

ENGINEERING CHEMISTRY

Editors

Dr. K. CHENNAKESAVULU

Dr. J. KARTHIKEYAN

Mrs. X. JANET SABINA

Dr. T. KRITHIGA

Dr. S. SUNITHA

Dr. S. SUPRIYA

Dr. M. KANNAN

DEPARTMENT OF CHEMISTRY
SATHYABAMA UNIVERSITY

PREFACE

Chemistry is the branch for science that deals with matter and its physical and chemical properties. It is important for budding engineers to have an understanding of Chemistry as it applies to their needs. Chemistry is considered as one of the essential elements of understanding the nature of various engineering materials. In this context, Engineering Chemistry is considered as one of the most important subjects for engineering students. This book is the concerted effort of various members of the Department of Chemistry. Their qualifications and experience has enabled them to write the book in an easy, interesting and simplified manner.

The book has been divided into five units covering all the basic areas of Engineering Chemistry. The content provided is primarily aimed at engineering students but will be of value to all those who wish to pursue a career in the chemical industry. This book gives sufficiently comprehensive information on all the units discussed. A question bank is also a part of this book and is given at the end of each chapter. This will help students check their understanding and prepare themselves for examination in this subject. For further exploration of the topics discussed, students will find the references useful. The five topics covered in this book are given below.

Unit I – Synthesis of Nanomaterials - The various methods of syntheses (Chemical vapour deposition, physical vapour deposition, Sol-gel method, Laser ablation method, etc) of nanowires, nanotubes and other nanomaterials are discussed in this chapter along with the properties and applications of all the nanomaterials discussed.

Unit II – Water Technology – This unit explains the various water quality parameters with special reference to the quality of boiler feed water. Water characteristics such as hardness are discussed along with the latest methods for its removal.

Unit III – Electrochemical Power Sources – This unit discusses the basic principles of electrochemistry and electrochemical cell. It then moves on to the most fundamental application of electrochemistry such as batteries and fuel cells. Starting with acid and alkaline batteries, this unit comprehensively discusses the latest Lithium ion batteries and the chemistry of hydrogen-oxygen and solid oxide fuel cells.

Unit IV – Corrosion Science – This unit explains the various types of corrosion, mechanism, factors promoting corrosion and corrosion control. Modern techniques employed to combat corrosion like sacrificial anode method, impressed current method are discussed exhaustively.

Unit V – Polymer Chemistry–This unit explores the various mechanisms involved in the synthesis of polymers such as free radical, anionic and cationic polymerization. The properties of polymers are also discussed comprehensively with special reference to conducting polymers.

The Faculty of the Department of Chemistry wish to thank the management for giving them the opportunity to write this book.

ACKNOWLEDGEMENT

The faculty members of Department of Chemistry are proud to dedicate this book to our beloved **Founder Chancellor** of Sathyabama University **Col. Dr. JEPPIAAR, M.A., B.L., Ph.D.**

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Introduction: Nanomaterials: Definition – Classification based on dimensions-Size dependent properties. Types of nanomaterials: Nanoparticles: Synthesis by chemical reduction method. Nanoporous materials: Synthesis by sol-gel method. Nanowires: Synthesis by VLS mechanism. Carbon Nanotubes (CNTs): Single walled and multi walled nanotubes – Mechanical and electrical properties of CNTs – Applications of CNTs – Synthesis of CNTs by electric arc discharge method and laser ablation method.

INTRODUCTION

Nano science and technology is a broad and interdisciplinary area growing explosively worldwide in the past few years. Nanomaterials are cornerstones of nanoscience and nanotechnology. Now a days in research & development the major sectors are energy, environment, water technology, pharmaceuticals etc. The usage of nanomaterials are enormous as energy storage devices such as fuel cells, detection of threats in defence, navy, drug delivery and water purification. Industrial revolution has made life easy and pleasant. Today's high speed personal computers and mobile communications would not have certainly been possible without the use of nano science and nano technology.

Almost 50 years after Einstein's prediction about the existence of atom, in 1959, Richard P. Feynman suggested that it should be possible to build machines small enough to manufacture object with atomic precision. R. P. Feynman pointed out there is "plenty of rooms at bottom". He described how the entire encyclopedia Britannica could be written on the head of pin and how all the books in the world could fit into a few pamphlets. The term "Nanotechnology" became popular. He got Nobel Prize in Physics 1965. The Government of India, in May, 2007 launched a mission on nanoscience and nanotechnology (Nano mission) with an allocation of Rs. 1000 crores for the first five years. One of the main objectives of this mission is to foster linkage between educational and research institutions and industry and promote public private partnerships.

A nanometer is one billionth of a meter $= 1/1000,000,000 = 10^{-9}$ m

Nanoscience – Deals about the chemical and physical properties of materials at the 1-100 nanometer (nm) scale. Materials at 1-100 nm are called nanostructures. They are the smallest things that can be made.

Nanotechnology – Deals about the develop and apply materials at this scale to develop new products or methods; i.e., turning nanostructures into useable tools and applications.

Porosity – It is the ratio of pore volume to its total volume. Here, pore volume is the difference between the total volume and solid volume.

$$\text{Porosity} = \frac{\text{Specified Area pore volume}}{\text{Total Pore Volume}}$$

Pore diameter - The average or effective diameter of the openings in a membrane, screen, or other porous material is known as pore diameter.

Classification of nanomaterials based on the dimensions

On the basis of reduction in size of materials in different dimension, nanomaterials are classified into three groups.

S.No.	Reduction in size in different coordinates	Size	Examples
1	3-dimensions	< 100 nm	Nanoparticles, Quantum dots
2	2-dimensions	< 100 nm	Thin films, Coatings, plates
3	1-dimension	< 100 nm	Nanotubes, Nanowires

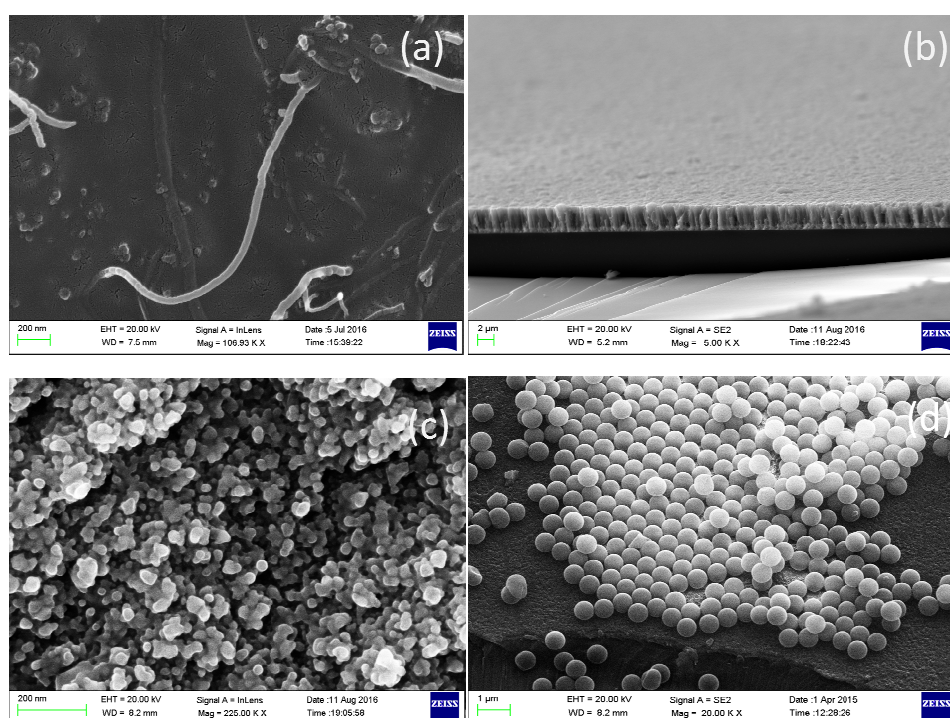


Fig.1 View of various nanomaterials (a) Multiwall Carbon Nanotube - Polymer composite (b) Zirconia thin film on Silica substrate (c) Zirconia morphology on Silica substrate (d) 3D Polystyrene spheres

Classification based on pore dimensions

According to IUPAC definition, nanoporous materials are classified in three main groups depending on their pore dimension:

Microporous materials (<2 nm): The average pore diameter has **less than 2 nm**. These materials have very narrow pores. They can host only small molecules, such as gases or linear molecules, and generally show slow diffusion kinetics and high interaction properties.

They are generally used in gas purification systems, membrane filters or gas-storage materials.

Example: Zeolite-Y, Zeolite-X and Alumino-silicates.

Mesoporous materials (2-50 nm): The average pore diameter has in between **2 nm to 50 nm**. The prefix meso- means “in-between”: These materials have pores with diameter size enough to host some big molecules, for example aromatic systems or large polymeric monomers. Diffusion kinetics of the adsorbed molecules is often due to capillarity, with an initial interaction with the pore wall followed by pore filling. These systems can be used as nano-reactors for the polymerization or adsorbing systems for liquids or vapours.

Example: Mobile composition matter-41(MCM-41), MCM-48, Santa barbara amorphous-15 (SBA-15) and carbon mesoporous materials etc.

Macroporous systems (>50 nm): The average pore diameter has **greater than 50nm**, Pores of these materials could host very large molecules, such as poly-aromatic systems or small biological molecules, and interactions with pore walls are often secondary with respect to the interactions with other molecules, overall in the case of very small guest molecules. These materials are principally used as matrices to store functional molecules, as scaffolds to graft functional groups, such as catalytic centres, and as sensing materials, thanks to the quick diffusion of chemical species in the pore system.

Example: Porous gels and porous glasses

Wafer - A wafer is a thin slice of **semiconductor** or substrate material.

Sol - It is a colloidal suspension of very small solid particles in liquid medium.

Ex: Ink, Blood and milk

Gel - It is a colloidal suspension of very small liquid particles in solid medium

Ex: agar, gelatin, jelly and tooth paste.

Aerogel - It is a synthetic porous ultra light material derived from a gel, in which the liquid component of the gel has been replaced with a gas.

Ex: Silica aerogel, Alumina aerogel and carbon aerogel.

Xerogel - A solid formed from a gel by drying with unhindered shrinkage is called a xerogel.

Surface area - The accessible or detectable area of solid surface per unit mass of material is called the surface area.

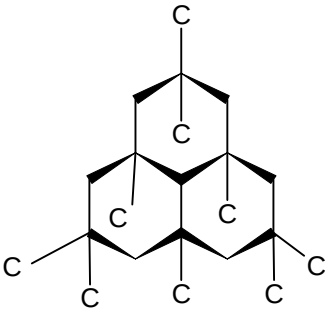
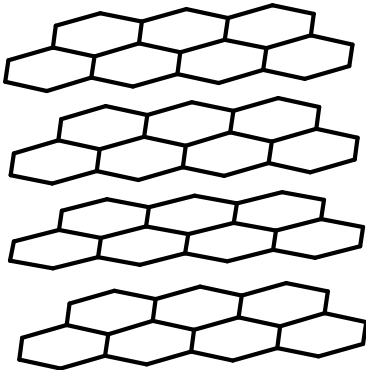
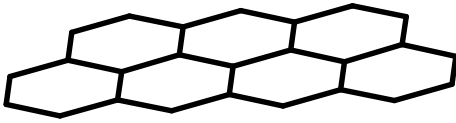
Aspect Ratio -The ratio between the length of the carbon nanotubes to the width (i.e. diameter) of the carbon nanotubes

Chiral - A chiral molecule is a type of molecule that has non-superimposable mirror images (i.e. **enantiomers**). Ex: A carbon having four different substituents

Helicity - It is a form of axial chirality or with respect to axis non-superimposable mirror images.Ex: Protein folding

Carbon Allotropes:

Carbon is capable of forming many allotropes due to its valency. Well-known forms are diamond, graphite, Fullerene, Carbon nanotubes.

Allotrope name	Structure	Properties
Diamond		Hybridization: sp^3 Structure: Tetrahedral C-C bond length: $1.545 \text{ \AA}$ Band gap: 5.47 eV Hardness: 10 Mhos Density: 3.5 gm/cc Electrical property: Insulator
Graphite		Hybridization: sp^2 Structure: Planar (hexagonal) C-C bond length: $1.421 \text{ \AA}$ Band gap: -0.04 eV Hardness: 1 to 2 Mho Density: 2.2 gm/cc The distance between two layers: 0.3354 nm
Graphene		Hybridization: sp^2 Structure: Planar C-C bond length: $1.42 \text{ \AA}$ Surface Area: $2630 \text{ m}^2/\text{gm}$.

Synthetic approaches for nanomaterials

Top-down approach: The process of making nanostructures starting with larger structures and breaking away to nano size is called top-down approach.

Ex: Mechanical grinding, Lithography, Ball milling, Epitaxy, etc.

Bottom-up approach: The building of nanostructures starting with small components such as atoms or molecules is called bottom-up approach.

Ex: Chemical vapour deposition, Sol-Gel Process, Chemical Reduction methods, etc.

Properties of a Nano structured materials

Depending on the Size and shape the properties of the materials tremendously altered and it describes how a material acts under certain conditions.

Types of properties:

- Chemical properties: Catalysis, Surface area, Particle size, Reaction rate
- Thermal property: Melting point, Thermal stability
- Electrical properties: Electrical conductivity, Band gap

- d) Optical properties: Absorption, Color and Scattering of light.
- e) Magnetic properties: Magnetization, Ferro magnetic, Para magnetic etc.

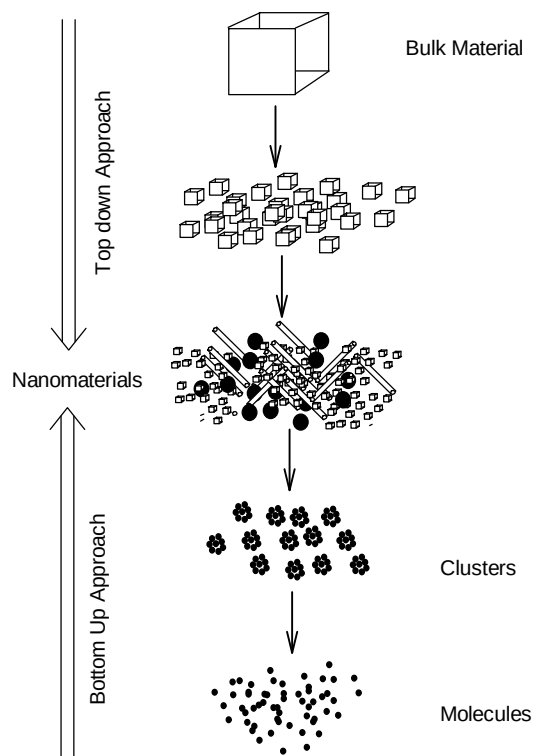


Fig.2 Representation of Synthetic approaches for nanomaterial synthesis

Characterization techniques for nanomaterials

S.No.	Techniques	Information acquired
1.	Scanning Electron Microscopy (SEM)	Surface topography
2.	Transmission Electron Microscopy (TEM)	Surface morphology
3.	Atomic Force Microscopy	Identification of individual surface atoms, 3D morphology
4.	Particle Size Analyzer	Particle Size distribution
5.	Raman Spectra	Distinguish single walled carbon nanotubes and multi walled carbon nanotubes
6.	Photoluminescence Spectra	CNT chirality or Asymmetry determination
7.	X-ray photoelectron spectroscopy	Electronic state of the element

Chemical Properties

The decrease in the particle size of a solid reactant increases the speed of reaction because breaking up a solid reactant into smaller pieces increases its total surface area.

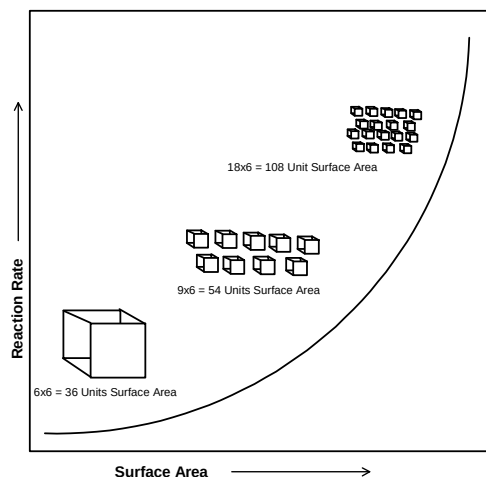


Fig. 3 Effect of Surface Area on the Reaction Rate

$$\text{Particle Size} \propto \frac{1}{\text{Surface Area}}$$

For Example, a single cube with 6 sides could have 6x6, 36 units square surface area, but 9 smaller cubes from the large one would have 9x6, which gives 54 units square of surface area (6 being the total of all six sides of the smaller cube).

