be supported. The bomb is placed in a copper calorimeter which is surrounded by an air jacket and water jacket to prevent heat loss due to radiation. The calorimeter is provided with an electrically operated stirrer and Beckmann's thermometer, sensitive enough to read up to 0.01°C



Bomb calorimeter

Working: A weighed amount of the fuel is taken in the clean crucible. The crucible is supported over the ring. A fine magnesium wire touching the fuel sample is then stretched across the electrodes. The bomb lid is tightly screwed and bomb is filled with oxygen to 25 atmospheric pressure. The bomb is then lowered into copper calorimeter, containing a known mass of water. The stirrer is worked and initial temperature of water is noted. The electrodes are then connected to six volt battery and circuit is completed. The sample burns and heat is liberated. Uniform stirring of water is continued and the maximum temperature attained is recorded.

Observation:

Weight of the fuel taken $= x\,gm$

Weight of water in calorimeter $= W\,gm$

Water equivalent of the calorimeter, stirrer, thermometer and bomb

$$= Wt.of\ apparatus \times Specific\ heat = W\ gm$$

Initial temperature of water in calorimeter $= t_1\ {}^0C$

Final temperature of water in calorimeter $= t_2\ {}^0C$

Let the higher calorific value of fuel $= L\,cal/g$

Calculations:

Heat gained by water $= W \times (t_2 - t_1)\, cal$

Heat gained by calorimeter $= w \times (t_2 - t_1)\, cal$

Total heat gained $= W(t_2 - t_1) + w(t_2 - t_1)\, cal$

$$= (W + w)(t_2 - t_1)\, cal$$

Heat liberated by fuel $= x \times L$

i.e., Heat liberated by fuel $=$ *Heat gained by water and calorimeter*

$$x \times L = (W + w)(t_2 - t_1)$$

$$HCV\,(L) = \frac{(W + w)(t_2 - t_1)}{x}\, cal/g$$

To calculate lower (net) calorific value:

Let the percentage of hydrogen in fuel $= H$

Weight of water produced from 1gm of fuel $= \frac{9H}{100}\, gm = 0.09\,H\, gm$

Heat taken by water in forming steam $= 0.09\,H \times 587\, cal$

[Latent heat of steam $= 587 cal/gm$]

Hence, $LCV = HCV - Latent\ heat\ of\ water\ formed$

$$= (L - 0.09H \times 587)\, cal/gm$$

Corrections: For accuracy, the following corrections must be taken into consideration.

(i) Cooling correction: Rate and time taken for cooling the water in calorimeter from maximum temperature to room temperature must be considered. From the rate of cooling (dt^0/minute) and the actual time taken for cooling (t minutes), the cooling correction of $dt \times t$ is added to the rise in temperature.

$$L = \frac{(W + w)(t_2 - t_1 + Cooling\ correction) - [Acid + Fuse\ corrections]}{Mass\ of\ fuel\,(x)}$$

(ii) Fuse wire correction: The heat liberated, as measured above includes the heat given out by ignition of the fuse wire used.

(iii) Acid correction: During ignition, sulphur and nitrogen (if present) in the fuel are oxidized to the corresponding acids along with the evolution of heat.

$$S + 2H + 2O_2 \xrightarrow{\quad} H_2SO_4 + Heat$$

$$2N + 2H + 3O_2 \xrightarrow{\quad} 2HNO_3 + Heat$$

So this heat is also included in the measured heat and hence must be subtracted. The amount of these acids are analyzed from washings of bomb by titration, while sulphuric acid alone is determined by precipitation as $BaSO_4$. Correction for 1 mg of S is 2.25 cal while for 1 ml N/10 HNO_3 formed is 1.43 cal.

LIQUID FUELS

Liquid fuels are characterized by low flash point, high calorific value, low viscosity at ordinary temperature and low moisture and sulphur content.

1. Petroleum

Petroleum or crude oil (derived from Latin Petra =rock and oleum =oil) is a dark greenish brown, viscous oil found deep in earth's crust. It is composed mainly of various hydrocarbons (like straight chain paraffins, cycloparaffins or naphthalenes, olefins and aromatics), together wit small amounts of organic compounds containing oxygen, nitrogen, and sulphur. The oil is usually, found floating upon a layer of brine and has a layer of gas top of it. The average composition of crude petroleum is: $C = 79.5 \, to \, 87.1$, $H = 11.5 \ to \ 14.8\%$, $S = 0.1 \ to \ 3.5\%$, $N + O = 0.1 \ to \ 0.5\%$.

Classification of petroleum: Petroleum is classified into three categories according to its compositions.

(i) Paraffinic base type of crude is mainly composed of the saturated hydrocarbon from CH_4 to $C_{35}H_{72}$ and a little of the naphthalenes and aromatics. The hydrocarbon from $C_{18}H_{38}$ to $C_{35}H_{72}$ are semisolids, called waxes.

(ii) Asphaltic base type crude contains mainly cycloparaffins or naphthalenes with smaller amount of paraffins and aromatic hydrocarbon.

(iii) Mixed base type crude contains both paraffinic and asphaltic hydrocarbons and are, generally, rich in semi solid waxes.

Mining of petroleum done by drilling holes in earth's crust and sinking pipes up to the oil bearing porous rocks. Oil, usually gushes out itself due to hydrostatic pressure of natural gas. Alternatively, it may be mechanically pumped up by using either lift pump or air lift pump. The latter consists of two co-axial pipes, lowered into the base of oil bed. Compressed air is forced through the outer pipe, whereby oil comes out through the inner pipe. The oil is conveyed to refinery by a system of pipelines.

Refining of crude oil: The crude oil is separated into various useful fractions by fractional distillation and finally converted into desired specific products. The process is called refining of crude oil and the plants set up for the purpose are called the oil refineries. The process of refining involves the following steps:

Step 1. Separation of water (Cottrell's process): The crude oil from the oil well is an extremely stable emulsion of oil and salt water. The process of freeing oil from water consists in allowing the crude to flow between two highly charged electrodes. The colloidal water droplets coalesce to form large drops, which separate out from oil.

Step 2. Removal of harmful sulphur compounds involves in treating oil with copper oxide. A reaction occurs with sulphur compounds, which results in the formation of copper sulphide (a solid), which is then removed by filtration.

Step 3. Fractional distillation: The crude oil is then heated to about 400-430°C in an iron retort, whereby all volatile constituents, except the residue (asphalt or coke) are evaporated. The hot vapours are then passed up a fractional column, which is a tall cylindrical tower containing a number of horizontal stainless steel trays at short distances. Each tray is provided with small chimney, covered with a loose cap. As the vapours go up, they become gradually cooler and fractional condensation takes place at different heights of column. Higher boiling fraction condenses first, while lower boiling fractions turn-by-turn. Various principal fractionation products thus obtained are given in Table.

Table : Fractions by distillation of crude

Name of fraction	Boiling range	Approx. composition	Uses
1.Uncondensed gases	below 30°C	C_1 to C_5	Domestic fuel (LPG), synthesis of organic chemicals, production of carbon black.
2. Petroleum ether	30-70°C	C_5 to C_7	As a solvent for oil, varnishes.
3.Gasoline or petrol	40-120°C	C_5 to C_{10}	Fuel for internal combustion engine of automobiles, aero-planes, solvent and dry cleaning
4. Naphtha	120-180°C	C_9 to C_{10}	As solvent and dry cleaning.
5. Kerosene	180-250°C	C_{10} to ${}_{16}$	Illuminant, fuel for stoves.
6. Diesel oil	250-320°C	C_{10} to ${}_{18}$	Fuel for diesel engine.
7. Heavy oil on refractionation gives:	320-400°C	C_{17} to ${}_{30}$	Lubrication.
(i) Lubricating oil	-	-	Lubricants, cosmetics.
(ii) Petroleum jelly	-	-	Medicines.
(iii) Grease	-	-	Lubricant.
(iv) Paraffin waxes	-	-	Candles, boot polish, wax paper, tarpolin cloth etc.
8. Residue may be either:	above 400°C	C_{30} and above	
(i) Asphalt or	-	-	Water proofing of roofs and road making.
(ii) Petroleum coke	-	-	As a fuel and in moulding arc light rods.

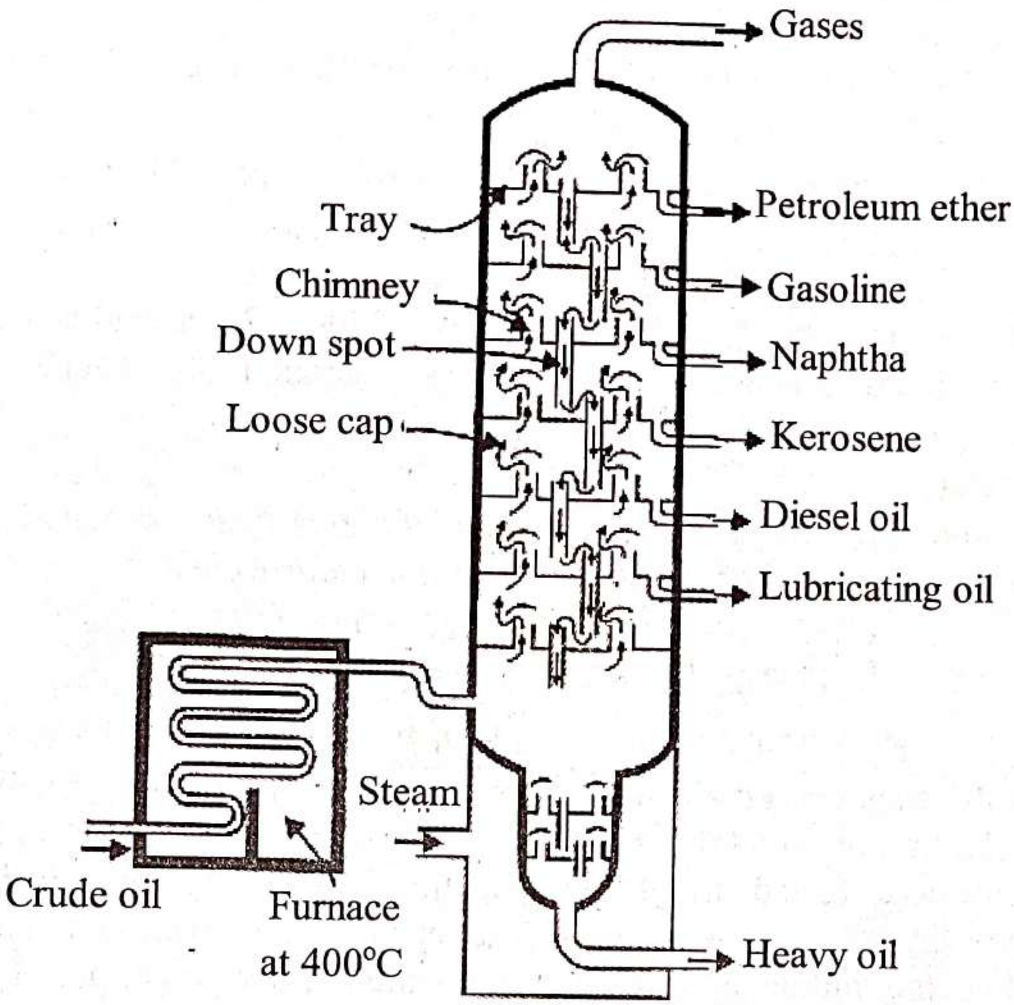


Fig.5A.3: Fractional distillation of crude petroleum

A brief description of four most important petreoleum products along with their uses:

(i) **Petroleum gas (LPG)**: Liquefied petroleum gas (LPG) is obtained as by product during the cracking of heavy oils or from natural gas and sold as bottled gas. These consist mainly of ethane, propane, butane and other volatile hydrocarbons. The main constituents of LPG are n-butane, isobutene butylenes, propane and very less ethane. LPG is supplied under pressure in containers under the trade name like Indanes, Hart gas etc. Its calorific value is about 27,800 kcal/m^3. LPG is dehydrated, desulphurised and traces of odorous organic sulphides (mercaptans) are added to give warning of gas leak. LPG is widely used as domestic and industrial fuel. Now a days this is also accepted as motor fuel.

(ii) **Gasoline or petrol**: Aviation fuel and motor petrol come under this group. This is a mixture of hydrocarbons such as C_5H_{12} to C_8H_{18}. Its approximate composition is: $C = 84\%$, $H = 15\%$, $N + S + O = 1\%$. Its calorific value is about 11,250 kcal/kg. It is highly volatile, inflammable and used as fuel for internal combustion engines of automobiles and aeroplanes.

(iii) **Kerosene**: This is the fraction obtained between 180-250°C and is a mixture of hydrocarbons such as $C_{10}H_{22}$ to $C_{16}H_{34}$. Its approximate composition is $C = 84\%, H = 16\%,$ with less than 1% of S. Its calorific value is 11,100kcal/kg. It has served as fuel for cooking especially where bottled gas is not obtainable. It finds use as jet engines fuel and for making oil gas.

(iv) **Diesel oil**: This is a fraction obtained between 250 – 320 °C and is a mixture of $C_{15}H_{32}$ to $C_{18}H_{38}$ hydrocarbons. Its calorific value is about 11,000 kcal/kg. It is used as a diesel engine fuel.

CRACKING

Cracking is defined as the decomposition of bigger hydrocarbon molecules into simpler, low boiling hydrocarbons of lower molecular weight.

$$\underset{\text{Decane}}{C_{10}H_{22}} \xrightarrow{\textit{Cracking}} \underbrace{\underset{\text{n-pentane}}{C_5H_{12}} \quad + \quad \underset{\text{Pentene}}{C_5H_{10}}}$$

$$B.P = 174^0 C \qquad\qquad B.P = 36^0 C$$

Of all the fractions obtained by fractionation of petroleum, gasoline has the largest demand as a motor fuel, but the yield of this fraction is only 20% of the crude. Also the quality of so called straight–run gasoline is not high. It has to be properly blended. Moreover, there is a surplus of heavier petroleum fractions. To overcome these difficulties, the middle and heavy fractions are cracked to get petrol. The petrol made by cracking has far better characteristics than straight-run petrol. There are two methods of cracking in use:

1. **Thermal cracking**: The heavy oils are subjected to high temperature and pressure, when the bigger hydrocarbon molecules break down to give smaller molecules of the paraffins, olefins plus some hydrogen. This process may be carried out either in liquid phase or vapour phase.

