

**GUDLAVALLERU ENGINEERING COLLEGE**  
(An Autonomous Institute with Permanent Affiliation to JNTUK, Kakinada)  
Seshadri Rao Knowledge Village, Gudlavalleru – 521 356.

**Department of Civil Engineering**



**HANDOUT**

**ON**

**ENGINEERING CHEMISTRY**

### **VISION OF THE DEPARTMENT**

To provide quality education embedded with knowledge, ethics and advanced skills and preparing students globally competitive to enrich the civil engineering research and practice.

### **MISSION OF THE DEPARTMENT**

- To aim at imparting integrated knowledge in basic and applied areas of civil engineering to cater the needs of industry, profession and the society at large.
- To develop faculty and infrastructure making the department a centre of excellence providing knowledge base with ethical values and transforming innovative and extension services to the community and nation.
- To make the department a collaborative hub with leading industries and organizations, promote research and development and combat the challenging problems in civil engineering which leads for sustenance of its excellence.

### **PROGRAM EDUCATIONAL OBJECTIVES**

- **PEOI** : Exhibit their competence in solving civil engineering problems in practice, be employed in industries and undergo higher studies.
- **PEOII** : Adapt to changing technologies with societal relevance for sustainable development in the field of their profession.
- **PEO III:** Develop multidisciplinary team work with ethical attitude & social responsibility and engage in life - long learning to promote research and development in the profession.

## HANDOUT OF ENGINEERING CHEMISTRY

Class & Sem. :I B.Tech. – I Semester

Year: 2018-19

Branch : CE

Credits: 2

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### 1. Brief history and scope of the subject

Chemistry is the study of matter, its properties and the changes that it may undergo and how these properties and changes are affected by its composition. It is important for engineers to have knowledge of chemistry, since they can expect to find problems in fields as diverse as the design and development of new materials, quality control and environmental engineering that are basically chemical in nature.

Chemistry is the back bone in designing and understanding the nature of various engineering materials. Many advances in engineering either produce a new chemical demand as in the case of polymers or wait upon chemical developments for their application as in the case of implants and alloys. Currently, the civil engineers are looking for materials that are environment friendly, economical but long lasting.

### 2. Pre-Requisites

Intermediate Chemistry

### 3. Course Objectives:

- To impart the knowledge of corrosion, treatment methods of water and green synthesis of products.
- To enable the students to obtain the knowledge of refractories, nano materials and instrumental methods of analysis.

### 4. Course Outcomes:

Students will be able to

- apply a suitable method of corrosion prevention for a given problem.
- explain the properties and engineering applications of polymers, fibre reinforced plastics and refractories.
- explain the methods of synthesis of nano materials, properties and applications of CNTs and quantum dots.
- explain the principles of green chemistry and suitable method for synthesis of green products.
- apply a suitable method of water treatment depending on the quality requirement.
- explain the principles and working of spectrophotometer and flame photometer for the determination of a given ion in a given solution.

### 5. Program Outcomes:

- a. An ability to apply knowledge of mathematics, science and engineering principles to civil engineering problems.

- b. An ability to analyze design and conduct experiments and interpret the resulting data.
- c. An ability to design a system, component or process to meet desired goals in civil engineering applications.
- d. An ability to function on multi disciplinary teams.
- e. An ability to identify, formulate and solve challenging engineering problems.
- f. An understanding of professional and ethical responsibility.
- g. An ability to communicate effectively through verbal, written and drawing presentations.
- h. An ability to understand the impact of engineering solutions in a global, economical and social context with a commitment on environmental and safety issues.
- i. An ability to recognize the need of engaging in lifelong learning and acquiring further knowledge in specialized areas.
- j. Ability to excel in competitive examinations, advanced studies and become a successful engineer in construction industry.
- k. An ability to use the techniques, skills and modern engineering tools and software for engineering design and practices.
- l. The understanding of basic finance & management techniques and construction practices including work procurement and legal issues.

#### 6. Mapping of Course Outcomes with Program Outcomes:

	a	b	c	d	e	f	g	h	i	i	k	l
CO1	H	H	H		H			L				
CO2	H				L			H	L			
CO3	H		L		L				H			
CO4	H				L			H				
CO5	H	H	L		L			H				
CO6	H				L			H				

#### 7. Prescribed Text Books

- Text book of Engineering Chemistry by Jain & Jain. Dhanpat Rai Publishing Company, 16<sup>th</sup> Edn., 2015.
- A Text book of Engineering Chemistry by Shashi Chawla. Dhanpat Rai Publications, 3<sup>rd</sup> Edn., 2013.

#### 8. Reference Text Books

- A Text book of Engineering Chemistry by S.S.Dara. S.Chand&Company Ltd., 12<sup>th</sup> Edn.,2010.
- Engineering Chemistry by J.C.Kurisasose and J.Rajaram. volumes 1 & 2, Tata Mc Graw-Hill Publishing.

#### 6. URLs and Other E-Learning Resource

<http://www.hunterwater.com.au/Water-and-Sewer/WaterSupply/Water>

<http://www.mpoweruk.com/chemistries.htm>

[http://chemwiki.ucdavis.edu/Core/Analytical\\_Chemistry/Electrochemistry/Case\\_Studies/Corrosion/Corrosion\\_Basics\\_II](http://chemwiki.ucdavis.edu/Core/Analytical_Chemistry/Electrochemistry/Case_Studies/Corrosion/Corrosion_Basics_II)  
<http://www.open.edu/openlearn/science-maths-technology/science/chemistry/introduction-polymers/content-section-0>

7. **Digital Learning Materials:**

[http://www.faadooengineers.com/threads/7899-Engineering-Chemistry-Ebook-pdf-free\\_download](http://www.faadooengineers.com/threads/7899-Engineering-Chemistry-Ebook-pdf-free_download)

8. **Lecture Schedule / Lesson Plan**

Topic	No. of Periods	
	Theory	Tutorial
<b>Unit-I: Corrosion and its prevention(8 Periods)</b>		
Introduction-Dry and wet corrosion and their mechanisms.	1	2
Pilling - Bedworth Rule- significance	1	
Types of Corrosion – galvanic corrosion, concentration cell corrosion, pitting corrosion and stress corrosion	1	
Factors influencing the rate of corrosion – Temperature, pH and dissolved oxygen.	1	
Corrosion of Reinforced cement concrete(RCC).	1	2
Corrosion Prevention methods – Cathodic protection – Sacrificial anodic method and Impressed current method.	1	
Metallic coatings –anodic and cathodic coatings.	1	
galvanization and tinning methods.	1	
<b>Unit-II: Polymers and Refractory materials (9 Periods)</b>		
Definitions of Polymer and Polymerization	1	2
Degree of Polymerization – Functionality.	1	
<b>Plastics</b> – definition- advantages-disadvantages	1	
Fibre reinforced plastics - Glass Fibres- preparation methods--properties – applications.	1	
Carbon fibres, aramid fibres- preparation methods--properties – applications.	1	2
preparation methods – hand layup method, matched metal die moulding method	1	
<b>Refractories:</b> Definition of a refractory – classification	1	
properties-refractoriness–RUL test–thermal spalling.	1	
Conditions leading to failure of a refractory and	1	2

applications of refractories.		
<b>Unit-III : Nano materials (7 Periods)</b>		
Concept of Nano materials	1	
synthesis of nano materials- Sol-gel	1	
Chemical vapour deposition method	1	
carbon nano tubes ( CNTs) – types	1	2
Preparation of CNTs	1	
properties, applications of CNTs	1	
Quantum dots – applications	1	
<b>UNIT-IV: Green Chemistry (6 Periods)</b>		
Introduction - Principles of Green Chemistry	1	2
methods of Green synthesis -supercritical fluid extraction	1	
IWM (Integrated Waste Management) of solid waste	1	
microwave induced methods	1	
ZWT (Zero Waste Technology)	1	2
Applications of green chemistry	1	
<b>Unit-V: Water and its treatment (9 Periods)</b>	1	
Hardness of water – calculation of hardness		
disadvantages of hard water	1	2
determination of hardness by EDTA method	1	
numerical problems	1	
softening methods – zeolite process	1	
Ion exchange process	1	2
desalination by reverse osmosis	1	
quality parameters of drinking water – (WHO standards and BIS standards)	1	
municipal water treatment (Sedimentation, filtration and sterilization by chlorination and bleaching powder).	1	
<b>Unit-VI: Instrumental methods of analysis (8 Periods)</b>	1	
Electronic transition in molecules		2
Absorption Spectra	1	
Beer Lambert's Law	1	
UV spectrophotometer – principle and working	1	
determination of Ferric Iron by spectrophotometry	1	2
Flame photometry	1	
principle and working	1	
estimation of sodium by flame photometry.	1	

<b>Total No. of Periods:</b>	<b>47</b>	<b>24</b>

**9. Seminar Topics :**

- Modern fabrication techniques of plastics.
- Nano materials preparation methods.

# ENGINEERING CHEMISTRY

## Unit – I

### CORROSION AND ITS PREVENTION

#### Objectives:

- To introduce the students to basic concept of corrosion, factors influencing the rate of corrosion, types of corrosion and the application of various chemical methods to prevent corrosion of metals.

#### UNIT I: Corrosion and its prevention

Dry and wet corrosion and their mechanisms. Pilling - Bedworth Rule. Types of Corrosion – galvanic corrosion, concentration cell corrosion, pitting corrosion and stress corrosion. Factors influencing the rate of corrosion – Temperature, pH and dissolved oxygen. Corrosion of Reinforced cement concrete(RCC). Corrosion Prevention methods – Cathodic protection – Sacrificial anodic method and Impressed current method. Metallic coatings – galvanization and tinning methods.

#### Course outcomes:

##### Students will be able to

- explain various types of corrosion
- explain the factors influencing the rate of corrosion
- apply various chemical methods to prevent corrosion of metals

#### Introduction:

- Corrosion is defined as the slow and gradual degradation or deterioration of metal due to its reaction with the environment.

#### Examples:

- ◆ Rusting of iron: A layer of reddish brown scale ( $\text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}$ ) formed on the surface of the iron.
- ◆ Formation of green layer of basic copper carbonate [ $\text{CuCO}_3 + \text{Cu}(\text{OH})_2$ ] on the surface of copper.
- ◆ Tarnishing of silver: Blackening of surface of silver due to the formation of black layer of silver sulphide on it.



**Reason for corrosion:**

- All the metals exist in nature in combined forms as oxides, carbonates, sulphides etc.
- High amount of energy is required to extract the metal from ore.
- Thus, the metal is in thermodynamically unstable state.
- It is the natural tendency of metal to revert back to thermodynamically stable state when it comes in contact with the elements in the environment.

**Disadvantages of corrosion:**

- Enormous waste of machineries and different types of metallic materials.
- It leads to sudden failure of machines.
- Metals lose metallic lustre and other important metallic properties.
- It leads to the decrease in efficiency of machine and frequent replacement of corroded equipment which is expensive.
- It may result leakage of inflammable gas from the corroded pipe lines resulting to fire accidents etc.
- It causes contamination of potable water.
- It has been estimated that 25% of annual world production of iron is wasted due to corrosion.

**Theories (or) Mechanism of corrosion:**

- \* Dry or Chemical theory
- \* Wet or Electrochemical theory

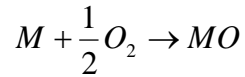
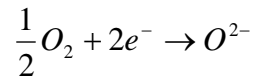
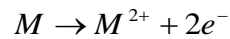
**Direct chemical attack theory (or) Mechanism of dry corrosion:**

- ◆ The direct chemical action of atmosphere gases like oxygen, halogen, H<sub>2</sub>S etc in a dry environment on metals is called dry corrosion. A solid film of the corrosion product is formed on the surface of the metal.
- ◆ This is known as chemical corrosion.

**1. Oxidation corrosion (Reaction with oxygen):**

- Some of the metals directly react with oxygen in the absence of moisture.
- Then the metal gets oxidized to metal ions and the electrons so released reduce oxygen to form oxide ion.
- The metal ion and oxide ion combine to form metal oxide on the metal

surface.



➤ The nature of metal oxide layer formed plays an important role in determining further corrosion.

**a) Protective (stable) and non porous oxide film:** Metals such as Al, Cr, Cu and W develop nonporous and stable oxide film on the surface. This film prevents further corrosion of the metal.

**b) Unstable oxide film:** Au & Pt develop unstable oxide film which instantaneously decomposes to form metal and oxygen and thereby no corrosion occurs.

**c) Volatile oxide film:** Molybdenum develops an oxide which immediately vaporizes. As a result, metal surface easily undergoes rapid and continuous corrosion.

**d) Porous and non protective film:** Alkali and alkaline earth metals form porous oxide layer which further increases the rate of corrosion of the metal due to porous nature of the film.

**Pilling Bedworth rule:** The ratio of volume of oxide film to the volume of metal consumed is known as Pilling-Bedworth rule (or ratio).

**Significance:**

The protective or non protective nature of oxide film is determined by this rule.

- If the ratio is  $<1$ , the metal oxide layer is porous and non protective. Ex. Oxide layer on alkaline metals.
- If the ratio is  $\geq 1$ , the metal oxide layer is non porous protective layer. It stops further corrosion of metal. Ex. Oxide layer on Al, Cr, Cu, W.

$$\text{Pilling Bedworth rule} = \frac{\text{Vol.of metal oxide layer}}{\text{Vol of metal consumed}}$$

## 2. Corrosion by other gases:

- This type of corrosion is due to the attack of other gases like  $\text{Cl}_2$ ,  $\text{SO}_2$ ,  $\text{H}_2\text{S}$ ,  $\text{NO}_x$  in dry atmosphere on the metal.
- The corrosion products may be protective or non-protective.
- Dry  $\text{Cl}_2$  reacts with Ag and forms AgCl which is protective layer, where as  $\text{SnCl}_4$  is volatile.

## 3. Liquid metal corrosion:

- This type of corrosion takes place, when molten metal passes through metallic pipes due to dissolution of solid metal by liquid molten metal or due to internal penetration of solid metal into liquid metal.

Ex.1 Liquid metal mercury dissolves most metals by forming amalgams, thereby corroding them.

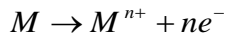
Ex.2 Coolant (sodium metal) leads to corrosion of cadmium (moderator) in nuclear reactors.

## Electrochemical Corrosion (or) Wet Corrosion(Mechanism of Wet corrosion by Electrochemical theory):

- This type of corrosion occurs when a metal is exposed to moisture (electrolytic medium).
- This corrosion occurs due to the existence of separate anodic and cathodic parts, between which current flows through the conducting medium.
- These anodic and cathodic regions are formed due to several factors like
  - on a metal surface if the concentration of oxygen is different.
  - due to contact of two different metals.
  - when a metal surface is subjected to stress.
- **At anodic area, oxidation reaction occurs**, thereby destroying the anodic metal due to dissolution. Hence, corrosion always occurs at anodic parts.
- **At cathodic area, reduction reaction occurs.**

### Anodic reaction:

- At anode, oxidation takes place so that metal is converted into metal ions with the liberation of electrons.
- These electrons migrate towards cathode.



**Cathodic reaction:**

At cathode, reduction takes place. Depending upon the nature of the corrosive environment, cathodic reaction takes place in the following way:

- Evolution of hydrogen.
- Absorption of oxygen depending upon the nature of corrosion environment.

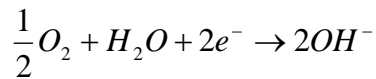
**a) Evolution of Hydrogen type:**

In acidic medium and in the absence of oxygen, H<sup>+</sup> ions are reduced to H<sub>2</sub> gas.



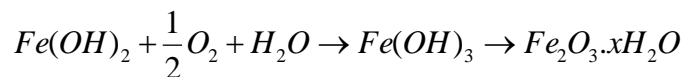
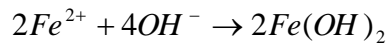
**b) Absorption of oxygen:**

In neutral and aerated or basic medium: If the solution is neutral and aerated, hydroxyl ions are formed as follows.



**Formation of corrosion product:**

- The hydroxyl ions react with metal ions and forms corrosion product.
- In case of iron, hydroxide ions react with ferrous ions and forms insoluble hydrated ferric oxide called brown rust.



**Differences between dry corrosion and wet corrosion:**

Dry corrosion	Wet corrosion
1.It occurs in dry condition.	1.It occurs in wet condition.

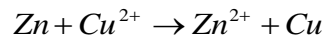
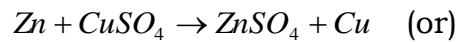
2.If the corrosion takes place due to direct chemical attack (in the absence of moisture), the corrosion is known as dry corrosion.	2.If the corrosion takes place due to electrochemical attack in presence of moisture or a conducting medium, the corrosion is known as wet corrosion
3.Explained by absorption mechanism	3.Explained by electrochemical mechanism
4.It occurs on both heterogeneous and homogeneous surfaces.	4.It occurs only on heterogeneous metal surfaces.
5.Corrosion is uniform.	5.Corrosion is not uniform.
6.It is a slow process.	6.It is a fast process.
7.Corrosion products accumulate at the place where corrosion occurs.	7.Corrosion take place at anode but products accumulate near the cathode

### Galvanic series

- Galvanic series is the series of metals that is made keeping in view the process of corrosion of a metal in a particular atmosphere, i.e., sea water. In galvanic series, oxidation potential of metals is arranged in the decreasing order of activity of a series of metals. The series is towards the increasing noble character. The series is given below:

**Mg,Mg alloys,Zn,Al, cast iron, stainless steel(active),Pb-Sn alloys, Pb, Sn, brass, Cu, bronze, Ag, stainless steel(passive), Monel, Graphite, Ti, Gold, Pt**

- A metal having higher position can replace (reduce) other metals that have lower position in the series.
- For example:

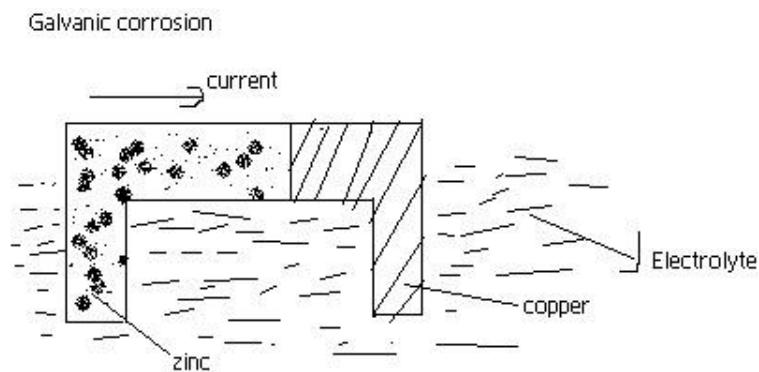


- Or in other words, zinc will corrode faster than copper.
- More anodic: Mg, Mg alloys, Zn, Al, Cd, Fe, Pb, Sn, Ni-Mo-Fe alloys.
- Brasses, Cu, Ni, Cr-alloy, Ag, Ti, Au, Pt towards noble nature.
- **From left to right of the series, anodic nature decreases, corrosion tendency decreases.**

## Types of Corrosion

### Galvanic corrosion:

- When two dissimilar metals are connected and exposed to an electrolyte, then the metal higher in electrochemical series undergoes corrosion. This type of corrosion is also called galvanic corrosion or bimetallic corrosion.
- For example, zinc and copper are connected and exposed to an electrolytic medium, the **more reactive zinc acts as anode and undergoes corrosion.**



- **The less reactive copper behaves as cathode and gets protected from corrosion.**
- The extent of corrosion depends on the potential difference between the two metals.
- This galvanic corrosion can be minimized by
  - Avoiding galvanic couple

- Selecting metals closely placed in electrochemical series as galvanic couple
- Providing an insulating material between the two metals

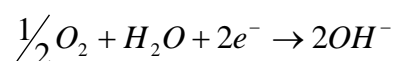
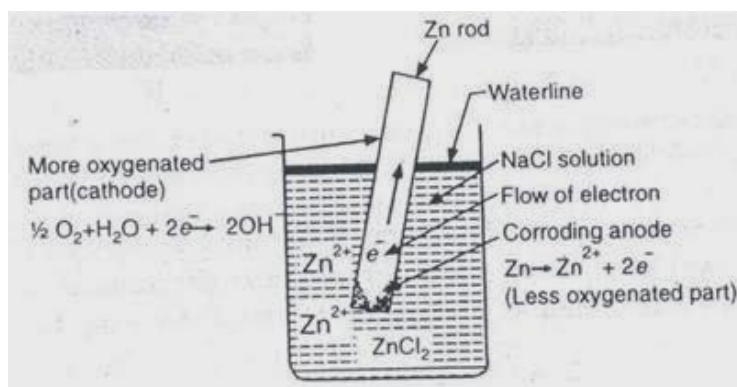
## Corrosion due to Differential Aeration (or) Concentration Cell

### Corrosion:

- This type of corrosion arises due to **exposure of metal to different concentrations of electrolyte or of varying aeration.**
- When metal is exposed to different concentrations of oxygen(air), part of the metal exposed to **less concentration of oxygen(air) acts as anode** and other parts exposed to **high concentration of oxygen(air) acts as cathode.**
- Anodic part undergoes corrosion.