Thermal Properties

The melting point of a material directly correlates with the bond strength. In bulk materials, the surface to volume ratio is small and hence the surface effects can be neglected. However, in nanomaterials the melting temperature is size dependent and it decreases with the decrease particle size diameters.

$$i.e \text{ Particle size} \propto \text{Melting point}$$

The reason is that in nanoscale materials, surface atoms are not bonded in direction normal to the surface plane and hence the surface atoms will have more freedom to move

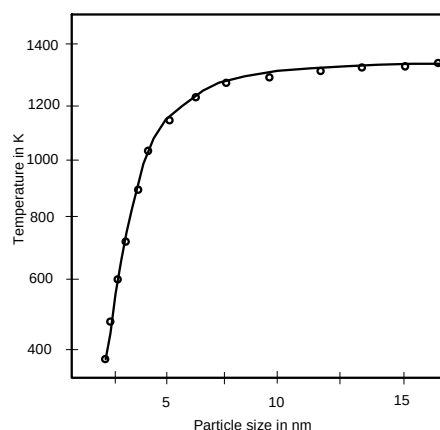


Fig. 4 Effect of Gold Particle Size on Melting Point

Electronic Properties

- (i) In bulk materials, conduction of electrons is delocalized freely in all directions, where as in the nano materials quantum effect dominates.

- (ii) For zero dimensional nanomaterials, all the dimensions are at the nanoscale and hence the electrons are confined in 3-D space. Therefore no electron delocalization (freedom to move) occurs.
- (iii) For one dimensional nanomaterials, electrons confinement occurs in 2-D space and hence electron delocalization takes place along the axis of nanotubes/nanorods/nanowires.
- (iv) Due to electron confinement, the energy bands are replaced by discrete energy states which make the conducting materials to behave like either semiconductors or insulators

Optical Properties

Because of the quantum confinement in nanomaterials exhibits various wavelenths for the same nano partilces. Here for example **silver** nano particles (Fig.5) shows increses in the particle size with the incremnet of wavelentgh (towards red shift) with chnage in the color.

i.e Particle size $\propto$ wavelength

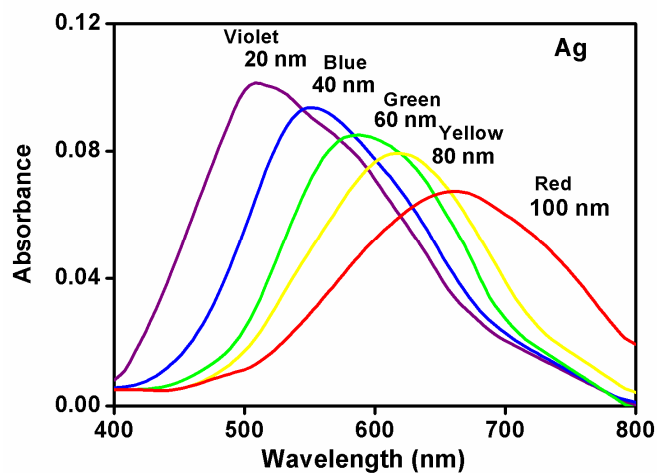


Fig. 5 Effect of particle size on wavelength and color

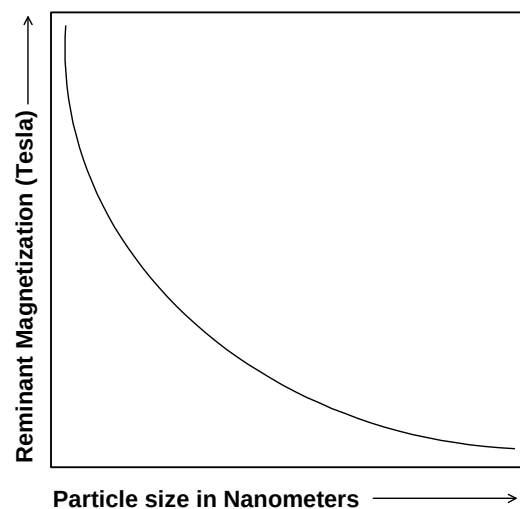


Fig. 6: Effect of particle size on magnetism

Magnetic Properties

The size of magnetic nanoparticles also influences the value magnetization. The Fig. 6 illustrates the effect of particle size on the saturation magnetization of **zinc ferrite**. The magnetization increases significantly below a grain size of 20nm. Hence, by decreasing the particle size of a granular magnetic material it is possible to improve the quality of magnets fabricated from it.

$$\text{Particle size} \propto \frac{1}{\text{Magnetism}}$$

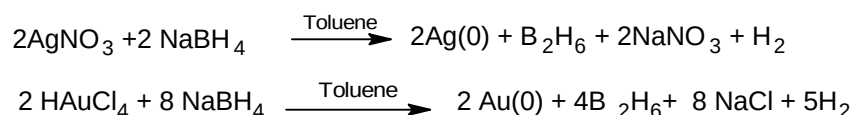
NANOPARTICLES

Particles or powders with particle size less than 100nm are called nanoparticles.

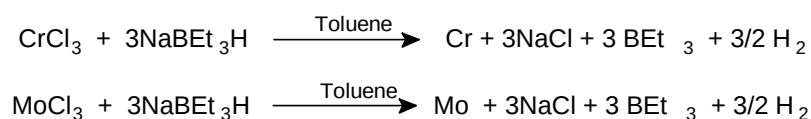
Synthesis of nanoparticles

Chemical reduction method

Silver nitrate and chloro auric acid can be reduced by the sodium boro hydrate to form the Silver and gold nano particles in the presences of toluene/aqueous medium.



The metal halides like CrCl_3 , MoCl_3 can be reduced into their corresponding metals by using NaBET_3H (sodium tri-ethyl boron hydride) with toluene as solvent at room temperature.



Properties of nanoparticles

- (i) As the particle size decreases, surface area increases. This enhances the catalytic activity of the nanoparticles.

Ex: Bulk SiO_2 partilces has less surface area than the nano fumed silica

- (ii) Reduction of particle size from micron to nanometer influences the optical properties.

Ex: **Bulk gold** appers in **yellowish** color, whereas **nano gold** appers **red** in color

- (iii) Reduction of particle size from micron to nanometer influences the thermal properties like melting point and thermal conductivity.

Applications of nanoparticles

- (i) **Silver** nanoparticles has good antibacterial properties, it is used in surgical instruments, refrigerators, air-conditioners, water purifiers etc.
- (ii) **Gold** nanoparticles are used in catalysis synthesis of silicon nano wires, sensors carrying the drugs and to detect tumors.

- (iii) **ZnO** nanoparticles are used in electronics, ultraviolet (UV) light emitters, piezoelectric devices and chemical sensors.
- (iv) **TiO₂** nanoparticles are used as photocatalyst and sunscreen cosmetics (UV blocking pigment).
- (v) Antimony-Tin-Oxide (ATO), Indium-Tin-Oxide (ITO) nanoparticles are used in car windows, liquid crystal displays and in solar cell preparations.

NANOWIRES

Nanowires are cylindrical solid wires with a diameter ranging from 1—100 nm and a length of few micrometers.

A well accepted mechanism for the growth of nanowires through gas phase reaction is vapour-liquid-solid process. To grow any nanowire, the material used must be soluble in the catalyst nanoparticles.

For example, to grow silicon nanowire, gold nanoparticles is used because silicon vapour is soluble in gold nanoparticles. To grow gallium nitride nanowire, iron nanoparticles are used because the reactants gallium and nitrogen are soluble in iron nanoparticles.

Synthesis of Si Nanowires (Vapour-Liquid-Solid Mechanism): It follows two step processes

- (i) In the first step, diffusion of vapour phase (SiH_4 reactants) takes place into the gold liquid phase (catalyst nanoparticles)
- (ii) In the second step, super saturation of Si reactants occur in the gold liquid phase which causes the precipitation of Si solid phase (nanowire).

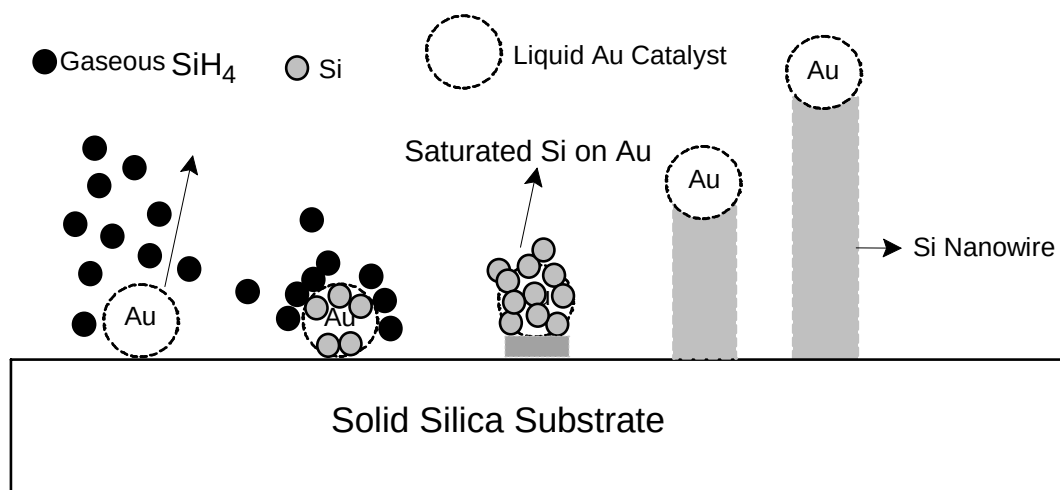


Fig.7 Vapour-Liquid-Solid Mechanism of Si nanowires

The substrate is first covered with a coating of gold nanoparticles and heated to a temperature in a furnace so that it becomes liquid. Simultaneously the precursor Silane (SiH_4) is introduced into the furnace where it vapourises to form silicon vapour. During the reaction, silicon vapour diffuses and dissolves in molten gold nanoparticles. When the

concentration of silicon becomes supersaturated, the excess material (silicon) precipitates and grows as nanowires.

Applications:

- (i) Nanowires are used in electron devices like field effect transistors, in sensors and detectors.
- (ii) Nanowires replace copper in computers and in electronics.

NANOPOROUS MATERIALS

Synthesis of nanoporous materials by sol gel process

Sol-Gel Process :

“Formation of an oxide network through polycondensation reactions of a molecular precursor in a liquid”.

Precursors:

The precursor used in sol-gel process for the synthesis of nanoporous materials are metal alkoxides $M(OR)_4$. They readily react with water to form gels.

Examples:

- (i) Tetra ethoxy silane $[Si(OC_2H_5)_4]$
- (ii) Tetra methoxy silane $[Si(OCH_3)_4]$

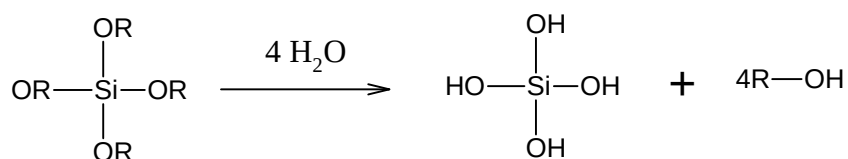
Process: (Synthesis of silica aerogel)

This process consists of four main steps

1. Hydrolysis of precursors
2. Condensation
3. Gelation followed by polycondensation
4. Super critical drying

1] Hydrolysis:

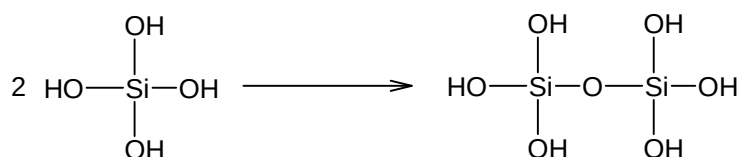
It occurs through the addition of water and to form silanol (Si-OH) particles.



Here R: Methyl/Ethyl

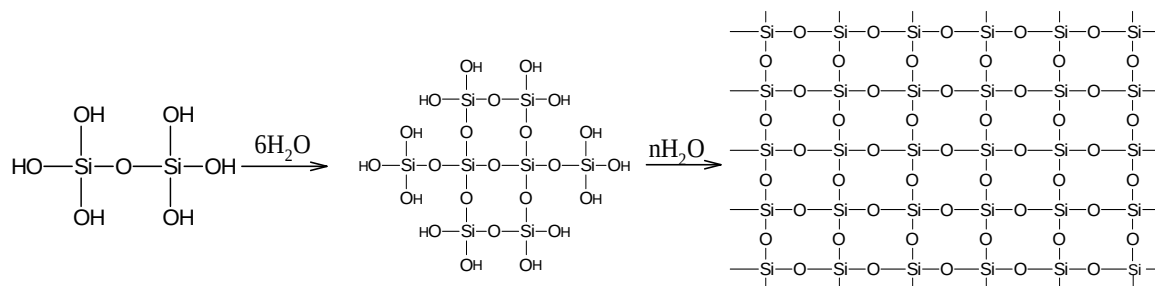
2] Condensation:

The self condensation of silanol groups produces siloxane linkages filled with by products of water and alcohol.



3] Polycondensation:

The condensation process continues to form poly condensed silica gel with Si-O-Si linkages.



4] Drying:

The gels are subjected to super critical drying in an autoclave. The critical pressure and critical temperature used are 78 bar and 294°C respectively in order to remove liquid from silica gel to form the network structure of silica aerogel.

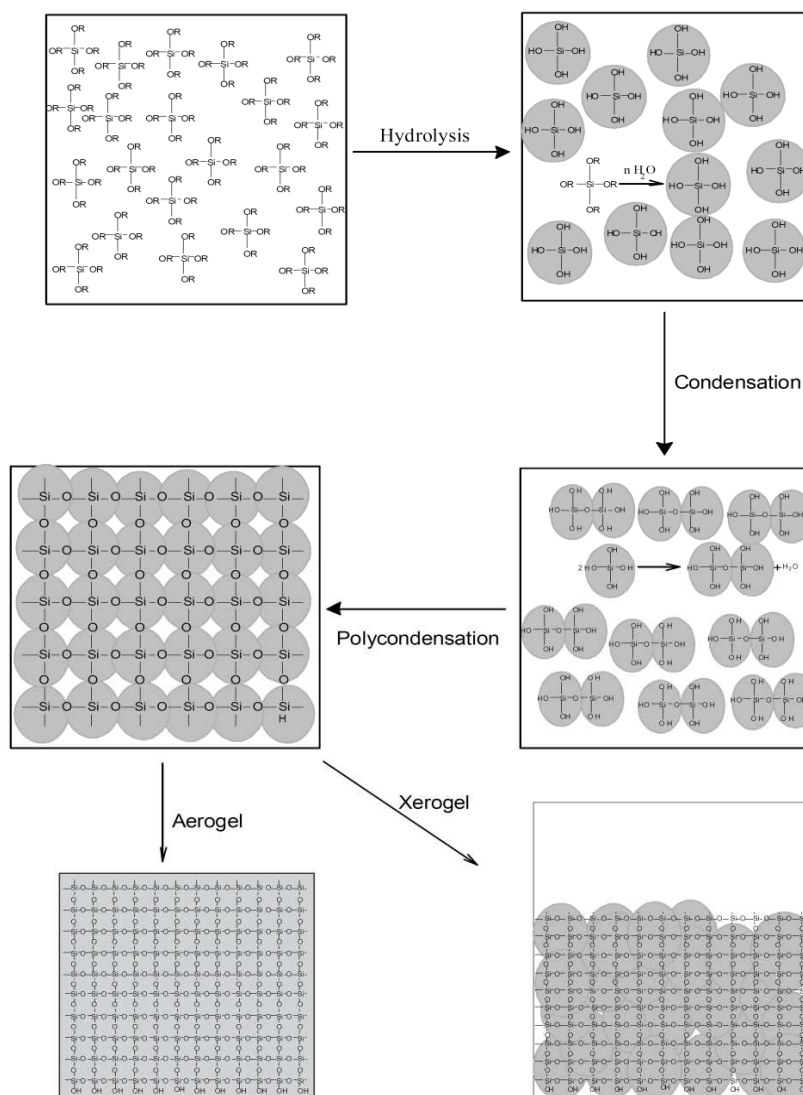


Fig.8 Schematic diagram of Sol-gel method

Properties and applications of nanoporous materials

- (i) Nanoporous materials have the surface area of 500-1000 m²/gm, which enhances the catalytic activity.
- (ii) Since they have very low thermal conductivity values, they are used in thermal insulators.
- (iii) Because of high porosity (90-99%), they are extensively used in membrane technology.
- (iv) They are of light weight materials (density: 0.003-0.8 gm/cc)

CARBON NANOTUBES

Carbon nanotubes (CNTs) were discovered by Iijima while studying the surface of graphite electrodes in an electric arc discharge. Since their discovery, CNTs have held a fundamental role in the field of nanotechnology due to their unique structural, mechanical and electronic properties. CNTs have high conductivity and high aspect ratio which help them to form a network of conductive tubes.

Definition: The rolled graphene sheet is known as Carbon Nanotube.

1. Single-Walled Carbon Nanotubes (SWCNT)

A single graphene layer rolled or folded in cylindrical manner

2. Multi-Walled Carbon Nanotubes (MWCNT)

Two or more graphene layers were rolled or folded in cylindrical manner.