(a) **Liquid phase thermal cracking**: The heavy oil or gas oil stock is cracked at a suitable temperature of 475-530°C and under pressure of 100kg/cm^2. The cracked products are then separated in a fractionating column. The yield is 50-60% and octane rating of the petrol produced is 65-70.

(b) **Vapour phase thermal cracking**: The cracking oil is first vapourised and then cracked at about 600-650°C and under a lower pressure of 10-20kg/cm^2. This process is suitable only for those oils, which may be readily vaporized. It requires less time than the liquid phase method. Petrol obtained from vapour phase cracking has better anti-knock properties, but poorer stability than petrol from liquid phase cracking.

2. **Catalytic cracking**: When cracking is done in the presence of a catalyst usually a mixture of silica and alumina or aluminium silicate, it is known as catalytic cracking. There are two methods of catalytic cracking in use:

(a) **Fixed-bed catalytic cracking**: The oil vapours are heated in a preheater to cracking temperatures (420-450°C) and then forced through a catalytic chamber (containing artificial clay mixed with zirconium oxide) maintained at 425-450°C and 1.5kg/cm^2 pressure. During their passage through the tower, about 40% of the charge is converted into gasoline and about 2-4% carbon is formed. The latter gets adsorbed on the catalyst bed. The vapours produced are then passed through a fractionating column, where heavy oil fractions condense. The vapours are then led through a cooler, where some of the gases are condensed along with gasoline and uncondensed gases move on. The gasoline containing some dissolved gases is then sent to a stabilizer, where the dissolved gases are removed and pure gasoline is obtained.

The catalyst, after 8-10 hours stops functioning, due to the deposition of black layer of carbon, formed during cracking. This is re-activated by burning off the deposited carbon. During the re-activation interval, the vapours are diverted through another catalyst chamber.

(b) **Moving-bed catalytic cracking**: The solid catalyst is very finely powdered, so that it behaves almost as a fluid, which can be circulated in gas stream. The vapours of cracking stock (gas oil, heavy oil etc.) mixed with fluidized catalyst is forced up into a large reactor bed in which cracking of the heavier into lighter molecules occurs. Near the top of the reactor, there is a centrifugal separator (called cyclone), which allows only the cracked oil vapours to pass on to the fractionating column, but retains all the catalyst powder in the reactor itself. The catalyst powder gradually becomes heavier, due to coating with carbon, and settles to the bottom, from where it is forced by an air blast to regenerator maintained at 600°C.

In regenerator, carbon is burnt and the regenerated catalyst then flows through a stand pipe for mixing with fresh batch of incoming cracking oil. At the top of the regenerator, there is a separator, which permits only gases (CO_2 etc.) to pass out, but holds back catalyst particles.

Advantages of catalytic cracking

(1) The yield of petrol is higher. (2) The quality of petrol produced is better.(3) No external fuel is necessary for cracking. The heat required for cracking is derived from coal, embedded in the catalyst. (4) A lower pressure (about 1-5kg/cm^2) is needed in catalytic cracking. (5) The catalytic process can easily be controlled, so that desired products can be obtained. (6) The evolution of by-product gases can be minimized; thereby the yield of desired petrol is higher. (7) The product of cracking contains a higher amount of aromatic and hence, it possesses better anti-knock properties. (8) The product contains a very little amount of undesirable sulphur, because a major portion of it escapes out as H_2S gas, during cracking. (9) Catalysts are selective in their action and, therefore, they permit cracking of only the high boiling hydrocarbons. (10) In the presence of catalyst, cracking is more of naphthalene materials than that of paraffinic. So the products of catalytic cracking are more paraffinic.

SYNTHETIC PETROL

Petrol is synthesized by any of the following three methods:

1. **Polymerization**: The gases obtained as a by-product from cracking of heavy oils, etc., contain olefins (like ethylene, propene and butene) and alkanes (such as methane, ethane, propane and butane). When this gaseous mixture is subjected to high pressure and high temperature, with or with out the presence of catalyst, it polymerise to form higher hydrocarbons, resembling gasoline, called polymer gasoline.

$$\underset{Propene}{CH_3.CH=CH_2} + \underset{1-Butene}{CH_3.CH_2.CH=CH_2} \xrightarrow{Pressure/\,heat/\,catalyst} \underset{5-methyl-1-hexene}{CH_2=CH.CH_2.CH_2.CH(CH_3)_2}$$

The polymerization is of two types:

(i) Thermal polymerization in which polymerization of cracked gases is carried out at 500-600°C and 75-350kg/cm^2 pressure. The products are gasoline and gas oil mixture, which are separated by fractionation.

(ii) Catalytic polymerization is carried out in presence of catalyst like phosphoric acid. In this case, lower temperature of 150-200°C is employed. Products are gasoline and unpolymerized gas. The latter is separated and recycled for polymerization.

2. **Fischer Tropsh method**: Water gas ($CO+H_2$), produced by passing steam over heated coke, is mixed with hydrogen. The gas is purified by passing through Fe_2O_3 (to remove H_2S) and then into a mixture of $Fe_2O_3.Na_2CO_3$ (to remove organic sulphur compounds). The purified gas is compressed to 5 to 25 atm and then led through a convertor (containing a catalyst, consisting of a mixture of 100 parts cobalt, 5 parts thoria, 8parts magnesia and parts keiselguhar earth), maintained at about 200-300°C. A mixture of saturated and unsaturated hydrocarbon results:

$$nCO + 2nH_2 \longrightarrow C_nH_{2n} + nH_2O$$

$$nCO + (2n+1)H_2 \longrightarrow C_nH_{2n+2} + nH_2O$$

The reaction is exothermic, so out coming hot gaseous mixture is led to a cooler, where a liquid resembling crude oil is obtained. The crude oil thus obtained is then fractionated to yield: (i) gasoline, and (ii) high boiling heavy oil. The heavy oil is reused for cracking to get more gasoline.

3. **Bergius process**: The low ash coal is finely powdered and made into a paste with heavy oil and then a catalyst (composed of tin or nickel oleate) is incorporated. The whole is heated with hydrogen at 450°C and under a pressure 200-250 atm about 1½ hours, during which hydrogen combines with coal to form saturated hydrocarbons, which decompose at prevailing high temperature and pressure to yield low boiling liquid hydrocarbons. The issuing gases (from the reaction vessel) are led to condenser, where a liquid resembling crude oil is obtained, which is then fractionated to get: (i) gasoline, (ii) middle oil, and (iii) heavy oil. The latter is used again for making paste with fresh coal dust. The middle oil is hydrogenated in vapour phase in

presence of a solid catalyst to yields more gasoline. The yields of gasoline in about 60% of the coal dust used.

KNOCKING

In an internal combustion engine, a mixture of gasoline vapour and air is used as a fuel. After the initiation of the combustion reaction, by spark in the cylinder, the flame should spread rapidly and smoothly through the gaseous mixture; thereby the expanding gas drives the piston down the cylinder. The ratio of the gaseous volume in the cylinder at the end of the suction stroke to the volume at the end of compression stroke of the piston is known the compression ratio. The efficiency of an internal combustion engine increases with the increase in compression ratio, which is dependent on the nature of the constituents present in the gasoline used. *In certain circumstances (due to the presence of some constituents in the gasoline used), the rate of oxidation becomes so great that the last portion of the fuel air mixture gets ignited instantaneously, producing an explosive violence, known as knocking. The knocking results in loss of efficiency.*

Chemical structure and knocking: The tendency of fuel constituents to knock is in the following order.

$Straight\ chain\ paraffins > Branched\ chain\ paraffins\,(i.e., iso-paraffins) > Olefins >$

$Cycloparaffins\,(i.e., naphthalenes) > Aromatics.$

Thus, olefins of the same carbon chain length possess better anti knock properties than the corresponding paraffins and so on.

OCTANE NUMBER (introduced by Edger in 1872): It has been found that n-heptane knocks very badly and hence, its anti knock value has arbitrarily been given zero. On the other hand, iso-octane (2,2,4-trimethyl pentane), gives very little knocking, so its anti knock value has been given as 100. Thus, *octane number of a fuel is the percentage by volume of isooctane present in a mixture of isooctane and n-heptane, which has the same knocking property as the fuel being tested, under similar experimental conditions in a special test engine.* In this way, an 80-octane fuel is one which has the same combustion characteristics as a 80:20 mixture of isooctane and n-heptane.

Improvement of anti-knock characteristics of a fuel: Octane number of internal combustion fuels can be raised by the addition of such extremely poisonous materials as tetra ethyl lead [$(C_2H_5)_4Pb$ or TEL] and diethyl telluride [$(C_2H_5)_2Te$]. In motor spirit, about 0.5 ml and in aviation fuels, about 1.0 to 1.5 ml of TEL is added per litre of petrol.

According to most accepted theory, TEL is converted into a cloud of finely divided lead oxide particles in the cylinder and these particles react with any hydrocarbon peroxide molecules formed, thereby slowing down the chain oxidation reaction and thus, decreasing the chances of any early detonation. However, deposit of lead oxide is harmful to the engine life. Consequently, in order to help the simultaneous elimination of lead oxide formed from the engine, a small amount of ethylene dibromide is also added to petrol. Ethylene dibromide removes lead oxide as a volatile lead bromide along with the exhaust gases. The presence of sulphur compounds in petrol reduces the effectiveness of the TEL

$$\underset{}{Pb} + \underset{\text{Ethylene dibromide}}{BrCH_2-CH_2Br} \longrightarrow \underset{\text{Lead bromide}}{PbBr_2} + \underset{\text{Ethylene}}{CH_2=CH_2}$$

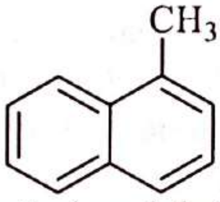
Unleaded petrol: Octane rating of petrol is in leaded petrol is increased by adding tetraethyl lead or tetramethyl lead. However, combustion of lead petrol leads to formation of litharge (PbO), which deposit the inner wall of cylinder and jams the piston. Also leaded petrol cannot be used in automobiles equipped cost catalytic converter, because lead present in exhaust gas poisons the catalyst, thereby destroying the active sites. Alternative method of increasing octane number of petrol is to add high octane compounds like isopentane, isooctane, ethyl benzene, isopropyl benzene, methyl tertiary butyl ether (MTBE). Out of these MTBE is preferred, because it contains oxygen in the form of ether group and supplies oxygen for the combustion of petrol in internal combustion engines, thereby reducing the extent of peroxy compound formation. Unleaded petrol is one where in the enhancement of octane rating is accomplished without the addition of lead compounds.

It may be pointed here that a major advantage of unleaded petrol is that it permits the use of catalytic converter attached to the exhaust in automobiles. A catalytic converter contains a catalyst (rhodium), which converts the toxic gases (CO and NO) to harmless gases (CO_2 and N_2 respectively), Moreover, it oxidizes unburnt hydrocarbon into CO_2 and H_2O.

DIESEL ENGINE FUEL AND CETANE NUMBER

In a diesel engine, the fuel is exploded not by a spark, but by the application of heat and pressure. Diesel engine fuels consist of longer chain hydrocarbons than internal combustion engine fuels. The main characteristics of diesel engine fuel is that it should easily ignite below compression temperature, and there should be as short an induction lag as possible. This means that it is essential that the hydrocarbon molecules in a diesel fuel should be as for as possible the straight chain ones, with a minimum admixture of aromatic and side chain hydrocarbon molecules.

The suitability of a diesel fuel is determined by its cetane number. *The cetane number of a diesel fuel is the percentage by volume of n- hexadecane in a mixture of n- hexadecane and 1-methyl naphthalene, which has the same ignition property as the fuel under test, under similar experimental conditions in a test engine.* The cetane number of a diesel fuel can be raised by the addition of small quantity of certain pre-ignition dopes like ethyl nitrite, isoamyl nitrite, acetone peroxide, etc.



1-methyl naphthalene
[Cetane No.=0]

$CH_3-[CH_2]_{14}-CH_3$
n-Hexadecane
[Cetane No.=100]

The usual diesel engine fuel is diesel oil or gas oil, a fraction obtained between 250-320°C during the fractional distillation of crude petroleum. This oil, generally, contains 85% C and 12% H. Its calorific value is about 11,000kcal/kg. Ignition quality order among hydrocarbon constituents of a diesel fuel is as follows:

$$n-Alkanes > Naphthalenes > Alkenes > Branched\ alkanes > Aromatics.$$

Thus, hydrocarbons which are poor gasoline fuels are quite good diesel fuels.

High speed and low speed diesels: In a high speed diesel engine, the time lag in getting the diesel droplets heated to ignition point in very brief, about 1/500th of a second. Such diesel engines require diesel with cetane number in excess of 45 (up to 60). On the other hand, low speed diesel requires cetane number of about 25. Cetane number of medium speed diesel is about 35.

GASEOUS FUELS

Gaseous fuels are classified into natural gas and artificial gases.

1. Natural gas:

Natural gas is a mixture of methane, ethane, propane, butane, pentane, carbon dioxide, nitrogen etc. is the most important fuel found mainly in the vicinity of coal mines or oil fields. It is also associated with petroleum deposits. The natural gas derived from oil wells may be either dry or wet. When natural gas occurs along with petroleum in oil wells it is called wet gas. The wet gas is treated to remove propane, propene, butane and butene which are used as LPG. On the other hand when the gas is associated with crude oil it is called dry gas. The calorific value of wet natural gas is higher than that of dry type because of higher percentage of the heavier unsaturated molecules. Before use, the natural gas is purified to remove objectionable ingredients such as water, dust, grit, H_2S, CO_2, N_2 and heavier liquefiable hydrocarbons (propane, butane, butene, etc.). The approximate composition of natural gas is: $CH_4 = 70-90\%$, $C_2H_6 = 5-10\%$, $H_2 = 3\%$, $CO + CO_2 = rest.$ The calorific value varies from 12,000 to 14,000 kcal/m^3.

Uses: (i) It is an excellent domestic fuel and can be conveyed over very large distances in pipelines. (ii) It is used for synthesis of a number of chemicals. (iii) It is used as a raw material for the manufacture of carbon black.

Compressed natural gas (CNG) *is natural gas compressed to a high pressure of about 1,000 atmospheres.* Natural gas consists mostly of methane, it also contains hydrocarbons such as ethane and propane as well as other gases such as nitrogen, helium, carbon dioxide, sulphur compounds, and water vapour. A sulphur-based odourant is normally added to CNG to facilitate leak detection. A steel cylinder containing 15kg of CNG contains about $2\times10^4 L$ or $20 m^3$ of natural gas at one atmospheric pressure. CNG is now being used as a substitute for petrol and diesel, since it is comparatively much less pollution causing fuel. During its combustion, no sulphur and nitrogen gases are evolved. Moreover, no carbon particles are ejected. Hence, it is a better fuel than petrol/ diesel for automobiles. However, initial cost of engine designed to use CNG as a fuel is comparatively higher than that of engine designed to use petrol/diesel.