### Example:

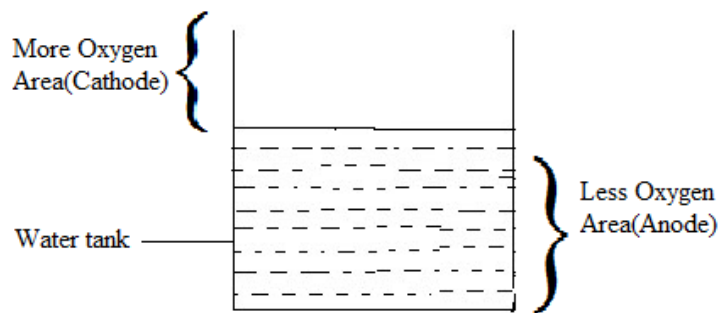
- If a metal is partially immersed in a dilute solution of a neutral salt solution, then the **parts above the solution are more strongly aerated hence, become cathodic.**
- The **metal part immersed in solution is less aerated and thus become anodic.**



**Examples:** Water line corrosion, water drop corrosion

♦ **Water line corrosion:**

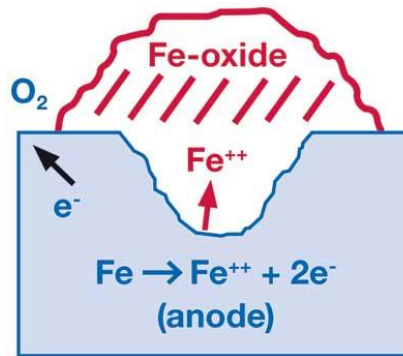
- The rusting of an iron tank partially filled with water takes place along the line just beneath the level of water in it.
- It is due to differential aeration.
- The **area above the waterline (well aerated) acts as cathode** whereas the **area below the waterline (less aerated) acts as anode and is corroded.**



**Pitting corrosion:**

- Pitting of metal occurs where there is a break in the protective layer.
- Pitting corrosion is a non uniform corrosion resulting from a localized accelerated attack and results in the formation of pits, cavities and pin holes in the metal.
- This gives rise to the formation of small anodic and large cathodic areas.
- The presence of the impurities (like sand, dust, scale etc) on the surfaces of metals also leads to pitting.
- A part below the impurity become the anodic area and undergoes corrosion and the surrounding part become the cathodic area.
- Once a small pit is formed, the rate of corrosion will be increased.





### Stress corrosion:

- Stress corrosion is observed in metals which undergo mechanical operations such as welding, bending, pressing etc.
- When a metal is subjected to uneven stress and exposed to corrosion environment, it undergoes stress corrosion.
- The stressed portion is in thermodynamically unstable state that's why **areas under stress act as the anode and unstressed areas act as the cathode.**
- Anode part undergoes corrosion.

### Factors influencing (effecting) the rate of corrosion:

- **Temperature:**
  - As temperature increases, the rate of almost every chemical reaction increases.
  - Thus, **the rate of corrosion also increases with increase in temperature.**
- **Effect of pH:**
  - Corrosion occurs at a **faster rate in acidic medium.**
  - Low pH accelerates corrosion by providing more hydrogen ions.
- **Effect of Dissolved Oxygen:**
  - **Dissolved oxygen (DO) refers to the volume of oxygen that is contained in water.**
  - Dissolved oxygen can destroy the protective hydrogen film that is formed on many metals.

- **As the amount of DO increases, the rate of corrosion also increases.**

**Corrosion of Reinforced Cement Concrete (RCC):** Concrete reinforced with steel is called reinforced cement concrete.

**Reinforcement (Iron or steel)** embedded in concrete is durable because of the protective Iron oxide coating present on reinforcement in the presence of  $\text{Ca(OH)}_2$ .

$\text{CO}_2$ , Chlorides and sulphates cause deterioration of RCC.

In porous and low quality concrete,  $\text{CO}_2$  diffuses easily and carbonation of lime occurs leading to decay of concrete and finally the decay of reinforcement.

In the presence of Chlorides, the protective oxide layer around iron becomes less protective and porous that causes electrochemical corrosion of iron.

Tricalcium Aluminate of Portland cement reacts with sulphate ions and forms Ettringite that leads to cracking and finally the deterioration of concrete and also the reinforcement.

#### **Prevention of decay of RCC:**

- By coating the surface of reinforcement and concrete with epoxy resin paint which makes surface impermeable to acidic water.
- By treating the surface of concrete with silicon fluoride, insoluble  $\text{CaF}_2$  is formed which prevents the penetration of acidic water into capillaries.

#### **Methods for prevention of corrosion:**

##### **1. Cathodic Protection**

##### **2. Coating methods (metallic coating)**

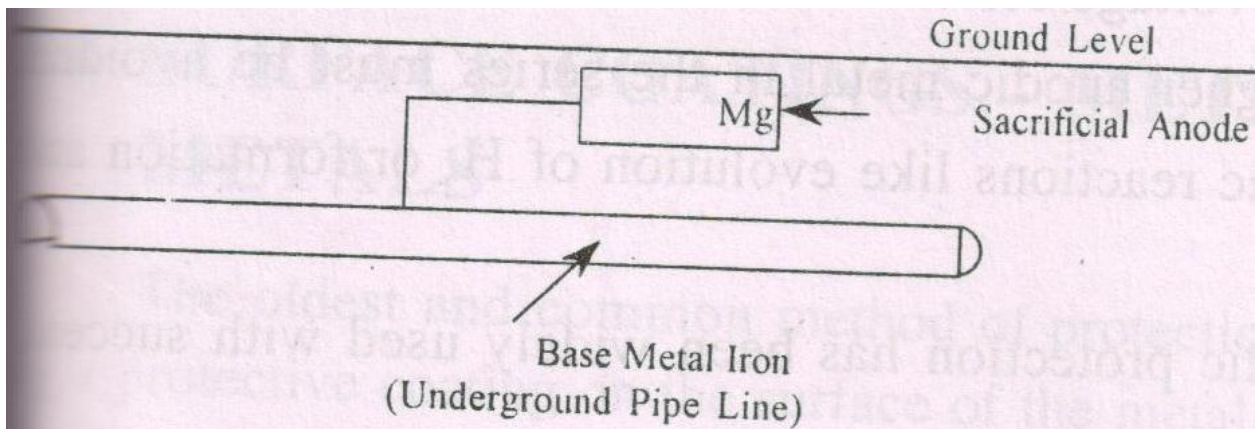
#### ➤ **Cathodic Protection:**

- The principle involved in this method is to force the metal to be protected to behave like a cathode, thereby corrosion does not occur.

- There are two types of cathodic protection.

**a) Sacrificial anodic protection method:**

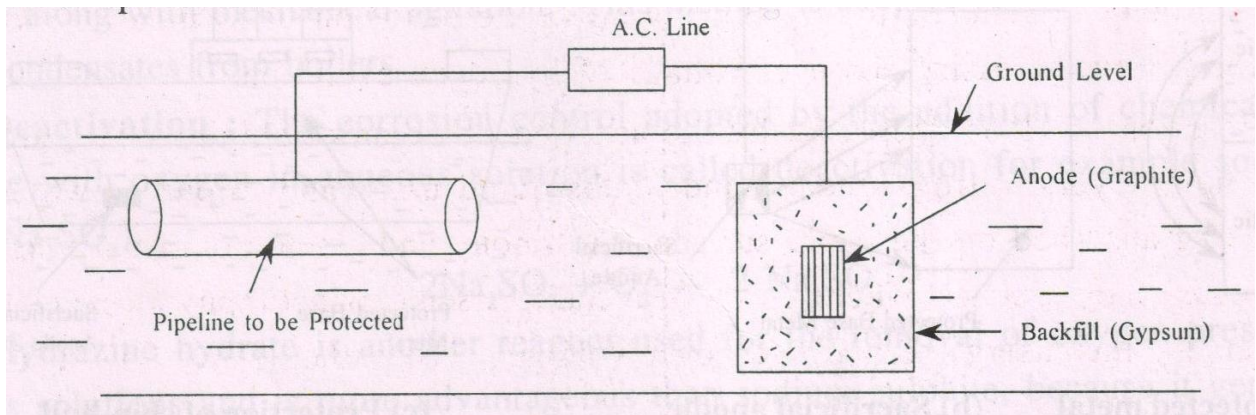
- In this method, the metallic structure to be protected is connected by a wire to a more anodic metal (more reactive metal).
- Thus during corrosion more anodic metal gets corroded. The **base metal becomes cathode and is protected.**
- The more **active metal used is known as sacrificial anode** which is to be replaced from time to time by fresh one.
- Metals commonly used as sacrificial anode are magnesium and zinc.
- This method is used for the protection of buried pipelines, ships and boat hulls, iron water tanks, etc.



Sacrificial anodic protection

**b) Impressed current cathodic protection:**

- In this method, the metallic object to be protected is made cathode by connecting it with the negative terminal of the DC source.
- The positive terminal is connected to an insoluble anode like graphite, scrap iron or platinum.
- The impressed current nullifies the corrosion current and converts the base metal from anode to cathode.
- The electrons flow to the metallic object. As a result, it acts as cathode and is protected.



- This method is used for the protection of buried pipelines, underground cables, transmission line towers, water tanks etc.

#### **Advantages of impressed voltage method:**

- Useful for long term operations.

#### **Limitations of impressed voltage method:**

- Capital investment and maintenance costs are high.
- Stray currents produced may corrode the neighbouring metallic structure.

#### ➤ **Surface coatings(or) protective coatings:**

- Coating the surface of the metal with continuous non porous material to protect the metal from corrosion is known as surface coating.

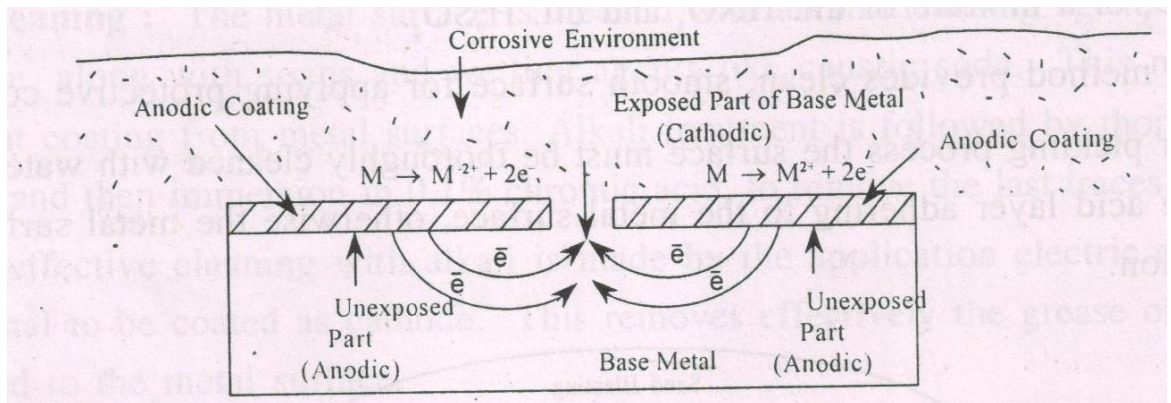
#### ➤ **Metallic coatings:**

- In metallic coatings, the base metal to be protected from corrosion is coated with another metal which is either anodic or cathodic to the base metal.
- The metallic coatings often used are of Zn, Sn, Ni, Cu etc.
- Metallic coatings are of two types.

#### ➤ **Anodic coating (Sacrificial coating):**

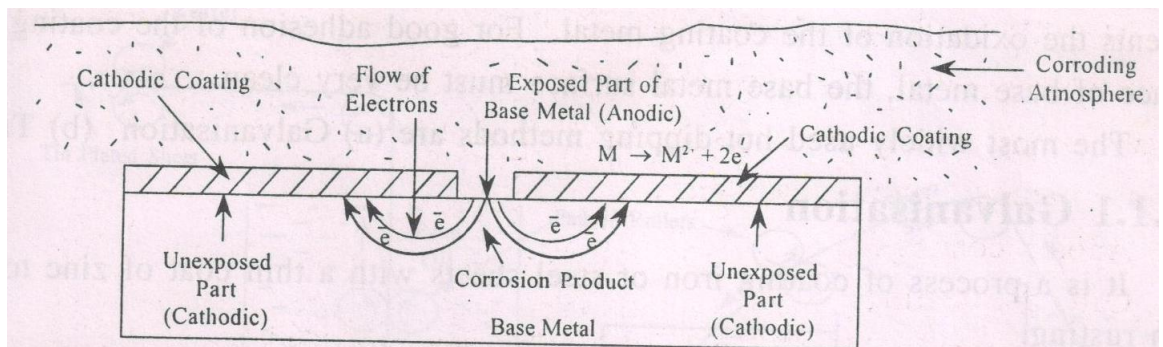
- Anodic coating is obtained by coating a more anodic metal on to the base metal.
- If the protective layer develops any cracks or pores, the base metal becomes cathode and it does not undergo corrosion.

- Ex: The coating of Zinc on to iron is known as galvanizing.



➤ **Cathodic coating (Noble coating):**

- Cathodic coating is obtained by coating a more cathodic metal on to the base metal.
- If the protective layer develops any cracks or pores, the base metal becomes anode and undergoes corrosion.
- Ex: The coating of tin on to iron is known as tinning.



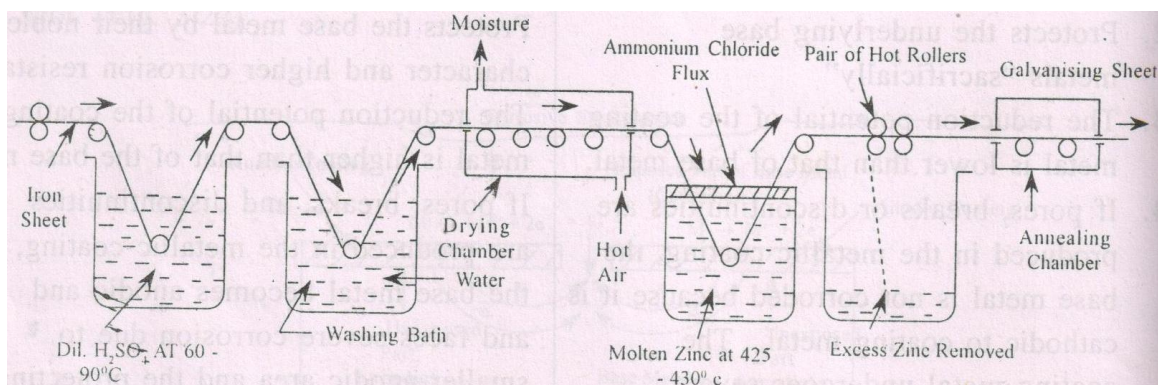
**Differences between anodic and cathodic coating:**

Anodic coating	Cathodic coating
1. Protects the underlying base metal sacrificially.	1. Protects underlying base metal due to noble character and higher corrosion resistant.
2. Electrode potential of coating metal is lower than the base metal.	2. Electrode potential of coating metal is higher than the base metal.

<p>3. If pores or breaks or discontinuity appear on the coating, base metal does not undergo corrosion until all the coating is consumed.</p>	<p>3. If pores or breaks or discontinuity appears on the coating metal, base metal undergoes corrosion.</p>
<p>4. Coating of Zn on Iron is an example.</p>	<p>4. Coating of Sn on Iron is an example.</p>

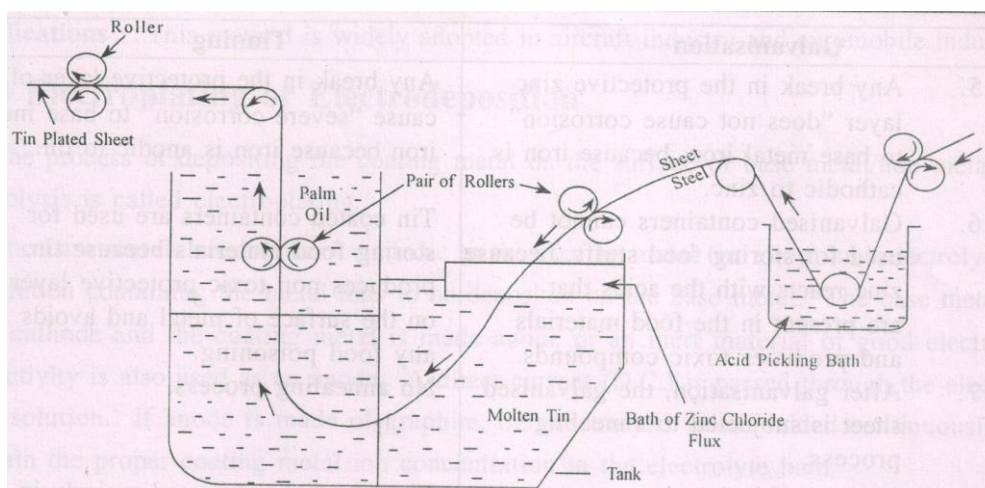
➤ **Galvanizing:**

- Iron article is treated with dil.  $H_2SO_4$  to remove the traces of rust and dust etc. at  $60-90^\circ C$  for about 15-20 minutes.
- It is then washed and dried.
- Then it is passed through molten bath of zinc at  $430^\circ C$  which is covered with an ammonium chloride flux to prevent oxide formation.
- The coated base metal is then passed through the rollers to correct the thickness of the film.
- Then the sheet is subjected to the annealing process and cooled slowly.
- It is used to protect iron used for roofing sheets, wires, pipes, tubes etc.



➤ **Tinning:**

- Iron article is treated with dil.  $H_2SO_4$  to remove the traces of rust and dust etc. at  $60-90^\circ C$  for about 15-20 minutes.
- Then it is passed through molten bath of tin maintained at a temperature of  $240^\circ C$  which is covered with a zinc chloride flux to prevent oxide formation.
- The coated base metal is then passed through the rollers immersed in palm oil bath .Palm oil helps to protect the tin coated surface against oxidation.
- The rollers remove excess of tin.
- The containers coated with tin are used for storing food stuff, pickles, oils etc.



**Differences between Galvanizing & Tinning:**

<b>Galvanizing</b>	<b>Tinning</b>
1.Coating of iron with zinc to prevent corrosion	1.Coating of iron with tin
2.Zinc protects the iron sacrificially	2.Tin protects iron due to its noble nature.
3.Protection continues even if cracks and pores develop on the surface of coating.	3.Protection is provided only when coating is perfect. Any break in the protective layer of tin, cause severe corrosion of base metal iron

	because iron is anodic to tin.
4. Food materials cannot be stored in zinc coated containers as zinc reacts with food items and produce compounds that are toxic.	4. Tin coating is non toxic and so food items can be stored.

## Assignment-cum-Tutorial Questions

### Section A

#### Questions testing the remembering / understanding level of students

#### I) Objective Questions

1. From the following, which is inert to oxidation?  
 A. Cu                      B. Fe                      C. Steel                      D. Pt
2. Chemical formula of Rust is,  
 A.  $\text{Fe}_2\text{O}_3$               B.  $\text{FeO}$               C.  $\text{Fe}_3\text{O}_4$               D.  $\text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}$
3. Corrosion process is nothing but -----.  
 A. Reduction              B. Oxidation              C. Protection              D. None of the above
4. Electrochemical corrosion takes place on,  
 A. Anodic area              B. Cathodic area              C. Near cathode              D. Near anode
5. Volatile oxidation corrosion product of a metal is,  
 A.  $\text{Fe}_2\text{O}_3$               B.  $\text{MoO}_3$               C.  $\text{Fe}_3\text{O}_4$               D.  $\text{FeO}$
6. Lower the pH, corrosion is,  
 A. Greater              B. Lower              C. Constant              D. None of above
7. Process of corrosion is enhanced by,  
 A. Air & Moisture                              B. Electrolytes in water  
 C. Gases like  $\text{CO}_2$  &  $\text{SO}_2$                               D. All of these
8. In differential aeration corrosion, poor oxygenated parts are,  
 A. Anodic              B. Cathodic              C. Corroded              D. None of above



9. In waterline corrosion, highly oxygenated parts acts as,  
 A. Cathodic      B. Anodic      C. Corroded      D. None of above
10. In galvanic series, a metal high in series is more -----.  
 A. Anodic      B. Cathodic      C. Corroded      D. None of the above
11. The metal at the top of Galvanic series is  
 A. most stable      B. best protective      C. most stable      D. most active
12. Identify the metal which is not employed as Sacrificial anode.  
 A. Mg      B. Zn      C. Al      D. Na
13. Which of the following metals could provide cathodic protection to Fe?  
 A. Al & Cu      B. Al & Zn      C. Zn & Cu      D. Al & Ni
14. The formation of ----- type of metal oxide film causes rapid and continuous corrosion.
15. ----- is the process of coating Fe or steel with a zinc coating.  
 A. Tinning      B. Hot dipping      C. Galvanizing      D. None of above
16. The buried pipeline is protected from corrosion by connecting to Mg block. It is called  
 A. impressed voltage protection      B. sacrificial cathodic protection  
 C. sacrificial anodic protection      D. any of these
17. Ratio of volumes of metal oxides to metal is known as -----
18. More active metal used in sacrificial anodic protection method is known as -----
19. ----- is the process of coating of tin over Fe or steel.
20. Anodic metal protects the underlying metal -----
21. During galvanic corrosion, the more noble metal acts as -----
22. During the electrochemical corrosion in acidic environment, evolution of ----- occurs.