Property	Single-Walled Carbon Nanotubes (SWCNT)	Multi-Walled Carbon Nanotubes (MWCNT)
No. of graphene layers	One	Two and more graphene layer
Diameter	0.4 to 2 nm	2 to 1000nm
Surface Area	>1000 m ² /gm	< 500 m ² /gm
Young Modulus	1 to 5 TPa	0.2 to 0.9 TPa
Tensile Strength	13 to 53 GPa	11 to 60 GPa
Morphology	TEM	FESEM
Visualization		

SYNTHESIS OF CARBON NANOTUBES

1. Electric Arc Discharge Method or Plasma Arcing

Carbon nanotubes are commonly prepared by striking or producing an arc between graphite electrodes in an inert atmosphere.

In this method, a potential of 20-25V is applied across the pure graphite electrodes of 5 to 20 μ m diameter and separated by 1mm at 500 Torr pressure of flowing helium gas. Under these conditions carbon atoms are ejected as vapour from the anode (Positive electrode)

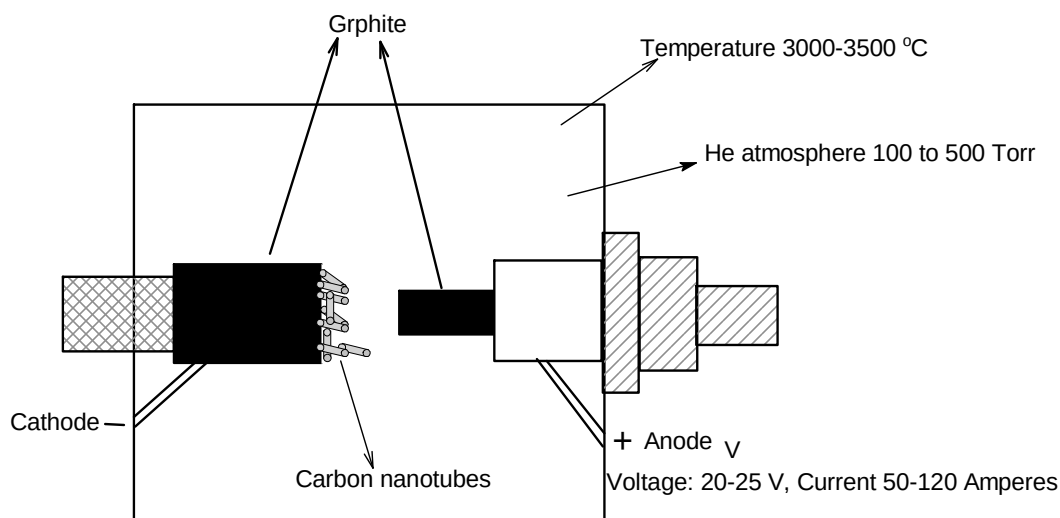


Fig.9 Electric Arc Discharge method or Plasma Arcing

and forms nanotube on the cathode (negative electrode). As the tube grows the length of cathode decreases. But the growth of CNT maintains a gap of 1mm between the two electrodes. To produce SWCNT a small amount of Co, Ni or Fe is incorporated as catalyst in the central region of anode. Presence of catalyst controls the anode reaction and releases carbon ions in a controlled manner so that it forms a SWNT at the negative electrode. If no catalysts are used, the tubes formed are MWCNT. The arc discharge method can produce SWCNT of diameter 1-5nm with a length of 1 μ m.

2. Laser Ablation

Laser ablation has several advantages, such as high quality SWNT production, diameter control, investigation of growth dynamics and the production of new materials. The

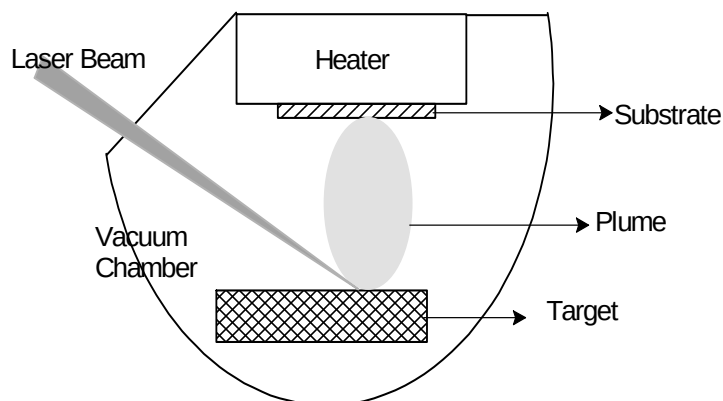


Fig.10. Schematic representation of Laser ablation method

laser ablation apparatus consist of a furnace, a quartz tube with a window, a graphite target doped with small amount of catalytic metals like cobalt and nickel, flow systems for argon gas to maintain constant pressures and flow rates and a water-cooled copper collector placed somewhat outside the furnace. (Fig. 10)

A laser beam of a pulsed or continuous Nd:YAG (Neodymium-doped-Yttrium Aluminium Garnet, $\text{Nd:Y}_3\text{Al}_5\text{O}_{12}$) or CO_2 is introduced through the window by focusing onto the target located in the center of the furnace. The furnace temperature is maintained at 1200°C . Due to the emission of a pulsed or continuous laser, the target is vaporized in high temperature. This leads to the formation of small carbon molecules and atoms. The argon gas then sweeps the carbon atoms from the high temperature zone to the colder copper collector where they condense to form carbon nanotubes. The argon flow rate and pressure are typically 1cm/sec and 500 Torr respectively.

PROPERTIES OF CARBON NANOTUBES

1. Electrical properties

Carbon nanotubes can be both metallic or semiconducting, depending upon the helicity (chirality) and diameter of the nanotubes. Helicity refers to rolling to hexagonal chains with respect to the tubes axis. Helicity results in three different kinds of CNTs. They are armchair, zig-zag and chiral nanotubes.

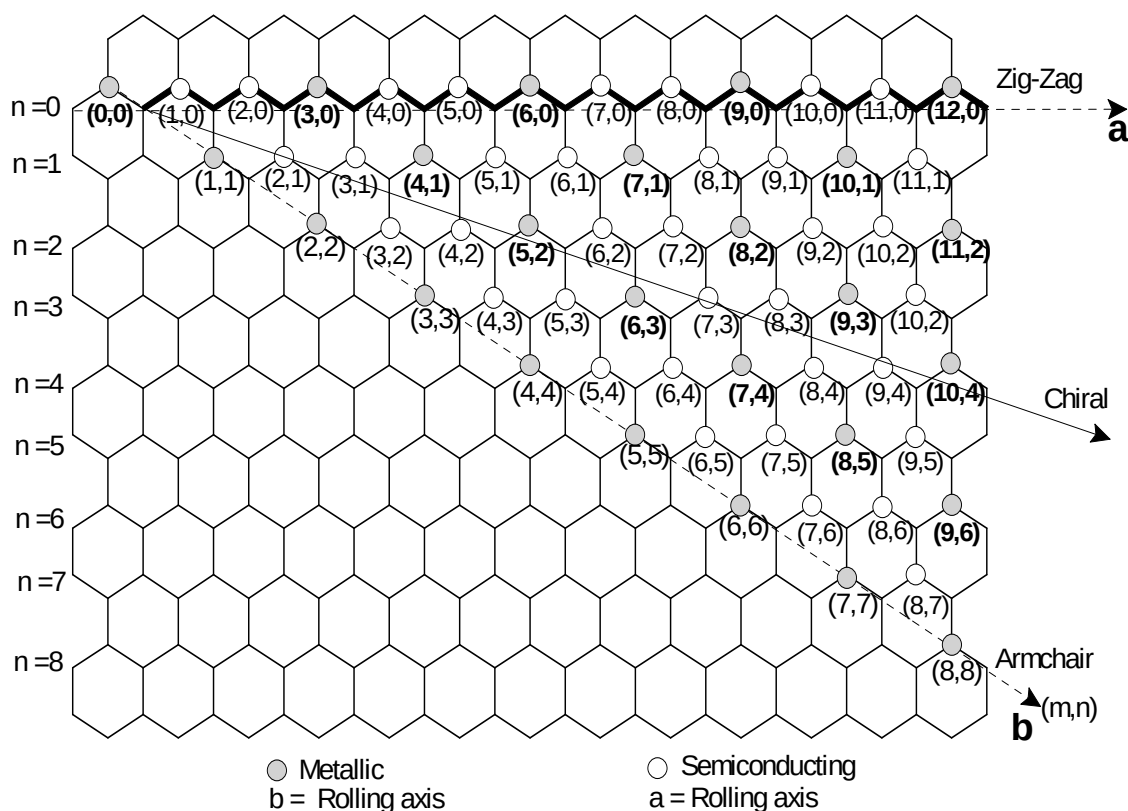


Fig. 11 Schematic representation of rolling graphene sheet and Based on its rolling axis Zig-Zag, Chiral and Arm chair CNTs

Table 1. Theoretical electronic conductivity of single-walled carbon nanotubes (SWNTs) depending on roll orientation of the graphene sheet (m, n).

(m, n)	Form of CNTs	Electrical Conductivity
(m, 0)	 Zig-Zag	Metallic properties dominate when $m - n = 0 \text{ or } \frac{m - n}{3} = \text{integer}$ Otherwise, zig-zag form is semiconducting. This zig-zag form is tubes show very small band gap due to the replacement of hexagonal carbon ring with a pentagonal or heptagonal rings at the edges of CNT.
(m, n)	 Arm-Chair	All armchair tubes or (m,n) tubes are metallic because of their symmetry. Ex: (1,1), (2,2), (3,3), (4,4) or (n,n) tubes are metallic. It is estimated that they can carry billion amperes of current per spare centimetre. The coper wire fails at one million amperes of current per square centimetre because resistive heating melts the wire.
(m, n) when $m \neq 0$, and n	 Chiral	Metallic properties dominate, when $\frac{2m + n}{3} = \text{integer}$ Otherwise chiral form is semiconducting.

Material	Electrical conductivity S/m	Thermal conductivity W/(m.K)
CNTs	10^6 to 10^7	>3000
Copper	5.96×10^7	400
Silver	6.30×10^7	429

2. Mechanical Properties

The Carbon nanotubes are the strongest and stiffest materials yet discovered in terms of tensile strength and elastic modulus respectively. The tensile strength of CNTs is

100 times stronger than that of steel of the same diameter. There are two things accounts for greater strength of CNTs

- (i) The strength is provided by the interlocking of carbon-carbon covalent bonds
- (ii) Each CNT is one large molecule. It means that, it does not have any weak spots like grain boundaries, dislocation etc, which all the other materials shows this properties.

Carbon nanotubes are made of a 2D matrix of carbon-carbon bonds formed into cylinders. This means they can bend and twist without breaking bonds, but they cannot stretch very far before bonds have to break. This means they are highly resistant to extension beyond a certain point. Their stability is not defined by their bonding mechanism but by the diameter of the tubes. Weak van der Waals forces are responsible for holding the tubes together. As with any material, the existence of a crystallographic defect affects the material properties. Defects can occur in the form of atomic vacancies. High levels of such defects can lower the tensile strength by up to 85%.

Young's Modulus:

It is a measure of how stiff or flexible (elastic) a material is. The larger the value of Young's modulus, the less flexible the material. CNTs have Young's modlus ranging from 1.28 to 1.80 TPa. One terapascal is a pressure very close to 10^7 times of atmospheric pressure. The Young's modulus of steel 0.21 TPs, which means that Young's Modulus of CNTs is almost 5 to 10 times of steel. That is, CNTs are very stiff and hard to bend.

Applications of CNTs

- i) *Catalyst supports:* CNTs can be sued a catalyst supports because they can provide higher surface areas and high chemical stability and controlled surface chemistry.
- ii) *Hydrogen storage:* Recently carbon nanotubes have been proposed to store hydrogen in hydrogen-oxygen fuel cell.
- iii) *AFM Probe tips:* To characterize surface of material 'Probes" are used. CNTs are widely used a materials for the manufacture of AFM (Atomic Force Microscope) Probes.
- iv) *Drug Delivery:* CNTs can be widely used as drug carriers for drug deliver, as they can easily adapt themselves and enter the nuclei of the cell.
- v) *Actuator/Artificial Muscles:* An actuator is a device that can induce motion. In the case of a carbon nanotube actuator, electrical energy is converted to mechanical energy causing the nanotubes to move.
- vi) *Chemical Senosrs/Biosensors:* Devices used to detect changes in physical and chemical quantities are called sensors. CNTs act as sensing materials in pressure, thermal, gas, optical, mass, position, stress, strain, chemical and biological sensors.
- vii) *Field Emission:* The high current density, low turn-on and operating voltage and steady, long-lived behaviour make CNTs ideal field emitter.

- viii) *Touch Screens*: Very thin CNT films (10 or 20nm) are transparent to visible light and can conduct enough electricity to make them useful for many applications which include thin film solar cells, organic LEDs and touch screens.
- ix) *Structural and Mechanical Applications*: CNTs are characterized with superior mechanical properties such as stiffness, toughness and strength. These properties lead in the production of very strong, lightweight materials that can be used in areas such as building, structural engineering and aerospace.
- x) *Aerospace Components*: CNTs have good fatigue strength over a long time which makes use of them as aircraft components.

Applications of Nanomaterials

- (i) Carbon Nanotubes (CNTs) can be used as catalyst supports because they can provide the advantages of large surface area, high chemical stability and controlled surface chemistry.
- (ii) Recently carbon nanotubes have been proposed to store hydrogen. In presence of certain metals, it can hold 8% by weight of hydrogen. The CNTs would absorb hydrogen, the way a sponge absorbs water and holds it (without leaking).
- (iii) CNTs are used in the development of flat panel displays used in televisions and computers.
- (iv) ZnO, TiO₂ nanoparticles are used in sunscreen cosmetics because they absorb UV-radiation and give protection to skin.
- (v) Silicon and gallium nitride nanowires are used in electron devices like field effect transistors, in sensors and detectors.
- (vi) Nano porous materials have the surface area of 500-1000m²/gm, which enhances the chemical reactivity and catalytic activity of various reactions.
- (vii) Nano porous materials have very low thermal conductivity values (presence of air in the pores makes the porous material less conductive); they are used as thermal insulators.

Questions

1. Explain the Chemical, Thermal, magnetic properties of nanomaterials?
2. What are nanoparticles. Explain the synthesis and applications of nanoparticles?
3. What are nanoporous Materials. Explain the synthesis of nanoporous silica by Sol-Gel method.
4. Explain the Synthesis of CNTs by Arch discharge and Laser ablation methods.
5. Explain the Electrical properties of CNTs.
6. Explain the Applications of Nanomaterials.
7. Explain the Mechanical Properties of CNTs.
8. Explain the synthesis of nanowires by VLS method.

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Introduction: Water quality parameters - Contamination of water by arsenic, lead, fluoride, mercury and their removal. Hardness: Types - Expression - Units. Estimation of hardness of water by EDTA method - Problems. Estimation of iron, calcium and magnesium: AAS method. Water softening: Zeolite process - Demineralization process; Desalination: Reverse osmosis - Electrodialysis.

INTRODUCTION

Water is one of nature's most important gifts to mankind which is a key component in determining the quality of our lives. Water reacts with minerals in the soil and rocks and dissolves numerous substances in large amounts thus pure water rarely occurs in nature. The surface and groundwater may contain many different dissolved substances which are normally used for industries, agriculture and domestic households. Industries that produce metals, wood, paper, chemicals, gasoline, oils, and most other products all use water in some part of their production process. Industrial water usage composes around 88% of water consumption worldwide. This chapter mainly deals with various qualities and quantities of impurities present in water and technologies used to eliminate them from water.

There are three main sources of water:

(i) Rain, (ii) Surface and (iii) Ground water

- ii) The UN estimates that by 2025, 75% of the world population won't have reliable, clean water
- iii) ~ 66% of the human body is made up of water.
- iv) At just ~ 2% dehydration your performance decreases by around 20%.
- v) We should drink at least > 2 litres of water a day.
- vi) 80% of all illness in developing countries is caused by water related diseases.
- vii) 90% of wastewater in developing countries is discharged directly into rivers and streams without treatment.
- viii) Two thirds of our planet is covered by water and 97.5% of the water is saltwater.
- ix) The majority of freshwater is beyond our reach, locked into polar snow and ice.

Effect of Impurities on Characteristics of Water

Physical Impurities:

1. Turbidity: Turbidity refers to the cloudiness of the water. The materials causing the cloudiness can be inorganic such as clay and sand or organic such as algae and plankton. These colloidal impurities scatter light. Turbidity is normally tested using nephelometer that passes a light through the water and measure the light refraction at a 90° angle from the light source. Surface waters usually have higher turbidity than groundwater. The turbidity in the water may shield bacteria and prevents disinfection chemicals from attacking and destroying the cells. Unit of turbidity: Nephelometric turbidity unit (NTU). Means of treatment: coagulation, settling and filtration.

2. Colour: Colour of water is due the dissolved and colloidal substance present in water like tannin, peat, algae, humus material, iron and manganese salts etc. Soluble iron salts

produce red, chromium salts give yellow and algae produce green colour to water. Colour of water is usually measured using tintometer. Unit of colour: Hazen units. Means of treatment: aeration, coagulation, adsorption and filtration.