Why is CNG preferred over LPG

(a) CNG is much safer fuel, since it ignites at a higher temperature than gasoline and diesel, (b) The conversion of gasoline operated automobiles into CNG operated vehicle is very easy, (c) The operated cost of CNG fuel is much lower compared to gasoline operation, (d) Combustion of CNG leads to lesser CO emissions than gasoline, (e) CNG mixes better with air than liquid fuels, (f) Emission from CNG operated vehicles contain no unregulated pollutants, e.g., smoke, SO_2, SO_3, C_6H_6, $HCHO$.

What is LNG?

Liquefied Natural Gas (LNG) is natural gas cooled to a liquid state. When natural gas is cooled to a temperature of approximately -256°F at atmospheric pressure, it condenses to a liquid. To liquefy natural gas, impurities that would freeze are removed, such as water, carbon dioxide, sulfur, and some of the heavier hydrocarbons. The volume of this liquid takes up about 1/600th of the volume of natural gas at a stove burner tip. LNG weighs about 45 percent as much as water and is odorless, colorless, non-corrosive, and non-toxic.

What is the composition of LNG?

LNG is natural gas cooled to a liquid state. Natural gas is composed primarily of methane (typically, at least 90 percent). Natural gas, and LNG, may also contain propane, ethane, and other heavier hydrocarbons as well as small quantities of nitrogen, oxygen, carbon dioxide, sulfur compounds, and water. During the liquefaction process, after oxygen, carbon dioxide, sulphur compounds, and water are removed and when natural gas is converted to a liquid state, a very clean product results.

What are the advantages of LNG?

LNG takes up 600 times less space than regular natural gas at ambient temperature and pressure, which makes it easier to transport and store than natural gas. LNG can be stored above or below ground in specially designed double walled storage tanks. LNG can be transported over long distances via double-hulled LNG ships, which are specially designed tankers that keep the LNG chilled during transport. LNG is also used to replace diesel in heavyduty trucks and buses and new gas-fueled locomotives as a lower emissions alternative.

BIODIESEL

Biodiesel refers to a vegetable oil - or animal fat-based diesel fuel consisting of long-chain alkyl (methyl, ethyl, or propyl) esters. Biodiesel is typically made by chemically reacting lipids (e.g., vegetable oil, soybean oil, animal fat (tallow)) with an alcohol producing fatty acid esters.

Biodiesel is meant to be used in standard diesel engines and is thus distinct from the vegetable and waste oils used to fuel *converted* diesel engines. Biodiesel can be used alone, or blended with petrodiesel in any proportions. Biodiesel blends can also be used as heating oil.

Blends of biodiesel and conventional hydrocarbon-based diesel are products most commonly distributed for use in the retail diesel fuel marketplace. Much of the world uses a system known as the "B" factor to state the amount of biodiesel in any fuel mix:

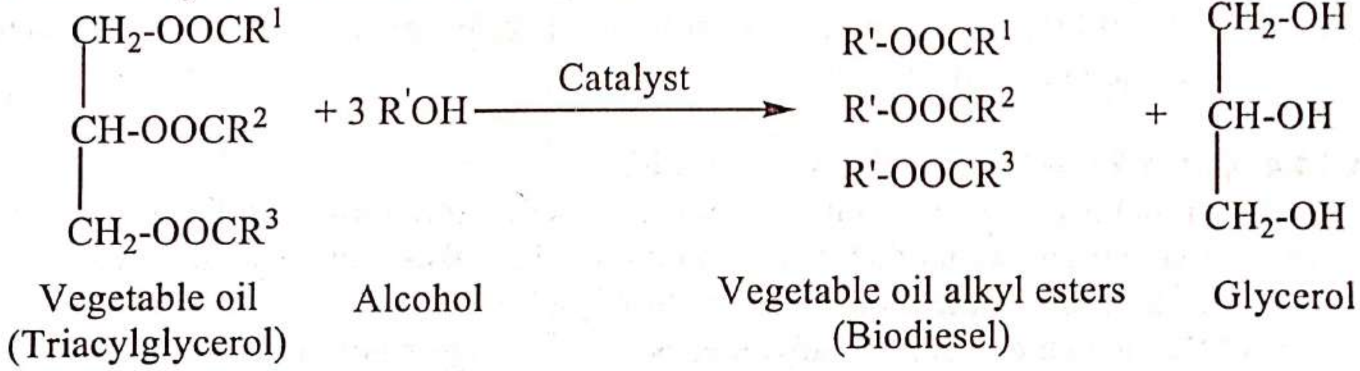
(a) 100% biodiesel is referred to as B100
(b) 20% biodiesel, 80% petrodiesel is labeled B20
(c) 5% biodiesel, 95% petrodiesel is labeled B5
(d) 2% biodiesel, 98% petrodiesel is labeled B2

Potential source of biodiesel

Vegetable oils-Classical (edible) commodity oils (palm, rape seed / canola, soybean, etc.), "Alternative" (inedible) oils (jatropha, karanja, pennycress, etc.), Animal fats, Used cooking oils, "Alternative" feedstocks - Algae

PREPARATION OF BIODIESEL

Vegetable oil, like biodiesel, belongs to a category of compounds called *esters*. Therefore, converting vegetable oil into biodiesel is called a *transesterification reaction*.



$$\begin{array}{l} CH_2\text{-}OOCR^1 \\ | \\ CH\text{-}OOCR^2 \\ | \\ CH_2\text{-}OOCR^3 \end{array} + 3\,R'OH \xrightarrow{\text{Catalyst}} \begin{array}{l} R'\text{-}OOCR^1 \\ R'\text{-}OOCR^2 \\ R'\text{-}OOCR^3 \end{array} + \begin{array}{l} CH_2\text{-}OH \\ | \\ CH\text{-}OH \\ | \\ CH_2\text{-}OH \end{array}$$

MAJOR ESTER COMPONENTS OF BIODIESEL FUELS

Fatty esters in from common vegetable oils (palm, soybean, canola/rapeseed, sunflower, etc):

Methyl palmitate (C16:0): $CH_3OOC\text{-}(CH_2)_{14}\text{-}CH_3$
Methyl stearate (C18:0): $CH_3OOC\text{-}(CH_2)_{16}\text{-}CH_3$
Methyl oleate (C18:1): $CH_3OOC\text{-}(CH_2)_7\text{-}CH{=}CH\text{-}(CH_2)_7\text{-}CH_3$
Methyl linoleate (C18:2; all cis): $CH_3OOC\text{-}(CH_2)_7\text{-}(CH{=}CH\text{-}CH_2)_2\text{-}(CH_2)_3\text{-}CH_3$
Methyl linolenate (C18:3; all cis): $CH_3OOC\text{-}(CH_2)_7\text{-}(CH{=}CH\text{-}CH_2\text{-})_3\text{-}CH_3$

From other oils:
Methyl laurate (C12:0): $CH_3OOC\text{-}(CH_2)_{10}\text{-}CH_3$
Methyl ricinoleate
(C18:1,12-OH;cis):$CH_3OOC\text{-}(CH_2)_7\text{-}CH{=}CH\text{-}CH_2\text{-}CHOH\text{-}(CH_2)_5\text{-}CH_3$
Algal Oils:
Methyl eicosapentaenoate (C20:5): $CH_3OOC\text{-}(CH_2)_3\text{-}(CH{=}CH\text{-}CH_2\text{-})_5\text{-}CH_3$
Methyl docosahexaenoate (C22:6): $CH_3OOC\text{-}(CH2)_2\text{-}(CH{=}CH\text{-}CH_2\text{-})_6\text{-}CH_3$

. PROPERTIES OF BIODIESEL

Biodiesel has promising lubricating properties and cetane ratings compared to low sulfur diesel fuels. Depending on the engine, this might include high pressure injection pumps, pump injectors (also called *unit injectors*) and fuel injectors.

The calorific value of biodiesel is about 37.27 MJ/kg. This is 9% lower than regular Number 2 petrodiesel. Variations in biodiesel energy density is more dependent on the feedstock used than the production process. Still, these variations are less than for petrodiesel. It has been claimed biodiesel gives better lubricity and more complete combustion thus increasing the engine energy output and partially compensating for the higher energy density of petrodiesel.

The color of biodiesel ranges from golden and dark brown, depending on the production method. It is slightly miscible with water, has a high boiling point and low vapor pressure. The flash point of biodiesel (>130 °C, >266 °F) is significantly higher than that of petroleum diesel (64 °C, 147 °F) or gasoline (−45 °C, -52 °F). Biodiesel has a density of ~ 0.88 g/cm³, higher than petrodiesel (~ 0.85 g/cm³).

Biodiesel contains virtually no sulfur, and it is often used as an additive to Ultra-Low Sulfur Diesel (ULSD) fuel to aid with lubrication, as the sulfur compounds in petrodiesel provide much of the lubricity.

. ADVANTAGES OF BIODIESEL FUEL

(a) Biodiesel fuel is a renewable energy source unlike petroleum-based diesel.
(b) An excessive production of soyabeans in the world makes it an economic way to utilize this surplus for manufacturing the biodiesel fuel.
(c) One of the main biodiesel fuel advantages is that it is less polluting than petroleum diesel.
(d) The lack of sulfur in 100% biodiesel extends the life of catalytic converters.
(e) Another of the advantages of biodiesel fuel is that it can also be blended with other energy resources and oil.
(f) Biodiesel fuel can also be used in existing oil heating systems and diesel engines without making any alterations.
(g) It can also be distributed through existing diesel fuel pumps, which is another biodiesel fuel advantage over other alternative fuels.
(g) The lubricating property of the biodiesel may lengthen the lifetime of engines.

INTRODUCTION

In all types of machines, the surfaces of moving or sliding or rolling parts rub against each other. Due to mutual rubbing of one part against another, a resistance is offered to their movement. This resistance, is known as friction. Friction causes a lot of wear and tear of surfaces of moving parts. And a large amounts of energy are dissipated in the form of heat, there by causing loss in the efficiency of machine. Moreover, the moving parts get heated up, damaged and even sometimes results in seizure (i.e., welding of two surfaces due to heat). The ill-effects of frictional resistance can be minimized by causing a suitable substance, which forms a thin layer in between the moving parts. *Any substance introduced between two moving/sliding surfaces with a view to reduce the frictional resistance between them, is known as a lubricants*. The main purpose of a lubricants is to keep the sliding/ moving surfaces apart, so that frictional resistance and consequent destruction of material is minimized. The process of reducing frictional resistance between moving/ sliding surfaces, by the introduction of lubricants in between them, is called lubrication.

Functions of a lubricants: (1) It reduces surface deformation, wear and tear, because the direct contact between the rubbing surfaces is avoided. (2) It reduces loss of energy in the form of heat. In other words, it acts as a coolant. (3) It reduces expansion of metal by local frictional heat. (4) It reduces waste of energy, so that efficiency of machine is enhanced. (5) It avoids seizure of moving surfaces, since the use of lubricant minimizes the liberation of frictional heat. (6) It avoids or reduces unsmooth relative motion of the moving/ sliding parts. (7) It reduces the maintenance and running cost of the machine. (8) It also, some times. Act as a seal. For example, lubricants used between piston and the cylindrical wall of an internal combustion engine act as a seal, there by preventing also the leakage of gases under high pressure from the cylinder.

CLASSIFICATION OF LUBRICANTS

Lubricants can be broadly classified, on the basis of their physical state, as follows: (1) Liquid lubricants or lubricating oils, (2) Semi-solid lubricants or greases, (3) Solid lubricants and (4) Gaseous lubricants. Man made lubricants are called synthetic lubricants.

1. Lubricating oils

Lubricating oils are also known as liquid lubricants and further classified into three categories viz. Animal and Vegetable oils, Mineral or Petroleum oils and blended oils.

Characteristic of good lubricating oils. High boiling point, low freezing point, adequate viscosity for proper functioning in service, high resistance to oxidation and heat, non-corrosive properties and stability to decomposition at the operating temperatures.

The types of lubricating oils are briefly described below:

(a) Animal and vegetable oils

Animal oils are extracted from the crude fat by rendering process in which the enclosing tissue is broken by treatment with steam or combined action of steam and water. Vegetable oils such as cotton seed oil and castor oils are obtained by crushing the seeds. These oils possess good oiliness and hence they can stick on metal surfaces effectively even under high temperatures and heavy loads. But they suffer from the disadvantages that they are costly, undergo easy oxidation to give gummy products and hydrolyse easily on contact with moist air or water. Hence they are only rarely used these days for lubrication. But they are still used as blending agents in petroleum based lubricants to get improved oiliness.

(b) Mineral or Petroleum oils

These are basically lower molecular weight hydrocarbons with about 12 to 50 carbon atoms. Their viscosity increases with the length of hydrocarbon chain. They are obtained by distillation of petroleum. As they are cheap, available in abundance and stable under service conditions, hence they are widely used. In comparison to animal and vegetable oils, oiliness of mineral oils are less. The addition of higher molecular weight compounds like oleic acids and stearic acid increases the oiliness of mineral oil.

(c) Blended oils

No single oil possesses all the properties required for a good lubricant and hence addition of proper additives is essential to make them perform well. Such additives added lubricating oils are called blended oils.

An additives is a material that imparts a new or desired property to the lubricating oil. It may also enhance a desirable property that the lubricating oil already possesses to some degree. Broadly speaking, they are two types of lubricants additives. Chemically active additives are those which chemically inert with metal (to form protective film) and with polar oxidation and degradation products (to make them harmless). Depressants, detergents, anti-wear agents, extreme pressure agents, oxidation inhibitors, corrosion inhibitor are few of the examples of chemically active additives. Chemically inert additives are those additives which improve the physical properties that are critical to the effective performance of the lubricant. These additives includes: viscosity index improvers, foam inhibitors, pour point depressants, emulsifiers etc.

The following are the commonly used additives.

(i) *Oiliness improver*: The oiliness property of lubricating oils is usually improved by adding vegetable oils like coconut oil, castor oil etc. or fatty acids like palmetic acid, stearic acid, oleic acids etc.