23. The buried pipe line is protected from corrosion by connecting it to Mg block. It is called -----

### **Section B**

#### **II) Descriptive Questions**

1. Define corrosion. Write the formula for rust.
2. Define Pilling Bedworth rule.
3. Explain the factors affecting the rate of corrosion.
4. Explain the mechanism of electro chemical corrosion.
5. Explain the mechanism of dry corrosion.
6. Define galvanic corrosion.
7. Define concentration cell corrosion. Give an example.
8. Discuss different methods of corrosion control.
9. Discuss cathodic protection method for the prevention of corrosion.
10. Explain with an example, the prevention of corrosion by sacrificial anode process.
11. Explain with an example, the prevention of corrosion by impressed current method.
12. Define Galvanic series. Mention its significance.
13. Describe the following metallic coatings (i) Tinning (ii) Galvanizing
14. Explain the significance of Pilling Bedworth rule.
15. Differentiate galvanic and concentration cell corrosion.
16. Explain the differences between wet and dry corrosion.
17. Of the zinc coating on iron and tin coating on iron, which type of coating protects iron even after the development of cracks on the surface of coating? Why?
18. Explain the process of corrosion occurring when:
  - (i) an iron pipe is connected to the copper plumbing.
  - (ii) iron tank is partially filled with water.
  - (iii) ship hull connected to a zinc plate.
19. Explain the advantages and limitations of impressed voltage method.
20. Differentiate anodic coating and cathodic coating.
21. Differentiate tinning and galvanizing.

## **Section C**

**Questions testing the ability of students in applying the concepts.**

### ***Descriptive Questions***

1. Corrosion of half-filled iron water tank occurs from below the water line. Why?
2. How do you protect the buried pipelines from corrosion?
3. Why food items should not be stored in galvanized containers?
4. Outline the reasons for the corrosion of reinforced cement concrete.  
How does the decay of RCC can be prevented?

# ENGINEERING CHEMISTRY (CE)

## Unit – II

### POLYMERS AND REFRACTORY MATERIALS

#### Objectives:

- To introduce the students to basic concept of polymer, polymerization, Fibre reinforced plastics, refractories their applications.

#### Unit-II: Polymers and Refractory materials

Definitions of Polymer and Polymerization - Degree of Polymerization - Functionality.

**Plastics** – Fibre reinforced plastics - Glass Fibres, Carbon fibres, aramid fibres – preparation methods – hand layup method, matched metal die moulding method – properties – applications.

**Refractories:** Definition of a refractory – classification and properties- refractoriness–RUL test–thermal spalling. Conditions leading to failure of a refractory – applications of refractories.

#### Course outcomes:

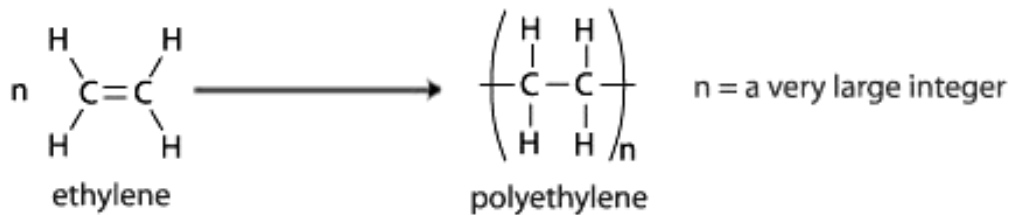
##### Students will be able to

- explain the terms - monomer, polymer and polymerization
- explain various types of fibre reinforced plastics and their applications.
- explain various types of refractories and their applications

#### Polymers:

- **The** word ‘**polymer**’ is coined from two **Greek words: poly** means **many** and **mer** means **unit or part**.
- The term **polymer is defined** as very large molecule having high molecular mass formed by the combination of many smaller molecules called monomers.
- The reaction in which many small molecules combine to form high molecular weight compound polymer is called Polymerization (or) The process in which a polymer is formed by repeating linkage of large number of monomers is called polymerisation.

Ex. formation of polyethene.



### Degree of Polymerization:-

- The number of monomeric units (or) repeating units present in a polymer is called degree of polymerization.
- In case of addition homo polymer, degree of polymerization ( $D_p$ ) is defined as the ratio of total molecular weight of a polymer to molecular weight of each repeating unit.

$$D_p = \frac{\text{total molecular weight of the polymer}}{\text{molecular weight of monomeric unit}}$$

### Significance of Degree of Polymerization:

Basing on Degree of Polymerization, the polymers are classified as

**(i) Oligo polymers:** The polymers whose Degree of Polymerization is less than 600 are called Oligo polymers. These polymers do not possess good engineering properties and hence cannot be used as engineering materials.

**(ii) High polymers:** The polymers whose Degree of Polymerization is greater than 600 are called High polymers. These polymers possess good engineering properties and hence widely used as engineering materials.

### Functionality:

- The number of active bonding sites of a monomer is termed as its functionality.
- A monomer should have atleast two reactive sites (or) bonding sites to form a polymer.

Ex. In Polyethene, a double bond is present and it is bifunctional.

### Plastics:

- The polymeric substance that can be moulded into the desired shape by the application of heat and pressure is called plastic.

- Plastics can be moulded [or] pressed [or] casted [or] extruded into various shapes like plates, tubes, bottle, boxes, fibres etc.

**Characteristics of Plastics materials:**

- Mechanical strength
- Insulation Property
- Low density
- Low cost
- Light weight
- Sufficient rigidity
- Resistance to chemicals, corrosion, insects

**Disadvantages of plastics:**

- Recycling of plastic is a costly process.
- Plastic undergo biodegradation after long time.
- Incineration of plastic causes pollution.
- Plastics are low heat resistance and brittle. They undergo deformation at low temperatures.

**Fibre reinforced plastics:**

- Fibre reinforced plastic [FRP] is a composite material.
- Composite material consists of physically distinct and mechanically separable two (or) more materials that retain their properties when combined together.
- FRP composites are anisotropic; therefore FRP composites properties are directional.
- Mechanical properties are in the direction of the fibre placement.
- FRP contains two components.

**Components of composite (FRP):**

**Fibre (reinforcement):**

- **Fibre (reinforcement)** is the substance that is used to strengthen plastic compounds.
- The properties of FRP are mainly influenced by the choice of fibres.
- There are three main types of fibres carbon, glass & Aramid fibres.

- They have different properties.
- All fibres have generally high stress capacity than the ordinary steel.

**Matrix:**

- The plastic material used in FRP is called **matrix**.
- Matrix is a relatively weak plastic that is reinforced by stronger fibres.
- It transfers the forces b/w the fibres and protects the fibre from the environment.
- Generally thermosetting plastics are used as matrix.
- Vinyl esters and epoxy resins are most commonly used matrixes.

**Advantages of Fibre reinforced plastics:**

Demand for FRP's is increasing because they replace metals and they do have good performance than metals.

FRP's have thermal stability, high tensile strength, dimensional stability etc.

Along with good mechanical properties, they possess design free reduced weight and corrosion resistance.

FRPs are commonly used in aerospace, automotive, marine and construction industries.

**Glass fibre reinforced plastics:**

**Preparation:**

- Glass fibre is made up of sand, limestone, folic acid and other minor ingredients.
- The mixture is heated till it melts at about 1260°C.
- The molten glass is then allowed to flow through fine holes in a platinum plate.
- The glass strands are cooled, gathered & wound.
- The fibres are woven into various forms for use in composites.
- Another glass fibre prepared from aluminium + lime + borosilicate has high insulating properties, low susceptibility to moisture and high mechanical strength.

**Properties:**

- They have high surface area to weight.

- Glass fibre has good thermal insulation due to the presence of air gaps.
- Glass fibre absorbs moisture.
- Glass fibre undergoes more elongation before it breaks.
- Glass fibre is drawn at moderately low viscosity. If it is too high, fibre will break during drawing. If it is too low, the glass will form droplets.

**Uses:**

- Bridges
- Airplane wings
- Boat hulls
- Corrosion resistant equipment
- Circuit boards
- Automobile industry

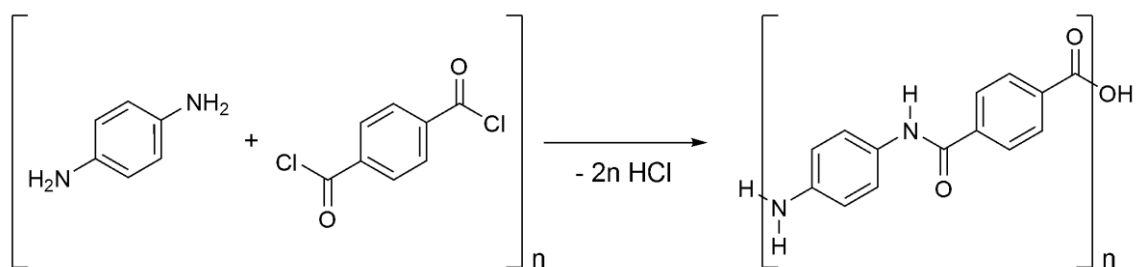
**Aramid fibre reinforced plastics [bullet proof plastic]:**

- Aramid is a short form of aromatic polyamide.
- Ex: Kevlar.

**Kevlar:**

**Preparation:**

- It is prepared by condensation polymerization of 1,4-diamino benzene and Isophthaloyl Chloride. In Kevlar, the repeating groups between the amide links are benzene rings





**Properties:**

- This is five times as strong as steel.
- Usually yellow in appearance
- Low density
- High strength
- Thermal resistance
- Good impact resistance
- Good abrasion resistance.
- Good chemical resistance.
- Compressive strength

**Uses:**

These are used in the manufacture of

- Bullet proof vests
- Boat hulls
- Aircraft body parts.
- Clutch plates, brake pads.
- Gaskets
- Adhesives & sealants

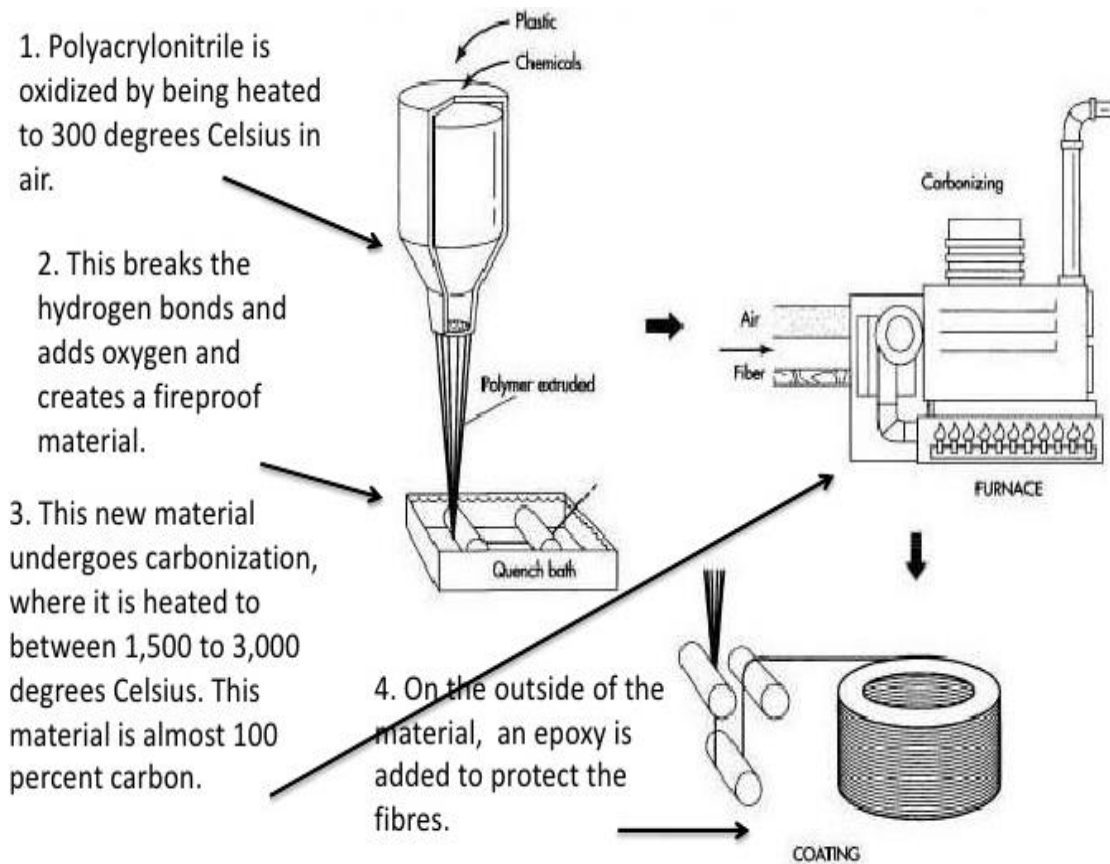
**Carbon fibre reinforced plastic (CFRP or CRP):**

The raw material used to make carbon fibre is called the precursor.

About 90% of the carbon fibres produced are made from polyacrylonitrile (PAN)

The remaining 10% are made from rayon or petroleum pitch.

**Preparation of CFRP:**



**Properties:**

- High strength
- High rigidity
- Corrosion resistance
- non poisonous
- not flammable
- good tensile strength

**Disadvantages:**

- Relatively expensive

**Uses:**

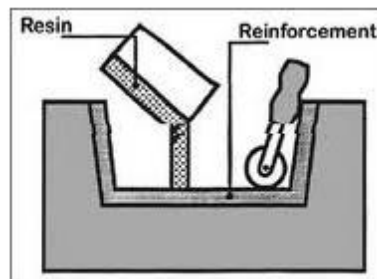
- Airspace and aircraft industries
- Automotive body parts
- Mobile cases
- Musical instruments
- Badminton racket

- Golf stick
- construction industry
- Wind mill and turbine blades
- Helmets

## Methods for producing FRP's:

### Hand lay up method:

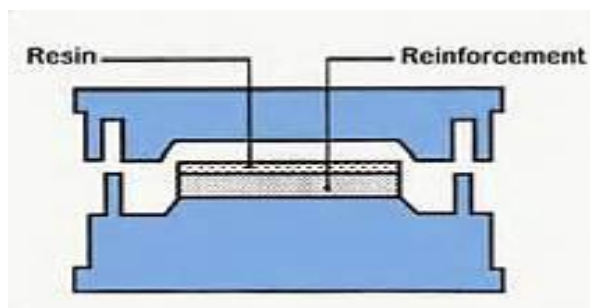
- This is a simple method for forming thermosetting plastics.
- The mould can be made of low cost wood (or) plaster.
- The reinforcing mat (or) fabric is cut to fit, laid in the mould and resin is applied by hand using a brush (or) roller (or) spray gun.
- Layers are built up to desired thickness and laminate is cured to render it hard.



Hand lay up

### Matched metal die moulding:

- ♦ It is the most common method used.
- ♦ With this process, the plastic and reinforcement are squeezed into its desired shape with the help of pressure and heat.
- ♦ The plastic and reinforcement are pressed in matched upper and lower moulds.
- ♦ This is heated to required temperature and required time.



## **Refractories:**

- **Refractories are** inorganic materials that can withstand high temperatures without softening, melting or deformation.
- Ex.  $\text{SiO}_2$ ,  $\text{CaCO}_3$
- These are used as bricks or lining inside the furnace used in metallurgy, cement and glass industries.
- The main objective of a refractory material is to resist heat losses and also to resist corrosion action of metals, chemicals and gases at higher temperatures.

## **Characteristics of a good Refractory:**

- Refractories should
  - have high refractoriness.
  - be chemically inert towards the corrosive gases, slags and liquids.
  - resist the abrasive action of the gases, flames etc.
  - not crack and suffer loss in size at the operating temperature.
  - expand and contract uniformly with rise or fall in temperature.
  - be able to withstand overlying load at operating temperature.

## **Classification of Refractories:**

There are three types based on their chemical composition

- **Acidic refractories:**
  - These are not attacked by acidic materials in the furnace.
  - Acidic refractories consist of acidic oxides like  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$ .
  - They are readily attacked by the bases or basic slags.
  - Ex:  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$
- **Basic refractories:**
  - These are not attacked by basic materials.

- They consist of basic oxides like CaO and MgO.
- Ex: MgCO<sub>3</sub>, CaCO<sub>3</sub>
- **Neutral refractories:**
  - These are not attacked by either acidic or basic materials.
  - These are made from weakly acidic or basic materials like carbon, chromites and Zirconia.
  - Ex: Graphite, Chromite, Zirconia & Carborundum.

## **Properties of Refractories:**

### **1. Refractoriness:**

- It is the ability of a material to with stand high temperatures without undergoing deformation or softening under working conditions.

### **2. Refractoriness under load(RUL) (Strength of refractory):**

- The refractory material used as lining inside the furnace has to withstand heavy loads of charged material.
- Hence, refractory material should possess high mechanical strengths to bear maximum possible load without deformation under working conditions.
- The load bearing capacity at high temperature is determined by refractory under load test (RUL Test).
- **In RUL test**, the specimen of refractory of size 5 cm<sup>2</sup> and height 75cm under a load of 1.75 Kg/ cm<sup>2</sup> is heated at a standard rate of 10°C/minute. The temperature at which at least 10% of the specimen starts getting destroyed or deformed is taken as the RUL value.
- On the basis of RUL test, the refractories are classified as (i)high heat-duty brick( that does not deform more than 10% at 1350°C) (ii)an intermediate heat-duty brick( that does not deform more than 10% at 1300°C) (iii)a moderate heat-duty brick( that does not deform more than 10% at 1100°C)

**Significance:** A good refractory should have high RUL value.

### **3. Thermal spalling:**

Thermal spalling is breaking, cracking, peeling off or fracturing under high temperature.

A good refractory shows a high resistance to thermal spalling.

Spalling is due to rapid changes in temperature which causes uneven expansion and contraction within the mass of refractory.

The spalling can be decreased by (i) avoiding sudden temperature changes by modifying furnace design so that stresses are not set up when the furnace is heated. (ii) by over firing the refractories.

### **Applications of Refractories:**

- Due to high temperature resistance, refractories are used in various mechanical, metallurgical, chemical and power industries.
- Acidic refractories like Alumina bricks and Silica bricks are used as linings for blast furnaces, open hearths, stoves, coke ovens, crucible furnaces. Acidic refractories are also used in lime kilns, glass furnaces, brass and copper furnaces.
- Basic refractories like Magnesite are used in electric furnace walls. Basic refractories are also used for refining noble metals such as Gold, Silver and Platinum.
- Neutral refractories like Zirconia is used for the manufacture of crucibles used for melting the noble metals.
- Graphite is used as linings of chemical resistant equipments, atomic reactors, electric furnaces etc.
- Refractories are used in hottest zones of cement rotary kilns, hearths etc.
- Refractories are used for lining basic electric furnace linings, ladle lining.
- Refractories are used in the manufacture of rocket nozzles, launch pads etc.

### **Conditions leading to the failure of a refractory:**

Failure of Refractories is mainly due to

- using refractories with less refractoriness than that of operating temperature
- rapid changes in temperature of furnace

- using bricks of high thermal expansion
- using bricks that are not properly fired
- using refractories with low RUL
- using bricks which undergo volume changes during their use at high temperature

## **Assignment-Cum-Tutorial Questions**

### **Section A**

### **Questions testing the remembering / understanding level of students**

#### **I) Objective Questions**

1. Functionality of ethylene monomer is  
 A. 1                      B. 2                      C. 3                      D. 4
2. The combination of polymeric substance with fibre is called  
 A. reinforced plastic    B. polymerization    C. vulcanisation  
 D. none
3. Which of the following polymer is used as bullet proof material?  
 A. Bakelite            B. Epoxy resin            C. aromatic  
 polyamide            D. glass
4. Usually stronger constituent of a composite is  
 A. Matrix    B. Reinforcement    C. Both are of equal strength  
 D. Can't define
5. Mechanical properties of fibre-reinforced composites depend on  
 A. Properties of constituents                      B. Interface strength  
 C. Fibre length, orientation, and volume fraction    D. All the  
 above
6. Kevlar is commercial name for ----- .  
 A. Glass fibres            B. Carbon fibres            C. Aramid fibres  
 D. Cermets
7. Alumina is a ----- type of refractory.

A. acid            B. basic            C. Neutral            D. None of  
the above

### **Section B**

#### **II) Descriptive Questions**

1. What is a polymer?
2. Define the term monomer.
3. What is degree of polymerization? Give its significance.
4. What is functionality? Give an example.
5. Discuss Fibre reinforced plastics.
6. Outline the preparation and Engineering applications of aramid fibre reinforced plastics.
7. Outline the preparation and uses of glass fibre reinforced plastics.
8. Discuss the preparation and uses of carbon fibre reinforced plastics.
9. Explain in brief the hand layup method for the preparation of fibre reinforced plastics.
10. Explain in brief the matched metal die moulding method for the preparation of fibre reinforced plastics.
11. What are refractories? Give an example.
12. Classify refractories with an example each.
13. Discuss the properties required for a good refractory.
14. Discuss the properties (i)refractoriness (ii)thermal spalling (iii)RUL
15. Explain the RUL test and mention its significance.
16. List out the applications of refractories.



17. List out the ways to reduce thermal spalling.
18. Why does thermal spalling of a refractory occur? Name two neutral refractories.
19. Discuss the acidic and neutral type of the refractories and their uses.
20. What are the characteristics of acidic, basic and neutral type refractories?

### **Section C**

**Question testing the ability of students in applying the concepts.**

#### ***Descriptive Questions***

1. Interpret the conditions leading to failure of a refractory.
2. Can an acidic refractory be used as a lining if the furnace is to be fed with basic materials? Why?

## Unit – III

### NANO MATERIALS

#### **Objectives:**

To enable the students to obtain the knowledge of nano materials, various synthesis methods for nano materials; properties, types and applications of carbon nano tubes, Quantum dots.

#### Unit-III: Nano materials

Concept of Nano materials - synthesis of nano materials – Sol-gel, Chemical vapour deposition methods, carbon nano tubes ( CNTs) – types, properties, applications of CNTs. Quantum dots – applications.