3. Taste and Odour: Pure water is tasteless and odourless. Taste and odour is imparted to water by the dissolved salts and organic matter. Iron and chlorine gives characteristic taste to water. Water contaminated with algae and other dead and decayed vegetable matter impart grassy odour. Presence of sulphides produces rotten egg smell to water. Means of treatment: aeration and cation exchange process

Chemical Impurities:

1. Alkalinity: Bicarbonates (HCO_3^-), carbonates (CO_3^{2-}), and hydroxides (OH^-) of calcium, magnesium, sodium and potassium makes water alkaline. Alkalinity is classified depending on the anion present into bicarbonate alkalinity, carbonate alkalinity and hydroxide alkalinity. The possible combinations of ions causing alkalinity are i) Hydroxide only, ii) Carbonate only, iii) Bicarbonate only, iv) Hydroxide and carbonate and v) Carbonate and bicarbonate. The possibility of combination of hydroxide and bicarbonate is ruled out as they form carbonates ($\text{OH}^- + \text{HCO}_3^- \rightarrow \text{CO}_3^{2-}$). Means of treatment: lime-soda softening, zeolite softening, demineralization anion exchange.

2. Acidity: The acidity of water due to the presence of dissolved CO_2 is called carbon dioxide acidity and due to the presence of mineral acid obtained by hydrolysis of Fe and Al salts is called mineral acidity. Acidity in water promotes corrosion due to the carbonic acid and mineral acids present. Means of treatment: Neutralization with alkalies.

3. Hardness: Hardness of water is caused by calcium and magnesium salts. It is the chief source of scale in heat exchange equipment, boilers, pipe lines and forms curds with soap, interferes with dyeing, etc. Means of treatment: softening; demineralization, internal boiler water treatment.

4. Dissolved gases:

Dissolved CO_2 : Surface water contain dissolved CO_2 derived from the atmosphere or biological oxidation of organic matter. The dissolved CO_2 in water changes carbonates in rocks into soluble bicarbonates and makes water alkaline. Action of CO_2 on aluminosilicates produce suspended clay and silica particles in water. Means of treatment: Aeration, deaeration and neutralizing by lime or alkali.

Dissolved O_2 : Water contains dissolved oxygen is essential for aquatic life. If the concentration of dissolved O_2 is high it causes corrosion in steam and condenser pipelines. Means of treatment: Deaeration, sodium sulphite treatment and cathodic protection.

Biological Impurities:

Biological contamination of the water is caused by the presence of living organisms, such as algae, bacteria, fungi, protozoan or viruses. Algae are quite abundant in a surface water

source and especially if the water contains nutrients that encourage their growth. Algae may cause taste and odor problems, clog filters, and produce nuisance slime growths on intake pipes and equipment. Disease-causing bacteria are called pathogenic bacteria which may cause typhoid fever, dysentery, cholera, and gastroenteritis. Their presence is determined by testing for the presence of an indicator organism, usually coliform bacteria. Presence of coliform bacteria indicates general bacterial contamination. Some bacteria, although not harmful, may cause taste and odor problems. For example sulphur bacteria which produce hydrogen sulphide and crenothrix iron bacteria which can produce disagreeable taste, odors and stains.

Tables 1: Some Water Quality Characteristics (Bureau of Indian Standards BIS 10500-1991)

Parameters	Disirable limit(approx)
Turbidity-NTU	5
pH	6.5-8.5
Dissolved Oxygen mg/L	4-5
Hardness (as CaCO ₃)mg/L	0.3
(Total Dissolved Salts)TDS mg/L	500 mg/L
Colour Hazen unit	5

Parameters	Disirable limit	Permissible limit
Nitrate	45	45
Chloride	250	1000
Flouride	1	1.5
Arsenic	0.05	0.05
Aluminium	0.03	0.2

Contamination of Water by Arsenic, Lead, Fluoride and Mercury

Mercury

Mercury is a liquid non-essential trace metal. It is usually found in natural deposits such as cinnabar (HgS) or embedded in igneous rocks.

Uses:

- Mercury is used in the chlor-alkali industries (Preparation of Chlorine and NaOH)
- It is also used in batteries, fluorescent tubes, mercury lamps, gear switches etc
- It finds applications in paper, pulp, pharmaceutical and plastic industries

Source: Mercury is discharged into water bodies both by natural and man-made sources.

- The main sources of mercury pollution by natural sources are weathering processes and terrestrial and submarine volcanic activity.
- The main source of mercury pollution by man-made sources are

- Effluents from the chlor-alkali industries, electrical and electronic industries, plastic industries etc
- Organomercurials in fungicides used for seed dressing in agriculture
- Organic mercury fumigants used for preservation of food grains
- Anthropogenic activities such as burning of coal and crude oil, dental amalgams, mercury containing ointments etc

Mercury poisoning:

Permissible limit: MCL is the maximum contaminant level set by EPA. It is the level of contaminants in drinking water at which no adverse health effects are likely to occur. The MCL given by US Environmental Protection Agency for mercury in drinking water is 0.002 mg/L.

Adverse health effects:

Short term effects: Mercury can cause adverse health effects when exposed to levels higher than MCL for short period of time.

- Mercury exposure for a few hours to 1-3 mg/L causes pulmonary irritation and destruction of lung tissue and central nervous system disorders.
- The two main effects of acute mercury poisoning are neurological and renal disturbances. The former is caused by methyl mercury and ethyl mercury salts and latter by inorganic mercury.
- Dermal exposure to alkylmercurials may give rise to acute toxic dermatitis and eczematous changes.

Long term effects:

- Chronic exposure to mercury concentrations above 0.1 mg/L causes tremors, mental disturbances and gingivitis.
- Long term exposure of lower mercury levels causes non-specific neurological and physiological symptoms.
- Chronic exposure of mercury above MCL leads to kidney damage.

Biochemical effects: The toxicity of mercury is based on the nature of chemical species is exist. Table (1) shows the various chemical species of mercury.

Table: 1 Various chemical species of mercury

S. No	Chemical species	Biochemical properties
1.	Elemental Mercury (Hg)	Relatively inert and non-toxic but its vapour is highly toxic when inhaled
2.	Mercurous ion (Hg_2^{2+})	Insoluble and low toxicity
3.	Mercuric ion	Toxic but does not transported across biological

	(Hg^{2+})	membranes
4.	Organomercurials (RHg^+)	Highly toxic and cause irreversible nerve and brain damage. Easily transported across biological membranes
5.	Diorganomercurials (R_2Hg)	Low toxicity but can be converted to RHg^+ in acidic medium
6.	Mercuric sulphide (HgS)	Highly insoluble and non-toxic

Biochemical effects of organomercurials:

- (i) Methyl mercury is a teratogen which is capable of crossing the placenta and causing embryo toxic effects and abortions. Teratogens are chemical.
- (ii) Organomercurials such as methyl mercury (CH_3Hg^+) are more soluble in fats, cell membranes and brain tissue. The Hg-C bond is not easily broken and thus retained in the cells for prolonged period of time. Thus they can cross placental barrier and cause irreversible damage to the central nervous system in babies.
- (iii) Minamita disease: A disease originated in Japanese fishing port of Minamita caused by methyl mercury poisoning which affects the central nervous system. A factory nearby bay synthesised aldehyde using $HgCl_2$ and $HgSO_4$ as catalyst. The effluent from factory continuously discharged catalyst into the bay which is biomethylated by bacteria to form methyl mercury. This is gradually bioconcentrated by the fish in the bay which provides the seafood for the people live near the bay. People consumed seafood are affected by various neurological disorder.

Antidote to mercury poisoning: Commonly used mercury-binding chemotherapeutic antidotes for mercury poisoning are

- (i) Sodium formaldehyde sulfoxide as local antidote
- (ii) Intramuscular injection of dimercaprol or penicillamine is administrated as chelating agents which chelate with mercury and excreted in urine.
- (iii) Isotonic NaCl to protect kidney from higher concentration of mercury

Lead

Lead is a non essential trace element which is toxic and found as deposits in rocks as galena (PbS).

Uses:

- (i) Lead is used in household plumbing materials or in water service lines used to bring water from the main to the home.
- (ii) It is used in acid storage batteries, solder and casting materials.

- (iii) It also finds application in the manufacture of leaded-porcelain enamel for protection against radiation in nuclear power reactors and in lead coated steel sheets used in construction of buildings.

- (iv) Lead salts are used in anti-corrosive and highway traffic safety paints

Source: The main source of lead in water is corrosion of household pipes, solder, fixtures, fittings etc. The amount of lead leaching into water depends on the water's acidity and temperature. The other sources of lead poisoning are

- (i) Smelting of lead ores
- (ii) Emissions from automobile exhaust containing tetra ethyl lead (TEL)
- (iii) Effluents from acid storage batteries
- (iv) Lead containing paints
- (v) Lead coated steel sheets used for sound attenuation in buildings

Lead poisoning:

Permissible limit: The MCL given by US Environmental Protection Agency for lead is zero. EPA has set this level based on the fact that there is no safe level of exposure to lead.

Adverse health effects:

Short term effects: Lead can cause adverse health effects when exposed to levels higher than MCL for short period of time. Lead in drinking water leads to delayed physical and mental development in babies and children. High blood lead levels in children cause learning disabilities, behavioural problems and mental retardation. Lead accumulates in the bones and interferes with the metabolism of calcium and vitamin D. In adults, it can cause kidney problems or high blood pressure. At very high levels, lead can cause convulsions, coma and death.

Long-term effects: Lead has the potential to cause stroke, kidney disease and cancer from a lifetime exposure at levels higher than MCL.

Biochemical effects:

1. Biochemical effects of Inorganic lead:
 - (i) Inorganic lead is absorbed by food or inhalation of particulate lead.
 - (ii) Lead interferes with the heme synthesis and disturbs the synthesis of haemoglobin and respiratory pigments such as cytochromes.
 - (iii) Inorganic lead replaces calcium in bones and accumulates in soft tissues such as liver and kidneys.
2. Biochemical effects of Organic lead:
 - (i) Organic lead such as tetra ethyl lead (TEL) and tetra methyl lead (TML) are more acutely poisonous than inorganic lead.
 - (ii) It is absorbed by inhalation or through the skin.
 - (iii) TEL attacks the central nervous system and cause severe mental disorder.
 - (iv) Organo lead compounds are suspected to cause genetic modifications.

Antidote to Lead poisoning:

- (i) Inorganic lead poisoning can be cured by treatment with calcium EDTA chelate in which lead replaces calcium in Ca-EDTA complex and the formed Pb-EDTA complex is excreted in urine. This treatment is called the Chelation therapy. Intramuscular dimercaprol also serves as antidote to lead poisoning.
- (ii) Organic lead does not form complex with chelating agents and this lead poisoning can be cured by sedative, anti-convulsant and fluid & electrolyte therapy.

Arsenic

Arsenic is a non-essential metalloid element which is toxic and occurs in nature as sulphide ores.

Uses:

- (i) Elemental arsenic is used in the manufacture of glass, electronics, semiconductors and photoconductors.
- (ii) Arsenic compounds are also used as wood preservative, fungicides, preservatives, insecticides, pesticides and herbicides.
- (iii) It finds applications in paints, dyes, metals, drugs, soaps and drugs.

Source:

The main source of arsenic pollution is from smelting of arsenic containing ores and burning of coal. The other sources of arsenic poisoning are

- (i) Arsenic compounds in fungicides, preservatives, pesticides, insecticides and herbicides
- (ii) Arsine (AsH_3) which is a byproduct of many industrial processes involving arsenic and action of fungi in sewage plants
- (iii) Arsenic release from metal refining, etching, soldering, galvanising and lead-plating operations.

Arsenic poisoning:

Permissible limit: The MCL given by US EPA for arsenic is 0.010 mg/L.

Adverse health effects:**1. Short term effects:**

Arsenic harms the central and peripheral nervous systems, heart and blood vessels. It also causes birth defects and reproductive problems.

2. Long-term effects:

Chronic exposure of arsenic poisoning causes problems in circulatory system. Long term exposure of arsenic level higher than 0.050 mg/L can cause skin, lung, kidney and bladder cancer.

Biochemical effects:

1. The major biochemical effects of arsenic poisoning are

- (i) **Complexation of coenzymes:** As (III) forms complex with enzymes and exerts its toxic effect by inhibiting enzyme action
 - (ii) **Uncoupling of phosphorylation:** Arsenic interferes in phosphorylation reaction which is the vital step in the generation of ATP
 - (iii) **Coagulation of proteins:** High concentration of arsenic compounds denatures the secondary and tertiary structures and coagulates protein.
2. Arsenic is cumulative protoplasmic poison which can cross placental membrane and thus is a teratogen.

Antidote to arsenic poisoning:

Arsenic poisoning can be cured by the treatment with 2,3-dimercapropional (BAL) which is capable of bonding to As(III). This is followed by restoration of fluid and electrolyte balance.

Fluoride

Fluoride is an essential non metal that does not occur in the elemental state in nature because of its high reactivity and combines with minerals in soil or rocks.

Uses:

- Fluoride is added to water in small concentration to protect the teeth from decay and to build bone strength.
- Inorganic fluoride compounds are used in Al production and glass fibre industries.
- Fluoride is also used in the production of phosphate fertilizers, bricks, tiles and ceramics.

Source:

- The main source of fluoride is drinking water contaminated from natural geological sources. Most of water bodies contain naturally occurring fluoride.
- It enters water sources from the effluents of fertilizers and aluminium factories.
- Fluoride compounds such as sodium fluoride and fluorosilicates easily dissolve into water flowing through rocks.
- Fluoride is added to drinking water to promote dental health.
- Burning of fluoride rich coal.

Fluoride poisoning or Fluorosis:

Permissible limit: The MCL set by US EPA for fluoride is 4 mg/L. Small amounts of fluoride (1 ppm) are good for teeth and it is added to toothpaste and drinking water.

Adverse Health effects:

- (i) High concentration of fluoride can cause pitting of teeth and severe skeleton problems such as crippling, stiff joints and restricted movement.
- (ii) Fluorosis is a major health problem resulting from long term exposure of high fluoride content.

- (iii) Fluorosis is characterised by dental mottling and skeleton manifestations such as crippling deformities, osteoporosis and osteosclerosis.
- (iv) Fluoride can rapidly cross the cell membrane and is distributed in skeletal and cardiac muscle, liver, skin and erythrocytes.

Antidote to Fluoride poisoning:

Fluorosis is not treatable but it is preventable. Defluoridation is difficult and expensive, so the best option for dealing with excess levels is pursuing alternative water sources if they are available. The goals of therapy in patients with fluoride toxicity are to reduce toxicity and prevent complications. No antidote for fluoride toxicity exists and activated charcoal does not adsorb fluoride. Electrolytes may be used to correct imbalances resulting from fluoride toxicity. The appearance of the fluorosis teeth can be improved by treatments such as tooth whitening, crowns, porcelain veneers, microabrasion, bonding with coats etc.

Removal of Lead, Mercury, Arsenic and Fluoride from water

It is essential to remove the hazardous pollutants such as mercury, lead, arsenic, fluoride etc from water to prevent public from adverse health defects caused by these. There are various methods to remove these pollutants from water. They are reverse osmosis, electrodialysis, coagulation/filtration, adsorption, ion exchange method, electrocoagulation etc. The removal of pollutants by Electrocoagulation method is described below. The other methods mentioned above are explained in different sections of the chapter.

Electrocoagulation Method:

Definition: Electrocoagulation is the process of destabilising suspended, emulsified, or dissolved contaminants in an aqueous medium by introducing an electric current into the medium.

Principle: Electrocoagulation is an electrochemical process that produces destabilising agents which neutralizes the electrical charge of the pollutant, coagulates and removes them. The cations (Fe^{2+} and Al^{3+}) produced from iron or aluminium anodes are responsible for the increasing of the coagulation of contaminants from an aqueous medium.

Electrocoagulation unit consists of an electrolytic cell with one anode (called sacrificial anode) and one cathode. When an electric current is applied it generates gas bubbles and coagulating agents which is capable of attracting oppositely charged pollutants and neutralizes them. The cations (Al^{3+} , Fe^{2+}) produced at the anode react with OH^- ions and form their respective hydroxides. These hydroxides undergo polymerization and condensation reactions and forms polymeric complexes.



The polymeric complexes $[\text{Al}_2(\text{O})(\text{OH})_4]$ and $[\text{Fe}_2(\text{O})(\text{OH})_2]$ remove pollutants from water mainly by either adsorption, surface complexation or by co-precipitation. In general, polymeric aluminium or iron complexes can have both positive and negative charges which

are capable of attracting the oppositely charged pollutants, agglomerate to form floc and remove them from water by filtration.

However, if electrocoagulation-flotation apparatus, is used the particulates would float to the top of the tank by means of hydrogen bubbles formed during the reaction from the anode. The floated particulates can be skimmed from the top of the tank.