(ii) *Extreme pressure additives*: under such extreme pressure, a thick film of oils is difficult to maintain, and oil need to have a high oiliness. Besides improving oiliness directly, high pressure additives are used. These additives contain certain materials, which are adsorbed on the metal surfaces or react chemically with metal, producing a surface layer of low shear- strength on the metal surface, thereby preventing the tearing up of the metal. The main substances added for high pressure lubrication are : (a) fatty ester, acids, etc., which form oxide film with the metal surfaces; (b) organic materials which contain sulphur; (c) organic chlorine compounds; (d) organic phosphorus compounds

(iii) *Pour point depressants*: Pour point depressant is lubricating oil additives used to lower the pour point of waxy oil. Alkylated naphthalene were the pour depressors used earlier. Now many polymeric material like polymethylacrylates, ethylene vinyl acetate copolymer, alkylated polystyrene, polyolefines, aliphatic amine oxides, oxidized wax etc., find use as pour point depressants.

(iv) *Viscosity index improvers* are certain high molecular weight compounds like hexanol.

(v) *Thickeners* such as polystyrene, polyesters,etc., are materials usually of molecular weight between 300 and 3000. They are added in order to give the lubricating oil a higher viscosity.

(vi) *Antioxidants or inhibitors*, when added to oil, retard oxidation of oil by getting themselves preferentially oxidized. They are particularly added in lubricants used in internal combustion engines, turbines, etc., where oxidation of oil is a serious problem. The antioxidants are aromatic, phenolic or amino compounds.

(vii) *Corrosion inhibitors* are organic compounds of phosphorus or antimony. They protect the metal from corrosion by preventing contact between the metal surfaces and the corrosion substances.

(viii) *Abrasion inhibitors* like tricresyl phosphate.

(ix) *Antifoaming agents* (like glycols and glycerol) help in decreasing foam formation.

(x) *Emulsifiers*: It is a substances used to promote or aid the emulsification of two liquids and to enhance the stability of the emulsion. Usually sodium salts of sulphonic acid are used for the purpose.

(xi) Deposit inhibitors are detergents such as the salts of phenol and carboxylic acids. Deposits are formed in internal combustion engines, due to imperfect combustion. Such additives disperses and cleans the deposit.

2. Grease or Semi-solid lubricants

A semi-solid lubricant obtained by combining lubricating oil with thickening agents is termed as grease. Lubricating oil is the principal component and it can be either petroleum oil or a synthetic hydrocarbon of low to high viscosity. The thickeners consist primarily of special soaps of lithium, sodium, calcium, barium, aluminium etc. Non-soap thickeners include carbon black, silica gel, polyureas and other synthetic polymers, bentonite clays etc.(They improve the heat resistance of a lubricant). The fibrous structure of the thickeners traps the oil and enables the lubricant to cling to moving parts.

Unlike lubricating oils that flow of their own accord (Newtonian fluids), most greases flow only under pressure (Non-Newtonian fluids). The fiber structure of thickeners is adversely affected by water contamination and the grease undergo degradation. Hence, (unless a grease has been formulated to function), it is not used in the presence of water. Shear or frictional resistance of grease is much higher than oils hence they can support much heavier load at lower speed. Coefficient of friction of greases is much higher than that of lubricating oils. Therefore, whenever possible, it is better to use oil instead of grease. Compared to lubricating oils, grease cannot effectively dissipate heat from the bearing. That is why the grease lubricated bearing works at relatively lower temperatures as compared to the oil lubricated bearing.

Preparation: Grease are made by saponification of fat with alkali (like caustic soda) followed by adding hot lubricating oils with constant mixing. Consistency of the finished grease is governed by the total amount of the mineral oil.

Greases are preferred in places where: (1) Oil cannot remain in place due to high load (2) Bearing and gears working at high temperatures (3) The bearings needs to be sealed against the entry of dust, dirt or moisture and (4) Spurting or dripping of oil is undesirable.

Depending on the nature of the soap used, greases can be classified as:

(i) *Sodium based greases* employ sodium soaps as thickening agent in petroleum oils. As the sodium soap content is soluble in water so these grease are not water resistant. These greases can be used up to 175°C. They are suitable for use in ball bearings which generates frictional heat.

(ii) *Lithium based greases* employ lithium soaps as thickening agent in petroleum oils. These greases are resistant to water and have good high temperature properties. These greases are stable in storage, have high mechanical and oxidation stability. They have high melting point, about 150°C. For aircraft applications at extreme heights, where temperature as low as -55°C may exists, lithium- base lubricant (properly formulated) can be used as they permit functioning of the controls under such conditions. These greases are used for special applications only, due to their high cost.

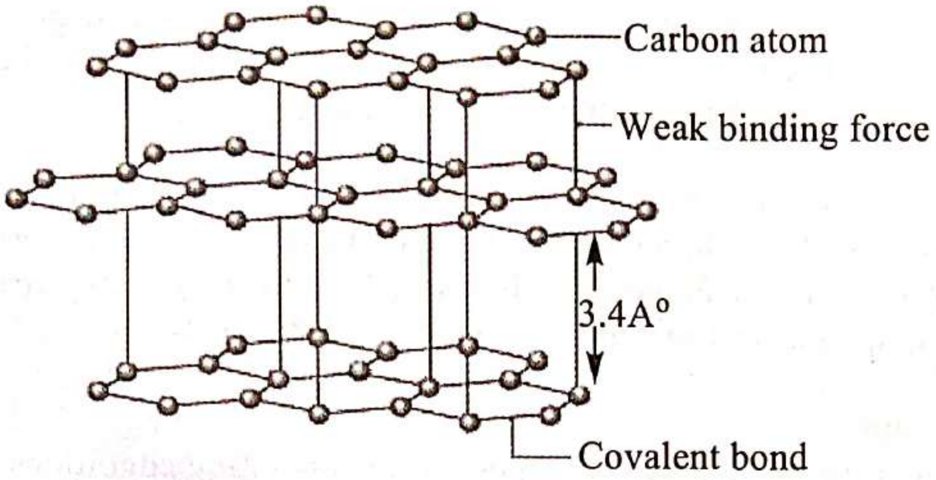
(iii) *Calcium based greases* employ calcium soaps as thickening agent in petroleum oils. These greases are also known as Cap-greases. These greases are the cheapest and most commonly used. These are water resistant and can be used up to 80°C. The amount of lime can be varied from 10 to 30% in calcium based greases for getting wide range of consistency, from soft paste to hard, smooth solid. These greases are suitable for lubricating caterpillar treads, tractors, water pumps etc.,

(iv) *Axle greases* are very cheap resin greases. They are prepared by adding lime to resin and fatty oils. After thorough mixing and standing, stiff mass grease floats out. Talc, mica or any other suitable filler is also added to them. They resistant to water and used for equipment working at low speeds and high loads.

3. Solid lubricants

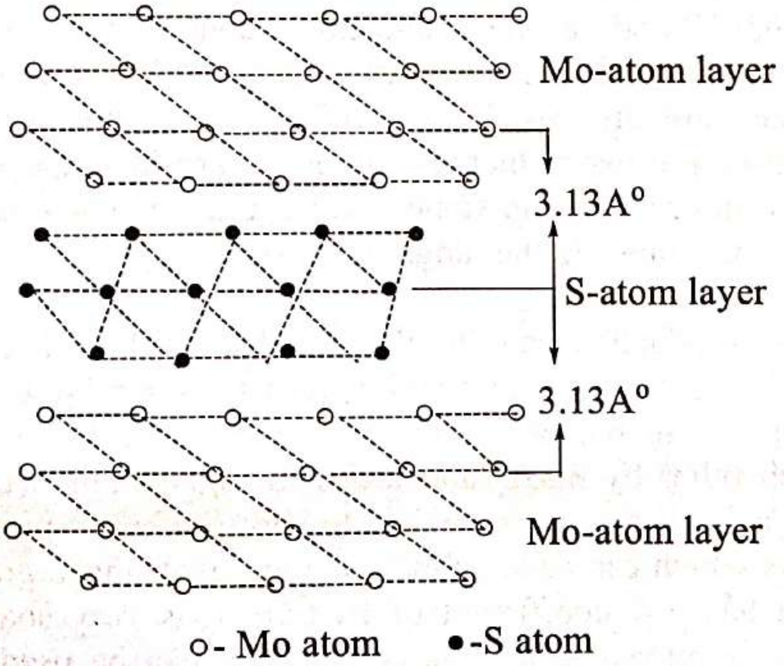
Solid lubricants are preferred where (i) the operating conditions are such that a lubricating film cannot be secured by use of lubricating oils or greases; (ii) contamination (by the entry of dust or grit particles) of lubricating oil or grease is unacceptable, e.g., in commutator bushes of electric generators and motors; (iii) the operating temperature or load is too high, even for a semi-solid lubricant to remain in position; and (iv) combustible lubricants must be avoided. They are used either in the dry powder form or with binders to make them stick firmly to the metal surfaces while in use. They are available as dispersions in non-volatile carriers like soaps, fats, waxes etc. and as soft metal films. The most common solid lubricants are graphite, molybdenum disulphide, tungsten disulphide and zinc oxide. They can withstand temperature up to 650°C and can be employed in continuously operating situations. Solid lubricants are preferred in metal working operating like wire drawing, extrusion and machining. They are also used as additives to mineral oils, synthetic liquid lubricants, and greases in order to increase the load carrying capacity of the material. Other solid lubricant in use are soap stone (talc) and mica. The coefficient of friction between solid lubricants comes in the range 0.005-0.01.

Graphite: It is the most widely used of all the solid lubricants and can be used either in the powdered form or in suspension. Graphite consists of number of plates made up of network of hexagons in which each carbon is in sp^2 hybridization state. The plates are separated from each other by $3.4A^o$ and are held together by weak vander Waal's forces, so that even a small force is sufficient to slide the layers parallel to each other. These parallel layers which can easily slide one over other make graphite an effective lubricant. Hence, it has low coefficient of friction. It is very soapy to touch, non-inflammable and not oxidized in air below 375°C. It can be used up to very much higher temperature in the absence of air. It is used in the powdered form or as suspension in oil or water along with tannin as emulsifying agent. Graphite grease (i.e., graphite mixed with grease) is useful for higher temperature applications. Graphite is used as lubricant in air compressors, railway track joints, open gears, cast iron bearings etc.



: Structure of graphite

Molybdenum disulphide: It has a sandwich-like structure in which a layer of molybdenum atoms lies between two layers of sulphur atoms. Poor inter laminar attraction helps these layers to slide over one another easily. The coefficient of friction of molybdenum disulphide is very low and it is stable up to a temperature of 400°C. Fine powder of molybdenum disulphide sprinkled on surfaces sliding at high velocities helps to fill the low spots on the metal surfaces and to form a thin film in between.



Structure of molybdenum disulphide

4. Gaseous lubricants

Gaseous lubricants are used in ultra centrifuges, nuclear reactors, gyroscopes, gas turbines, get engines etc. Their circulation ability, high and low temperature properties and resistance to reaction make them attractive as lubricants in these cases. Examples of gaseous lubricants are air (most preferred), halogenated hydrocarbon, sulphur hexa fluoride and nitrogen.

SYNTHETIC LUBRICANTS

Petroleum based lubricants can be used under abnormal conditions like extremely high temperature, chemically reactive atmosphere, etc. by employing certain specific additives. However, synthetic lubricants have been developed which alone can meet the most drastic and severe conditions such as those existing in aircraft engines, in which the same lubricant may have to used in the temperature range of -50°C to 250°C.

In general, synthetic lubricants possess the following properties:

(a). Thermal stability even at high operating temperatures, (b). Chemical stability even in corrosive environments, (c). High viscosity index, (d). Non-inflammability and high flash points, (e). Low freezing point.

Important synthetic lubricants are given below:

(1) Polymerized hydrocarbon like polyethylene, polypropylene, polybutylene in the molecular weight range 500 to 50,000 are residue free, light in colour, free from non-hydrocarbon impurities, chemically non-reactive and high temperature lubricants.

(2) Polyglycols and related compounds like polyethylene glycol, polypropylene glycol, polyglycidyl ethers, and higher polyalkylene oxides can be used as water soluble as well as water insoluble lubricants in rubber bearing and joints. Polyglycidyl ethers and higher polyalkylene oxides are water insoluble, but they can absorb a considerable amount of water, their viscosity index is high and these are used in roller bearings of sheet glass manufacturing machines. It may be pointed that polyethylene oxides undergo thermal decomposition (at high temperature) to evolve volatile oxidisable products, so that these are not useful as lubricants at high temperatures.

(3) Organic amines, imines and amides are good synthetic lubricants, since they possess low pour-point and high viscosity index. They can be used under temperature conditions of -50°C to 250°C.

(4) Silicones are very good synthetic lubricants, because are not oxidized below 200°C and possess high viscosity index. These are frequently used for low temperature lubrication purposes. It may be pointed that silicones are oxidised quickly above 200°C and undergo cracking process at about 230°C, so that they are not employed for high temperature applications.

(5) Fluorocarbons are not decomposed by heat, not easily oxidisable and chemically inert and resistant to chemicals, except molten sodium.

PROPERTIES OF LUBRICATING OILS

1. **Viscosity**: *Viscosity is the property of liquid or fluid by virtue of which it offers resistance to its own flow*. A liquid in a state of steady flow on a surface may be supposed to consist of a series of parallel layers moving one above the other. Any two layers will move with different velocities; top layer moves faster than the next lower layer, due to viscous drag (i.e., internal friction). Consider two layers of a liquid

separated by a distance, d and moving with a relative velocity difference, v. Then force per unit area (F) required to maintain this velocity difference is given by:

$$F = \frac{\eta v}{d}$$

Where η (eta) is a constant of the liquid, called coefficient of viscosity. If $v = 1$ unit (e.g., cm/s), $d = 1$ unit (e.g., cm.) then, $F = \eta$, Hence, coefficient of viscosity (η) may be defined as the force per unit area required to maintain a unit velocity gradient (i.e., velocity difference of one unit in the fluid or liquid layers, which are unit distance apart)between two parallel layers. The unit of viscosity is poise.

Viscosity is the most important single property of any lubricating oil, because it is the main determinant of the operating characteristics of the lubricant: (i) If the viscosity of the oil is too low, a liquid oil film cannot be maintained between two moving/sliding surfaces, and consequently, excessive wear will take place. On the other hand, (ii) if the viscosity is too high, excessive friction will result.