#### **Course outcomes:**

##### **Students will be able to**

- explain the methods of synthesis of nano materials.
- explain the properties and applications of CNTs and quantum dots.

**Nano materials:** If the particle sizes are in the 1-100 nm range at least in one dimension, they are called nano particles or **nano materials**.

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

Nano sized particles of any given substance exhibit different properties and behavior than larger particles of the same substance.

Materials can be produced that are nano scale in one dimension , in two dimensions or in three dimensions.

- **Nano materials in one dimension:** In this type, only one dimension is confined and the other two are free to move for the electrons.
- Examples are layers like thin films or surface coatings.  
Thin films (sizes 1–100 nm) or monolayer is now common place in the field of solar cells offering, different technological applications, such as chemical and biological sensors, information storage systems, magneto-optic and optical device, fibre-optic systems.

- **Nano materials in two dimensions:** In this type, only one dimension is free to move and two dimensions are confined for electrons.

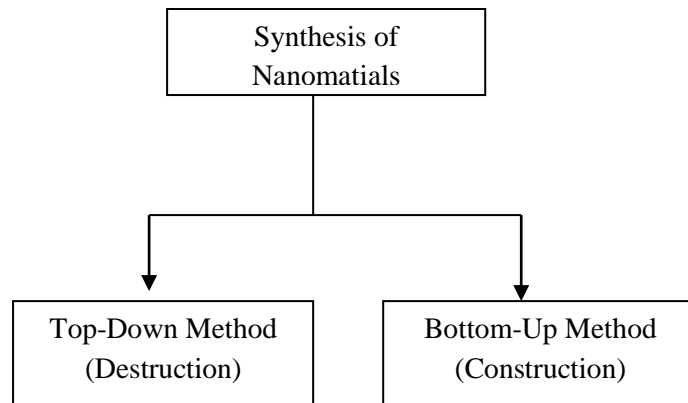
Examples are carbon nano tubes and nano wires.

- **Nano materials in three dimensions:** In three dimensional nano materials, all the three dimensions are confined for electrons.

Ex. particles like precipitates, colloids, fullerenes and quantum dots.

### **General methods of preparation of nano materials:**

There are basically two major types of approach for the preparation of nano materials.

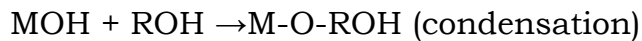
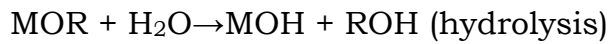


1. **Top -Down Method:** In this method, bulk materials are converted to powder and then to nano particles by using different methods. This method is used in the microelectronic industry.
2. **Bottom - Up Method:** In this method, very small particles like individual molecules or atoms are assembled to get cluster which in turn are aggregated to get nano particles.

### **Sol- gel method for the preparation of nano particles:**

- Sol gel method is bottom up approach for the synthesis of nano materials.

- It is an important industrial process for the generation of colloidal nano particles from liquid phase for the production of advanced nano materials and coatings. It refers to the hydrolysis and condensation of alkoxide based precursors such as  $\text{Si}(\text{OEt})_4$ . The reactions involved in the sol-gel process based on the hydrolysis and condensation of metal alkoxides  $\text{M}(\text{OR})$  is described as follows:



- A colloid suspended in a liquid is called as **sol**.
- A suspension that keeps its shape is called **gel**.
- Thus sol-gel is suspensions of colloids in liquids that keep their shape.
- The sol-gel formation occurs in different stages.

**Step – I:** Precursor (metal oxide) undergoes hydrolysis by continuously stirring for 24 hours and forms sol.

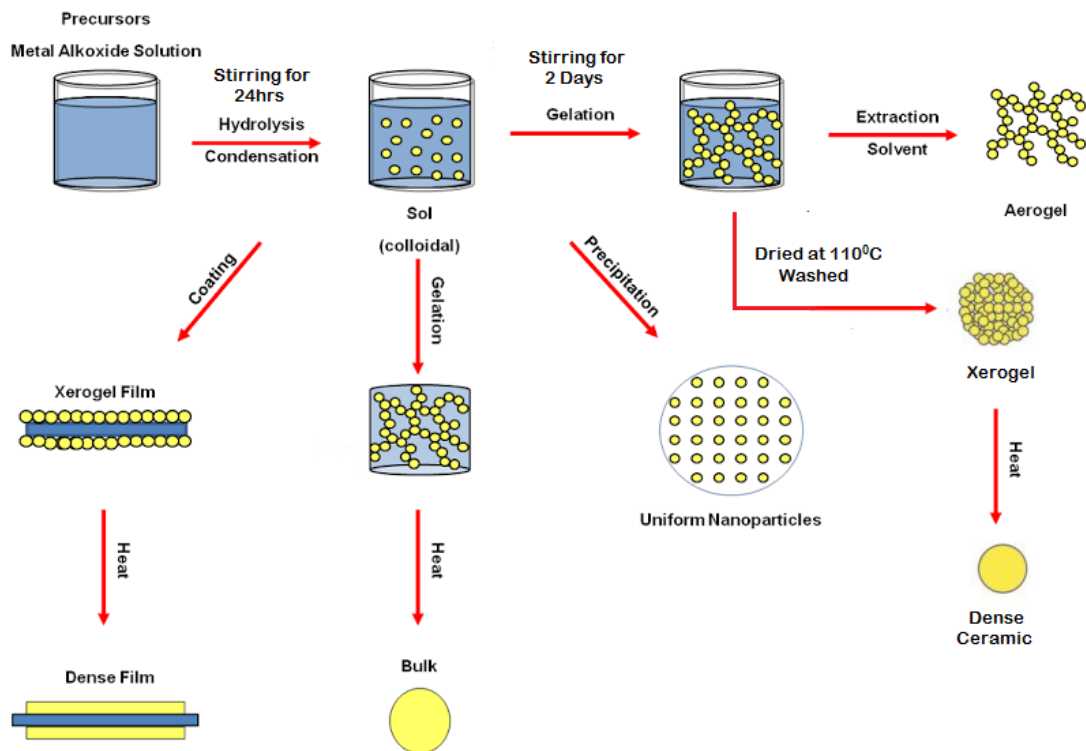
**Step – II:** On continuous stirring for 2 days, sol is converted into gel. This results in increase in the viscosity of solution.

**Step – III:** On drying at  $110^\circ\text{C}$ , gel is termed as Xerogel.

**Step – IV:** On extraction of solvent from the gel, it is termed as aerogel.

**Step – V:** Sol on precipitation forms uniform nano particles.

**Step – VI:** Sol is coated on a material and heated, to form a dense layer.



### Advantages of Sol-gel process :

- Sol-gel process can be used for the preparation of oxide nano particles and composite nano powders synthesis.
- This method can be used to synthesise non metallic inorganic materials like glasses, glass ceramics.
- It is a cheap and low temperature technique that allows for the control of the product's chemical composition.

### Applications

Sol-gel derived materials have applications in optics, electronics, energy, space, bio sensors etc.

### Limitations :

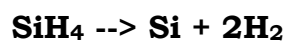
- Low yield of nano powders is obtained.
- Problem in ensuring the completion of reactions.

### Thin Film preparation Chemical Vapour Deposition method (CVD) :

Chemical vapour deposition is a technique for depositing thin films of materials on wafers or other substrates. Source gases are introduced into a reaction chamber and energy is applied through heat, high frequency high voltage or other techniques that result in the decomposition of the source gas and reaction of the chemicals to form a film.

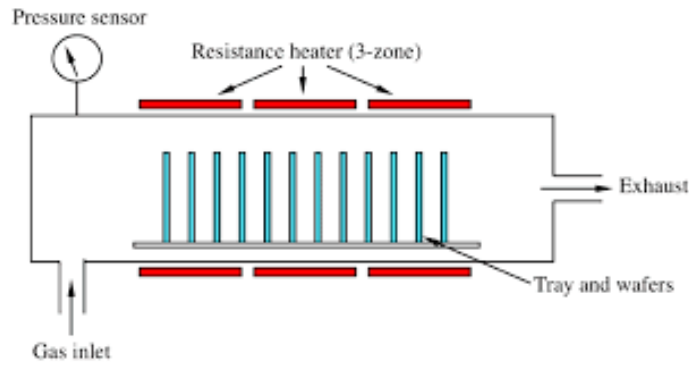
- In a **CVD** process, the wafer (substrate) is exposed to one or more volatile precursors, which react and/or decompose on the substrate surface to produce the desired deposit.
- A wafer is a thin slice of semiconductor material, such as a silicon crystal, used in the manufacture of integrated circuits and other micro devices.
- Generally, temperatures inside a chemical vapor deposition machine are high, while pressures are very low.
- Frequently, volatile by-products are also produced, which are removed by gas flow through the reaction chamber.

**Ex.1** The **chemical vapor deposition** process is used in the synthesis of polycrystalline silicon from silane (SiH<sub>4</sub>), using this reaction:

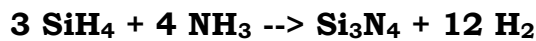


In the silane reaction, the medium would either be pure silane gas, or silane with 70-80% nitrogen. Using a temperature between 600 and 650 °C and very less pressure (less than a thousandth of an atmosphere), pure silicon can be deposited at a rate of between 10 and 20 nm per minute.

This method is used for many circuit board components, whose thickness is measured in microns.



**Ex.2 Silicon nitride:** Silicon nitride is often used as an insulator and chemical barrier in manufacturing Integrated Circuits. It is prepared as follows:



#### **Applications of CVD:**

Chemical Vapour Deposition is often used in the semiconductor industry (i.e. in the design and fabrication of semiconductor devices) to produce thin films. A thin film is a layer of material ranging from fractions of a nanometer to several micrometers in thickness.

- Micro fabrication is the term that describes processes of fabrication of miniature structures, of micrometre sizes and smaller. Micro fabrication processes widely use **Chemical Vapour Deposition** to deposit materials.
- Silicon nitride is often used as an insulator and chemical barrier in manufacturing Integrated Circuits is prepared by CVD method.
- CVD is also commonly used in optoelectronics applications, optical coatings, and coatings of wear resistant parts.

#### **Carbon nano tubes (CNTs):**

- Carbon nano tubes were discovered in 1991 by S.Iijima.
- Carbon nano tubes are long thin cylinders of carbon. Rolled graphite sheets are called Carbon nano tubes.
- CNTs are allotropes of carbon with a nano structure having a length to diameter ratio greater than lakh.

- CNT have very broad range of electronic, thermal and structural properties which vary with the dimensions of tubes.

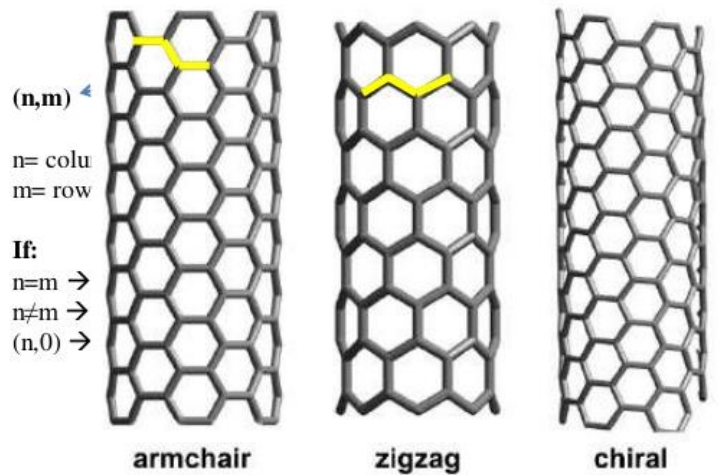
### **Types of carbon nano tubes:**

- Depending upon the arrangement of carbon atoms, these are classified into two types.
- Single walled nano tubes (SWNTs)
- Multi walled nano tubes (MWNTs)

### **Single walled nano tubes (SWNTs)**

- SWNT have diameter close to one nano meter.
- The structure of SWNT is obtained by wrapping one atom thick layer of graphite called graphene into a smooth cylinder.
- One important application of SWNTs is in the development of first intermolecular field effect transistors (FET).
- Based on the way the graphene sheet is wrapped, SWNTs are of three types.
  - a) Zig – Zag
  - b) Arm Chair
  - c) Chiral





Graphene sheet consisting of pair of indices  $(n, m)$  called the chiral vector.

### Arm chair

- If  $n=m$  the nano tubes are called armchair.
- The lines of hexagons are parallel to the axis of the nano tube.

### Zig - Zag

- If  $m=0$  the nano tube are called zig-zag.
- The lines of carbon bonds are arranged down the centre.

### Chiral

- Remaining all are Chiral.
- It has twist or spiral around the nano tube.

### Multi walled nano tube (MWNTs)

- It consists of multiple rolled layers of graphite.
- These are concentric tubes.
- The distance between two layers is  $3.3 \text{ \AA}$ .
- There are two models.

- a) Russian doll model                      b) Parchment model

### **Russian doll model**

- Sheets of graphite are arranged in concentric cylinders.
- A tube is arranged inside the larger tube.

### **Parchment model**

- A single sheet of graphite is rolled in around itself, resembling like a rolled news paper.

### **Synthesis of carbon nano tubes:**

Carbon nano tubes are synthesized by the following three methods.

- 1) Arc Discharge Method 2) Laser ablation method 3) Chemical vapour deposition method

### **Properties of carbon nano tubes (nano materials):**

CNTs have unique chemical, optical, electrical and structural properties which are useful in bio sensing and drug delivery systems for treating various diseases.

### **Mechanical Properties**

#### **Strength:**

- Carbon nano tubes are the strongest materials.
- They possess high tensile strength and Young's modulus.
- This strength is due to covalent  $sp^2$  bonds formed between the individual carbon atoms.
- CNTs have hollow structure because of which they undergo buckling under compression.
- CNTs have low density.
- CNTs are very light.

## **Electrical Properties**

- CNTs are metallic or semi conducting depending on their structure.
- the arm chair model nano tube is metallic while other models are semiconducting.
- Some nano tubes have higher conductivities than that of copper.

## **Vibrational Properties**

- Atoms in CNT are continuously vibrating back and forth and are Raman active.

## **Engineering applications of carbon nano tubes (nano materials):**

- The small size, strength and unique properties of the nano materials find greater applications in various fields of engineering.
  1. They find application in conductive and high strength composites.
  2. They are used in sensors, emission displays, and semi conducting devices.
  3. They are used as nano probes in metrology, biological and chemical investigations.
  4. They are used as efficient tools for transporting therapeutic molecules.
  5. They are used in the manufacture of reinforced plastics, car and aeroplane parts and sports goods.

### **Applications in Fuel Cell**

- SWNTs are effective as a hydrogen storage material, which is in turn used for fuel cells to run electric vehicles.
- Electrodes constructed with nano tubes are light in weight thereby making the fuel cells lighter.
- CNTs are resistant to corrosion and can efficiently be used in fuel cells.

### **Applications in Catalysis**

- A catalyst having CNT makes reaction milder, safer and more selective.
- CNTs are used as catalyst or catalyst additives or catalyst promoter.
- Some chemical reactions are carried out inside the nano tubes.
  - Ex.Reduction of NiO to Ni
  - Ex.Reduction of AlCl<sub>3</sub> to Al

#### **Application in Medicines**

- CNTs deliver drugs to the cancer cells without damaging other healthy cells.
- CNTs are useful in selective destruction of cancer cells by IR radiation.
- CNTs attached with peptides, proteins, nucleic acids, drugs are used to deliver the materials to cells or organs.
- CNTs are used in nano biotechnology and nano medicine.

#### **Application in Civil Engineering:**

carbon nanotubes are used for mechanical durability and crack prevention in concrete, enhanced mechanical and thermal properties in ceramics.

#### **Quantum Dot (Three Dimensional Nano Materials):**

- The size of the quantum dot is one billionth of a meter (1 nm).
- The key to the quantum dot is in the electrons.
- Electrons occupy in two bands (valency band & conduction band) in a crystal.
- By supplying energy, an electron is excited from valency band (VB) to conduction band (CB).
- As it moves from one band to the other, it creates a hole which is positively charged.
- Together, the hole and the electron are referred to as an exciton.
- The electron and the hole in the exciton normally keep their distance from each other.
- This is called the exciton Bohr radius.
- If the crystal is reduced in size, it removes this gap.

- Once that happens, it changes the crystals ability to absorb and emit energy.
- At this point, quantum dot is created.
- Quantum dots are composed of a hundred to a thousand atoms.
- These semiconductor materials can be made from an element, such as silicon or germanium, or a compound, such as CdS or CdSe.
- These tiny particles can differ in colour depending on their size.

### **Applications**

- **Quantum dots are of much interest for the other unusual properties** that they possess. These other properties **include electrical and nonlinear optical properties.** These unique properties of nano sized particles are partly the result of the unusually high surface to volume ratios for these particles, as many as one-third of the atoms are on the surface of the particle. As a result electrons and "holes" are confined in a limited space inside the cluster. These quantum electrical properties make these quantum dots of particular interest in the electronics industry.
- Quantum dots can emit light if excited. It is possible to make light-emitting diodes (LEDs) from quantum dots. They may also be used to emit white light for backlighting laptop computer screens.
- **Used to track trespassers in restricted areas.**
- **Used as light emitting diodes in sign display.** The result of using quantum dot is a display that's brighter, more power efficient and incredibly vibrant.
- **Used as cell staining for life science.**
- **Used in Solar cells.**

## **Assignment-Cum-Tutorial Questions**

### **Section A**

**Questions testing the remembering / understanding level of students**

#### ***Objective Questions***

1. The size of nanoparticles is between ----- nm. [       ]  
 [A] 100 to 1000 [B] 0.1 to 10 [C] 1 to 100 [D] 0.01 to 1

2. Which ratio decides the efficiency of nano substances? [ ]  
 [A] Weight/volume [B] Surface area/volume [C] Volume/weight [D] pressure/volume
3. Nano wires and nano tubes are ---- dimensional on nano scale  
 [A] three [B] one [C] two [D] four
4. The size of a quantum dot is ----- nm. [ ]  
 [A] 1 [B] 10 [C] 50 [D] 100
5. Nanomaterials are used in medicine as. [ ]  
 [A] drug carriers [B] for diagnosis [C] for treatment [D] all of the above
6. Nanoscience can be studied with the help of... [ ]  
 [A] quantum mechanics [B] Newtonian mechanics [C] macro-dynamics [D] geophysics
7. The diameter of human hair is \_\_\_\_ nm. [ ]  
 [A] 50 [B] 100 [C] 1000 [D] 1,00,000
8. The properties like melting point, solubility, color, etc changes on varying the [ ]  
 [A] Size  
 [B] Composition  
 [C] Surface properties  
 [D] None of the mentioned
9. Which of the following is the principal factor which causes the properties of nanomaterials to differ significantly from other materials? [ ]  
 [A] Size distribution  
 [B] Specific surface feature  
 [C] Quantum size effects  
 [D] All the mentioned
10. What are the advantages of nano-composite packages? [ ]  
 [A] Lighter and biodegradable  
 [B] Enhanced thermal stability, conductivity and mechanical strength  
 [C] Gas barrier properties  
 [D] All of the mentioned

## **Section B**

### ***Descriptive Questions***

1. What are nano materials? Explain about different methods to produce nano materials.
2. Discuss the advantages and limitations of sol-gel method.
3. What are carbon nano tubes? Describe sol-gel method for preparation of nano materials.
4. What are nano materials? Explain the types of nano materials with examples.
5. Describe thin film preparation by chemical vapour deposition method.
6. Discuss the engineering applications of CNTs.
7. Illustrate the different types of CNTs.
8. Discuss the significance and applications of quantum dot.
9. Explain medicinal applications of CNTs.
10. Discuss about the properties of carbon nano tubes.
11. Discuss the applications of thin film materials in industry.
12. Explain the following
  - a) SWNTs
  - b) MWNTs
13. Explain the applications of nano materials in engineering.

# ENGINEERING CHEMISTRY

## Unit – IV

### GREEN CHEMISTRY

#### **Objectives:**

To familiarize the students with the importance of green chemistry and its applications.

#### Unit-IV: Green Chemistry

Introduction - Principles of green Chemistry, methods of green synthesis (supercritical fluid extraction and microwave induced methods), IWM (Integrated Waste Management), ZWT (Zero Waste Technology). Applications of green chemistry.

#### **Course outcomes:**

##### **Students will be able to**

- explain the need of green chemistry.
- explain the principles of green chemistry and suitable method for synthesis of green products.
- apply the green principles for integrated waste management and zero waste technology

#### **Introduction:**

- Green chemistry is an approach to pollution prevention.
- It controls the pollution at the beginning of the process.
- **“Green chemistry is an approach to the design, manufacture and use of chemical products to reduce or eliminate chemical hazards”.**
- Green chemistry is an essential program to protect human health and environment.

#### **Need of Green Chemistry:**

- Green chemistry aims to eliminate hazards right at the design stage. The practice of eliminating hazards from the beginning of the chemical design process has benefits for our health and the environment, throughout the design, production, use/reuse and disposal processes.
- It focuses on prevention of waste, less hazardous chemical syntheses, and designing safer chemicals including safer solvents.
- It focuses on the design of chemical products to safely degrade in the environment.



## Principles of Green Chemistry:

Paul T. Anasthas and John Warner proposed the following twelve principles of Green Chemistry.

### 1. **Prevention**

It is better to prevent waste than to treat or clean up waste after it has been created.