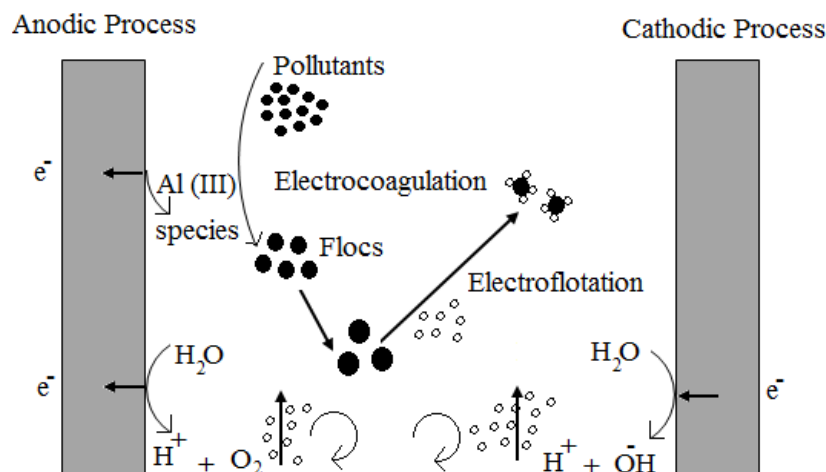
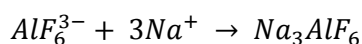
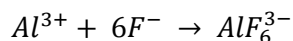
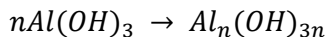
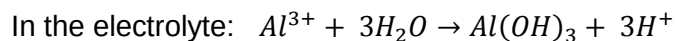
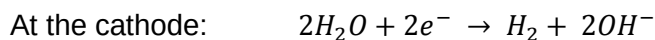


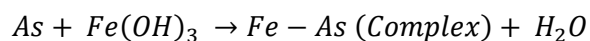
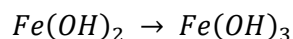
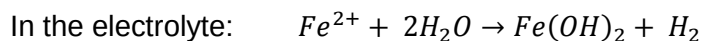
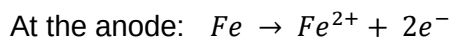
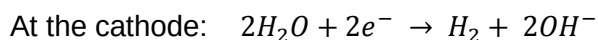
Fig. 2 Electro coagulation Unit

Mechanism:

Removal of Fluoride by Electrocoagulation

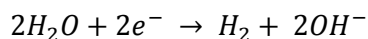


Removal of Arsenic by Electrocoagulation



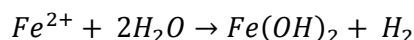
Removal of Heavy metals (Pb and Hg) by Electrocoagulation

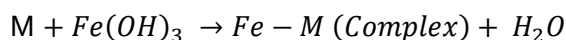
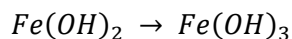
At the cathode: (Stainless Steel)



At the anode: (Mild Steel) $Fe \rightarrow Fe^{2+} + 2e^-$

In the electrolyte:





Where M= Pb,Cr,Hg, etc.,

Advantages:

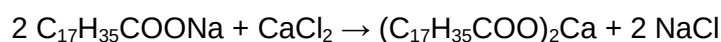
1. Electrocoagulation requires simple equipment and is easy to operate.
2. Electrocoagulation requires low installation and operating cost.
3. It does not require any chemicals thus no problem of neutralizing excess chemicals.
4. There is no possibility of secondary pollution caused by chemical substances.
5. The gas bubbles produced during electrolysis can carry the pollutant to the top of the solution where it can be collected and removed.

Disadvantages:

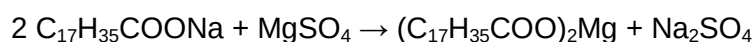
1. Due to oxidation, sacrificial anode dissolved in the water, so need to be regularly replaced.
2. The use of electricity may be expensive in some cases.

Hardness of Water

Hardness in water is the characteristic property which prevents the lathering of soap. This is caused by bicarbonates, chlorides and sulphates of calcium and magnesium. When hard water is treated with soap it does not produce lather but forms white scum or precipitate of insoluble calcium and magnesium soaps.



Sodium soap Insoluble Calcium soap



Sodium soap Insoluble Magnesium soap

Lather is not produced until all the hardness causing Ca^{2+} and Mg^{2+} ions are completely removed as insoluble soap. Hence a large quantity of soap is consumed to produce lather with hard water.

Hard Water and Soft Water

Water which does not produce lather with soap but forms a white precipitate is called as **hard water**. It contains dissolved salts of calcium and magnesium. Common hardness causing impurities are $CaCl_2$, $MgCl_2$, $Ca(HCO_3)_2$, $Mg(HCO_3)_2$, $CaSO_4$ and $MgSO_4$. Water which gives lather readily with soap is called as **soft water**. This water does not contain dissolved calcium and magnesium salts in it.

Types of Hardness

Hardness is classified into temporary hardness and permanent hardness.

Temporary or carbonate hardness

Temporary hardness is due to the presence of dissolved bicarbonates of calcium and magnesium and thus referred as carbonate hardness. This hardness can be removed by boiling which converts the bicarbonates into insoluble carbonates or hydroxides.



Permanent or non-carbonate hardness

Permanent hardness is due to the presence of dissolved chlorides and sulphates of calcium and magnesium. Permanent hardness cannot be removed by boiling. Since this hardness is caused by salts other than carbonates they are also called as non-carbonate hardness.

Expression of Hardness or Equivalents of CaCO_3

Hardness caused by various dissolved salts is expressed in terms of CaCO_3 equivalents. CaCO_3 is chosen as standard because its molecular weight is 100 (equivalent weight=50) and it is the most insoluble salt that can be precipitated in water treatment.

$$\text{Hardness of } \text{CaCO}_3 \text{ eq} = \frac{\text{Mass of hardness producing substance } \left(\frac{\text{mg}}{\text{L}}\right) \times \text{Molecular weight of } \text{CaCO}_3}{\text{Molecular weight of hardness producing substance}}.$$

Calculation of hardness of various salts in CaCO_3 equivalents

Dissolved salt	Molecular weight	Equivalent weight	Multiplication factor
$\text{Ca}(\text{HCO}_3)_2$	162	81	100/162
$\text{Mg}(\text{HCO}_3)_2$	146	73	100/146
CaCO_3	100	50	100/100
MgCO_3	84	42	100/84
CaSO_4	136	68	100/136
MgSO_4	120	60	100/120
CaCl_2	111	55.5	100/111
MgCl_2	95	47.5	100/95

Units of Hardness

Parts per million (ppm) is the number of parts of calcium carbonate equivalent hardness per 10^6 parts of water.

1 ppm = 1 part of CaCO_3 eq hardness per 10^6 parts of water.

Milligrams per litre (mg/L) is the number of milligrams of calcium carbonate equivalents per litre of water.

1 mg/L = 1 mg of CaCO_3 eq hardness per litre of water.

Clarke's degree ($^\circ\text{C}$) is the number of parts of calcium carbonate equivalents per 70,000 parts of water.

Degree French ($^\circ\text{Fr}$) is the number of parts of calcium carbonate equivalents per 10^5 parts of water.

Relationship between ppm and mg/L

1 mg/L = 1 mg of CaCO_3 eq hardness per litre of water.

But 1 litre of water weighs = 1 Kg = 1000 g = 1000 × 1000 mg = 10^6 mg.

1 mg/L = 1 mg of CaCO_3 eq hardness per 10^6 mg of water.

1 mg/L = 1 part of CaCO_3 eq hardness per 10^6 parts of water

[But 1 ppm = 1 part of CaCO_3 eq hardness per 10^6 parts of water]

1 mg/L = 1 ppm

PROBLEMS: Conversion of Hardness Producing Salts into CaCO_3 Equivalents

Note:

1. When hardness causing impurities are given as CaCO_3 and MgCO_3 they are to be treated as $\text{Ca}(\text{HCO}_3)_2$ and $\text{Mg}(\text{HCO}_3)_2$
2. NaCl , KCl , Na_2SO_4 , SiO_2 , Fe_2O_3 etc. do not make water hard. Therefore they should not be taken into account while calculating hardness.

Hardness producing salts and their CaCO_3 equivalents.

S.No	Mole equivalents	Weight equivalents
1.	$1\text{Ca}(\text{HCO}_3)_2 \equiv 1 \text{CaCO}_3$ 162 parts $\equiv$ 100 parts X parts $\equiv$?	$(100/162) \times X$ parts
2.	$1 \text{Mg}(\text{HCO}_3)_2 \equiv 1 \text{CaCO}_3$ 146 gm $\equiv$ 100 gm X gm $\equiv$?	$(100/146) \times X$ gm
3	$1 \text{CaCl}_2 \equiv 1 \text{CaCO}_3$ 111mg $\equiv$ 100 mg X mg $\equiv$?	$(100/111) \times X$ mg
4	$1 \text{CaSO}_4 \equiv 1 \text{CaCO}_3$ 136 parts $\equiv$ 100 parts X parts $\equiv$?	$(100/136) \times X$ parts
5	$1\text{MgCl}_2 \equiv 1 \text{CaCO}_3$ 95parts $\equiv$ 100 parts X parts $\equiv$?	$(100/95) \times X$ parts
6	$1 \text{MgSO}_4 \equiv 1 \text{CaCO}_3$ 120 parts $\equiv$ 100 parts X parts $\equiv$?	$(100/120) \times X$ parts
7	$1 \text{FeSO}_4 \cdot 7\text{H}_2\text{O} \equiv 1 \text{CaCO}_3$ 278 parts $\equiv$ 100 parts X parts $\equiv$?	$(100/278) \times X$ parts

1) Calculate temporary and permanent hardness in terms of CaCO_3 for a water sample containing the following. i) $\text{Ca}(\text{HCO}_3)_2 = 16.2 \text{ mg/L}$ ii) $\text{Mg}(\text{HCO}_3)_2 = 14.6 \text{ mg/L}$ iii) $\text{MgCl}_2 = 19 \text{ mg/L}$ iv) $\text{CaSO}_4 = 68 \text{ mg/L}$ v) $\text{NaCl} = 58.5 \text{ mg/L}$

Solution:

i) 162 mg/L of $\text{Ca}(\text{HCO}_3)_2 \equiv 100 \text{ mg /L of } \text{CaCO}_3$

$$16.2 \text{ mg/L of } \text{Ca}(\text{HCO}_3)_2 = (100 / 162) \times 16.2 \text{ mg of } \text{CaCO}_3 \\ \equiv 10 \text{ mg /L of } \text{CaCO}_3$$

ii) 146 mg/L of $\text{Mg}(\text{HCO}_3)_2 \equiv 100 \text{ mg /L of } \text{CaCO}_3$

$$14.6 \text{ mg/L of } \text{Mg}(\text{HCO}_3)_2 = (100 / 146) \times 14.6 \text{ mg /L of } \text{CaCO}_3 \\ = 10 \text{ mg /L of } \text{CaCO}_3$$

iii) 95 mg /L of $\text{MgCl}_2 \equiv 100 \text{ mg /L of } \text{CaCO}_3$

$$19 \text{ mg/L of } \text{MgCl}_2 = (100/95) \times 19 \text{ mg /L of } \text{CaCO}_3 \\ = 20 \text{ mg/L of } \text{CaCO}_3$$

iv) 136 mg/L of $\text{CaSO}_4 \equiv 100 \text{ mg /L of } \text{CaCO}_3$

$$68 \text{ mg/L of } \text{CaSO}_4 = (100/ 136) \times 68 \text{ mg /L of } \text{CaCO}_3 \\ = 50 \text{ mg /L of } \text{CaCO}_3$$

v) NaCl does not produce hardness.

$$\text{Temporary hardness} = \text{Ca}(\text{HCO}_3)_2 + \text{Mg}(\text{HCO}_3)_2 = 10+10 = 20 \text{ mg/L or ppm}$$

$$\text{Permanent hardness} = \text{MgCl}_2 + \text{CaSO}_4 = 20 +50 = 70 \text{ mg /L or ppm}$$

2) Calculate carbonate and non carbonate hardness caused by the following salts in water. i) $\text{Ca}(\text{HCO}_3)_2 = 20 \text{ mg/L}$ ii) $\text{Mg}(\text{HCO}_3)_2 = 18 \text{ mg/L}$ iii) $\text{MgSO}_4 = 19 \text{ mg/L}$ iv) $\text{CaCl}_2 = 40 \text{ mg/L}$ v) $\text{NaCl} = 30.5 \text{ mg/L}$

Solution:

Hardness producing salt	Molecular weight	Hardness in terms of CaCO_3 eq (mg/L)	Carbonate/non carbonate hardness
$\text{Ca}(\text{HCO}_3)_2$	162	$(100/ 162) \times 20 = 12.35$	Carbonate hardness
$\text{Mg}(\text{HCO}_3)_2$	146	$(100/ 146) \times 18 = 12.33$	Carbonate hardness
MgSO_4	120	$(100/ 120) \times 19 = 15.83$	non carbonate hardness
CaCl_2	111	$(100/ 111) \times 40 = 36.04$	non carbonate hardness
NaCl	Does not produce hardness		

$$\text{Carbonate hardness} = \text{Ca}(\text{HCO}_3)_2 + \text{Mg}(\text{HCO}_3)_2 = 12.35 + 12.33 = 24.68 \text{ mg/L or ppm}$$

$$\text{Non carbonate hardness} = \text{CaCl}_2 + \text{MgSO}_4 = 36.04 + 15.83 = 51.87 \text{ mg /L or ppm}$$

3) Find out the sample which is more hard.

Water sample 1	Water sample 2
----------------	----------------

$\text{Ca}(\text{HCO}_3)_2 = 16.2 \text{ ppm}$	$\text{Mg}(\text{HCO}_3)_2 = 16.2 \text{ ppm}$
$\text{CaCl}_2 = 55.5 \text{ ppm}$	$\text{MgCl}_2 = 55.5 \text{ ppm}$
$\text{CaSO}_4 = 13.6 \text{ ppm}$	$\text{MgSO}_4 = 13.6 \text{ ppm}$
$\text{NaCl} = 58.5 \text{ ppm}$	$\text{KCl} = 58.5 \text{ ppm}$

Solution:

i) Water sample 1:

$$\begin{aligned}\text{Hardness} &= \text{Ca}(\text{HCO}_3)_2 + \text{CaCl}_2 + \text{CaSO}_4 + \text{NaCl} \\ &= [(100/162) \times 16.2] + [(100/111) \times 55.5] + [(100/136) \times 13.6] + 0 \\ &= 10 + 50 + 10 + 0 = 70 \text{ ppm}\end{aligned}$$

ii) Water sample 2:

$$\begin{aligned}\text{Hardness} &= \text{Mg}(\text{HCO}_3)_2 + \text{MgCl}_2 + \text{MgSO}_4 + \text{KCl} \\ &= [(100/146) \times 16.2] + [(100/95) \times 55.5] + [(100/120) \times 13.6] + 0 \\ &= 11 + 58.4 + 11.3 = 80.7 \text{ ppm}\end{aligned}$$

Therefore, the water sample which is more hard is '2'

Estimation of Hardness

The EDTA method is a complexometric titration which is more preferred and accurate than soap titration method. In this method usually disodium salt of ethylene diamine tetra acetic acid is used because it is more soluble in water. The eriochrome black -T is an organic azo dye which is used as an indicator. The structure of disodium salt of EDTA is given below.

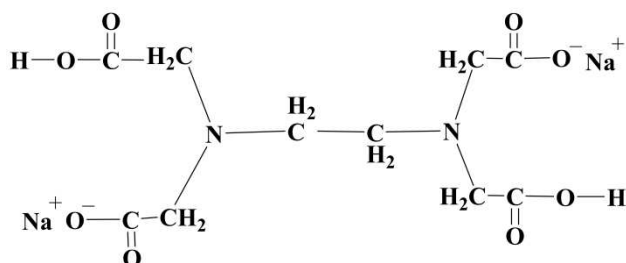
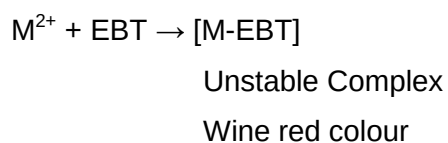


Fig. 3 Structure of disodium salt of EDTA

Principle: In this method a sample of hard water is titrated against disodium salt of EDTA in presence of a buffer using eriochrome black-T (EBT) as an indicator. The buffer (NH_4OH - NH_4Cl buffer) provides a pH = 9-10 required for the complex formation. The indicator forms an unstable wine red coloured complex $[\text{M-EBT}]$ with M^{2+} $\{\text{Ca}^{2+}$ and $\text{Mg}^{2+}\}$ ions present in the hard water sample.



EDTA added forms a stable metal EDTA complex [M-EDTA] with free M^{2+} ions remaining in the water. Further addition of EDTA forms a stable [M-EDTA] complex releasing EBT from the unstable [M-EBT] complex.