Effect of temperature on viscosity: Viscosity of liquids decreases with increasing temperature and, consequently, the lubricating oil becomes thinner as the operating temperature increases. Hence, viscosity of good lubricating oil should not change much with change in temperature, so that it can be used continuously, under varying conditions of temperature. *The rate at which the viscosity of an oil changes with temperature is measured by an arbitrary scale, known as the viscosity-index(V.I.).* If the viscosity of an oil falls rapidly as the temperature is raised, it has a low viscosity index. On the other hand, if viscosity of an oil is only slightly affected on raising the temperature, its viscosity index is high.

Determination of viscosity index: For determining the viscosity index, a series of two types of standard oils namely paraffinic-base Pennsylvanian oils(V.I=100) and naphthalenic – base Gulf oils (V.I=0) are used. The former type is called as 'H' –oils while latter is called 'L'-oils.

Step 1: The viscosities of the oil under-test at 100°F and also at 210°F are first found out, Let these values be 'U' and 'V' respectively. The difference between the two values should be low, if the oil is good; and high, if the oil is poor.

Step II: Now from the list of H-oils (with V.I.=100), the oil which has the same viscosity at 210°F as the oil under test is selected, and its corresponding viscosity at 100°F is read off. Let it be H.

Step III: Then, from the list of L-oils (i.e., with V.I.=0), the oil which has same viscosity at 210°F as the oil under test is selected, and its corresponding viscosity at 100°F is read off. Let it be L, Then:

$$\text{V.I} = \frac{\text{L} - \text{U}}{\text{L} - \text{H}} \times 100$$

Where U = Viscosity at 100°F of the oil under test,

L = Viscosity at 100°F of the low viscosity standard oil (Gulf oil) having a V.I. of 0 and also having the same viscosity at 210°F as the oil under test.

H = Viscosity at 100°F of the high viscosity standard oil (Pennysylvanian oil) having a V. I. of 100 and also having the same viscosity at 210°F as the oil under test.

Viscosity- Index and molecular structure of oil: The molecular structure of lubricating oils has a direct bearing on their viscosity and viscosity index. (i) Molecules of a linear or rod like structure, possessing flexibility, through free rotation about the chemical bonds, exhibit high V.I. (ii) A low freezing point or high viscosity of an oil can be secured by attaching short side chains to the chain of the linear molecule. This is due to the fact that side-chains tend to prevent alignment of the neighboring molecules. In general, an oil of high molecular weight possesses a high boiling point and high viscosity.

How to increase viscosity – index of an oil: viscosity – index of lubricating oils can be increased by adding certain polymers, which are only partially soluble in the oil. (i) At low temperature, when the solubility of the added polymer in oil is slight, so the effect of the polymer on the viscosity of the oil is also slight. (ii) At high temperature, when the solubility of the polymer in oils is considerable, its effect will be to increase viscosity of the oil. Thus, by the correct addition of organic polymers, it is possible to produce oil-polymer blends, which have a very slight temperature coefficient of viscosity.

Exercise.1: An oil of unknown viscosity-index has a saybolt universal viscosity of 60 seconds at 210°F and of 600 seconds at 100°F. The high viscosity index standard (i.e.,Pennysylvanian) oil has Saybolt viscosity of 60 seconds at 210°F and 500 seconds at 100°F. The low viscosity-index standard (i.e., Gulf) oil has a Saybolt universal viscosity of 60seconds at 210°F and 800seconds at 100°F. Calculate viscosity index of unknown oil.

Solution: Here L=800 s, H=500 s and U=600 s

Viscosity-index of unknown oil,

$$\text{V.I}=\frac{\text{L}-\text{U}}{\text{L}-\text{H}}\times 100=\frac{800-600}{800-500}\times 100=\frac{200}{300}\times 100=66.7$$

Exercise.2: An oil of unknown viscosity-index has a saybolt universal viscosity of 58seconds at 210°F and of 580 seconds at 100°F. The high viscosity index standard (i.e.,Pennysylvanian) oil has Saybolt viscosity of 58 seconds at 210°F and 430 seconds at 100°F. The low viscosity-index standard (i.e., Gulf) oil has a Saybolt universal viscosity of 58 seconds at 210°F and 780 seconds at 100°F. Calculate viscosity index of unknown oil.

Solution: Here L=780 s, H=430 s and U=580 s

Viscosity-index of unknown oil,

$$V.I = \frac{L-U}{L-H} \times 100 = \frac{780-580}{780-430} \times 100 = \frac{200}{350} \times 100 = 57.14$$

Exercise.3: An oil sample under test has a saybolt universal viscosity same as that of standard Gulf oil (low viscosity standard) and Pennysylvanian oil (high viscosity standard) at 210°F. Their Saybolt universal viscosities at 100°F are 61, 758 and 420 seconds respectively. Calculate viscosity index of the sample oil.

Solution: Here U=61 s, L=758 s and H= 420 s

Viscosity-index of unknown oil,

$$V.I = \frac{L-U}{L-H} \times 100 = \frac{758-61}{758-420} \times 100 = \frac{697}{338} \times 100 = 206.21$$

2. Flash and fire points: *Flash point is the lowest temperature at which the oil lubricant gives off enough vapours that ignite for a moment, when a tiny flame is brought near it; while fire-point is the lowest temperature at which the vapours of the oil burn continuously for at least five seconds, when a tiny flame is brought near it.* In most cases, the fire points are 5°C to 40°C higher than the flash points. The flash and fire points do not have any bearing with the lubricating property of the oil, but these are important when oil is exposed to high temperature service. A good lubricant should have flash point at least above the temperature at which it is to be used. This safeguards against risk of fire, during the use of lubricant.

3. **Cloud and pour points**: *When an oil is cooled slowly, the temperature at which it becomes cloudy or hazy in appearance, is called its cloud point; while the temperature at which the oil cease to flow or pour, is called its pour point.* Cloud and pour points indicate the suitability of lubricants in cold conditions. Lubricant used in a machine working at low temperatures should possess low pour point; otherwise solidification of lubricant will cause jamming of machine. It has been found that presence of waxes in the lubricating oil raise pour point.

4. Aniline point: *Aniline point of an oil is defined as the minimum equilibrium solution temperature for equal volumes of aniline and oil samples.* Aniline point gives an indication of the possible deterioration of oil in contact with rubber sealing, packing, etc. Aromatic hydrocarbons have a tendency to dissolve natural rubber and certain types of synthetic rubbers. Consequently, low aromatic content in the lubricants is desirable. A higher aniline point means a higher percentage of parafinic hydrocarbons and hence, a lower percentage of aromatic hydrocarbons.

Aniline point is determined by mixing mechanically equal volumes of the oil samples and aniline in a test tube. The mixture is heated, till homogeneous solution is obtained. Then, the tube is allowed to cool at a controlled rate. The temperature at which the two phases (oil and aniline) separate out is recorded at the aniline point.

MODULE VI

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).

$$\underset{\text{(Soap)}}{2C_{17}H_{35}COONa} + CaCl_2 \rightarrow \underset{\text{(Ca- Soap)}}{(C_{17}H_{35}COO)_2Ca} + 2NaCl$$

$$2C_{17}H_{35}COONa + MgSO_4 \rightarrow (C_{17}H_{35}COO)_2Mg + Na_2SO_4$$

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.

$$Ca(HCO_3)_2 \rightarrow CaCO_3 + H_2O + CO_2$$

$$Mg(HCO_3)_2 \rightarrow Mg(OH)_2 + 2CO_2$$

Removal of temporary hardness

1. Boiling

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

$$Ca(HCO_3)_2 \rightarrow CaCO_3 + H_2O + CO_2$$

$$Mg(HCO_3)_2 \rightarrow Mg(OH)_2 + 2CO_2$$

2. Clark's process

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

$$Ca(HCO_3)_2 + Ca(OH)_2 \rightarrow 2CaCO_3 + 2H_2O$$

$$Mg(HCO_3)_2 + Ca(OH)_2 \rightarrow MgCO_3 + CaCO_3 + H_2O$$

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 **$CaCO_3$** equivalent hardness. The concentration of hardness producing ions and non-hardness producing ions are expressed in terms of equivalent amount of **$CaCO_3$** and is called **$CaCO_3$** equivalent hardness. The choice of **$CaCO_3$** 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.

$$\mathbf{CaCO_3\ equivalent\ hardness} = \frac{Mass\ of\ HPS\ X\ Equivalent\ weight\ of\ CaCO3}{Equivalent\ weight\ of\ HPS}$$

Where **HPS** is hardness producing substance.

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

$$\mathbf{CaCO_3\ equivalent\ hardness} = \frac{Mass\ of\ HPS\ X\ Molecular\ weight\ of\ CaCO3}{Molecular\ weight\ of\ HPS}$$

Let X be the mass of HPS, then **$CaCO_3$ equivalent hardness** $= \frac{X\ x\ 100}{M\ HPS}$

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 $CaCO_3$ equivalent hardness present per million parts of water.

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

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

Mg/L:

It is the number of milligrams of $CaCO_3$ equivalent hardness present per litre of water.

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

Degree French:

It is the number of parts of $CaCO_3$ equivalent hardness present per 10^5 partsof water.

$1°F = \frac{1}{10^5}$

$$\boxed{10^5 °F = 1}$$

Degree Clark:

It is the number of parts of $CaCO_3$ equivalent hardness present per 70000 parts of water.

$$1°Cl = \frac{1}{70000}$$

Equivalents per million:

It is the number of equivalents of $CaCO_3$ equivalent hardness present per million parts of water.

$$1\ epm = \frac{50}{10^6} \qquad \boxed{\frac{10^6}{50} epm = 1}$$

$$\boxed{70000°Cl = 1}$$

Inter conversion of various units of hardness

$$10^6 Ppm = 10^6 mg/L = 10^5 °F = 70000°Cl = \frac{10^6}{50}\ epm = 1$$

$$1ppm = 1mg/L = 0.1°F = 0.07°Cl = 0.02epm$$

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 leads 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, $Mg(HCO_3)_2$ – 1.4mg/L, $MgCl_2$ – 9.5mg/L.

Constituents	Quantity	M_{HPS}	$CaCO_3$ equivalent hardness = Quantity X $\frac{100}{MHPS}$
$CaSO_4$	16.2mg/L	136	$16.2X\frac{100}{136} = 11.9$ ppm
$Mg(HCO_3)_2$	1.4mg/L	146	$1.42\ X\frac{100}{146} = 0.97$ ppm
$MgCl_2$	9.5mg/L	95	$9.5\ X\frac{100}{95} = 10$ ppm

Total hardness = 11.9 + 0.97 + 10 = 22.87 ppm

Temporary hardness = 0.97 ppm

Permanent hardness = Total hardness - Temporary hardness = 22.87 – 0.97 = 21.9 ppm

2. A sample of water on analysis gives the following results: Ca^{2+} = 30mg/L, Mg^{2+} = 18mg/L, HCO_3^- =244mg/L, Na^+ =11.5mg/L. Calculate the temperory and permanent hardness of water sample.

Constituents	Quantity (mg/L)	M_{HPS}	$CaCO_3$ equivalent hardness = Quantity X $\frac{100}{MHPS}$
Ca^{2+}	30	40	$30\ X\frac{100}{40} = 75$
Mg^{2+}	18	24	$18\ X\frac{100}{24} = 75$
HCO_3^-	122	61	$122\ X\frac{100}{2\ X\ 61} = 100$
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 $NaHCO_3$ 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 $NaHCO_3$.

Increase in temporary hardness = $\frac{42\ X\ 100}{2\ X\ 84} = 25$ ppm

New temporary hardness = 100 + 25 = 125 mg/L

New permanent hardness = Total hardness - New temporary hardness = 500 – 125 =375mg/L

4. A water sample contains$(HCO_3)_2$– 36.5 ppm, $Ca(HCO_3)_2$ – 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 X $\frac{100}{MHPS}$
$Ca(HCO_3)_2$	40.5	162	$40.5X\ ^{100}/_{162} = 25$ ppm
$Mg(HCO_3)_2$	36.5	146	$36.5X\ ^{100}/_{146} = 25$ ppm
$MgSO_4$	30.3	120	$30.0\ X\ ^{100}/_{120} = 25$ ppm
$CaSO_4$	34.0	136	$34.0X\ ^{100}/_{136} = 25$ ppm
$CaCl_2$	27.75	111	$27.75\ X\ ^{100}/_{111} = 25$ ppm
NaCl	10	-	-

Temporary hardness = Hardness due to $Ca(HCO_3)_2$+ Hardness due to $Mg(HCO_3)_2$
= 25 +25 = 50 ppm

Permanent hardness = Hardness due to $MgSO_4$+ Hardness due to $CaSO_4$ + Hardness due to $CaCl_2$ = 25 + 25 + 25 = 75 ppm

5. A sample of water on analysis gives the following results: Ca^{2+} = 400mg/L, Mg^{2+} = 240mg/L, HCO_3^- = 244mg/L, Na^+ =92mg/L. Calculate the temperory and permanent hardness of water sample.

Constituents	Quantity (ppm)	M_{HPS}	$CaCO_3$ equivalent hardness = Quantity X $\frac{100}{MHPS}$
Ca^{2+}	400	40	$400\ X \frac{100}{40} = 1000$
Mg^{2+}	240	24	$240\ X \frac{100}{24} = 1000$
HCO_3^-	244	61	$244\ X \frac{100}{2\ X\ 61} = 200$
Na^+	92	-	-

Total hardness = 1000 + 1000 = 2000 ppm

Temporary hardness = 200 ppm

Permanent hardness = 2000 – 200 = 1800 ppm

6. A water sample contains $Mg(HCO_3)_2$ – 43.8mg/L, $Ca(HCO_3)_2$ – 48.6 ppm, $MgSO_4$ – 24.0 ppm, $CaSO_4$ – 27.2mg/L, $NaHCO_3$ – 16.8mg/L. Calculate the temperory and permanent hardness of water sample.

Constituents	Quantity (mg/L)	M_{HPS}	$CaCO_3$ equivalent hardness = Quantity X $\frac{100}{MHPS}$
$Ca(HCO_3)_2$	48.6	162	$48.6\ X \frac{100}{162} = 30$ ppm
$Mg(HCO_3)_2$	43.8	146	$43.8\ X \frac{100}{146} = 30$ ppm
$MgSO_4$	24.0	120	$24.0\ X \frac{100}{120} = 20$ ppm
$CaSO_4$	27.2	136	$27.2\ X \frac{100}{136} = 20$ ppm
$NaHCO_3$	16.8	84	$16.8\ X \frac{100}{2\ X\ 84} = 10$ 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: Ca^{2+} = 320mg/L, Mg^{2+} = 72mg/L, HCO_3^-=610mg/L, Na^+ =23mg/L. Calculate the temporary and permanent hardness of water sample.