### 2. **Atom Economy**

Synthetic methods should be designed to maximize the incorporation of all materials used in the process into the final product.

$\% \text{ atom economy} = \frac{\text{formula weight of desired product} \times 100}{\text{sum of the formula weights of all the reactants used in the reaction.}}$

### 3. **Less hazardous chemical synthesis**

Wherever practicable, synthetic methods should be designed to use and generate substances that possess little or no toxicity to human health and the environment.

For example adipic acid is widely used in polymer industries for the manufacture of nylon, polyurethane etc. was earlier synthesized from benzene which is carcinogenic. In Green technology, it is being synthesized from glucose.

### 4. **Designing safer chemicals**

Chemical products should be designed to affect their desired function while minimizing their toxicity.

For example, DDT is a powerful insecticide but it kills other useful insects also. So, it should be replaced with other substances that kill only the target organisms.

### 5. **Safer solvents and auxiliaries**

The use of auxiliary substances (e.g., solvents, separation agents, etc.) should be made unnecessary wherever possible and harmless when used.

This principle aims to use green solvents (water, super critical CO<sub>2</sub>) in place of volatile organic solvents.

### 6. **Design for energy efficiency**

Energy requirements of chemical processes should be recognized for their environmental and economic impacts and should be minimized.

If possible, synthetic methods should be conducted at ambient temperature and pressure.

**7. Use of renewable feedstocks**

A raw material or feedstock should be renewable rather than depleting whenever technically and economically practicable.

For example renewable resources like Solar energy, wind energy can be used in place of non renewable fossil fuels.

**8. Reduce derivatives**

Unnecessary derivatization (use of blocking groups, protection/ deprotection, temporary modification of physical/chemical processes) should be minimized or avoided if possible, because such steps require additional reagents and can generate waste.

**9. Catalysis**

Catalytic reagents (as selective as possible) are superior to stoichiometric reagents. Suitable catalyst must be used for the chemical reaction to proceed in lesser time and that gives high yield.

**10 . Design for degradation**

Chemical products should be designed so that at the end of their function they break down into harmless degradation products and do not persist in the environment. Biodegradable products must be preferred.

For example, DDT is an effective pesticide but its stability in the environment causes several hazards.

**11. Real-time analysis for pollution prevention**

Analytical methodologies need to be further developed to allow for real-time, in-process monitoring and control prior to the formation of hazardous substances.

**12. Inherently safer Chemistry for accident prevention**

Substances and the form of a substance used in a chemical process should be chosen to minimize the potential for chemical accidents, including releases, explosions, and fires.

## Methods of Green Synthesis or Green Reactions

Chemical synthesis that is consistent with the goals of green chemistry is called Green synthesis. The basic idea of cleaner production is to increase the production efficiency and to reduce the use and generation of hazardous substances and bi-products.

**Green Synthesis** is possible only by replacing the organic solvents like pyridine, benzene toluene etc. as much as possible by water or to eliminate the use of solvents altogether.

### Super Critical Fluid Extraction Method (SFE)

- Generally organic solvents have been used for the extraction of compounds like caffeine, cholesterol etc.
- But these solvents pollute air, land and water.
- To avoid the pollution, SFE method was developed.
- Super critical fluid has combined properties of liquid and gas.
- Super critical fluids are produced by heating a gas above its critical temperature or compressing a liquid above its critical pressure.
- Super critical fluids have both the gaseous property of being able to penetrate any material and the liquid property of being able to dissolve materials into their components.
- The most commonly used SCF is CO<sub>2</sub> because of its solubilizing property similar to organic solvents with lower critical temperature and critical pressure.
- Water can also be used as SCF.
- The basic principle of SCF extraction is that when the feed material is contacted with SCF then the volatile substances will separate into super critical phase.
- After dissolution of soluble material, the SCF containing dissolved substances is removed from the feed material.
- The extracted component is completely separated from the SCF by changing temperature and pressure.
- The SCF may be recompressed to the extraction conditions and recycled.

### **Advantages of SCF Extraction process:**

1. Dissolving power of SCF is controlled by pressure or temperature.
2. It is relatively a rapid process.
3. Quality and yield of the product can be increased.
4. SCF is easily recoverable from the extract due to its volatility.
5. SCF is non destructive process.
6. Separation of the fluid substances from the product is relatively easy and the solvent residues in the product are small.

### **Applications of Super Critical Fluid Extraction:**

1. It is used for the extraction of essential oils, flavones and some natural products from plants.
2. It is used for the production of de-nicotined tobacco.
3. Used in the removal of caffeine from coffee.
4. Used in pharmaceutical industry for production of active ingredients from herbal plants.
5. Used in the extraction of bi-products from polymer components.
6. Used in purification of contaminated oils.

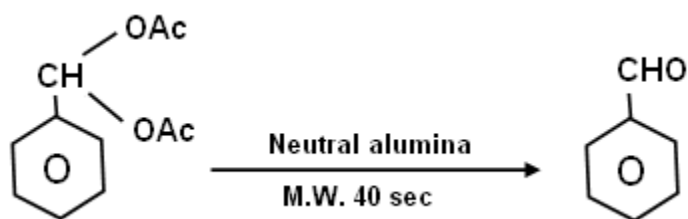
### **Microwave induced method for green synthesis:**

- Microwaves are used for heating.
- Their wave length is 1 cm to 1m.
- Polar molecules absorb Microwaves and non polar molecules are inert to Microwaves.
- In absence of electric field, the polar molecules are in Brownian motion.
- But in presence of electric field, all the polar molecules are lined up together in the same direction.
- As the field oscillates, their orientation changes rapidly leading to homogeneous heating.

Microwaves are used to carry out organic reactions. There are 3 types.

1. Microwave – assisted reactions in organic solvents.
2. Microwave – assisted reaction in aqueous phase.
3. Microwave – solvent free reactions (solid state reactions).

For example Deacylation



Use of microwaves irradiation reduces the time for Deacylation and the yields are good.

#### **Advantages:**

1. It is a clean, economical and safe procedure.
2. Rapid and homogeneous heating lead the reaction very fast.
3. High purity products are obtained.
4. Good yield is obtained.

#### **Limitations:**

Sometimes solvents reach their boiling points, leading to explosion.

#### **Zero Waste Technology:**

In this concept, a waste product is said to be zero waste technology, when a byproduct or waste product of any unit is used as raw material (or starting material) for another unit.

Ex.

- Molasses generated in sugar industry is used as raw material in manufacturing of alcohol.
- Bagasse obtained as solid waste in the sugar industry can be utilized as a raw material for manufacturing of paper and as a bio sorbent in treatment of waste water.
- Ash produced in thermal power stations can be used in manufacturing of bricks and as an adsorbent in waste water treatment.
- CO<sub>2</sub> produced in industries can be used as a blowing agent in manufacturing foam materials instead of using harmful chlorofluoro carbons.
- Agricultural byproducts can be used in manufacturing of biodegradable polymers.

#### **Integrated Waste Mangement:**

If waste is generated in the industry it should be properly managed before dumping in to the environment. Gaseous, liquid and solid wastes are generated in the industries.

## Management of gaseous waste products:

Flue gases should be treated before discharging in to air by using Cottrell's electrostatic smoke precipitators.

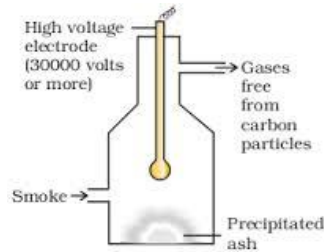


Fig. Cottrell smoke precipitator

## Management of waste water:

Waste water generated in the industries should be treated and can be reused in industries. Management of waste water includes (i) collection of waste water, (ii) Treatment of waste water using zeolite process or lime soda process etc. and finally (iii) Disposal of waste water. Treatment of waste water involves Preliminary, primary, secondary and tertiary treatments.

## Solid waste management:

Solid waste can be defined as any unwanted or discarded material from residential, commercial, industrial, mining and agricultural activities to the environment, causing problems. Solid waste management comprises of systematic control of generation, separation of waste into different categories, recycling, recovery and finally disposal of waste.

- I. **Collection of solid waste:** solid waste should be collected at least once a week from domestic, municipal, industrial, agricultural and special waste(e-waste, biological products etc.). After the collection, different materials must be separated depending on their nature. Eg. plastic, rubbish and bio waste etc.
- II. **Management of solid waste:** It involves three techniques
  - (a)**Reduce:** Reduction in the use of raw materials will decrease the production of waste from various types of industrial processes.
  - (b) **Reuse:** useful materials are recovered from solid waste and used in different applicatons.  
Ex. making rubber rings from the discarded cycle tubes, which are used by the newspaper vendors, instead of rubber bands, reduces the waste generation.
  - (c) **Recycle:** Plastic materials are separated from the solid waste and can be recycled. Recycling of paper will reduce cutting of trees for making fresh paper.

- III. **Disposal of solid waste:** After the separation and utilization of solid waste, the remaining waste material should be disposed in an ecofriendly manner. Thermal processes (Incineration and Pyrolysis) or open dumping or sanitary land filling or composting etc. methods are used in solid waste management.

### **Engineering Applications of green chemistry:**

- ◆ Engineers apply scientific and engineering principles to the design of manufacturing and combustion processes to reduce air pollutant emissions to acceptable levels.
- ◆ Engineers have developed various air pollution dispersion modes to remove vehicle gases like NO<sub>2</sub>, SO<sub>2</sub>, and other air pollutants.
- ◆ Improving industrial processes to eliminate waste and reduce consumption of organic solvents.
- ◆ By using biotechnology processes, the biomass is converted into useful products by the action of enzymes.
- ◆ Preparation of bio ethanol is an ecofriendly process that can be used as the gasoline replacement.
- ◆ With the help of bacteria, yeast and other microorganisms, many products are being prepared. These processes are less expensive, ecofriendly and more productive.
- ◆ Pesticides like DDT should be replaced by compounds that are less harmful and destroy only the target organisms.
- ◆ Biopolymers produced from byproducts of starch industry are used as packing material.
- ◆ Engineers are trying their level best to develop many such ecofriendly processes which keep the plant earth in safe position.

## Assignment-Cum-Tutorial Questions

### A. Questions testing the remembering / understanding level of students

#### I) Objective Questions

1. One of the following is a concept of green chemistry [ ]
  - a. Use of chemicals that are harmful
  - b. Improper technical designing
  - c. Production of by products in large amounts
  - d. Use of recycled or recyclable products
2. Green chemistry is called [ ]
  - a. Sustainable Chemistry
  - b. Un sustainable Chemistry
  - c. Developing Chemistry
  - d. Conceptual Chemistry
3. Physical Character of SCFs [ ]
  - a. Liquid
  - b. Gas
  - c. Combination of liquid and gas
  - d. Vapour
4. Which of the following is SCF [ ]
  - a) Benzene b) toluene c) CO<sub>2</sub> d) petroleum ether
5. Which of the following is not one of the twelve principles of green chemistry? [ ]
  - a) Using high temperatures to speed up reactions
  - b) Minimising toxic reagents used in a synthesis
  - c) Maximisation of atom economy
  - d) Minimising the use of solvents
6. Which of the following is the greenest solvent? [ ]
  - a) Formaldehyde b) Benzene c) Ethanol d) Water

#### II. Descriptive Questions:

1. Define green chemistry.
2. Discuss the need of green chemistry.
3. What is a Super Critical Fluid? Give an example?
4. What are green solvents? Give an example?
5. What is the aim of Integrated Waste Management?



6. What is the concept of zero waste technology?
7. Discuss any six applications of green chemistry.
8. What is the concept of green chemistry and its applications to the industry?
9. Explain briefly about the methods for green chemistry.
10. List out the advantages and applications of Micro Wave Induced method.
11. Discuss about the integrated waste management.
12. What are the main advantages and applications of Zero Waste Technology?
13. List out the engineering applications of green chemistry.

**II. Questions testing the ability of students in applying the concepts:**

**A. Level one questions:**

1. What is an atom economy?
2. What are the examples for super critical fluids?
3. Explain any six principles of green chemistry.

**B. Level two questions:**

1. List out the characteristics of Super Critical Fluid.
2. Discuss the main features of green Solvent.
3. What are the main advantages of Microwave induced method in green chemistry?

# Engineering Chemistry

## Unit- V

### WATER AND ITS TREATMENT

#### Objectives:

- To introduce different types and characteristics of water and its treatment methods for various applications.

#### Unit-V: Water and its treatment

Hardness of water – calculation of hardness – disadvantages of hard water – determination of hardness by EDTA method – numerical problems – softening methods – zeolite process – Ion exchange process – desalination by reverse osmosis – quality parameters of drinking water – (WHO standards and BIS standards) –municipal water treatment (Sedimentation, filtration and sterilization by chlorination and bleaching powder).

#### Course outcomes:

##### The students will be able to

- identify soft water and hard water.
- determine the temporary hardness, permanent hardness and total hardness by EDTA method.
- apply a suitable method of water treatment depending on the quality requirement.
- apply the knowledge of water treatment methods for domestic and drinking purpose.
- understand Reverse Osmosis process for conversion of sea water into pure water.

#### Introduction:

- Water is the most abundant and most useful natural component for the existence of all living beings.
- It also occupies a vital position in industries.
- It is important for the steam generation and thereby used to produce electricity.

#### Sources of Water:

The chief sources of water classified in to two groups

1. Surface water
2. Ground water

## **Surface water:**

The water present on the earth surface is known as surface water. It is available in many types

1. **Rain water:** The rain water is obtained by the evaporation of the surface water, it is considered as the purest form of the natural water. But Rain water during its downward path to the earth dissolves considerable amount of gases (e.g.; CO<sub>2</sub>, SO<sub>2</sub>, NO, NO<sub>2</sub>....) and also suspended solid particles present in the atmosphere.
2. **River water:** The source of the river water is ultimately the rain water and spring water. Rain water contains dissolved impurities and also contains the organic products (From the decomposition of the plants and animals bodies) and small particles of sand and rock in suspension.
3. **Lake water:** Lake Water is static water. In this type of the water, the main impurities observed are the organic matter (bacteria etc.).
4. **Sea water:** Sea water is the most impure form of natural water. Sea water is found to have about 3.5% of dissolved salts, out of which 2.6% is NaCl and hence sea water is always saltish in taste.

**Ground Water:** A part of rain water which falls on earth surface percolates into the earth and continues its journey till it meets a hard rock where it may be stored or come in the form of the spring. During its downward journey, it dissolves a number of salts.

## **Impurities in water:**

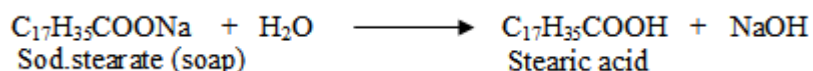
The common impurities present in natural water may be classified as follows.

- **Dissolved minerals:** Mostly comprise of carbonates, bicarbonates, chlorides and sulphates of calcium, Magnesium, sodium and potassium.
- **Dissolved gases:** Mostly O<sub>2</sub> and CO<sub>2</sub>.
- **Suspended matter:** Mostly comprise of mineral matter, giving turbidity to the water. Organic matter may also be present. They impart turbidity, colour and odour to the water.
- **Microscopic matter:** Consists of plants and bacterial life giving colour, taste and odour.

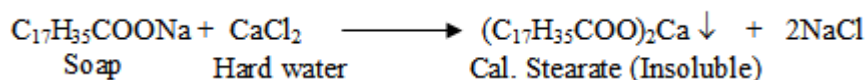
## **HARD WATER:**

- **The water which does not produce lather easily with soap is called hard water.** Hard water contains salts like Ca(HCO<sub>3</sub>)<sub>2</sub>, Mg(HCO<sub>3</sub>)<sub>2</sub>, CaCl<sub>2</sub>, MgCl<sub>2</sub>, CaSO<sub>4</sub>, MgSO<sub>4</sub> etc.
- **Water which produces lather easily with soap is called soft water.**

- Soap is a sodium salt of higher fatty acid i.e., Sodium or Potassium salts of stearic or palmitic or oleic acid. Soap is highly soluble in soft water and forms lather immediately.



- Soap forms insoluble salts with hard water and does not form lather.



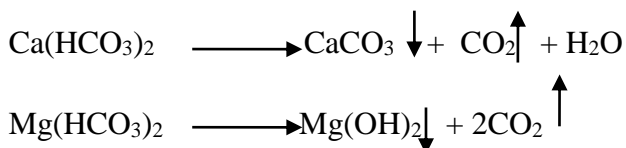
## Types of hardness:

The hardness of water may be of two types

1. Temporary hardness (carbonate hardness)
2. Permanent hardness (non-carbonate hardness)

### Temporary hardness:

This type of hardness is due to the presence of soluble bicarbonates of calcium and magnesium in water. It can be removed easily by boiling of water. In this process bicarbonates are decomposed to insoluble carbonates and hydroxides that can be removed by filtration.



### Permanent hardness:

This type of hardness is due to the presence of chlorides and sulphates of calcium and magnesium in water. Permanent hardness cannot be removed by boiling. It can be removed only by special methods like Zeolite process, Ion-exchange process etc.

### Degree of hardness (or) Expression of hardness:

The total hardness of water is caused by different dissolved salts of calcium and magnesium. [  $\text{Ca}(\text{HCO}_3)_2$ ,  $\text{Mg}(\text{HCO}_3)_2$ ,  $\text{CaCl}_2$ ,  $\text{MgCl}_2$ ,  $\text{CaSO}_4$ ,  $\text{MgSO}_4$  ].

The concentration of Hardness causing salts in water is expressed in terms of  $\text{CaCO}_3$  equivalents.

#### Reason:

- Because  $\text{CaCO}_3$  molecular weight is 100, it is easy for calculation.

Hardness of hardness causing salts in terms of CaCO<sub>3</sub> equivalents is

$$= \left[ \frac{\text{Amount of the hardness causing salt in mg/l}}{\text{Molecular weight of hardness causing salt}} \right] \times 100 \text{ ppm}$$

### Units of hardness:

There are four different units in which the hardness of water is expressed as given below:

- **Parts per million (ppm):** The number of parts by weight of CaCO<sub>3</sub> equivalents of hardness causing salts present in one million parts of water (10<sup>6</sup> parts).
- **Milligrams per litre (mg/l):** The number of parts by weight of CaCO<sub>3</sub> equivalents of hardness causing salts in milligrams present in one litre of water.  
1 mg/L = 1 ppm
- **Degree Clark (°Cl):** It is expressed as the number parts of CaCO<sub>3</sub> equivalents of hardness causing salt in 70,000 parts of water.
- **Degree French (°Fr):** It is expressed as the number of parts of CaCO<sub>3</sub> equivalents of hardness causing salt in 10<sup>5</sup> parts of water.
- The relationship between different units of hardness is

$$1 \text{ ppm} = 1 \text{ mg/L} = 0.07^\circ\text{Cl} = 0.1^\circ\text{Fr}$$
$$1^\circ\text{Cl} = 1.43^\circ\text{Fr} = 14.3 \text{ ppm} = 14.3 \text{ mg/L}$$

### Example:

A sample of hard water contains 120 mg/L of hardness. Express the hardness in ppm, degree French, degree Clark.

Sol:

Hardness of water sample = 120 mg/l

Conversion = 1 ppm = 1 mg/l = 0.07°Cl = 0.1 °Fr

Hardness of water in degree Clark = 120 × 0.07 = 8.4°Cl

Hardness of water in degree French = 120 × 0.1 = 12°Fr

Hardness of water in ppm = 120 ppm

### Disadvantages of using hard water in domestic use:

#### Washing:

When hard water is used for washing purpose, it does not produce lather freely with soap and it produces sticky precipitates of calcium and magnesium soaps. This cause a wastage of lot of soap.

#### Cooking:

Due to presence of dissolved hardness the boiling point of water is elevated. Therefore, more fuel and time are required for cooking.

#### Drinking:

Hard water causes bad effect on our digestive system and also possibility of forming calcium oxalate crystals in urinary tracks is increased.

### **Disadvantages of using hard water in Industries:**

#### **Disadvantages of hard water in steam generation in boilers:**

If hard water directly fed into the boilers it may cause many troubles as follows:

- Scale and sludge formation
- Corrosion
- Priming and foaming
- Caustic embrittlement

#### **Textile industry:**

The precipitates of calcium and magnesium soaps adhere to the fabrics. These fabrics when dyed do not produce exact shades of colour.

#### **Sugar industry:**

If hard water is used in sugar refining, it causes difficulties in the crystallization of sugar and the produced sugar may be deliquescent.

#### **Dyeing industry:**

Hard water if used in dyeing produces impure shades and give spots on the fabrics being dyed.

#### **Laundry:**

Hard water if used in laundry causes much wasting of the soap used in washing and may even cause coloration of clothes.

#### **Concrete making:**

It affects the hydration of cement and the final strength of the hardened concrete.

#### **Pharmaceutical industry:**

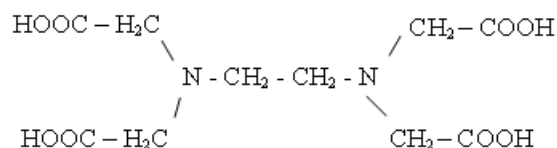
If hard water is used for preparing pharmaceutical products like drugs or injection may produce certain undesirable products in them.