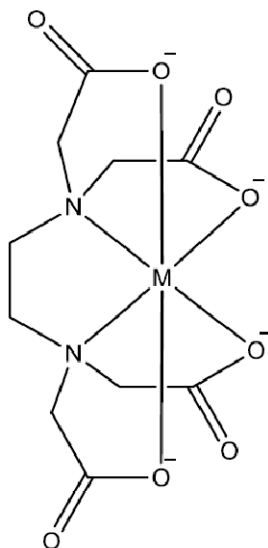
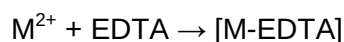
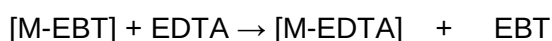


Fig. 4 Metal-EDTA complex [M-EDTA] where $M = Ca^{2+}$ or Mg^{2+} ion

When all the M^{2+} ions are complexed by EDTA the free indicator released gives steel blue colour. Thus the end point is change of wine red colour to steel blue.



Stable complex



Free indicator

Steel blue colour

Steps involved in EDTA method

1. Reagents required for EDTA titration

Preparation of standard hard water: Dissolve 1 g of pure $CaCO_3$ minimum quantity of dilute HCl and then evaporated to dryness. Dissolve the residue in distilled water and make up to 1000 ml. Thus

1 ml of standard hard water = 1 mg of $CaCO_3$ equivalent hardness

Preparation of EDTA solution: Dissolve 4 g of EDTA crystals + 0.1 g of $MgCl_2$ in 1000 ml of distilled water.

Preparation of EBT: Dissolve 0.5 g of EBT in 100 ml of alcohol.

Preparation of buffer solution: Add 67.5 g of NH_4Cl to 570 ml of concentrated ammonia and dilute with distilled water to 1000 ml.

2. Standardization of EDTA solution:

Pipette out 50 ml of standard hard water into a clean conical flask. Add 5 ml of NH_4OH - NH_4Cl buffer and a few drops of EBT indicator. This solution is titrated against EDTA taken in a burette till the colour changes from wine red to steel blue. Let volume of EDTA consumed for 50 ml of standard hard water is V_1 ml.

1 ml of standard hard water = 1 mg of CaCO_3 equivalent hardness ----- 1

50 ml of standard hard water = 50 mg of CaCO_3 equivalent hardness ----- 2

50 ml of standard hard water consumes = V_1 ml of EDTA ----- 3

From equation 1 and 2

V_1 ml of EDTA = 50 mg of CaCO_3 equivalent hardness

1 ml of EDTA = $\frac{50}{V_1}$ mg of CaCO_3 equivalent hardness

3. Estimation of Total hardness

Pipette out 50 ml of sample hard water into a clean conical flask. Add 5 ml of NH_4OH - NH_4Cl buffer and a few drops of EBT indicator. This solution is titrated against EDTA taken in a burette till the colour changes from wine red to steel blue. Let volume of EDTA consumed for 50 ml of sample hard water is V_2 ml.

50 ml of sample hard water consumes = V_2 ml of EDTA

50 ml of sample hard water = $V_2 \times 1$ ml of EDTA

50 ml of sample hard water = $V_2 \times \frac{50}{V_1}$ mg of CaCO_3 equivalent hardness

1000 ml of sample hard water = $V_2 \times \frac{50}{V_1} \times \frac{1000}{50}$ mg of CaCO_3 equivalent hardness

Total hardness of water sample = $\frac{V_2}{V_1} \times 1000$ ppm

4. Estimation of permanent hardness

Take 250 ml of water sample in a beaker and boil it to convert temporary hardness causing Ca and Mg bicarbonates into insoluble CaCO_3 and $\text{Mg}(\text{OH})_2$. Filter the precipitate and wash with distilled water and make upto 100 ml in a standard flask.

Pipette out 50 ml of this boiled sample into a clean conical flask. Add 5 ml of NH_4OH - NH_4Cl buffer and a few drops of EBT indicator. This solution is titrated against EDTA taken in a burette till the colour changes from wine red to steel blue. Let volume of EDTA consumed for 50 ml of boiled sample hard water is V_3 ml.

50 ml of boiled sample hard water consumes = V_3 ml of EDTA

50 ml of boiled sample hard water = $V_3 \times 1$ ml of EDTA

50 ml of boiled sample hard water = $V_3 \times \frac{50}{V_1}$ mg of CaCO_3 equivalent hardness

1000 ml of boiled sample hard water =

$V_3 \times \frac{50}{V_1} \times \frac{1000}{50}$ mg of CaCO_3 equivalent hardness

Permanent hardness of water sample = $\frac{V_3}{V_1} \times 1000$ ppm

5. Temporary hardness of water sample

Temporary hardness of water sample = Total hardness – Permanent hardness

$$= \frac{V_2 - V_3}{V_1} \times 1000 \text{ ppm}$$

PROBLEMS BASED ON EDTA METHOD

Note:

1 Ca or 1 Mg combines with 1 EDTA molecule

i.e 1 Ca $\equiv$ 1 Mg $\equiv$ 1 EDTA

1 ml of 1 M $\text{CaCO}_3 \equiv$ 1 ml of 2 N CaCO_3

$\equiv$ 1 ml of 1M EDTA

$\equiv$ 1 ml of 2N EDTA

$\equiv$ 100 mg of CaCO_3

1 ml of N/50 EDTA $\equiv$ 1 ml of M/100 EDTA

1 ml of N/50 EDTA $\equiv$ 1 mg of CaCO_3

1) 0.5 gm of CaCO_3 was dissolved in dil.Hcl and diluted to 500 ml. 50ml of this solution required 48 ml of EDTA for titration. 50 ml of a hard water required 15 ml of the EDTA for titration. 50 ml of the same water sample after boiling and filtering required 10 ml of EDTA solution. Calculate the total hardness in ppm.

Solution:

500 ml of std. hard water contains 0.5 g of CaCO_3

1 ml of standard hard water = 1 mg of CaCO_3 equivalent hardness

50 ml of standard hard water = 50 mg of CaCO_3 equivalent hardness

50 ml of standard hard water consumes = 48 ml of EDTA

From equation 1 and 2

48 ml of EDTA = 50 mg of CaCO_3 equivalent hardness

1 ml of EDTA = $\frac{50}{48}$ mg of CaCO_3 equivalent hardness

= 1.041 mg of CaCO_3 equivalent hardness

Estimation of total hardness

50 ml of sample hard water consumes = 15 ml of EDTA

50 ml of sample hard water = 15 x 1 ml of EDTA

50 ml of sample hard water = $15 \times \frac{50}{48}$ mg of CaCO_3 equivalent hardness

1000 ml of sample hard water = $15 \times \frac{50}{48} \times 1000$ mg of CaCO_3 equivalent hardness

Total hardness of water sample = $\frac{15}{48} \times 1000 \text{ ppm} = 312.5 \text{ ppm}$

Estimation of permanent hardness

50 ml of sample hard water consumes = 10 ml of EDTA

50 ml of sample hard water = 10 x 1 ml of EDTA

50 ml of sample hard water = $10 \times \frac{50}{48}$ mg of CaCO_3 equivalent hardness

$$1000 \text{ ml of sample hard water} = 10 \times \frac{50}{48} \times 1000 \text{ mg of CaCO}_3 \text{ equivalent hardness}$$

$$\text{Permanent hardness of water sample} = \frac{10}{48} \times 1000 \text{ ppm} = 208.2 \text{ ppm}$$

$$\text{Temporary hardness of water sample} = \text{Total hardness} - \text{Permanent hardness}$$

$$= \frac{V_2 - V_3}{48} \times 1000 \text{ ppm}$$

$$= \frac{15 - 10}{48} \times 1000 \text{ ppm} = 104.2 \text{ ppm}$$

2) 50 ml of a standard hard water containing 1.1 mg of CaCO₃ per ml consumed 45ml of EDTA. 50 ml of a water sample consumed 25 ml of EDTA and 50 ml of boiled off water sample consumed 18 ml of EDTA. Calculate total, permanent and temporary hardness of water.

Solution:

1 ml of standard hard water = 1.1 mg of CaCO₃ equivalent hardness

50 ml of standard hard water = 55 mg of CaCO₃ equivalent hardness

50 ml of standard hard water consumes = 45 ml of EDTA

From equation 1 and 2

45 ml of EDTA = 55 mg of CaCO₃ equivalent hardness

$$1 \text{ ml of EDTA} = \frac{55}{45} \text{ mg of CaCO}_3 \text{ equivalent hardness}$$

$$= 1.222 \text{ mg of CaCO}_3 \text{ equivalent hardness}$$

Estimation of total hardness

50 ml of sample hard water consumes = 25 ml of EDTA

50 ml of sample hard water = 25 x 1 ml of EDTA

$$50 \text{ ml of sample hard water} = 25 \times \frac{55}{45} \text{ mg of CaCO}_3 \text{ equivalent hardness}$$

$$1000 \text{ ml of sample hard water} = 25 \times \frac{55}{45} \times \frac{1000}{50} \text{ mg of CaCO}_3 \text{ equivalent hardness}$$

$$\text{Total hardness of water sample} = 611.11 \text{ ppm}$$

Estimation of permanent hardness

50 ml of sample hard water consumes = 18 ml of EDTA

50 ml of sample hard water = 18 x 1 ml of EDTA

$$50 \text{ ml of sample hard water} = 18 \times \frac{55}{45} \text{ mg of CaCO}_3 \text{ equivalent hardness}$$

$$1000 \text{ ml of sample hard water} = 18 \times \frac{55}{45} \times \frac{1000}{50} \text{ mg of CaCO}_3 \text{ equivalent hardness}$$

$$\text{Permanent hardness of water sample} = 440 \text{ ppm}$$

$$\text{Temporary hardness of water sample} = \text{Total hardness} - \text{Permanent hardness}$$

$$= 171.11 \text{ ppm}$$

3) Calculate permanent hardness from the following: 250 ml of a water sample is boiled for one hour. It is then cooled and filtered to remove precipitate. The filtrate is made upto 250 ml again with distilled water. 50 ml of this solution required 4 ml of N/50 EDTA with NH₄OH buffer and EBT indicator.

Solution:

We know that

1 ml of N/50 EDTA $\equiv$ 1 mg of CaCO_3

4 ml of N/50 EDTA $\equiv$ 4 mg of CaCO_3

50 ml of boiled off water sample consumes = 4 ml of EDTA $\equiv$ 4 mg of CaCO_3

1000 ml of boiled off water sample = $\frac{4}{50} \times 1000 = 80$ ppm

Permanent hardness of water sample = 80 ppm.

4) 50 ml of sample water consumes 13 ml of 0.02 M EDTA before boiling and 8 ml of the same EDTA after boiling. Calculate the degree of total hardness, permanent and temporary hardness.

Solution:

Estimation of Total hardness

50 ml of sample hard water (before boiling) $\equiv$ 13 ml of 0.02 M EDTA

(1 ml of 0.01 M EDTA $\equiv$ 1 mg of CaCO_3)

1 ml of 0.02 M EDTA $\equiv$ 2 mg of CaCO_3

13 ml of 0.02 M EDTA $\equiv$ 13×2 mg of CaCO_3

50 ml of sample hard water (before boiling) = 13×2 mg of CaCO_3

1000 ml of sample hard water (before boiling) = $13 \times 2 \times \frac{1000}{50}$ mg of CaCO_3

Total hardness of water sample = 520 ppm.

Estimation of permanent hardness

50 ml of sample hard water (after boiling) $\equiv$ 8 ml of 0.02 M EDTA

(1 ml of 0.01 M EDTA $\equiv$ 1 mg of CaCO_3)

1 ml of 0.02 M EDTA $\equiv$ 2 mg of CaCO_3

8 ml of 0.02 M EDTA $\equiv$ 8×2 mg of CaCO_3

50 ml of sample hard water ((after boiling) = 8×2 mg of CaCO_3

1000 ml of sample hard water (after boiling) = $8 \times 2 \times \frac{1000}{50}$ mg of CaCO_3

Permanent hardness of water sample = 320 ppm.

Temporary hardness of water sample = $520 - 320 = 200$ ppm.

Atomic Absorption Spectrometry (AAS)

Atomic Absorption Spectrometry is one of the most widely used methods for quantitative elemental analysis. There are a number of situations where elemental composition is important such as iron content in an ore sample, lead in drinking water, calcium in intracellular fluids etc. An obvious application of the determination of calcium and magnesium in water is testing for hardness in hard water.

Principle and Working

- (i) Atomic absorption spectrometry is based on the absorption of light by free metallic atoms.
- (ii) Monochromatic light for a particular element (to be analyzed) is produced by means of a hollow cathode lamp. It is constructed of a metal cathode composed of the metal element to be analyzed and contained in a transparent tube filled with an inert gas.
- (iii) Calcium and magnesium are both determined with a combination hollow cathode lamp but iron requires a separate lamp and different operating wavelength.
- (iv) In AAS, a substance is vaporized and decomposed into gaseous atoms in a flame, furnace, or plasma. Concentrations of atoms are measured by absorption or emission of specific wavelengths of radiation.
- (v) This monochromatic light is passed through a long flame into which the solution to be analyzed is aspirated.
- (vi) The heat energy dissociates the molecules and converts the components into atoms.
- (vii) These atoms absorb the particular wavelength of light as in the hollow cathode lamp.
- (viii) The amount of light absorbed varies directly with metal ion concentration in the flame.
- (ix) The transmitted light that is not absorbed reaches the monochromator and strikes the detector.
- (x) The decrease in transmitted light is directly proportional to the measure of metal ion concentration in the solution.

Instrumentation

- A simple atomic absorption spectrophotometer consists of a source emitting radiation (Hollow cathode lamp), Flame and spray chamber, monochromator, detector (Photomultiplier) and Recorder (Fig. 5).

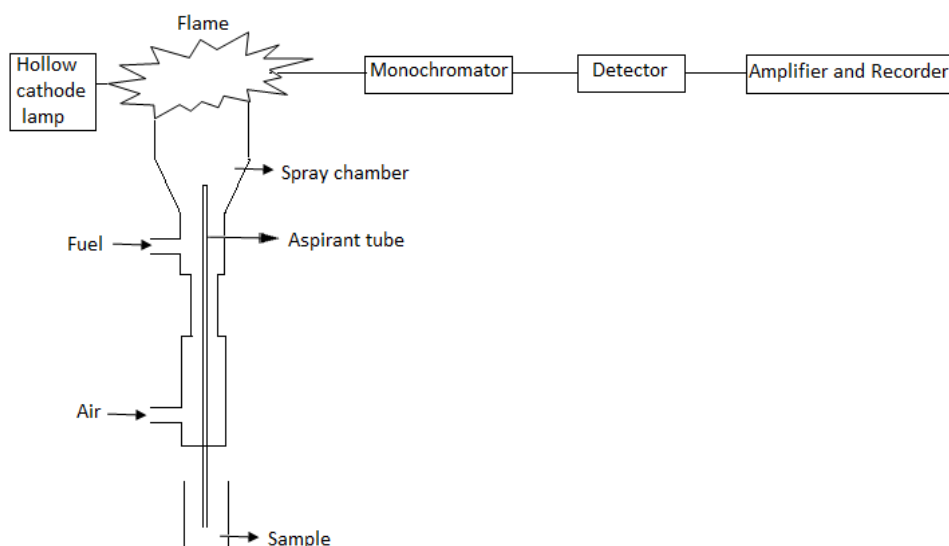


Fig. 5 Atomic Absorption Spectrophotometer

Light source (Hollow Cathode Lamp)

- (i) The hollow cathode lamp (electric discharge lamp) is widely used as light source in AAS.
- (ii) It is designed to emit the atomic spectrum of a particular element.

Flame

- For the vaporization of sample, the sample is sprayed into the burner system.
- The flame is produced using one of the gaseous mixture namely Air-acetylene (gives flame temperature of about 2400°K), air-propane (1900°K) and nitrous oxide-acetylene (2900°K).

Monochromator

- The monochromator is used to disperse several wavelengths of lights that are emitted from the light source to isolate a particular line of interest.

Detector and Amplifier

- The detector produces an electrical current that is dependent on the light intensity.
- This electrical current is amplified and processed to produce a signal.
- It is a measure of the light attenuation occurring in the sample cell. This signal is further processed to generate readout in concentration units.

Limitations

- ✓ The sample to be analyzed must be prepared in the form of solution.
- ✓ Individual source lamp and filters are needed for each element. This is because each and every metal has its own characteristic absorption.

Applications

- ✓ AAS is the most widely used technique for the quantitative determination of various metals at trace levels (0.1 to 100 ppm).

✓ AAS is extensively used in:

- Water analysis (e.g: Ca, Mg, Fe, Si, Al, Ba content).
- Analysis of animal feedstuffs (e.g: Mn, Fe, Cu, Cr, Se, Zn).
- Analysis of additives in lubricating oils and greases (Ba, Ca, Na, Li).
- Analysis of contaminated soils.
- Clinical analysis (blood samples: whole blood, plasma, serum; Ca, Mg, Li, Na, K, Fe).

Estimation of Calcium, Magnesium and Iron by Atomic Absorption Spectroscopy

Principle

- In AAS, the sample is first converted into an atomic vapour and then it is absorbed with a suitable hollow cathode lamp and measured at a selected wavelength which is the characteristic of each individual element.
- The measured absorbance is proportional to the concentration of the solution.