Constituents	Quantity (mg/L)	MHPS	$CaCO_3$ equivalent hardness = Quantity X $\frac{100}{MHPS}$
Ca^{2+}	320	40	$320 \text{ X } \frac{100}{40} = 800$
Mg^{2+}	72	24	$72 \text{ X } \frac{100}{24} = 300$
HCO_3^-	610	61	$610 \text{ X } \frac{100}{2 \text{ X } 61} = 500$
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 $CaCl_2$ solution.

Hardness = Normality X Eqnt Wt $_{CaCO_3}$ X 1000

= 0.1 X 2 X 50 X 1000 =10000 ppm

9. Calculate the hardness of 0.4 N Ca^{2+}solution.

Hardness = Normality X Eqnt Wt $_{CaCO_3}$ X 1000

= 0.4 X 50 X 1000 =20000 ppm

10. A sample of water is found to contain $Mg(HCO_3)_2$ – 7.3mg/L, $Ca(HCO_3)_2$ – 16.2 mg/L, $MgCl_2$ – 9.5 ppm and $CaSO_4$ – 13.6mg/L. Calculate the temperory and permanent hardness of water sample. What happen to the temperory and permanent hardness of water sample if 10.6mg/L Na_2CO_3 is added?

Constituents	Quantity (mg/L)	MHPS	$CaCO_3$ equivalent hardness = Quantity X $\frac{100}{MHPS}$
$Ca(HCO_3)_2$	16.2	162	$16.2 \text{ X } \frac{100}{162} = 10$ ppm
$Mg(HCO_3)_2$	7.3	146	$7.3 \text{ X } \frac{100}{146} = 5$ ppm
$MgCl_2$	9.5	95	$9.5 \text{ X } \frac{100}{95} = 10$ ppm
$CaSO_4$	13.6	136	$13.6 \text{ X } \frac{100}{136} = 10$ ppm
Na_2CO_3	10.6	106	$10.6 \text{ X } \frac{100}{106} = 10$ ppm

Total hardness = 10+5+10+10 = 35 ppm

Temporary hardness = 10+5 = 15 ppm

Permanent hardness = 35 – 15 = 20 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 Na_2CO_3= 10 ppm. Thus 10 ppm permanent Ca is removed as $CaCO_3$.

New total hardness = 35 – 10 = 25 ppm

Temporary hardness = 15 ppm

New permanent hardness = 25 – 15 = 10 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.

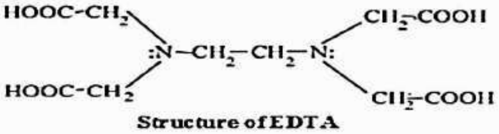
Principle and method of EDTA process:

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.

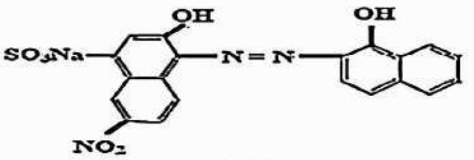
$$M^{2+} + EBT \longrightarrow \underset{\text{(Weak \& Wine red)}}{M\text{-}EBT}$$

$$M\text{-}EBT + EDTA \longrightarrow M\text{-}EDTA + \underset{\text{(Blue)}}{EBT}$$

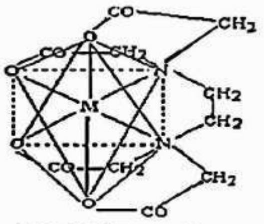
The PH is maintained around 10 using NH4Cl and NH4OH buffer, since indicator effective only at this PH. Initially M-EBT complex is formed, which is unstable. Then the addition of EDTA replaces EBT from the M-EBT complex produces M-EDTA complex and the colour changes from wine red to blue.



Structure of EDTA



Structure of Eriochrome Black-T



M-EDTA complex

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 ml EDTA (N_1) = $\frac{50}{V1}$ mg $CaCO_3$ 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 ml UHW = V_2 ml EDTA

$V_{UHW} \times N_{UHW} = V_{EDTA} \times N_{EDTA}$

$50 \times N_2 = V_2 \times \frac{50}{V1}$

1 ml UHW (N_2) = $\frac{V2}{V1}$

1 litre of UHW = $\frac{V2}{V1}$ x 1000mg $CaCO_3$ equivalent hardness

Total hardness = $\frac{V2}{V1}$ **x 1000mg/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 ml UHW = V_2 ml EDTA

$V_{BHW} \times N_{BHW} = V_{EDTA} \times N_{EDTA}$

$50 \times N_3 = V_3 \times \frac{50}{V1}$

1 ml BHW (N_3) = $\frac{V3}{V1}$

1 litre of BHW = $\frac{V3}{V1}$ x 1000mg $CaCO_3$ equivalent hardness

Permanent hardness = $\frac{V3}{V1}$ **x 1000mg/L** or **ppm**

V. Determination of temporary hardness

Temporary hardness = Total hardness – Permanent hardness

$$= \{ \frac{V2}{V1} \times 1000 - \frac{V3}{V1} \times 1000 \} \text{ mg/L or ppm}$$

$$= \frac{V2-V3}{V1} \times 1000 \text{mg/L or ppm}$$

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.

Hardness = Normality X Eqnt. Wt. $_{CaCO3}$ X 1000= Molarity X 2 X Eqnt. Wt. $_{CaCO3}$ X 1000

= 0.1 X 2 X 50 X 1000 =10000 ppm

2. Calculate the hardness of 0.4 N Ca^{2+}solution.

Hardness = Normality X Eqnt. Wt. $_{CaCO3}$ X 1000

= 0.4 X 50 X 1000 =20000 ppm

3. A standard hard water containing 15g $CaCO_3$ 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 $CaCO_3$
1000 ml SHW = 15000mg $CaCO_3$
1 ml SHW = 15mg $CaCO_3$
Normality of SHW = 15mg $CaCO_3$

Step II: Standardisation of EDTA

20 ml SHW = 25 ml EDTA
$V_{SHW} \times N_{SHW} = V_{EDTA} \times N_{EDTA}$
$20 \times 15 = 25 \times N_{EDTA}$
$N_{EDTA} = \frac{20 \times 15}{25} = 12$mg $CaCO_3$

Step III: Estimation of total hardness

100 ml UHW = 18 ml EDTA
$V_{UHW} \times N_{UHW} = V_{EDTA} \times N_{EDTA}$
$100 \times N_{UHW} = 18 \times 12$
$N_{UHW} = \frac{18 \times 12}{100} = 2.16$mg
Total Hardness = 2.16 X 1000 = 2160 ppm

Step IV: Determination of permanent hardness

100 ml BHW = 12 ml EDTA
$V_{BHW} \times N_{BHW} = V_{EDTA} \times N_{EDTA}$
$100 \times N_{BHW} = 12 \times 12$
$N_{BHW} = \frac{12 \times 12}{100} = 1.44$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 $CaCO_3$ in dil. HCl. It is then evaporated and made upto 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 $CaCO_3$
1000 ml SHW = 1000mg $CaCO_3$
1 ml SHW = 1mg $CaCO_3$
Normality of SHW = 1mg $CaCO_3$

Step II: Standardisation of EDTA

50 ml SHW = 48 ml EDTA
$V_{SHW} \times N_{SHW} = V_{EDTA} \times N_{EDTA}$
$50 \times 1 = 48 \times N_{EDTA}$
$N_{EDTA} = \frac{50 \times 1}{48} = 1.04$mg $CaCO_3$

Step III: Estimation of total hardness

50 ml UHW = 15 ml EDTA
$V_{UHW} \times N_{UHW} = V_{EDTA} \times N_{EDTA}$
$50 \times N_{UHW} = 15 \times 1.04$
$N_{UHW} = \frac{15 \times 1.04}{50} = 0.312$mg
Total Hardness = 0.312 X 1000 = 312 ppm

Step IV: Determination of permanent hardness

50 ml BHW = 10 ml EDTA

$V_{BHW} \times N_{BHW} = V_{EDTA} \times N_{EDTA}$

$50 \times N_{BHW} = 10 \times 1.04$

$N_{BHW} = \frac{10 \times 1.04}{50} = 0.208$mg

Permanent Hardness = 0.208 X 1000 = 208 ppm

Step V: Determination of temporary hardness

Temporary hardness = Total hardness - Permanent hardness = 312 – 208= 104 ppm

5. 2.8g $CaCO_3$ 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 litre SHW = 2.8g $CaCO_3$

1000 ml SHW = 2800mg $CaCO_3$

1 ml SHW = 2.8mg $CaCO_3$

Normality of SHW = 2.8mg $CaCO_3$

Step II: Standardisation of EDTA

100 ml SHW = 28 ml EDTA

$V_{SHW} \times N_{SHW} = V_{EDTA} \times N_{EDTA}$

$100 \times 2.8 = 28 \times N_{EDTA}$

$N_{EDTA} = \frac{100 \times 2.8}{28} = 10$mg $CaCO_3$

Step III: Estimation of total hardness

100 ml UHW = 35 ml EDTA

$V_{UHW} \times N_{UHW} = V_{EDTA} \times N_{EDTA}$

$100 \times N_{UHW} = 35 \times 10$

$N_{UHW} = \frac{35 \times 10}{100} = 3.5$mg

Total Hardness = 3.5 X 1000 = 3500 ppm

Step IV: Determination of permanent hardness

100 ml BHW = 10 ml EDTA

$V_{BHW} \times N_{BHW} = V_{EDTA} \times N_{EDTA}$

$100 \times N_{BHW} = 10 \times 10$

$N_{BHW} = \frac{10 \times 10}{100} = 1$mg

Permanent Hardness = 1 X 1000 = 1000 ppm

Step V: Determination of temporary hardness

Temporary hardness = Total hardness - Permanent hardness = 3500 –1000= 2500 ppm

6. 0.30g $CaCO_3$ 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 litre SHW = 0.30g $CaCO_3$

1000 ml SHW = 300mg $CaCO_3$

1 ml SHW = 0.3mg $CaCO_3$

Normality of SHW = 0.3mg $CaCO_3$

Step II: Standardisation of EDTA

100 ml SHW = 30 ml EDTA

$V_{SHW} \text{ X } N_{SHW} = V_{EDTA} \text{ X } N_{EDTA}$

$100 \text{ X } 0.3 = 30 \text{ x } N_{EDTA}$

$N_{EDTA} = \frac{100 \text{ X } 0.3}{30} = 1\text{mg } CaCO_3$

Step III: Estimation of total hardness

100 ml UHW = 33 ml EDTA

$V_{UHW} \text{ X } N_{UHW} = V_{EDTA} \text{ X } N_{EDTA}$

$100 \text{ X } N_{UHW} = 33 \text{ X } 1$

$N_{UHW} = \frac{33 \text{ X } 1}{100} = 0.33\text{mg}$

Total Hardness = 0.33 X 1000 = 330 ppm

Step IV: Determination of permanent hardness

100 ml BHW = 10 ml EDTA

$V_{BHW} \text{ X } N_{BHW} = V_{EDTA} \text{ X } N_{EDTA}$

$100 \text{ X } N_{BHW} = 10 \text{ X } 1$

$N_{BHW} = \frac{10 \text{ X } 1}{100} = 0.1\text{mg}$

Permanent Hardness = 0.1 X 1000 = 100 ppm

Step V: Determination of temporary hardness

Temporary hardness = Total hardness - Permanent hardness = 330 – 100= 230 ppm

7. In an EDTA experiment, the following values are obtained. Calculate the different types of hardness.

i) 20ml standard hard water (10g $CaCO_3$ 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 litre SHW = 10g $CaCO_3$

1000 ml SHW = 10000mg $CaCO_3$

1 ml SHW = 10mg $CaCO_3$

Normality of SHW = 10mg $CaCO_3$

Step II: Standardisation of EDTA

20 ml SHW = 25 ml EDTA

$V_{SHW} \text{ X } N_{SHW} = V_{EDTA} \text{ X } N_{EDTA}$

$20 \text{ X } 10 = 25 \text{ x } N_{EDTA}$

$N_{EDTA} = \frac{20 \text{ X } 10}{25} = 8 \text{ mg } CaCO_3$

Step III: Estimation of total hardness

50 ml UHW = 25 ml EDTA

$V_{UHW} \text{ X } N_{UHW} = V_{EDTA} \text{ X } N_{EDTA}$

$50 \text{ X } N_{UHW} = 25 \text{ X } 8$

$N_{UHW} = \frac{25 \text{ X } 8}{50} = 4 \text{ mg}$

Total Hardness = 4 X 1000 = 4000 ppm

Step IV: Determination of permanent hardness

50 ml BHW = 14 ml EDTA

$V_{BHW} \text{ X } N_{BHW} = V_{EDTA} \text{ X } N_{EDTA}$

$50 \text{ X } N_{BHW} = 14 \text{ X } 8$

$N_{BHW} = \frac{14 \text{ X } 8}{50} = 2.24\text{mg}$

Permanent Hardness = 2.24 X 1000 = 2240 ppm

Step V: Determination of temporary hardness

Temporary hardness = Total hardness - Permanent hardness = 4000 – 2240 = 1760 ppm

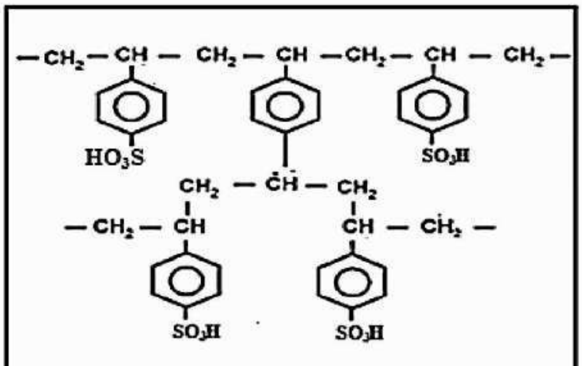
Water softening processes

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.

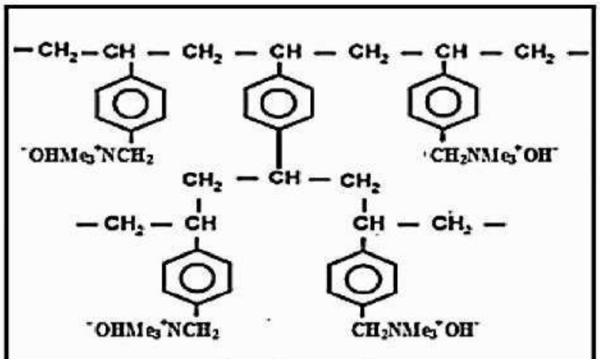
Ion exchange process : Ion exchange resins are insoluble cross linked long chain organic polymers having micro porous structure, where the functional group attached to the chain are responsible for their ion exchange capacity. Cation exchange resin (RH^+) contains acidic functional groups like –COOH, $-SO_3H$, etc. Anion exchange resin (ROH^-) contains basic functional groups like –OH, $-NH_2$, 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 or carboxylation 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 quartarnary ammonium group, which on treatment with NaOH attain the capability to exchange its OH^- ions with cations of water.