### **ESTIMATION OF HARDNESS OF WATER BY EDTA METHOD:**

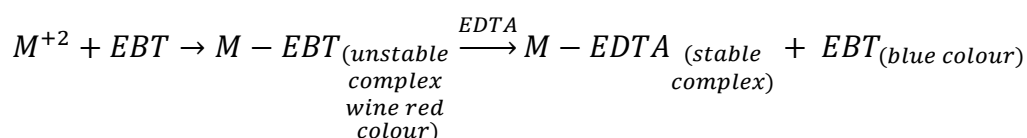
- This is a complexometric method where the disodium salt of ethylene diamine tetra acetic acid (EDTA) is the reagent.

#### **Principle:**

- EDTA acts as complexing agent or chelating agent.
- It forms complexes with various metal ions present in water.
- From the amount of the EDTA consumed during complex formation, the hardness of the water sample can be calculated.
- Structural formula of EDTA, ethylene diamine tetra acetic acid is



- $\text{Ca}^{2+}$  &  $\text{Mg}^{2+}$  ions form stable complexes with EDTA at pH = 9-10.
  - To maintain the pH 9-10 ( $\text{NH}_4\text{Cl} + \text{NH}_4\text{OH}$ ) basic buffer is used.
  - An alcoholic solution of **Erichrome Black -T (EBT)** is used as an indicator.
- When hard water comes in contact with EDTA at pH = 9-10, the  $\text{Ca}^{2+}$  &  $\text{Mg}^{2+}$  ions forms stable colorless complex with EDTA.
- To the hard water sample the blue coloured indicator Eriochrome Black-T is added along with the Basic buffer solution. EBT forms an unstable wine red colour complex with  $\text{Ca}^{++}$  and  $\text{Mg}^{++}$ .
- Now this solution is titrated with EDTA solution, then EDTA replaces EBT from the complex to form colourless and stable complex with calcium and magnesium ions. After completion of the titration, EBT is separated completely, which is evident by the appearance of blue colour in solution. Hence the colour change at the end point is **wine red to sky blue colour**.



### Reagents required:

- Standard hard water
- EDTA solution
- Water sample
- Eriochrome Black-T indicator
- Basic buffer solution

### Procedure & calculations:

#### 1. Standardization of EDTA solution:

Pipette out 20 ml of standard hard water into a conical flask. Add 2-3 ml of buffer solution and 1-2 drops of EBT indicator. Titrate this mixture against EDTA present in burette. At the end point the colour changes from wine red to sky blue. Note down the burette reading (say x ml) repeat the titration to get two concurrent values.

Observations: 
$$\frac{M_1 V_1}{n_1} = \frac{M_2 V_2}{n_2}$$

$n_1$  &  $n_2$  are no. of moles of  $\text{Ca}^{2+}$  &  $\text{Mg}^{2+} = \text{EDTA} = 1$  each

$$\begin{aligned} \text{(Molarity of EDTA)} \quad M_2 &= \frac{M_1 V_1}{V_2} \\ &= \frac{M_1 \times 20}{x} \text{ M} \end{aligned}$$

## 2. Estimation of total hardness of water sample:

Pipette out 20 ml of the water sample collected from the tap in a conical flask. Add 2-3ml of buffer solution and 2-3 drops of EBT indicator. Titrate the wine red coloured solution with EDTA. At the end point, it changes to sky blue colour. Note down burette reading. Let the volume of EDTA say  $y$  ml; repeat the titration to get two concurrent values.

$$\frac{M_3 V_3}{n_3} = \frac{M_2 V_2}{n_2}$$

$$n_2 = n_3 = 1$$

$$\begin{aligned} \text{Molarity of hard water} \quad M_3 &= \frac{M_2 V_2}{V_3} \\ &= \frac{M_2 \times y}{V_3} \text{ M} \end{aligned}$$

$$\text{Total hardness of water} = M_3 \times 100 \times 1000 \text{ mg/lit}$$

## 3. Estimation of permanent hardness:

Pipette out 100ml of hard water of water sample in a beaker and boil till the volume reduces to 20ml [all the bicarbonates of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  are precipitated to  $\text{CaCO}_3$  and  $\text{Mg}(\text{OH})_2$  respectively]. Cool the solution and filter the water into a conical flask. Finally make up the volume to 100 ml by adding distilled water. Pipette out 20 ml of boiled water sample into a conical flask. Add 2-3 ml of buffer solution and 2-3 drops of EBT indicator and titrate with EDTA solution taken in the burette till a clear blue colour end point is obtained. Note the volume of burette say  $z$  ml. Repeat the titration to get two concurrent values.

$$\frac{M_4 V_4}{n_4} = \frac{M_2 V_2}{n_2}$$

$$n_4 = n_2 = 1$$

$$\begin{aligned} \text{Molarity of permanent hard water} \quad M_4 &= \frac{M_2 V_2}{V_4} \\ &= \frac{M_2 \times z}{V_4} \text{ M} \end{aligned}$$

$$\text{Permanent hardness of water} = M_4 \times 100 \times 1000 \text{ mg/lit}$$

$$\text{Temporary hardness} = \text{Total hardness} - \text{permanent hardness}$$

$$= M_3 \times 100 \times 1000 - M_4 \times 100 \times 1000 \text{ mg/lit}$$



## Softening of hard water:

- Water required for industrial purposes (such as for steam generation) should be very soft. The process of removing hardness producing salts from hard water is known as softening of hard water. In industry, the important methods employed for softening of water are, (i) Zeolite process, (ii) Ion-exchange process.

## PERMUTIT OR ZEOLITE PROCESS:

- Hydrated sodium aluminosilicates with the general formula  $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot x\text{SiO}_2 \cdot y\text{H}_2\text{O}$  (where  $x=2-10$  and  $y=2-6$ ) are known as zeolite.

### Types of zeolite:

#### Natural zeolites:

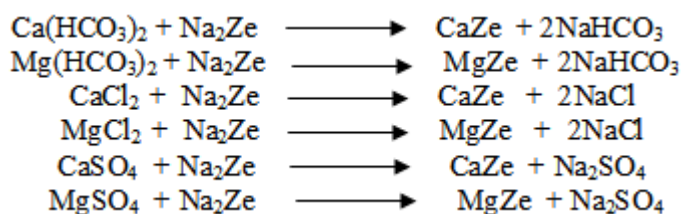
- Ex: Natrolith -  $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{SiO}_2 \cdot 2\text{H}_2\text{O}$

#### Synthetic Zeolites:

- Synthetic form of zeolite is known as **permutit**.
- It can be synthesized by heating together solutions of sodium silicate, sodium aluminate and aluminium sulphate.
- It is porous in nature.

### Principle:

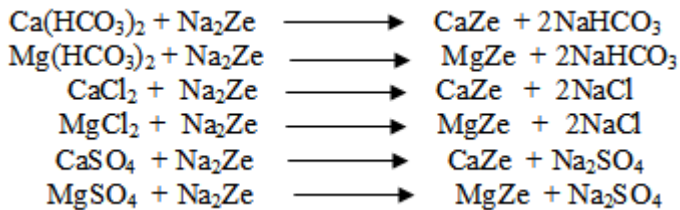
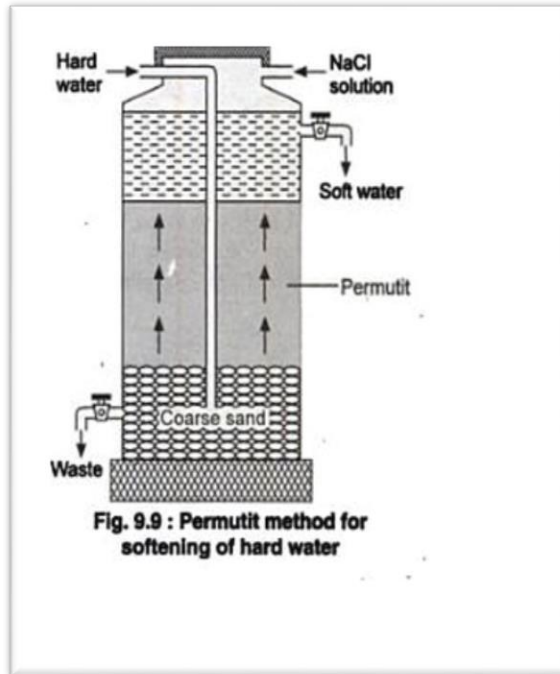
- Zeolites are represented as  $\text{Na}_2\text{Ze}$ .
- These are capable of replacing its sodium ions with cations in water, thereby reducing hardness of water.
- When hard water is passed through zeolite bed,  $\text{Na}^+$  ions are replaced by  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  ions to form  $\text{CaZe}$  and  $\text{MgZe}$ .



- Sodium salts formed in the above reactions remain dissolved in the softened water and do not impart any hardness to the treated water.

**Process:**

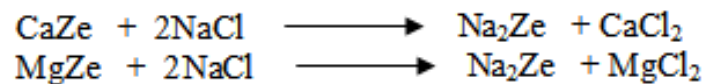
- When hard water is passed through Zeolite bed,  $\text{Na}^+$  ions are replaced by  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  ions to form  $\text{CaZe}$  and  $\text{MgZe}$ .



- After the process continues, the bed gets exhausted. Exhausted bed cannot further soften the water; hence it needs to be regenerated.

**Regeneration of exhausted zeolite:**

- The exhausted zeolite bed can be regenerated into sodium zeolite bed by passing brine solution (10%  $\text{NaCl}$ ) through the bed.



✦ **Advantages:**

- ✓ Residual water hardness of about 15 ppm can be obtained.
- ✓ The equipment occupies less space.
- ✓ Softening time is less.

✓ No sludge is formed.

✦ **Disadvantages:**

✓ Only cations are removed.

✓ As sodium ions are replaced, treated water contains more sodium salts leading to the boiler troubles like caustic embrittlement and boiler corrosion.

✓ Mineral acids destroy the zeolite bed.

✓ Turbid water is not suitable to treat by this method.

**ION EXCHANGE PROCESS OR DEMINERALIZATION PROCESS:**

✦ In the method ion exchange resins are used for softening of water.

✦ Ion exchange resins are high molecular weight, insoluble, cross linked long chain organic polymers.

✦ Types of ion exchange resins:

**Cation exchange resins:**

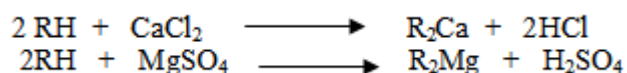
Resins containing acidic groups like  $-\text{COOH}$ ,  $-\text{SO}_3\text{H}$ , are capable of exchanging their  $\text{H}^+$  ions with other cations in water. These resins are denoted as RH.

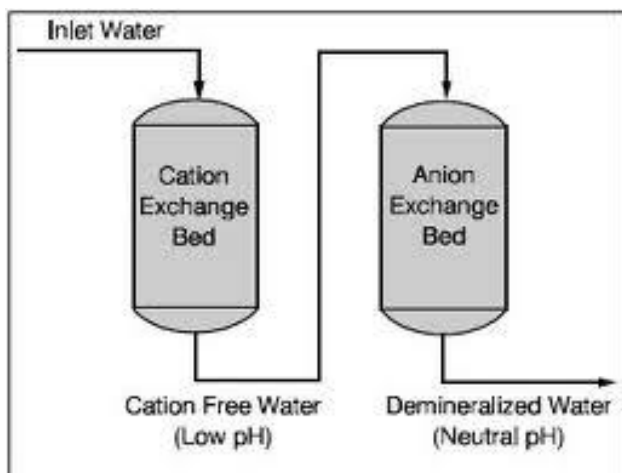
**Anion exchange resins:**

Resins containing basic groups like  $-\text{OH}$ , are capable of exchanging their  $\text{OH}^-$  ions with other anions present in water. These resins are denoted as ROH.

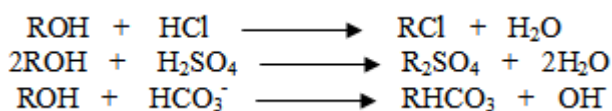
**Principle and Process:**

The apparatus used for deionization of water is shown in the following figure. It consists of two types of cylinders. Cation exchange cylinder and anion exchange cylinder. The hard water is passed first through cation exchange cylinder, where all the cations like  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Na}^+$ ,  $\text{K}^+$  etc., are removed off by exchanging with  $\text{H}^+$  ions of resin and equivalent number of  $\text{H}^+$  ions are released to the water.





Water coming from cation exchange resin, is passed through anion exchange resin. The anions like  $\text{HCO}_3^-$ ,  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$  etc. present in the water are removed off by exchanging with  $\text{OH}^-$  ions of resin and equivalent amount of  $\text{OH}^-$  ions are released to water.



$\text{H}^+$  and  $\text{OH}^-$  ions released from cation and anion exchange column, respectively combine to produce water molecule.

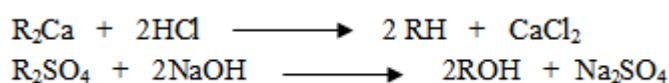


Thus, the water obtained in this process is free from ions. This water is called **deionized** or **demineralized** water.

- When all the  $\text{H}^+$  ions of cation exchange resin and  $\text{OH}^-$  ions of anion exchange resin are replaced, the resins are said to be exhausted.

#### **Regeneration of exhausted ion-exchange resins:**

Regeneration of exhausted cation exchange resin and anion exchange resin are carried out by passing dil.HCl and dil.NaOH solution respectively into the bed and washing with distilled water.



- ✦ Advantages:

- Water softened by this method is completely free from cations and anions.
- Highly acidic or alkaline water samples can be purified by this method.
- Residual hardness of water softened by this method is less than 2 ppm.
- Water obtained by this method is suitable for high pressure boilers.

✦ Disadvantages:

- The cost of equipment and chemicals used for regeneration are very expensive.
- Turbid water is not suitable for this process because these particles block the pores present in the resin.

**Desalination of Brackish Water by Reverse Osmosis:**

- The water containing dissolved salts with a particular salty or brackish taste is called brackish water.
- The process of removal of dissolved salts from brackish water (sea water or saline water) is known as desalination of brackish water.

**Desalination:**

- The process of removal of dissolved salt from the water is known as desalination.

Desalination can be done by **Reverse Osmosis**

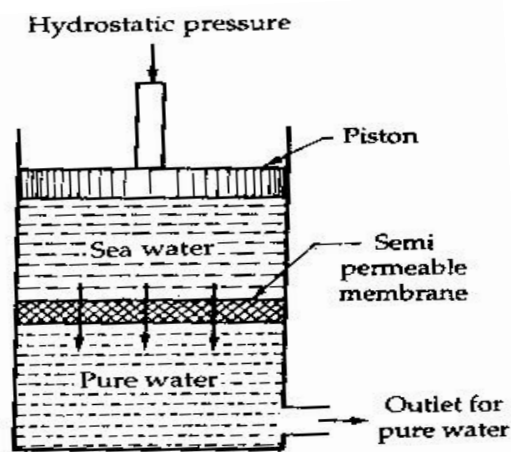
**REVERSE OSMOSIS**

- The flow of solvent molecules from a dilute solution to the concentrated solution when these two are separated by a semi permeable membrane is called **osmosis**.
- The external pressure is applied to stop away the osmosis is called **Osmotic Pressure**.
- If a pressure higher than the osmotic pressure is applied on the concentrated solution side, solvent flows in reverse direction i.e. from high concentration solution to lower concentration solution. This process is known as **reverse osmosis**.
- This membrane filtration is also called **super filtration or hyper filtration**.

**Process:**

- The reverse osmosis chamber consists of semi permeable membrane fitted in the middle, above which the sea water is taken and pressure of about 15 to 40kg/cm<sup>2</sup> is applied on sea water side. The pure water is forced through the semi-permeable membrane by using piston.
- The pure water is collected at the bottom of the tank.

- The membranes are made of poly methacrylate, poly amide polymers.



❖ **Advantages:**

- Maintenance cost is low.
- Life time of membrane is high.
- It removes ionic, non ionic, colloidal and organic matter from water.
- The water used in high pressure boilers is produced by reverse osmosis.

**Potable Water:**

The water which is suitable for drinking or domestic use and free from pathogenic bacteria is known as **potable water**.

**Essential qualities of drinking water:**

- It should be colorless, odorless and tasteless.
- Turbidity should be less than 10ppm.
- Hardness should be less than 125ppm.
- It should not contain disease causing germs.
- Total dissolved salts should be less than 500ppm
- pH of the solution should be between 7 and 8.5
- It should be free from objectionable dissolved gases like H<sub>2</sub>S
- Its chloride, fluoride and sulphate contents should be less than 250ppm, 1.5 ppm and 250ppm respectively.

**Parameters of drinking water as per WHO(World Health Organisation) specifications:**

Sl.No.	Parameters	Standards
1	pH	6.5-8.5
2	Total hardness	300
3	Total dissolved salts	500
4	calcium	75
5	Magnesium	50
6	Dissolved Oxygen	5
7	Biochemical Oxygen demand	5
8	Sulphate	150

9	nitrate	45
10	Chlorides	250
11	Electrical conductivity	300
12	Total alkalinity	120

**Parameters of drinking water as per BIS (Bureau of Indian Standards) specifications:**

**INDIAN STANDARD SPECIFICATIONS FOR DRINKING WATER IS. 10500**

S.NO.	Parameter	Requirement desirable Limit	Remarks
1.	Colour	5	May be extended up to 50 if toxic substances are suspected
2.	Turbidity	10	May be relaxed up to 25 in the absence of alternate
3.	pH	6.5 to 8.5	May be relaxed up to 9.2 in the absence
4.	Total Hardness	300	May be extended up to 600
5.	Calcium as Ca	75	May be extended up to 200
6.	Magnesium as Mg	30	May be extended up to 100
7.	Copper as Cu	0.05	May be relaxed up to 1.5
8.	Iron	0.3	May be extended up to 1
9.	Manganese	0.1	May be extended up to 0.5
10.	Chlorides	250	May be extended up to 1000
11.	Sulphates	150	May be extended up to 400
12.	Nitrates	45	No relaxation
13.	Fluoride	0.6 to 1.2	If the limit is below 0.6 water should be rejected, Max. Limit is extended to 1.5
14.	Phenols	0.001	May be relaxed up to 0.002
15.	Mercury	0.001	No relaxation

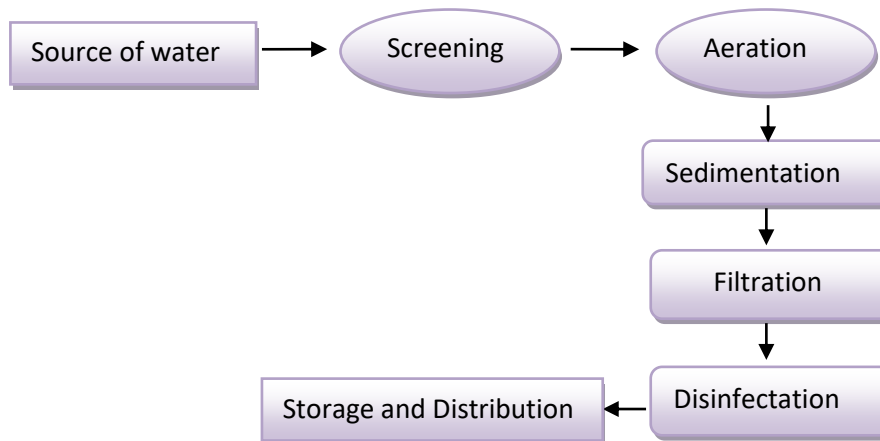
## MUNICIPAL WATER TREATMENT:

The treatment of water for municipal supply mainly involves the removal of suspended impurities, colloidal impurities and harmful pathogenic bacteria.

Three stages are involved in purifying a water sample for drinking purpose is

1. Sedimentation
2. Filtration
3. Sterilization

### Flow diagram of treatment of water:

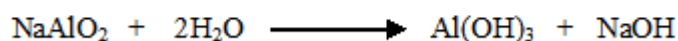
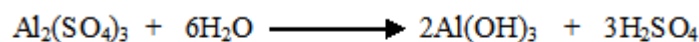


### 1. Sedimentation

- The basic principle of this treatment is to make water flow at a very slow velocity, so that the heavier particles are settled down under gravitation.
- For setting fine particles, coagulants like alum, sodium aluminate and salts of iron are added. They attract the colloidal particles and settle down. Then the top clear water is sent to next filtration tank.

#### Sedimentation by coagulation:

- This is the process of removal of suspended colloidal impurities by using coagulants like
  - Alum ( $K_2SO_4 \cdot Al_2SO_4)_3 \cdot 2H_2O$ )
  - Ferrous sulphate( $FeSO_4$ )
  - Sodium aluminate( $NaAlO_2$ )
- When coagulant is added to water, floc formation takes place due to hydroxide formation which can gather tiny particles together to form bigger particles and settle down quickly.

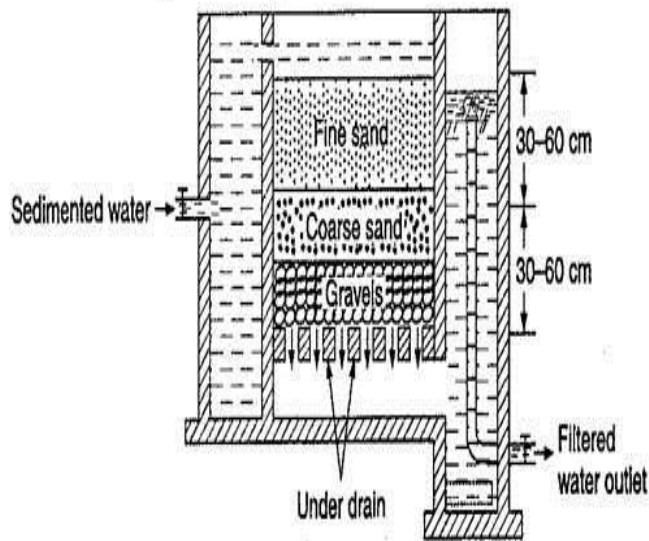


### 2. Filtration

- During filtration process, water containing fine impurities (after sedimentation) is removed by passing it through a porous filtering medium. Common materials used for filtration are fine sand, coarse sand, and gravel. Filtration takes place due to gravity or



due to the difference in pressures of water above and below the filter bed.