Preparation of Standard Stock Solution

- **Calcium stock solution:** Accurately weigh about 0.252g of dry primary standard calcium carbonate. Dissolve in a minimum amount of 6 M HCl then dilute to 100 mL in a standard flask with deionized water
- **Magnesium stock solution:** Accurately weigh out about 0.1g of dry magnesium oxide. Dissolve in a minimum amount of 6 M HCl then dilute to 1000-mL in standard flask with deionized water.
- **NaCl stock solution:** Accurately weigh about 0.510g of NaCl and make up to 200 mL in standard flask with deionized water.
- **Standard iron solution:** Accurately weigh out about 0.1g FAS and dissolve it with about 10 mL of 2 M H₂SO₄ and make up to 500 mL with deionized water.

Preparation of calcium/magnesium/iron Calibration Solutions

- Prepare a series of standard calcium and magnesium ion solution in the concentration range 3-12 ppm.

Preparation of Given Unknown Solution

- *Transfer the given unknown solution into a 100 ml standard measuring flask.*
- *Dilute carefully to the mark with de-ionized water and mix thoroughly.*

Procedure

- Switch on AAS and warm up for about 10 minutes.
- Appropriate hollow cathode lamp is chosen based on the analyte to be estimated.
- Fix the wavelength and then adjust the meter to zero absorbance or 100% transmittance.
- Now the standard solutions are aspirated (introduced) into the air-acetylene flame one by one.
- A part of the light from hollow cathode lamp is absorbed by the excited metal atoms, resulting in a proportionate decrease of the light intensity.

- The decrease of the light intensity is measured as absorbance.
- The absorbance values for different concentrations are used to construct the calibration curves.
- The unknown solution is also aspirated into the flame and the absorbance is measured as performed with standard solutions.
- With the help of calibration curve, the calcium and magnesium content of test solution is measured (Fig. 6).

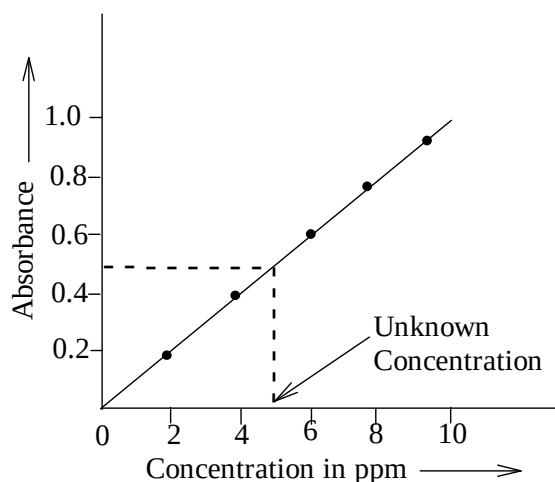


Fig. 6 Absorbance versus Concentration

Disadvantages of Hard Water in Domestic Use

- 1. Washing and bathing:** Hard water does not lather with soap but forms sticky white precipitate of calcium and magnesium soaps. After complete removal of Ca^{2+} and Mg^{2+} ions from water sodium soap gives lather with water. This causes wastage of soap. Presence of iron produce yellowish red colour to fabrics.
- 2. Cooking:** Presence of dissolved salts elevate boiling point of water thereby increasing fuel and time required for cooking. The dissolved salts deposit as scales on the inner walls of the utensils. Pulses and peas are not cooked soft in hard water.
- 3. Drinking:** Hard water is not suitable for drinking purpose. The dissolved salts cause the formation of calcium oxalate crystals in urinary track. These crystals form stones in kidney and urinary tract.

Specification of Water for Industries

Industry	Requisites of water	Disadvantages/Troubles
Textile	Soft water	Hardness in water causes wastage of soap. It also affects dyeing of fabrics
	Free from Fe and Mn salts	Causes stains on fabrics
Paper	Free from alkalinity	Alkaline water consume more alum thereby increasing cost of

			production
		Free from Hardness	Ca and Mg salts increase ash content of Paper
		Free from Fe and Mn salts	Affects brightness and colour of paper
Boiler	feed	Free from dissolved gases	Causes boiler corrosion
water		Free from dissolved salts and silica	Causes scales and sludges
Laundry		Soft water	Hardness in water consumes lot of soap
		Free from colour, Fe and Mn salts	Impart grey or yellow colour to fabric
Beverages		Should not be alkaline	Alkalinity neutralize the fruit acids and modifies the taste
Sugar industry		Free from sulphates, nitrates and alkali carbonates	Causes difficulties in crystallization of sugar

Water Softening

Water used for steam generation must be free from dissolved salts to minimize troubles like scale formation in boilers and industries such as textiles, laundries, paper, distilleries etc essentially require soft water. Thus water should be freed from the hardness producing salts before use. The process of removing of hardness producing salts from water is known as softening of water. There are three main methods used in industries for water softening. They are i) Lime-soda process ii) Zeolite process and iii) Demineralization process.

Lime-Soda Process:

The hardness causing Ca and Mg salts are converted into insoluble precipitate by calculated amounts of lime Ca(OH)_2 and soda Na_2CO_3 and the precipitate formed is filtered.

Zeolite or Permutit Process:

Zeolites are crystalline microporous aluminosilicates built up of three dimensional framework of $[\text{SiO}_4]^{4-}$ and $[\text{AlO}_4]^{5-}$ tetrahedra linked by sharing of oxygen atoms. . The linking of these tetrahedra results in pores of the zeolite which permits the movement of water molecules and ions. Zeolite contains weakly bonded (readily exchangeable) cations (Na^+) in pores of the structure. They are capable of exchanging reversibly its Na^+ ions for hardness causing Ca^{2+} and Mg^{2+} ions in hard water. The cation exchange capacity (CEC) is a measure of number of cations per unit weight available for exchange which depends on the Al content (i.e. more Na^+ needed to balance the charge). Zeolites are of two types;

- i) Natural zeolites are non-porous. Example: Natrolite $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2 \cdot 2\text{H}_2\text{O}$
- ii) Synthetic zeolites are porous and possess gel structure. They are synthesized by heating together china clay, feldspar and soda ash. They possess higher exchange capacity per unit weight than natural zeolites.

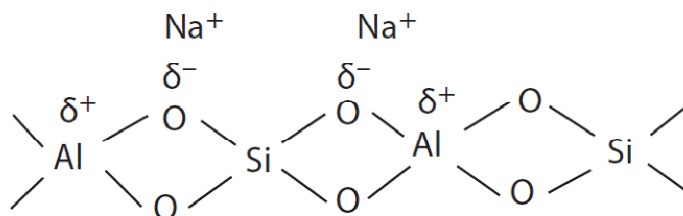


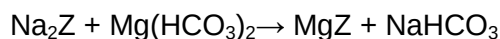
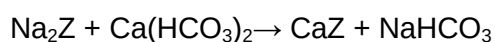
Fig. 7 Structure of zeolite

Principle:

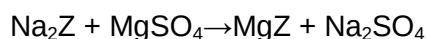
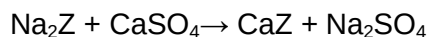
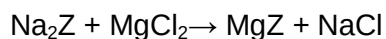
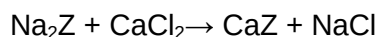
Sodium zeolite is hydrated sodium aluminosilicate having general formula $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot x\text{SiO}_2 \cdot y\text{H}_2\text{O}$ where $x=2-10$ and $y=2-6$. Sodium zeolite is represented as Na_2Z where Z stands for insoluble zeolite framework. They are capable of exchanging reversibly its Na^+ ions for hardness causing Ca^{2+} and Mg^{2+} ions in hard water.

Softening process: When hard water is passed through the bed of zeolite, the hardness causing Ca^{2+} and Mg^{2+} ions are retained in the zeolite bed as CaZ and MgZ and an equivalent amount of Na^+ ions are released in the outgoing water. The exchange reactions taking place during the softening process are

Removal of Carbonate hardness



Removal of Non-carbonate hardness



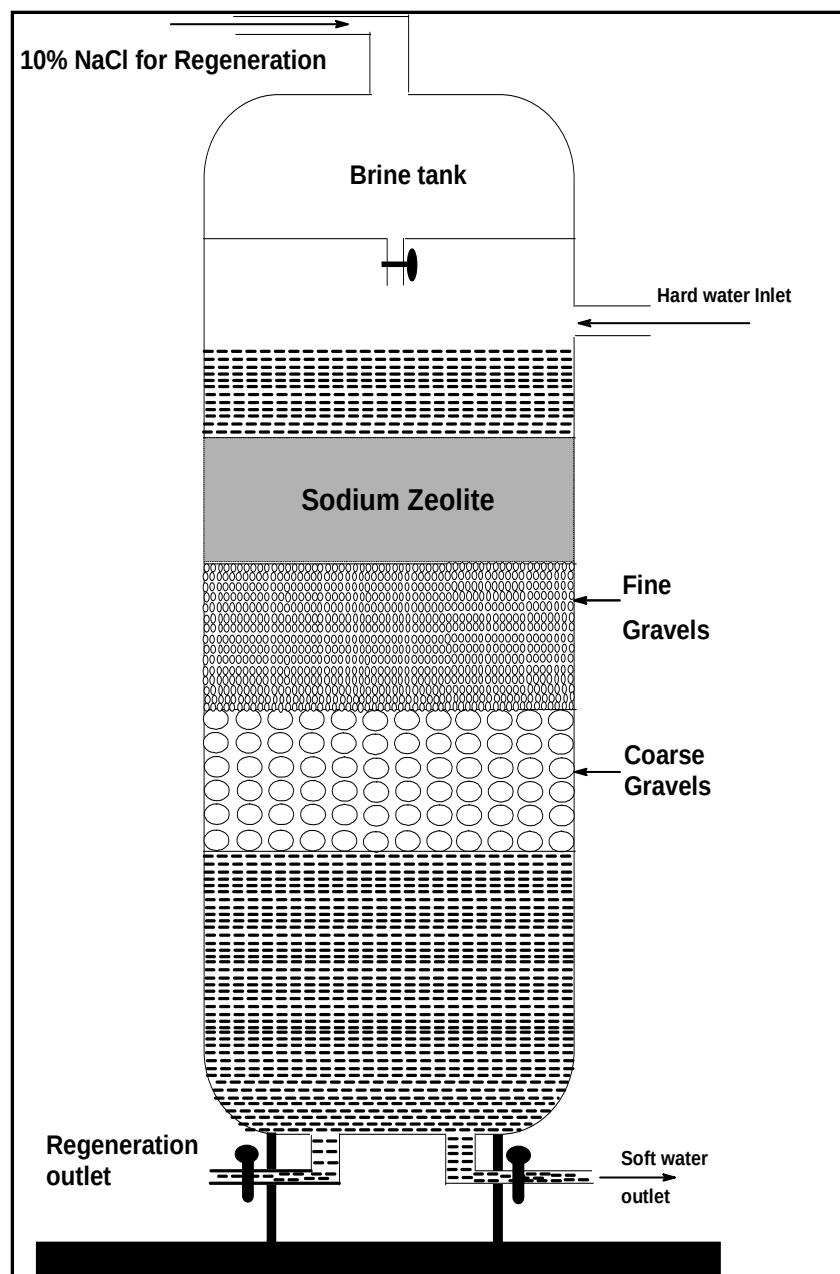
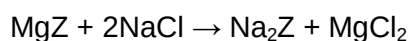
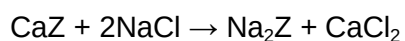


Fig. 8 Zeolite softener

Regeneration process: When the zeolite is completely exhausted it loses its exchange capacity and thus has to be regenerated. This is indicated by an increase in hardness of the softened water obtained. The exhausted zeolite is regenerated by treating with 10% brine (NaCl) solution and reused. The washing containing CaCl_2 and MgCl_2 are led to drain.



Advantages of zeolite process

1. Water softened by zeolite process has residual hardness of 10 ppm.
2. Equipment is compact and requires less time for softening.

3. Process does not involve any precipitate or sludge.
4. Requires less skill for maintenance and operation.

Disadvantages of Zeolite Process:

1. Water softened contains large amount of sodium salts which is not suitable for boilers as it leads to boiler corrosion.
2. Turbid water cannot be treated. Turbidity clogs the pores of zeolite and the rate of flow decreases. Thus turbidity of water should be removed by coagulation and filtration before subjecting to softening.
3. It is a Base Exchange process and therefore anions (CO_3^{3-} , SO_4^{2-} , Cl^- , etc.) are not removed by zeolite process.
4. Brackish water (salt water containing NaCl) cannot be treated by this method.
5. If water contains Fe and Mn salts they form irreversible iron and manganese zeolite which cannot be easily regenerated.

Demineralization Process or Ion Exchange Process:

Demineralization process is an ion exchange process in which porous, insoluble, cross linked long chain high molecular weight synthetic resins are used as ion exchangers. The functional groups attached to the polymers are responsible for Ion exchange property. Resins containing acidic groups are capable of exchanging their H^+ ions with cations in water where as those containing basic groups are capable of exchanging their OH^- ions with anions in water. The organic ion exchange resins are:

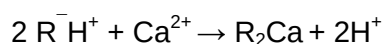
Cation exchange resin: These are cross linked styrene - divinyl benzene copolymers containing sulphonic acid group (SO_3H) or carboxylic acid group (COOH) which is capable of exchanging reversibly its H^+ ions for cations in water. It is represented as R^+H^+ .

Anion exchange resin: These are cross linked styrene - divinyl benzene copolymers containing amino, substituted amino or quaternary ammonium group as integral part of resin. This copolymer on treatment with dilute NaOH becomes capable of exchanging reversibly its OH^- ions for anions in water. It is represented as R^+OH^- .

Softening Process

The cation and anion exchange resins are kept in two vertical exchangers.

Cation exchange reaction: : Hard water is first percolated through cation exchange resin where the cations are retained in the resin and an equivalent amount of H^+ ions are released in the outgoing water.



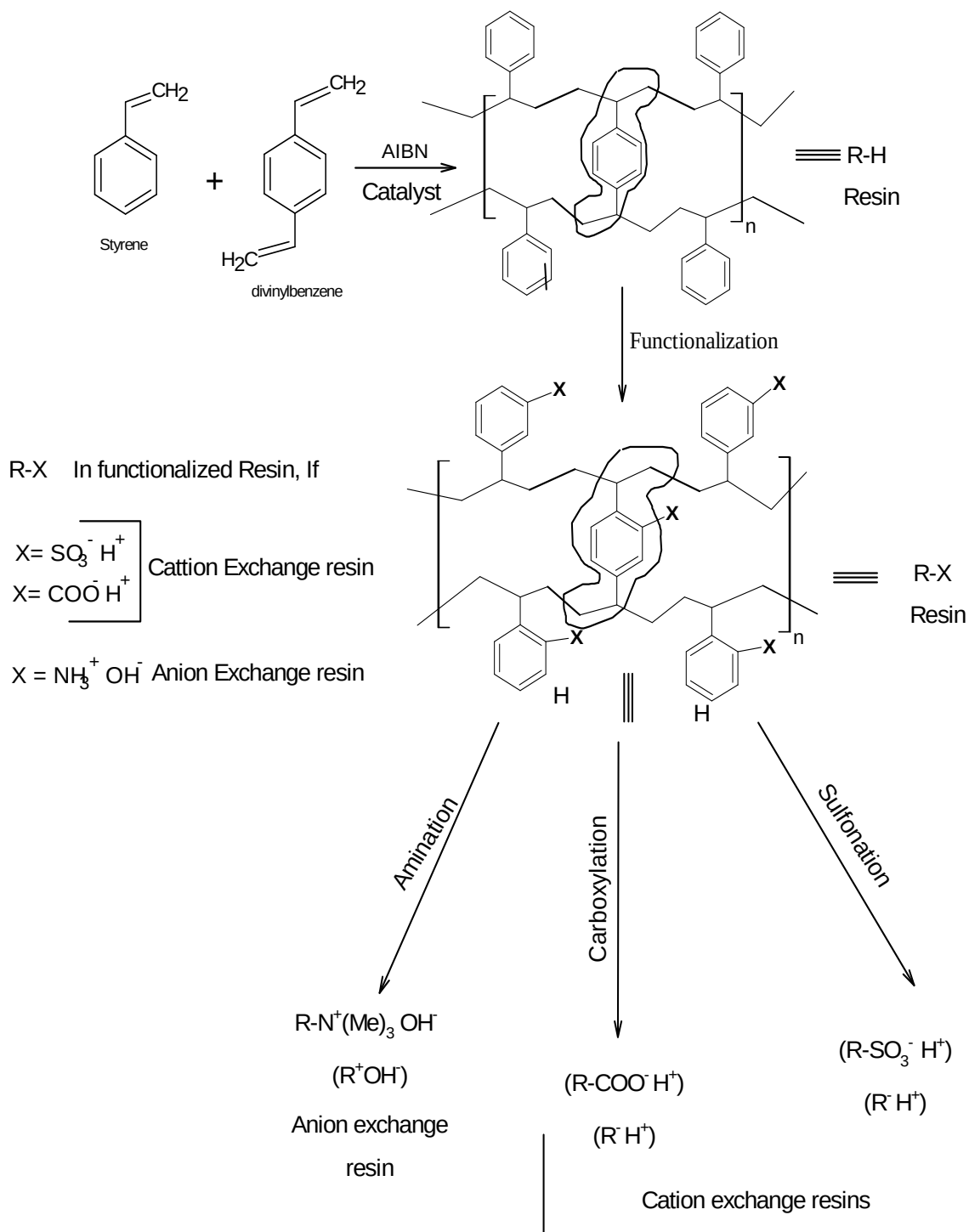
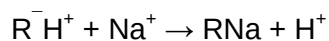
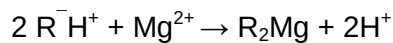
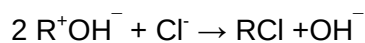
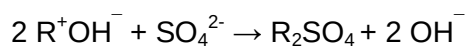
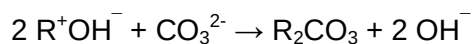


Fig. 9 Schematic Representation of synthesis of Cationic and Anionic exchange Resin

Anion exchange reaction: The water from cation exchange resin is passed through anion exchange resin which retains the anions and releases an equivalent amount of OH^- ions in the water.