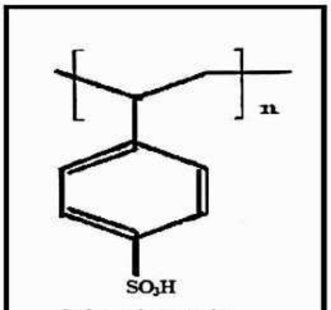
Cation exchange resin



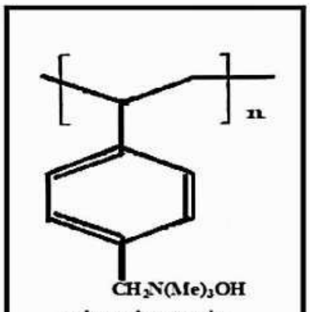
anion exchange resin

OR

Simply we can draw the structure of cation exchange resin and anion exchange resin in the following manner.



Cation exchange resin



anion exchange resin

Procedure:

Initially hard water is allowed to pass through cation exchange resin column to remove all the cations like Ca^{2+}, Mg^{2+}, etc.

$$\mathbf{2RH^+ + Ca^{2+} \rightarrow R_2Ca + 2H^+}$$

$$\mathbf{2RH^+ + Mg^{2+} \rightarrow R_2Mg + 2H^+}$$

Then the hard water is allowed to pass through anion exchange resin column to remove all the anions like SO_4^{2-}, Cl^-, etc.

$$\mathbf{ROH^- + Cl^- \rightarrow RCl + OH^-}$$
$$\mathbf{2ROH^- + SO_4^{2-} \rightarrow R_2\,SO_4^{2-} + 2OH^-}$$
$$\mathbf{2ROH^- + CO_3^{2-} \rightarrow R_2CO_3^{2-} + 2OH^-}$$

The H^+ ions and OH^- ions produced from cation and anion exchange resin column combine to form water.

$$\mathbf{H^+ + OH^- \rightarrow H_2O}$$

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_4through the column.

$$\mathbf{R_2Ca + 2H^+ \rightarrow 2RH^+ + Ca^{2+}}$$

Anion exchangers are regenerated by passing dil.NaOH through the column.

$$\mathbf{R_2\,SO_4^{2-} + 2OH^- \rightarrow 2ROH^- + SO_4^{2-}}$$

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 Ca2+ and Mg2+ ions of hard water produces $Ca(OH)_2$ and $Mg(OH)_2$ 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 P^H 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 ($K_2SO_4Al_2(SO_4)_3$. $24H_2O$), $FeSO_4$, $NaAlO_2$, etc. These coagulants when added to water produce insoluble, gelatinous, floculant precipitates, which descents 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.

$$CaOCl_2 + H_2O \rightarrow Ca(OH)_2 + Cl_2$$

$$H_2O + Cl_2 \rightarrow HCl + HOCl$$

$$HOCl + \text{Germs} \rightarrow \text{Germs are killed} \rightarrow \text{water purified}$$

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.

$$H_2O + Cl_2 \rightarrow HOCl + HCl$$

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.

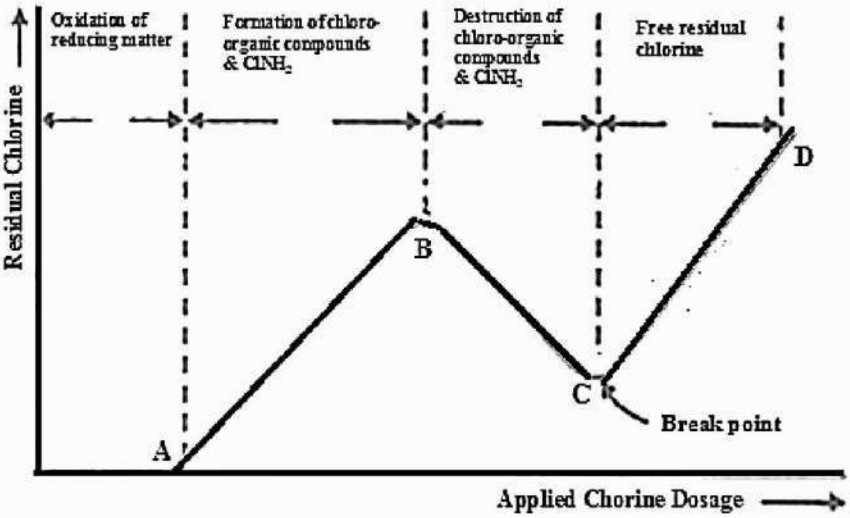
Break point of chlorination:

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.



C

Breakpoint of chlorination

4. Addition of $ClNH_2$

Chlorine on reaction with ammonia produces $ClNH_2$.

$$Cl_2 + NH_3 \rightarrow ClNH_2$$
$$ClNH_2 + H_2O \rightarrow HOCl + NH_3$$

<u>ClNH$_2$ is a better disinfectant than chlorine</u>, 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.

$$3O_2 \xrightarrow[\text{discharge}]{\text{silent elctric}} \underset{\text{ozone}}{2O_3}$$
$$O_3 \longrightarrow O_2 + [O] \text{ (nascent oxygen)}$$

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 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.

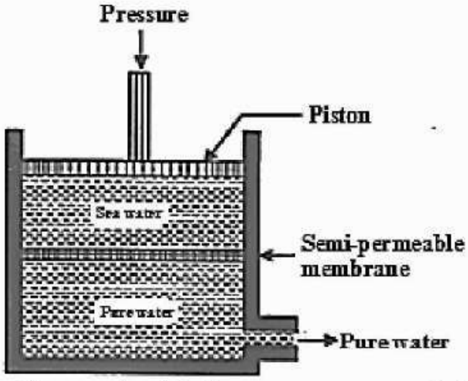
Brackish water treatment

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 15-40kgm^{-2} is required. Membranes made up of cellulose acetate or polymethacryte 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 15-40kgm^{-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
• It occurs in presence of excess oxygen.	• It occurs in presence of limited quantity oxygen.
• Oxidation by aerobic bacteria.	• Oxidation by anaerobic bacteria.
• The products of oxidation are CO_2, nitrates, phosphates, sulphates.	• The products of oxidation are acetic acid, methane, H_2S, NH_3, phosphine.
• The products are non-offensive smelling.	• The products are offensive smelling.
• During decomposition, carbohydrates are converted as $CO_2$and water.	• During decomposition, carbohydrates are converted as $CO_2$and methane.
• Energy released is more and rate of decomposition is slow.	• Energy released is less and rate of decomposition is fast.
• No bio-gas fuel is produced.	• 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.

$$MnSO_4 + 2KOH \rightarrow Mn(OH)_2 + K_2SO_4$$

The DO present in the sample oxidizes some of the Mn2+ to Mn4+, which is precipitated as brown hydrated manganese dioxide.

$$Mn(OH)_2 + O2 \rightarrow 2MnO(OH)_2$$

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.

$$2MnO(OH)_2 + H_2SO_4 \rightarrow MnSO_4 + 2H_2O + [O]$$

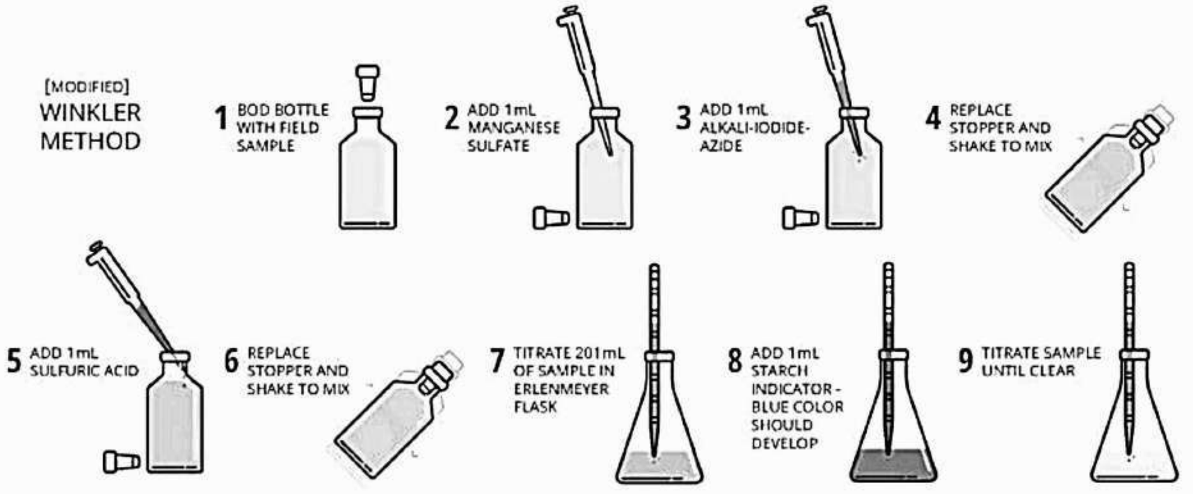
The nascent oxygen reacts with KI in the solution in presence of H_2SO_4 to liberate iodine.

$$2KI + H_2SO_4 + [O] \rightarrow K_2SO_4 + H_2O + I_2$$

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.

$$I_2 + 2Na_2S_2O_3 \rightarrow 2NaI + Na_2S_4O_6$$

$$1\text{ml of } 0.01N\ Na_2S_2O_3 \text{ solution} = 0.1\text{mg Dissolved Oxygen}$$



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.

$$\text{BOD} = \frac{(\text{D1} - \text{D2}) \text{ Volume of the sample after dilution}}{\text{Volume of the sample before dilution}}$$

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 $K_2Cr_2O_7$ 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 $K_2Cr_2O_7$ 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 $K_2Cr_2O_7$ 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.

$$\text{COD} = \frac{(\text{V1} - \text{V2}) \text{ X N X 8}}{\text{Ve}} \text{ X } 1000$$

Where V1& V2 are the volumes of Mohr salt used by the blank and test samples respectively. Ve 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.

$$CH_2O + O_2 \longrightarrow CO_2 + H_2O$$

30 g CH_2O reacts with 32 g O_2

Therefore, 60 mg carbohydrate requires $60 \text{ X } \frac{32}{30} = 64$ 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.

$$CH_2O + O_2 \longrightarrow CO_2 + H_2O$$

30 g CH_2O reacts with 32 g O_2

Therefore, 75 mg carbohydrate requires $75 \text{ X } \frac{32}{30} = 80$ 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.

$$\text{COD} = \frac{(V1-V2)\ X\ N\ X\ 8}{Ve}\ \mathbf{X\ 1000}$$

$$\text{COD} = \frac{(25-15)\ X\ 0.1\ X\ 8}{100}\ \mathbf{X\ 1000 = 80\ ppm}$$

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.

$$\text{BOD} = \frac{\text{(D1 -D2) Volume of the sample after dilution}}{\text{Volume of the sample before dilution}}$$

$$\text{BOD} = \frac{(7.5-3.5)\ 500}{100} = 20 \text{ ppm}$$

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.

$$Al_2(SO_4)_3 + 6H_2O \rightarrow 2Al(OH)_3 + 6H_2SO_4$$

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.

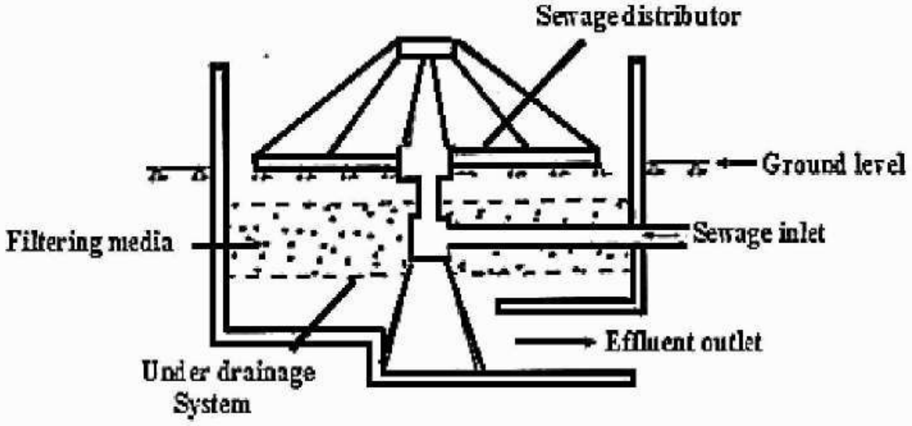
$$NH_2\text{-}CO\text{-}NH_2 \xrightarrow{\text{Aerobic oxidation}} 2NH_3 \div CO_2$$

$$NH_3 \xrightarrow{\text{Oxidation}} HNO_2 \div HNO_3$$

$$HNO_2 \div HNO_3 \xrightarrow[\text{Bases present in soil}]{} NH_4NO_2 \div NH_4NO_3$$

a. Trickling filter process

It is a type of biological treatment carried out using a special type of filter called trickling filter.



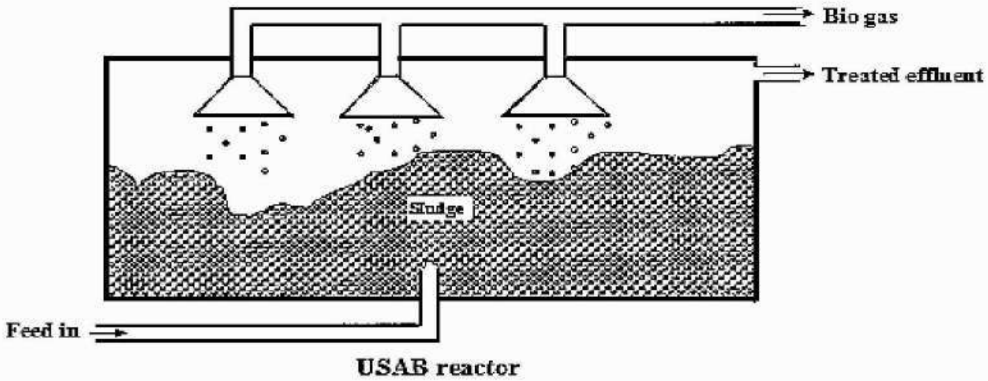
Trickling Filter

It is rectangular in shape with 2m depth. It is filled with crushed rocks, brocken 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 Anaerbic 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 $Ca_3(PO_4)_2$.