### Slow sand filtration:

- Slow sand filtration (SSF) tank contains thick beds of fine sand (at top), coarse sand (in middle), gravel (at bottom). When water passes through the filtering medium, it flows through various beds due to gravity. The rate of filtration slowly decreases since impurities trap in sand bed. When the rate of flow becomes very slow, filtration is stopped and the bed is cleaned by removing thin layer of sand bed (top layer) and replacing it with clean sand.

*(Note: In industrial areas where large amount of drinking water is required in short period, Pressure filters are used in which water is sent through filter beds using external pressure.)*

### STERILIZATION AND DISINFECTION

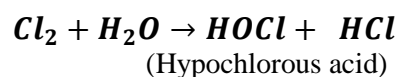
The process of removing or killing bacteria, viruses and micro-organisms etc, in water is called sterilization or disinfection.

Sterilization is done in the following ways

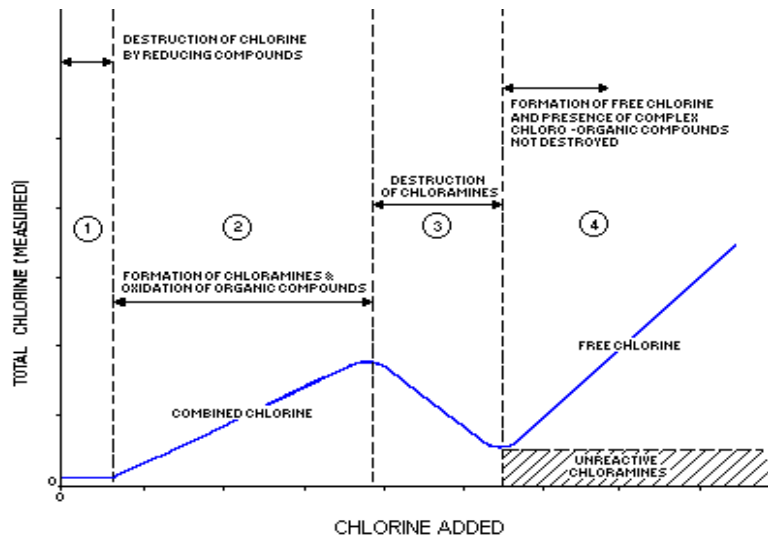
- Boiling
- Aeration or UV treatment
- Ozonisation
- Chlorination
- bleaching powder

### Chlorination:

- The process of utilizing chlorine as a powerful disinfectant is called chlorination. When chlorine is treated with water, it produces **hypochlorous acid which kills germs.**



- Chlorine is a powerful disinfectant. But the residual chlorine gives unpleasant taste to water and toxic to human beings. Hence calculated amount must be added to water carefully.
- The amount of chlorine required to kill bacteria and to remove organic matter is called “Break point chlorination”. It can be determined by plotting a graph between applied chlorine and residual chlorine.

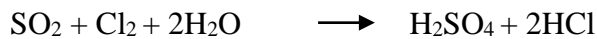


#### Advantages of Break point chlorination:

- It removes bad taste, colour, oxidizes completely organic compounds, ammonia and other reducing impurities.
- It destroys completely (100%) all disease producing bacteria.
- It prevents growth of any weeds in water.

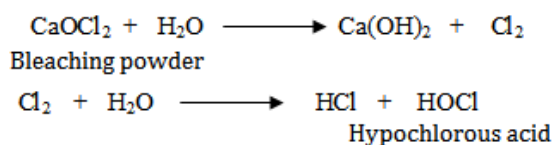
#### Dechlorination:

Overchlorination after break point produces unpleasant taste, odour, and toxicity to water. The overchlorination is removed by passing water through a bed of granular carbon and also by the addition of  $\text{SO}_2$  and sodium thiosulphate.



#### Sterilisation by adding bleaching powder:

- Bleaching powder contains 80% chlorine.
- When it is used as disinfectant, hypochlorous acid so formed in the process that acts as disinfecting agent.



## Assignment-Cum-Tutorial Questions

### A. Questions testing the remembering / understanding level of students

#### I) Objective Questions

- Potable water treatment does not involve [ ]  
(a) Demineralization (b) Sedimentation (c) Filtration (d) Disinfection
- Hard water is unfit for use in boilers for generating steam because [ ]  
(I) Its boiling point is higher.  
(II) Hard water does not produce lather inside the boiler.  
(III) Water decomposes into O<sub>2</sub> and H<sub>2</sub>.  
(IV) It produces scales inside the boiler.
- Hardness in water is caused due to the presence of [ ]  
(I) Un-dissolved salts of calcium and magnesium.  
(II) Dissolved sulphates of potassium.  
(III) Dissolved salts of calcium and magnesium.  
(IV) Un-dissolved calcium carbonate.
- The purest form of the naturally occurring water is [ ]  
(a) Rain water (b) Lake water (c) Pond water (d) Well water.
- One part of CaCO<sub>3</sub> equivalent hardness per 10<sup>5</sup> parts of water is called [ ]  
(a) Degree Clark (b) PPM (c) Degree French (d) mgs/L
- The Purification of brackish water by reverse osmosis is also called as [ ]  
(a) Super – Filtration (b) Supra – Filtration (c) Hypo – filtration (d) Filtration
- The compound used in regenerating of Permutit is [ ]  
(a) NaCl (b) HCl (c) NaOH (d) CaCl<sub>2</sub>
- Rain water picks up gases like CO<sub>2</sub>, O<sub>2</sub> etc. from \_\_\_\_\_.
- Anion exchange resin is regenerated by using \_\_\_\_\_.
- The chemical formula of Zeolite is \_\_\_\_\_.
- The chemical composition of basic buffer is \_\_\_\_\_.
- The solvent molecules move from low concentration region to high concentration region through the semi permeable membrane is called \_\_\_\_\_.
- On addition of chlorine to water \_\_\_\_\_ acid is produced which is a powerful disinfectant.
- Which of the following method separates both ionic and non –ionic impurities from water. [ ]  
(I) Electro dialysis (b) Deionization (c) Reverse osmosis (d) Zeolite process
- Which of the following statement is correct for ion exchange bed? [ ]  
(I) Cross linked polymers with micro porous structure.  
(II) Branched polymers with porous structure.  
(III) Cross linked polymers with non-porous structure.  
(IV) Branched polymers with non-porous structure.  
(a) Only I (b) both I & III (c) only II (d) both II & IV
- Hard water can be softened by passing it through [ ]  
(I) Distillation.  
(II) Sodium aluminate.  
(III) Ion exchange resin.  
(IV) Sodium silicate.  
(a) Only I (b) both I & II (c) both I & III (d) only IV
- Which of the following statement is correct? [ ]  
(I) Temporary hardness in water cannot be removed by boiling.  
(II) Temporary hardness in water can be removed by boiling.

(III) Hard water gives lather easily with soap solution.

(IV) Temporary hardness is also called as bi carbonate hardness.

(a) Only II (b) both I & IV (c) c (d) both I & III

18. Match the list-I and list-II of the following. [ ]

List-I	List-II
(1) Coagulant	(A) EBT
(2) EDTA	(B) Alum
(3) Disinfectant	(C) Chloramine.

(a) 1-A,2-B,3-C (b) 1-B,2-A,3-C (c) 1-B,2-C,3-A (d) 1-C,2-B,3-A

19. Match the list-I and list-II of the following. [ ]

List-I	List-II
(1) Natrolite	(A) Sodium Chloride
(2) Basic buffer	(B) Natural Zeolite
(3) Sea Water	(C) Styrene divinyl benzene
(4) Ion exchange resin	(D) $P^H=10$

(a) 1-B,2-D,3-A,4-C (b) 1-A,2-C,3-D,4-B (c) 1-C,2-A,3-D,4-B (d) 1-A,2-B,3-C,4-D

## II) *Descriptive Questions*

1. Define carbonate and non carbonate hardness of water; list out the various disadvantages of hard water for domestic use?
2. What is hard water? Give the action of hard water on soap.
3. Identify the hardness causing salts among the following.  $\text{NaHCO}_3$ ,  $\text{Ca}(\text{HCO}_3)_2$ ,  $\text{Na}_2\text{CO}_3$ ,  $\text{NaCl}$ ,  $\text{MgCl}_2$ .
4. Explain the determination of hardness by EDTA method.
5. Explain why  $\text{NH}_4\text{Cl} + \text{NH}_4\text{OH}$  buffer is added in the determination of hardness in water by EDTA method?
6. Explain the softening of hard water by Zeolite process?
7. What are the chemicals used for regeneration of ion exchange resins?
8. What is the principle of reverse osmosis? How it is used for the conversion of sea water to pure water?
9. What is potable water? Give its characteristics.
10. List out the parameters of potable water as per WHO and BIS specifications.
11. Define break point chlorination? What are its advantages?
12. What is reverse osmosis? Explain desalination of brackish water by reverse osmosis method.
13. What are the different steps involved for the treatment of water for municipal supply? Explain in detail.
14. How can you apply the Ion –exchange process for the softening of hard water? Explain in detail.

## B. Question testing the ability of students in applying the concepts.

1. Estimate the hardness of water in terms of ppm,  $^\circ\text{Fr}$ , if the hardness of water sample is 14 degree Clark.
2. A sample of water contains 100ppm of total hardness and 25ppm of temporary hardness. Calculate the permanent hardness of water in degree Clark and degree French.
3. 20ml of a sample water consumed 15ml of 0.02M EDTA before boiling and 5ml of the same EDTA after boiling. Calculate the permanent hardness and temporary hardness of water.
4. Find the  $\text{CaCO}_3$  equiv. of 83 mg of  $\text{Mg}(\text{HCO}_3)_2$  (Molecular weight 146).

5. If 50 mL of a sample of hard water consumed 15 mL of 0.01M EDTA. What is the hardness of water?
6. Find out the hardness of water if it contains 0.0010 g of dissolved  $\text{MgCl}_2$  per 500mL of it. Express it in ppm of  $\text{CaCO}_3$  equivalent.
7. Calculate the temporary, permanent and total hardness of a water sample having the following analysis.  
 $\text{Ca}(\text{HCO}_3)_2 = 16.2\text{mg}$ ,  $\text{CaCl}_2=11.1\text{mg}$ ,  $\text{MgSO}_4=60\text{mg}$ ,  $\text{MgCl}_2=19\text{mg}$ .
8. Calculate the temporary hardness of a water sample having the following analysis.  
 $\text{Ca}(\text{HCO}_3)_2=162\text{mg/L}$ ,  $\text{Mg}(\text{HCO}_3)_2=7.3\text{mg/L}$ ,  $\text{CaCl}_2= 22.2\text{mg/L}$  and  $\text{MgCl}_2=95\text{mg/L}$ .
9. A sample of hard water contains the following dissolved salts per litre. $\text{CaCl}_2=111\text{mg}$ ,  $\text{CaSO}_4=1.36\text{mg}$ , $\text{Ca}(\text{HCO}_3)_2=16.2\text{mg}$ , $\text{Mg}(\text{HCO}_3)_2=14.6\text{mg}$ , $\text{Silica}=40\text{mg}$ ,  
 $\text{Turbidity}=10\text{mg}$ . Calculate the temporary, Permanent and total hardness of water in ppm, degree Clark and degree French.
10. Calculate the temporary, permanent and total hardness of water in ppm from the following determination. 20ml of 0.05M solution of standard hard water required 40ml of EDTA for titration, 20ml of a sample of hard water consumed 30ml of the same EDTA and 20ml of hard water after boiling filtering etc., required 20ml of EDTA for titration.
11. A sample of water on analysis has been found to contain following in ppm.  
 $\text{Ca}(\text{HCO}_3)_2=4.86$ ;  $\text{Mg}(\text{HCO}_3)_2=5.84$ ;  $\text{CaSO}_4=6.80$ ;  $\text{MgSO}_4=8.40$ ; Calculate the temporary and permanent hardness of water.  
 (Atomic weights:  $\text{Ca}=40$ ;  $\text{Mg}=24$ ;  $\text{C}=12$ ;  $\text{S}=32$ ;  $\text{O}=16$ ,  $\text{H}=1$ ).

### C. Questions testing the analyzing / evaluating ability of students

1. One litre of water from an underground reservoir in Nalgonda town in Telangana was found to have the following dissolved salts.  $\text{Mg}(\text{HCO}_3)_2=0.0146\text{g}$ ,  $\text{Ca}(\text{HCO}_3)_2=0.0081\text{g}$ ,  $\text{MgSO}_4=0.0012\text{g}$ ,  $\text{CaSO}_4=0.0136\text{g}$ , organic impurities 100g. Calculate the temporary, permanent and total hardness of water in degree French. Give permissible level of water based on result.
2. One litre of water from khammam Dist. in Telangana showed the following analysis:  $\text{Mg}(\text{HCO}_3)_2=0.0256\text{g}$ ,  $\text{Ca}(\text{HCO}_3)_2=0.0156\text{g}$ ,  $\text{NaCl}=0.0167\text{g}$ ,  $\text{CaSO}_4=0.0065\text{g}$ , and  $\text{MgSO}_4=0.0054\text{g}$ . Calculate the temporary and permanent hardness of 100 litres of water.

# Engineering Chemistry

## Unit- VI

### Instrumental methods of analysis

#### Objectives:

- To enable the students to obtain the knowledge of instrumental methods of analysis.

#### Unit-VI: Instrumental methods of analysis

Electronic transition in molecules – Absorption Spectra, Beer Lambert's Law, UV spectrophotometer – principle and working – determination of Ferric Iron by spectrophotometry – Flame photometry – principle and working, estimation of sodium by flame photometry.

#### Course outcomes:

#### The students will be able to

- explain electronic transition in molecules
- explain the principles and working of spectrophotometer and flame photometer for the determination of a given ion in a given solution.

#### Introduction:

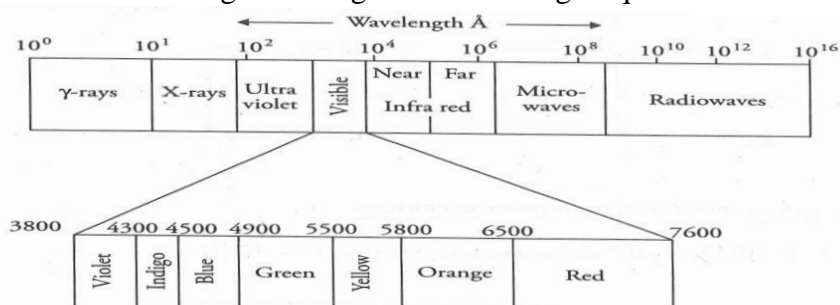
When light either visible or ultraviolet is absorbed by valence (outer) electrons, these electrons are promoted from their normal (ground) states to higher energy (excited) states. The energies of the orbitals involved in electronic transitions have fixed values. Ultraviolet- visible spectroscopy or ultraviolet - visible spectrophotometry (UV-Vis or UV/Vis) involves the spectroscopy of photons in the UV-visible region. There is an interaction between UV visible light and sample which is in solution form. As a result of this interaction some photons (photons of UV-Vis EMR) are absorbed and this absorption of UV visible is measured by an instrument named UV visible spectrophotometer. UV visible is low energy EMR(electro magnetic radiation) hence generally no ionization take place but electronic transition of lone pair and  $\pi$  electron take place (200-800 nm).

**Electromagnetic radiation:** It is a kind of radiation including visible light, radio waves, gamma rays, and X-rays, **in which electric and magnetic fields vary simultaneously.**

Generally, **electromagnetic radiation** is classified by wavelength into radio wave, microwave, terahertz (or sub-millimeter) radiation, infrared, the visible region, ultraviolet, X-rays and gamma rays. The behaviour of EM radiation depends on its wavelength.

#### The Electromagnetic Spectrum

An electromagnetic spectrum is obtained when all types of electromagnetic radiations are arranged in the order of increasing wavelength or decreasing frequencies.



**Absorption Spectrum:** Absorption spectroscopy refers to spectroscopic techniques that measure the absorption of radiation, as a function of frequency or wavelength, due to its interaction with a sample. The sample absorbs energy, i.e., photons, from the radiating field. The intensity of the absorption varies as a function of frequency, and this variation is the **absorption spectrum**. Absorption spectroscopy is performed across the electromagnetic spectrum.

Absorption spectroscopy is used as an analytical chemistry tool to determine the presence of a particular substance in a sample and, to quantify the amount of the substance present. Infrared and ultraviolet-visible spectroscopy are particularly common in analytical applications.

The most common arrangement for measuring absorption spectra is to direct a generated beam of radiation at a sample and detect the intensity of the radiation that passes through it. The transmitted energy can be used to calculate the absorption.

### **Theory (principle) of Ultraviolet-Visible (UV-Vis) Spectroscopy**

Ultraviolet and visible radiation interacts with matter and causes electronic transitions (promotion of electrons from the ground state to a high energy state).

**It involves the measurement of absorption of light in the visible and ultraviolet regions (visible region 400-800 nm; UV region 200-400 nm) by the substances under investigation.**

Since the absorption of light involves the transition from one electronic energy level to another within a molecule, UV spectroscopy is also known as electronic spectroscopy

#### **Electronic transitions in molecules:**

The following electronic transitions are possible:

$\pi \rightarrow \pi^*$  (pi to pi star transition)

$n \rightarrow \pi^*$  (n to pi star transition)

$\sigma \rightarrow \sigma^*$  (sigma to sigma star transition)

$n \rightarrow \sigma^*$  (n to sigma star transition)

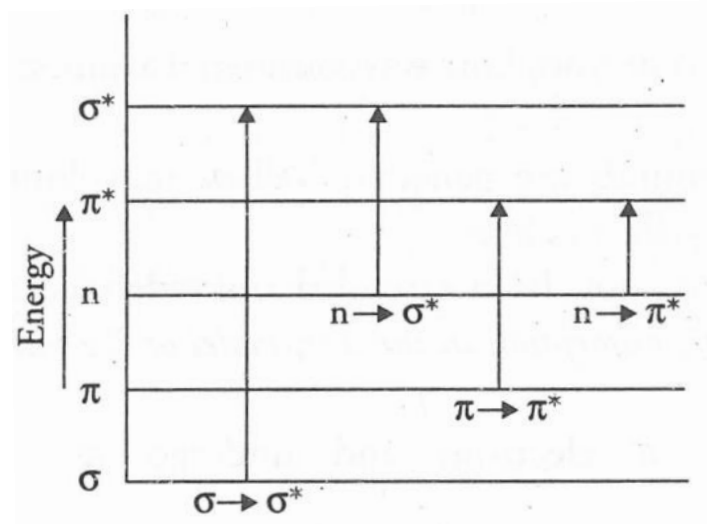
**$\sigma \rightarrow \sigma^*$  transitions:** The  $\sigma$  bonded electrons are held firmly in the molecule. Hence, the transitions from  $\sigma$  to  $\sigma^*$  require large amount of energy. These transitions require high energy radiations and therefore, occur in the far ultraviolet region.  $\sigma \rightarrow \sigma^*$  transitions occur in hydrocarbons like methane, propane and are less informative.

**$n \rightarrow \sigma^*$  transitions:** This type of transitions occur in saturated compounds with one hetero atom having unshared pairs of electrons (n electrons) like alcohols, ethers, amines, ketones, aldehydes, etc. The energy required for these transitions is lesser than the energy required for  $\sigma \rightarrow \sigma^*$  transitions.

**$\pi \rightarrow \pi^*$  transitions:** These transitions take place in compounds containing double and triple bonds. The excitation of  $\pi$  electrons required lesser energy; hence they occur at longer wavelength.

**$n \rightarrow \pi^*$  transitions:** In these transitions, the electrons of the unshared electron pair on the hetero atom is excited to  $\pi^*$  anti-bonding orbital. As non-bonding electrons are loosely held, these require least energy and occur at larger wavelengths. They occur in unsaturated compounds with hetero atoms having unshared pairs of electrons like C=O, C=S.

The electronic transitions are shown in the energy diagram:



Change in energy for different transitions are in the order:

$$n \rightarrow \pi^* < \pi \rightarrow \pi^* < n \rightarrow \sigma^* \ll \sigma \rightarrow \sigma^*$$

The  $\sigma$  to  $\sigma^*$  transition requires an absorption of a photon with a wavelength which does not fall in the UV-vis range. Thus, only  $\pi$  to  $\pi^*$  and  $n$  to  $\pi^*$  transitions occur in the UV-vis region.

#### Transition probability:

Depending upon the value of the extinction coefficient, transitions are classified as

- (a) Allowed transitions
- (b) Forbidden transitions

Allowed transitions are transitions with values of extinction coefficient  $\epsilon_{max}$  more than  $10^4$ .

The value of  $\epsilon_{max}$  for forbidden transitions is below  $10^4$ .

**Beer-Lambert's Law:** "equal fractions of the incident light are absorbed by layers of solution with equal concentration and same thickness".