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.

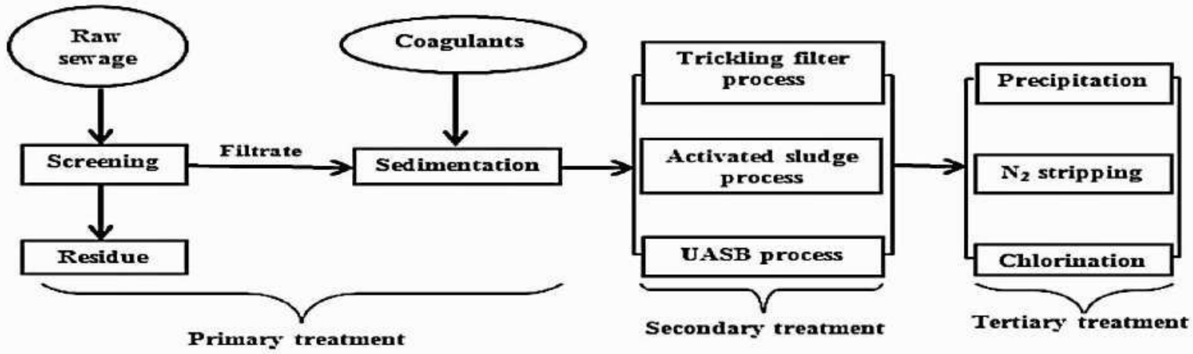
c) Chlorination

Disinfection of effluent is done by treating it with chlorine.

$$H_2O + Cl_2 \rightarrow HOCl + HCl$$

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, $Mg(HCO_3)_2$ – 1.4mg/L, $MgCl_2$ – 9.5mg/L.

Constituents	Quantity	M_{HPS}	$CaCO_3$ equivalent hardness = Quantity X $\frac{100}{MHPS}$
$CaSO_4$	16.2mg/L	136	$16.2X\frac{100}{136} = 11.9$ ppm
$Mg(HCO_3)_2$	1.4mg/L	146	$1.42 X \frac{100}{146} = 0.97$ ppm
$MgCl_2$	9.5mg/L	95	$9.5 X \frac{100}{95} = 10$ ppm

Total hardness = 11.9 + 0.97 + 10 = 22.87 ppm

Temporary hardness = 0.97 ppm

Permanent hardness = Total hardness - Temporary hardness = 22.87 – 0.97 = 21.9 ppm

2. A sample of water on analysis gives the following results: Ca^{2+} = 30mg/L, Mg^{2+} = 18mg/L, HCO_3^- =244mg/L, Na^+ =11.5mg/L. Calculate the temperory and permanent hardness of water sample.

Constituents	Quantity (mg/L)	M_{HPS}	$CaCO_3$ equivalent hardness = Quantity X $\frac{100}{MHPS}$
Ca^{2+}	30	40	$30 X \frac{100}{40} = 75$
Mg^{2+}	18	24	$18 X \frac{100}{24} = 75$

HCO_3^-	122	61	$122 \text{ X } \frac{100}{2 X 61} = 100$
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 $NaHCO_3$ 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 $NaHCO_3$.

Increase in temporary hardness = $\frac{42 X 100}{2 X 84}$ = 25 ppm

New temporary hardness = 100 + 25 = 125 mg/L

New permanent hardness = Total hardness - New temporary hardness = 500 – 125 = 375mg/L

4. A water sample contains $Mg(HCO_3)_2$– 36.5 ppm, $Ca(HCO_3)_2$ – 40.5 ppm, $MgSO_4$ – 30.0 ppm, $CaSO_4$ – 34.0 ppm, $CaCl_2$ –27.75 ppm, NaCl – 10 ppm. Calculate the temperory 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	$40.5 \text{X } 100/_{162}$ = 25 ppm
$Mg(HCO_3)_2$	36.5	146	$36.5 \text{X } 100/_{146}$ = 25 ppm
$MgSO_4$	30.3	120	$30.0 \text{ X } 100/_{120}$ = 25 ppm
$CaSO_4$	34.0	136	$34.0 \text{X } 100/_{136}$ = 25 ppm
$CaCl_2$	27.75	111	$27.75 \text{ X } 100/_{111}$= 25 ppm
NaCl	10	-	-

Temporary hardness = Hardness due to $Ca(HCO_3)_2$+ Hardness due to $Mg(HCO_3)_2$
= 25 +25 = 50 ppm

Permanent hardness = Hardness due to $MgSO_4$+ Hardness due to $CaSO_4$ + Hardness due to $CaCl_2$= 25 + 25 + 25 = 75 ppm

5. A sample of water on analysis gives the following results: Ca^{2+} = 400mg/L, Mg^{2+} = 240 mg/L, HCO_3^- = 244mg/L, Na^+ =92mg/L. Calculate the temperory and permanent hardness of water sample.

Constituents	Quantity (ppm)	M_{HPS}	$CaCO_3$ equivalent hardness = Quantity X $\frac{100}{MHPS}$
Ca^{2+}	400	40	$400 \text{ X } \frac{100}{40} = 1000$
Mg^{2+}	240	24	$240 \text{ X } \frac{100}{24} = 1000$
HCO_3^-	244	61	$244 \text{ X } \frac{100}{2 X 61} = 200$
Na^+	92	-	-

Total hardness = 1000 + 1000 = 2000 ppm

Temporary hardness = 200 ppm

Permanent hardness = 2000 – 200 = 1800 ppm

6. A water sample contains $Mg(HCO_3)_2$ – 43.8mg/L, $Ca(HCO_3)_2$ – 48.6 ppm, $MgSO_4$ – 24.0 ppm, $CaSO_4$ – 27.2mg/L, $NaHCO_3$ – 16.8mg/L. Calculate the temperory and permanent hardness of water sample.

Constituents	Quantity (mg/L)	M_{HPS}	$CaCO_3$ equivalent hardness = Quantity X $\frac{100}{MHPS}$

$Ca(HCO_3)_2$	48.6	162	$48.6 \text{ X } \frac{100}{162} = 30$ ppm
$Mg(HCO_3)_2$	43.8	146	$43.8 \text{ X } \frac{100}{146} = 30$ ppm
$MgSO_4$	24.0	120	$24.0 \text{ X } \frac{100}{120} = 20$ ppm
$CaSO_4$	27.2	136	$27.2 \text{ X } \frac{100}{136} = 20$ ppm
$NaHCO_3$	16.8	84	$16.8 \text{ X } \frac{100}{2 X 84} = 10$ 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: Ca^{2+} = 320mg/L, Mg^{2+} = 72mg/L, HCO_3^-=610mg/L, Na^+ =23mg/L. Calculate the temperory and permanent hardness of water sample.

Constituents	Quantity (mg/L)	M_{HPS}	$CaCO_3$ equivalent hardness = Quantity X $\frac{100}{MHPS}$
Ca^{2+}	320	40	$320 \text{ X } \frac{100}{40} = 800$
Mg^{2+}	72	24	$72 \text{ X } \frac{100}{24} = 300$
HCO_3^-	610	61	$610 \text{ X } \frac{100}{2 X 61} = 500$
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 $CaCl_2$ solution.
Hardness = Molarity X M_{CaCO3} X 1000
= 0.1 X 100 X 1000 =10000 ppm

9. Calculate the hardness of 0.4 N Ca^{2+}solution.
Hardness = Normality X Eqnt. Wt. $_{CaCO3}$ X 1000
= 0.4 X 50 X 1000 =20000 ppm

10. A standard hard water containing 15g $CaCO_3$ 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 litre SHW = 15g $CaCO_3$
1000 ml SHW = 15000mg $CaCO_3$
1 ml SHW = 15mg $CaCO_3$
Normality of SHW = 15mg $CaCO_3$

Step II: Standardisation of EDTA

20 ml SHW = 25 ml EDTA
V_{SHW} X N_{SHW} = V_{EDTA} X N_{EDTA}
20 X 15 = 25 x N_{EDTA}
$N_{EDTA} = \frac{20 X 15}{25} = 12$mg $CaCO_3$

Step III: Estimation of total hardness

100 ml UHW = 18 ml EDTA
V_{UHW} X N_{UHW} = V_{EDTA} X N_{EDTA}
100 X N_{UHW}= 18 X 12
$N_{UHW} = \frac{18 X 12}{100} = 2.16$mg
Total Hardness = 2.16 X 1000 = 2160 ppm

Step IV: Determination of permanent hardness

100 ml BHW = 12 ml EDTA

V_{BHW} X N_{BHW} = V_{EDTA} X N_{EDTA}

100 X N_{BHW}= 12 X 12

$N_{BHW}= \frac{12\ X\ 12}{100} = 1.44$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

11. A standard hard water was prepared by dissolving 1g $CaCO_3$ in dil. HCl. It is then evaporated and made upto 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 $CaCO_3$

1000 ml SHW = 1000mg $CaCO_3$

1 ml SHW = 1mg $CaCO_3$

Normality of SHW = 1mg $CaCO_3$

Step II: Standardisation of EDTA

50 ml SHW = 48 ml EDTA

V_{SHW} X N_{SHW} = V_{EDTA} X N_{EDTA}

50 X 1 = 48 x N_{EDTA}

$N_{EDTA}= \frac{50\ X\ 1}{48} = 1.04$mg $CaCO_3$

Step III: Estimation of total hardness

50 ml UHW = 15 ml EDTA

V_{UHW} X N_{UHW} = V_{EDTA} X N_{EDTA}

50 X N_{UHW}= 15 X 1.04

$N_{UHW}= \frac{15\ X\ 1.04}{50} = 0.312$mg

Total Hardness = 0.312 X 1000 = 312 ppm

Step IV: Determination of permanent hardness

50 ml BHW = 10 ml EDTA

V_{BHW} X N_{BHW} = V_{EDTA} X N_{EDTA}

50 X N_{BHW}= 10 X 1.04

$N_{BHW}= \frac{10\ X\ 1.04}{50} = 0.208$mg

Permanent Hardness = 0.208 X 1000 = 208 ppm

Step V: Determination of temporary hardness

Temporary hardness = Total hardness - Permanent hardness = 312 – 208= 104 ppm

12. 2.8g $CaCO_3$ 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 litre SHW = 2.8g $CaCO_3$

1000 ml SHW = 2800mg $CaCO_3$

1 ml SHW = 2.8mg $CaCO_3$

Normality of SHW = 2.8mg $CaCO_3$

Step II: Standardisation of EDTA

100 ml SHW = 28 ml EDTA

V_{SHW} X N_{SHW} = V_{EDTA} X N_{EDTA}

100 X 2.8 = 28 x N_{EDTA}

$N_{EDTA} = \frac{100\ X\ 2.8}{28}$ = 10mg $CaCO_3$

Step III: Estimation of total hardness

100 ml UHW = 35 ml EDTA

V_{UHW} X N_{UHW} = V_{EDTA} X N_{EDTA}

100 X N_{UHW}= 35 X 10

$N_{UHW} = \frac{35\ X\ 10}{100}$ = 3.5mg

Total Hardness = 3.5 X 1000 = 3500 ppm

Step IV: Determination of permanent hardness

100 ml BHW = 10 ml EDTA

V_{BHW} X N_{BHW} = V_{EDTA} X N_{EDTA}

100 X N_{BHW}= 10 X 10

$N_{BHW} = \frac{10\ X\ 10}{100}$ = 1mg

Permanent Hardness = 1 X 1000 = 1000 ppm

Step V: Determination of temporary hardness

Temporary hardness = Total hardness - Permanent hardness= 3500 –1000= 2500 ppm

13. 0.30g $CaCO_3$ 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 litre SHW = 0.30g $CaCO_3$

1000 ml SHW = 300mg $CaCO_3$

1 ml SHW = 0.3mg $CaCO_3$

Normality of SHW = 0.3mg $CaCO_3$

Step II: Standardisation of EDTA

100 ml SHW = 30 ml EDTA

V_{SHW} X N_{SHW} = V_{EDTA} X N_{EDTA}

100 X 0.3 = 30 x N_{EDTA}

$N_{EDTA} = \frac{100\ X\ 0.3}{30}$ = 1mg $CaCO_3$

Step III: Estimation of total hardness

100 ml UHW = 33 ml EDTA

V_{UHW} X N_{UHW} = V_{EDTA} X N_{EDTA}

100 X N_{UHW}= 33 X 1

$N_{UHW} = \frac{33\ X\ 1}{100}$ = 0.33mg

Total Hardness = 0.33 X 1000 = 330 ppm

Step IV: Determination of permanent hardness

100 ml BHW = 10 ml EDTA

V_{BHW} X N_{BHW} = V_{EDTA} X N_{EDTA}

100 X N_{BHW}= 10 X 1

$N_{BHW} = \frac{10\ X\ 1}{100}$ = 0.1mg

Permanent Hardness = 0.1 X 1000 = 100 ppm

Step V: Determination of temporary hardness

Temporary hardness = Total hardness - Permanent hardness = 330 – 100= 230 ppm

14. A sample of water is found to contain $Mg(HCO_3)_2$ – 7.3mg/L, $Ca(HCO_3)_2$ – 16.2 mg/L, $MgCl_2$ – 9.5 ppm and $CaSO_4$ – 13.6mg/L. Calculate the temperory and permanent hardness of

water sample. What happen to the temperory 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 X $\frac{100}{MHPS}$
$Ca(HCO_3)_2$	16.2	162	16.2 X $\frac{100}{162}$ = 10 ppm
$Mg(HCO_3)_2$	7.3	146	7.3 X $\frac{100}{146}$ = 5 ppm
$MgCl_2$	9.5	95	9.5 X $\frac{100}{95}$ = 10 ppm
$CaSO_4$	13.6	136	13.6 X $\frac{100}{136}$ = 10 ppm
Na_2CO_3	10.6	106	10.6 X $\frac{100}{106}$ = 10 ppm

Total hardness = 10+5+10+10 = 35 ppm
Temporary hardness = 10+5 = 15 ppm
Permanent hardness = 35 – 15 = 20 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 Na_2CO_3= 10 ppm
Thus 10 ppm permanent Ca is removed as $CaCO_3$.
New total hardness = 35 – 10 = 25 ppm
Temporary hardness = 15 ppm
New permanent hardness = 25 – 15 = 10 ppm