According to it, when a beam of monochromatic light is passed through a solution, the decrease in intensity of radiation with thickness of the absorbing material is directly proportional to the intensity of incident radiation as well as to the concentration of the solution.

$$\log I_0/I \propto c \quad (\text{Beer's Law})$$

$$\log I_0/I \propto l \quad (\text{Lambert's Law})$$

$$\log I_0/I \propto cl \quad (\text{Beer Lambert's Law})$$

$$\log I_0/I = \epsilon cl$$

$$\log I_0/I = \text{Optical Density or absorbance (A)}$$

$$\text{Therefore, } \log I_0/I = \epsilon cl = A$$

$$A = \epsilon cl$$

A = Absorbance (optical density)

$I_0$  = Intensity of incident light on the sample cell

I = Intensity of light leaving the sample cell (transmitted light)



$c$  = molar concentration of solution

$l$  = length of sample cell (cm)

$\epsilon$  = molar absorption coefficient

### Applications of Beer Lambert's Law

- Using the Beer Lambert's law equation, the concentration of the species absorbing in the UV or visible region can be determined.

(First, a series of standard solutions of known concentrations have to be prepared and their absorbance measured. A graph (calibration plot) of various absorbance values Vs concentration is obtained. Then the absorbance of the unknown concentration of the species is determined. The concentration value corresponding to the absorbance of the unknown solution is directly read from the graph.)

### Limitations of Beer Lambert's Law:

The linearity of the Beer-Lambert law is limited by chemical and instrumental factors. Causes of nonlinearity include:

- deviations in absorptivity coefficients at **high concentrations** due to electrostatic interactions between molecules in close proximity.
- **scattering of light due to particulates** in the sample.
- **fluorescence or phosphorescence** of the sample.

**Spectrophotometer:** With Spectrophotometers, it is possible to measure optical density or transmittance at a specific wavelength.

The essential Components of a Spectrophotometer are:

**1) Energy Sources:** Argon, Xenon, Deuterium, or Tungsten lamps

- Deuterium Lamps or hydrogen discharge tubes are used for continuous spectrum in the ultraviolet region .
- Tungsten Filament Lamps are the most common source of visible and near infrared radiation.

**2) Monochromators:** Quartz prisms and all gratings

A monochromator is a device that produces a narrow beam of radiation with a provision to vary the wavelength of the radiation.

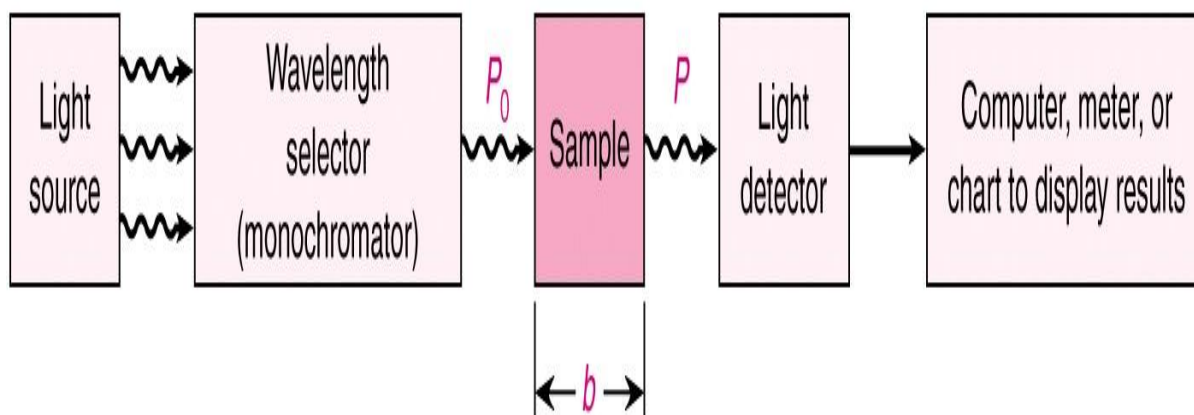
The important parts of a monochromator are (i) an entrance slit (ii) a concave mirror to focus the light (iii) a dispersing element which may be prism or grating. and an (iv) exit slit

**3) Sample Containers (cells):** Quartz, Borosilicate.

The essential requirement of a cell or sample container is that it should be transparent to UV-Visible radiations. Quartz cells are commonly used.

**4) Detector and recorder:** Detector continuously measures the intensity ratio of the beams transmitted through the sample and the solvent respectively and the recorder records the data.

Ex. Photo tube and photo multiplier detectors.



### **Applications of spectroscopy:**

UV/Vis spectroscopy is routinely used in analytical chemistry for the quantitative determination of different analytes, such as transition metal ions, highly conjugated organic compounds, and biological macromolecules.

UV/Vis spectroscopy can be used for finding the **extent of conjugation**.

**It is also used for:**

**Identification of unknown compounds:** Unknown compounds can be identified by comparing its spectra with the spectra of known compounds.

**Determination of geometrical isomers:** Effective  $\pi \rightarrow \pi^*$  transitions take place when the molecule is coplanar. The steric strain in cis-isomer prevents coplanarity. Thus, cis isomers absorb at a shorter wavelength when compared to the trans-isomer. For example, cis-stilbene absorbs at 280 nm and trans stilbene absorbs at 295 nm.

**Detection of impurities:** Ethanol contains benzene as an impurity. Since benzene is toxic in nature, it is essential to detect its presence. The presence of benzene can be detected through the UV spectrum of the sample at 280 nm. Ethanol is transparent at this wavelength but benzene shows an absorption band with  $\epsilon_{max}=230$

### **Determination of concentration of ferric Iron in a given solution Spectrophotometrically(Spectrophotometric Analysis of Iron (III))**

**Aim:** To determine concentration of ferric Iron in a given solution Spectrophotometrically.

**Requirements:** Visible spectrophotometer, beaker, distilled water, standard solution, tissue paper.

**Principle:** The study of variation in intensity of a given coloured solution with the change in concentration of the given coloured component is termed as colorimetric analysis. A spectrometer is a device which detects the percentage transmittance of light radiation when light of certain intensity and frequency range is passed through the sample. Thus the instrument compares the intensity of the transmitted light with that of the incident light.

**Procedure:**

Part A: Initial setting of the instrument

1. Before starting the experiment ensure that meter initially reads zero on transmittance scale (T). If zero is not adjusted, set mechanical zero with adjusting knob.
2. Connect the instrument to the power supply through a three pin plug. Set the switch to the ON position and ensure that red light indicator on the meter glows.
3. Adjust the wave length knob to the required wave length region on scale (approximate). Choose the position of gain selector (wave length) switch correspondingly either to 340 – 400 nm or 400 – 960 nm.
4. Adjust the 'set zero' knob so that meter reads zero on T scale and 100 on O.D. scale.

Final setting of the instrument

5. Open the lid of the sample housing and insert a cuvette containing blank solution (distilled water). Close the lid so that it fits properly.
6. Adjust the control knob (Set 100) in appropriate direction to bring the reading to 100% transmittance or zero optical density (OD).
7. Open the lid and remove the cuvette. Close the lid tightly again.
8. Check zero on the meter. Adjust zero if disturbed.

9. Repeat step 4 and 8 till zero and 100% transmittance.

Part B: Determination of  $\lambda_{\max}$

10. Insert the cuvette containing standard solution in the similar fashion and note the reading.

11. Change the wavelength by about 20nm every time and note down corresponding optical density. Repeat step 4 to 8 for each wave length measurement. Plot a graph between wavelength on the x-axis and O.D. on y-axis.

Part C: Verification of Beer's law

12. Fix the wavelength at  $\lambda_{\max}$  position.

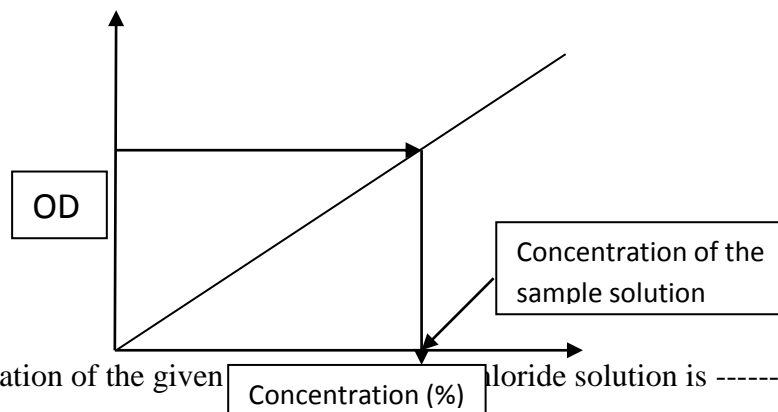
13. Make 20 ml solution of Ferric chloride with concentration 0.2M, 0.5M, 1.0M, 1.5M, 2.0M, 2.5M, 3.0M, etc.,

14. Note down optical density of series of solutions of Ferric chloride prepared above.

15. Plot the O.D. against concentration. Line connecting the point should be a straight line.

16. Now take a solution of unknown concentration and note down optical density. Find out the concentration of the unknown solution from graph.

17. Report the results of unknown solution in moles / litre.



**Result:** Concentration of the given ferride solution is -----M.

## FLAME PHOTOMETRY (or) FLAME EMISSION SPECTROSCOPY

It is a type of emission spectroscopy widely used for analysis of metals particularly sodium, potassium, calcium, Barium, Lithium present in biological fluids, tissues and other samples. In this method, a flame is used as the excitation source and an electronic photodetector is used as the measuring device. It is suitable for qualitative and quantitative determination of several cations, especially for metals that are easily excited to higher energy levels at flame temperature.

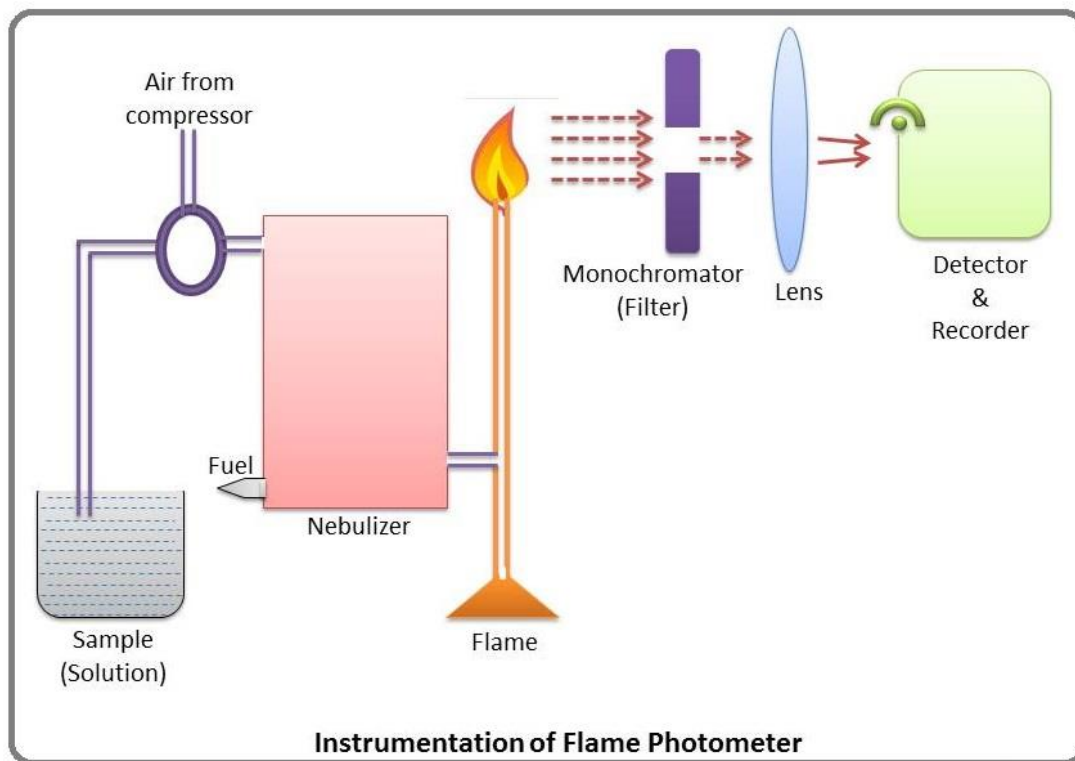
### Principle

A metal is analyzed on the basis of radiation emitted by it when the sample is atomized into a flame. When a solution containing a metallic salt is sprayed into a flame; the salt gets vaporized. This causes some of the metal atoms to get excited to an energy level. When these electrons return to the lower energy level, they radiate energy of different wavelengths. The radiated energy, on passing through monochromator, emitted the characteristic wavelength radiation which is amplified and recorded. The emission is proportional to the number of excited atoms, which is proportional to the total number of atoms in the flame i.e. the sample concentration.

The energy to which the atoms are subjected must be less than the ionization potential. The resonance wave - length (at which the most intense absorption and emission occur) is: 671 nm for lithium, 589 nm for sodium and 767 nm for potassium.

### FLAME PHOTOMETER INSTRUMENTATION:

1. Pressure regulators and flow meters
2. Nebuliser and Burner system
3. Monochromators
4. Detectors
5. Recorder and display.



Namrata Heda

#### 1. Pressure regulators and flow meters:

A constant thermal environment and an uniform spray have to be maintained when the flame photometer is operated.

Therefore, the gas pressure and gas flow have to be maintained at the same level.

The fuel to be used is usually contained in a cylinder under pressure.

The oxidant, air may be directly used from a compressor.

To obtain a constant flow, a diaphragm pressure regulatory valve is used.

**2. Nebuliser and Burner system:** This is a part which produces excited atoms. Here the sample solution is sprayed into fuel and oxidant combination. A homogenous flame of stable intensity is produced.

The fuel, air and the test solution in the form of aerosol are all passed through separate channels to an opening on which the flame is produced.

A Propane-air flame, acetylene-air flame that produce a temperature of 2000K can be used.

#### 3. Monochromators:

Filters and monochromators are needed to isolate the light of specific wavelength from

remaining light of the flame. For this simple filters are sufficient for the study of elements like Ca, Na, K and Li. So a filter wheel with filter for each element is taken. When a particular element is analyzed, the particular filter is used so that it filters all other wavelengths.

**4.Detectors:** Photovoltaic cell can be used for detecting the radiation characteristic of the test metal in the range of 200nm to 750nm.

**5.Recorders and display:** These are the devices to read out the recording from detectors.

### **Applications of flame photometry:**

1. It is useful in industries for detection of elements present in fuels, cement, glass, metallurgical samples etc.
2. It is used for analysis of Na, K, Ca etc. present in soil, water.
3. It can be used for analysis of elements present in plant materials.
4. It can be used for analysis of elements like Na, K, Ca present in blood and urine samples.

### **Limitations of flame photometry:**

- The number of excited atoms in flame is very small.
- It needs perfect control of flame temperature.
- Interference by other elements is not easy to be eliminated.

## **Estimation of sodium concentration in a given sample by flame photometry:**

**Aim:** To determine the sodium concentration in a given sample by flame photometry.

**Requirements:** Flame photometer, beaker, distilled water, standard solution.

**Principle:** The technique of the flame photometry is based upon the measurement of emitted radiations when a solution of metal compound is introduced into the flame in the form of droplets.

The quantitative results can be obtained by plotting a calibration curve between the concentration of the element and flame intensity.

The processes involved in flame photometry follow the following steps:

1. Liquid sample containing element, is aspirated into a flame to the formation of the liquid droplets.
2. Evaporation of liquid droplets, resulting formation of salt residue.
3. The decomposition of residue to formation of free neutral atoms or radicals. These neutral atoms are excited by the thermal energy of the flame. The excited atoms which are unstable quickly emit photons (radiation) and return to the lower energy state. The measurement of emitted radiation in terms of wavelength or intensity is basis of flame photometry.

If  $E_2$  and  $E_1$  represent the energy of the higher and lower energy state, the radiation emitted during the changing energy levels may be defined by equation as;

$$E_2 - E_1 = h\nu$$

Where  $h$  is the Planck's constant, and  $\nu$  is the frequency of emitted light which is defined as follows.

$$\nu = \frac{c}{\lambda}$$

We get,

$$E_2 - E_1 = hc/\lambda$$

$$\text{or } \lambda = hc / E_2 - E_1$$

From the above equation, calculate the wavelength of the emitted radiation which is characteristic of the particular ion from which it was emitted.

### PROCEDURE

1. Weigh accurately 100mg of sodium chloride and dissolve in 100 ml of distilled water.
2. Take 10 ml of the solution and dilute to 100 ml with distilled water.
3. Prepare a series of standard solutions of 10, 20, 30, 40, 50  $\mu\text{g} / \text{ml}$  concentrations.
4. Switch on the flame photometer and select the sodium filter.
5. Set the gas in flame in order to get non-luminous flame and air pressure at 0.4 to 0.5  $\text{kg} / \text{cm}^2$ .
6. Atomize the flame intensity to 0% using distilled water with the knob.
7. Atomize the flame intensity to 100% using 50  $\mu\text{g} / \text{ml}$  standard solution (highest concentration).
8. Measure the per cent flame intensity of all the standard solutions (10  $\mu\text{g} / \text{ml}$ , 20  $\mu\text{g} / \text{ml}$ , 30  $\mu\text{g} / \text{ml}$ , 40  $\mu\text{g} / \text{ml}$ , and 50  $\mu\text{g} / \text{ml}$  concentration ) and unknown sample solution.
9. Plot the graph between concentration and per cent flame intensity.
10. From the graph, mark the percentage flame intensity of the unknown sample and by extrapolating, determine the corresponding concentration.

### Preparation of standard solution

100 mg standard in 100 ml water = 1 mg / ml = 1000  $\mu\text{g} / \text{ml}$

10 ml of 1 mg / ml diluted to 100 ml water = 100  $\mu\text{g} / \text{ml}$

1 ml of 100  $\mu\text{g} / \text{ml}$  diluted to 10 ml = 10  $\mu\text{g} / \text{ml}$

2 ml of 100  $\mu\text{g} / \text{ml}$  diluted to 10 ml = 20  $\mu\text{g} / \text{ml}$

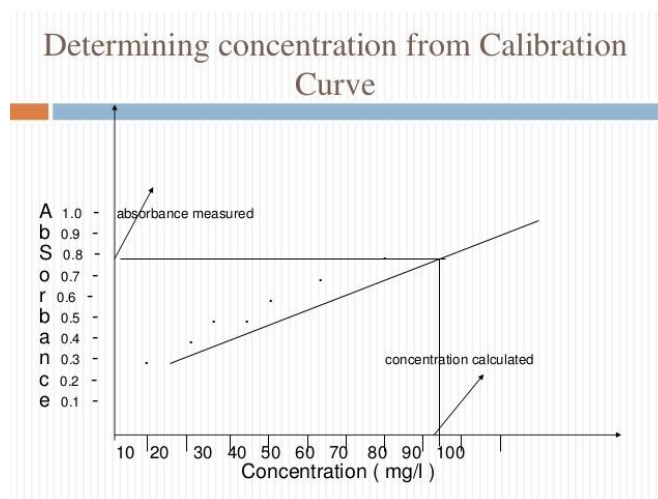
3 ml of 100  $\mu\text{g} / \text{ml}$  diluted to 10 ml = 30  $\mu\text{g} / \text{ml}$

4 ml of 100  $\mu\text{g} / \text{ml}$  diluted to 10 ml = 40  $\mu\text{g} / \text{ml}$

5 ml of 100  $\mu\text{g} / \text{ml}$  diluted to 10 ml = 50  $\mu\text{g} / \text{ml}$

### OBSERVATIONS

S.No	Concentration ( $\mu\text{g} / \text{ml}$ )	Flame Intensity(%)
1.	0	0
2.	10	
3.	20	
4.	30	
5.	40	
6.	50	
7.	Unknown (Sample)	



Result: the concentration of sodium ions in the given sample of NaCl solution was found to be .....  $\mu\text{g} / \text{ml}$

### Assignment-Cum-Tutorial Questions

#### A. Questions testing the remembering / understanding level of students

##### I) Objective Questions

1. According to the Beer-Lambert Law, on which of the following does absorbance not depend?
 

**A.** colour of the solution                      **B.** extinction coefficient of the sample  
**C.** distance that the light has travelled through the sample    **D.** solution concentration
2. The visible portion of the electromagnetic spectrum occurs between \_\_\_nm and \_\_\_nm
 

**A.** 1, 10                      **B.** 10,300                      **C.** 400,740                      **D.** 800, 1200
3. A blank contains the \_\_\_\_\_ but not the dissolved chemical.
 

**A.** solvent                      **B.** solute                      **C.** filter                      **D.** absorption spectrum
4. Basically, what is the path of light through a spectrophotometer?
 

**A.** meter, photodetector, filter, sample, light source    **B.** meter, filter, sample, photodetector, light source  
**C.** light source , filter, sample, photodetector, meter.  
**D.** light source , sample, filter, photodetector, meter.

##### II) Descriptive Questions

1. Define spectroscopy.
2. What is meant by absorption spectrum?
3. Define Beer-Lambert's law.
4. List out any two applications of flame photometry.
5. List out any two applications of UV-spectrophotometry.
6. Discuss the principle of UV-spectrophotometry.
7. What is the principle of Flame photometry?
8. What is an electromagnetic radiation?
9. What is a monochromator?

10. Elaborate on the visible wavelength range.
11. Explain the electronic transition in molecules.
12. Discuss the principle and working of UV-spectrophotometer.
13. Discuss the principle and working of flame photometer.
14. Determine the concentration of ferric ion by spectrophotometry.
15. Draw a block diagram of flame photometry. Estimate the amount of sodium by flame photometry.
16. What is Beer's-Lambert's law? Derive the formula.
17. List out the limitations of Beer- Lambert's law.
18. Discuss the applications of flame photometer.