H^+ and OH^- ions from cation exchange and anion exchange resins combine to form deionized water which is free from cations and anions.

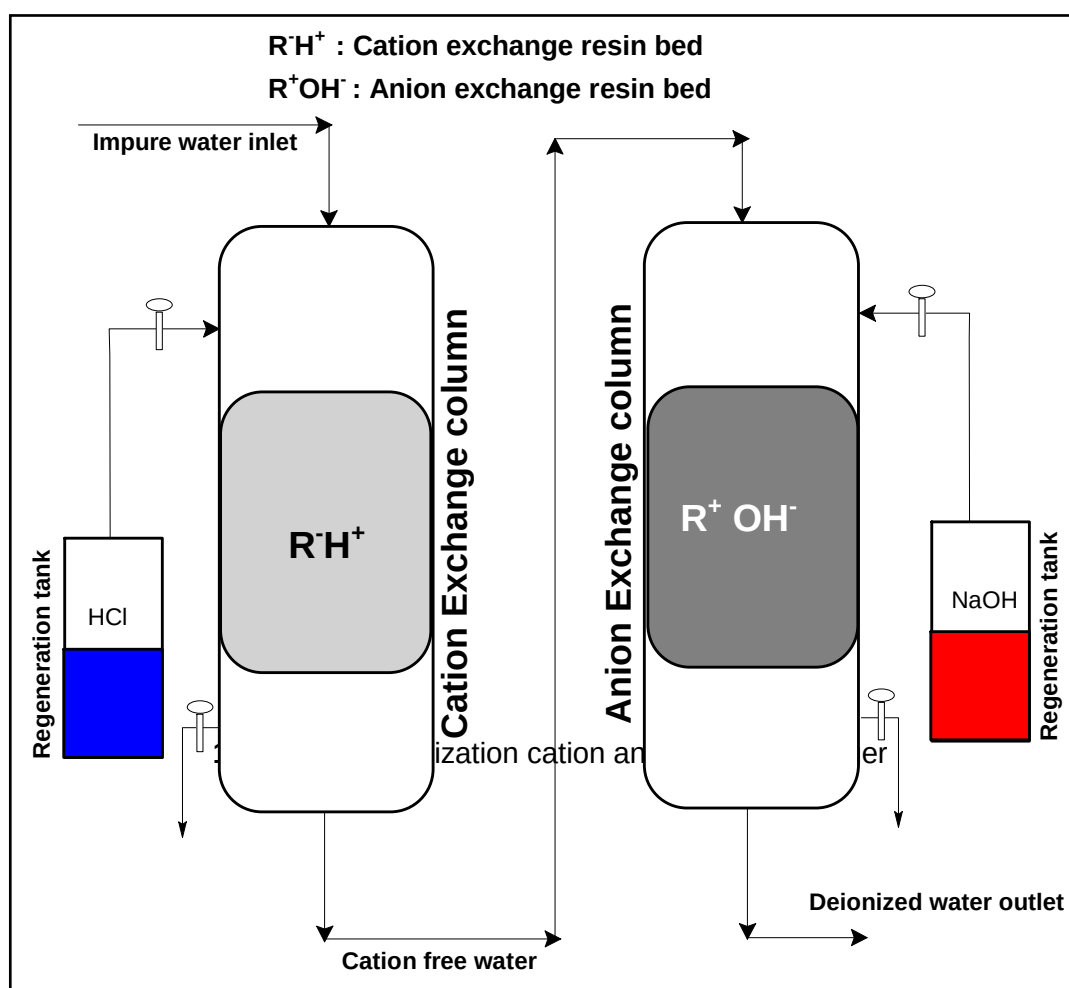
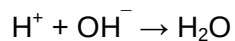
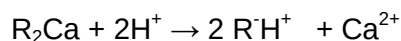


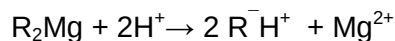
Fig. 10 Schematic Representation of Ion Exchange Resin process

The order of exchange process should not be interchanged as water coming out from cation exchange resin is acidic which does not affect the anion exchange resin. Whereas when the order is changed the water coming from the anion exchange resin is alkaline this harms the cation exchange resin in the subsequent step.

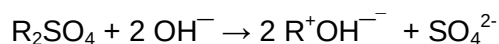
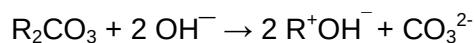
Regeneration Process: When the resin is completely exhausted it loses its ion exchange capacity and are regenerated and reused.

Cation exchange resin: The exhausted cation exchange resins are regenerated by passing dilute HCl or H_2SO_4 .





Anion exchange resin: The exhausted cation exchange resins are regenerated by passing dilute NaOH.



Advantages of Demineralisation process

1. Water obtained from demineralisation process contain residual hardness of 2ppm. This can be used in high pressure boilers.
2. Acidic and alkaline waters can be softened by this method.

Disadvantages of Demineralisation process

1. The cost of equipment and resins are expensive.
2. Fe and Mn containing water cannot be treated by this method as they are irreversibly exchanged.
3. Turbid water cannot be treated as they reduce the efficiency of the process.

Desalination

The process of removal of dissolved solids (mainly NaCl) from sea water or brackish water is known as **desalination**.

This is done by two ways

1. Separation of water from brackish water
Methods: Reverse osmosis, distillation, evaporation, freezing.
2. Separation of salt from brackish water
Methods: Electrodialysis

Osmosis

Osmosis is a natural process. When two liquids of different concentration are separated by a semi-permeable membrane, the solvent has a tendency to move from lower to higher solute concentration for chemical potential equilibrium. This phenomenon is known as **Osmosis**. The driving force for osmosis is called as osmotic pressure.

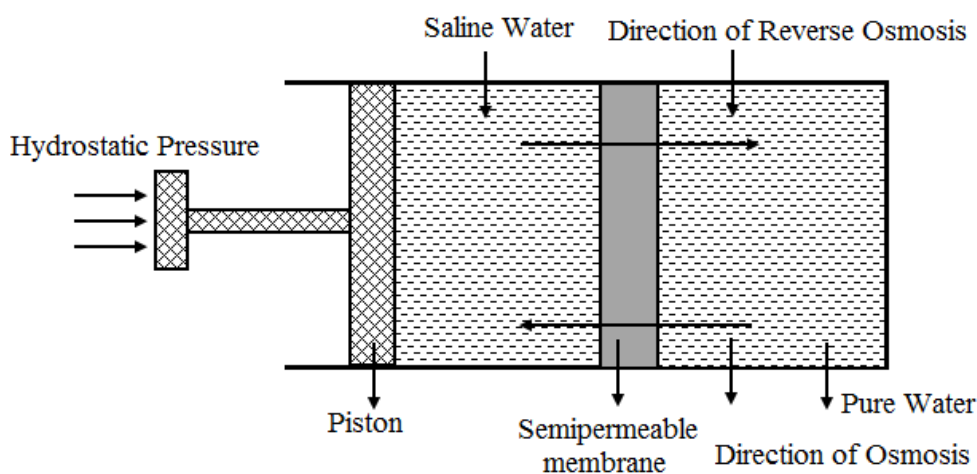


Fig. 11 Reverse osmosis process

Reverse Osmosis

Reverse osmosis is the process of forcing a solvent from a region of higher solute concentration to a region of lower solute concentration through a semi-permeable membrane by applying a hydrostatic pressure in excess of the osmotic pressure on higher concentration side. The semi-permeable membrane used for reverse osmosis has a dense layer in the polymer matrix containing cellulose acetate, methyl acrylate or polyamides etc.

The largest and most important application of reverse osmosis is the separation of pure water from seawater and brackish water. This process requires a high pressure to be exerted on the higher concentration side of the membrane, usually 2–17 bars for fresh and brackish water and 40–82 bar for seawater. The thickness of the cellulose acetate membrane should be of 100 to 150 microns to withstand the pressure applied. The hydrostatic pressure is applied on the seawater or brackish water side to force the pure water out through the semi-permeable membrane leaving behind the ionic and non ionic dissolved solids. Thus potable drinking water emerges out from the pure water side.

Advantages

1. The life of the membrane is high and it can be replaced with in few minutes.
2. It removes ionic as well as non –ionic and colloidal impurities.
3. Due to low capital cost and simplicity, it is highly reliable for converting seawater to fresh water.

Disadvantages

1. Reverse osmosis is a costlier process since the rigid plastic membranes are expensive.
2. Thin plastic membrane cannot withstand very high pressure therefore it has to be replaced frequently.
3. Frequent fouling of membrane occurs due to the deposition of impurities.

Electrodialysis

Definition: *Electrodialysis* is a desalination method used to transport ions from salt solution through ion-selective membranes to another solution in an applied electric field.

Principle: Electrodialysis is related to the principle of electrolysis. In this process the ions in salt water are attracted to opposite electrodes in an applied electric field. The electrical potential acts as the driving force for the movement of ions. When an electric field is applied to saline water, cations such as Na^+ , Ca^{2+} , Mg^{2+} moves towards cathode and anions such as Cl^- , SO_4^{2-} moves towards anode through ion-selective membranes. Subsequently the concentration of saline water decreases in the middle compartments and that of the adjacent compartments increases.

Ion-selective membrane: The ion-selective membrane allows either cations or anions to pass through it and not both simultaneously. Thus cation selective membrane (C) is permeable only to cations and not anions whereas anion selective membrane (A) is permeable to anions but not cations. These membranes are made of polystyrene backbone with charged groups. Sulphonated polystyrene is an example for cation selective membrane and polystyrene with quaternary ammonium group is an example for anion selective membrane.

Description and working: An electrodialysis unit consists of a series of compartments made of anion selective and cation selective membranes alternating each other. The outermost compartments are connected to charged electrodes. Care should be taken to connect (C) to cathode and (A) to anode. All the compartments are filled with saline water and an electric field is applied perpendicular to the direction of flow of saline water. Now cations move towards cathode and anions move towards anode through the membranes. From compartments 2, 4 and 6 the cations pass through cation selective membrane and anions pass through anion selective membrane to the adjacent compartments. Thus in compartments 1, 3, 5 and 7 the concentration of salt increases (brine) whereas in compartments 2, 4 and 6 pure water is obtained. The concentrated brine and pure water are collected from the outlets.

Advantages

1. Electrodialysis unit is compact.
2. If electricity is easily available the process can be extended to sea water.
3. The cost of installation is economical.

Disadvantages

1. Electrodialysis process is costly.

Applications

1. Electrodialysis is used in the brackish water and sea water desalination.
2. It finds applications in waste water reduction or recovery.
3. It is also very useful to reduce salt contents of process streams with high amounts of salts.
4. It is used in salt production.
5. This method is effective for small and medium scale drinking water production.

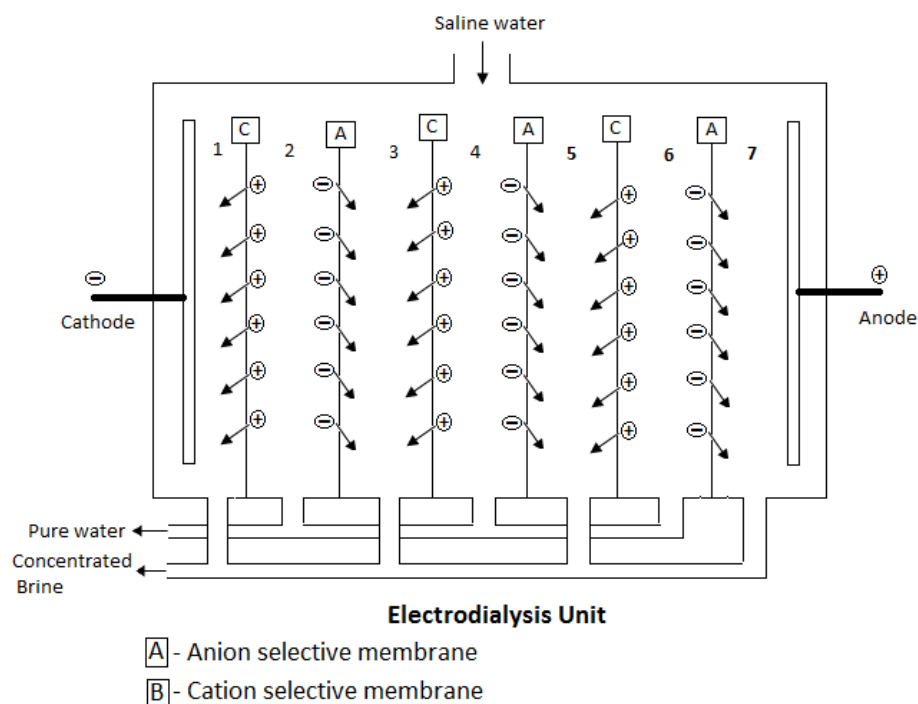


Fig. 12 Electrodialysis Unit

Exercises

1. Calculate temporary and permanent hardness in terms of CaCO_3 for a water sample containing the following. i) $\text{CaCl}_2 = 11.1 \text{ mg/L}$ ii) $\text{MgSO}_4 = 12 \text{ mg/L}$ iii) $\text{MgCl}_2 = 9.5 \text{ mg/L}$ v) $\text{NaCl} = 60 \text{ mg/L}$
2. Calculate carbonate and non carbonate hardness in terms of CaCO_3 for a water sample containing the following. i) $\text{Ca}(\text{HCO}_3)_2 = 252 \text{ mg/L}$ ii) $\text{Mg}(\text{HCO}_3)_2 = 200 \text{ mg/L}$ iii) $\text{MgCl}_2 = 30 \text{ mg/L}$ iv) $\text{CaSO}_4 = 76 \text{ mg/L}$.
3. A water sample contains 29 mg/L of CaSO_4 . Calculate the hardness caused in terms of CaCO_3 equivalents.
4. 2 g of CaCO_3 was dissolved in 500 ml of distilled water. 20 ml of this solution consumed 12 ml of EDTA. 20 ml of hard water sample consumed 6 ml of EDTA. 20 ml of the same hard water sample after boiling and filtering consumed 2 ml of EDTA. Calculate the total, permanent and temporary hardness of the given water sample.
5. 0.25 g of CaCO_3 was dissolved in 250 ml of distilled water. 25 ml of this solution consumed 16 ml of EDTA. 25 ml of hard water sample consumed 9 ml of EDTA. 25 ml of the same hard water sample after boiling and filtering consumed 4 ml of EDTA. Calculate the carbonate and non carbonate hardness of the given water sample.
6. 50 ml of sample of hard water consumed 15 ml of 0.03 M EDTA. Calculate the hardness of the water sample.

Questions

1. How is total hardness of water estimated by EDTA method?
2. Explain the estimation of iron, calcium and magnesium by AAS method.

3. Describe the principle and instrumentation of atomic absorption spectrometry.
4. Describe the demineralization process of water softening with a neat labelled diagram.
5. What is sodium zeolite? Explain the water softening by zeolite process.
6. Write short notes on reverse osmosis.
7. Explain the principle and working of Electrodialysis unit.
8. Discuss the source, biochemical effects and removal of mercury from water.
9. Write notes on the contamination of water by arsenic and fluoride.
10. Briefly explain the source, adverse effects and removal of lead poisoning.
11. Compare zeolite process and demineralization process.
12. Write short notes on specifications and disadvantages of hard water for industries.

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Electrochemistry: Galvanic cell- Electrochemical cell representation - EMF series and its significance. Batteries: Terminology- Lead-acid accumulator- Nickel-Cadmium batteries, Lithium batteries: Li/SOCl₂ cell - Li/I₂ cell- Lithium ion batteries. Fuel cells: Hydrogen-oxygen fuel cell, Solid oxide fuel cell (SOFC).

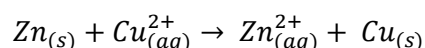
The science of electrochemistry was born at the end of the eighteenth century due to the key discovery of the voltaic pile, the first modern electrical battery by Volta in 1793. Nicholson and Carlisle, in 1800 showed that electric current could convert water into oxygen and hydrogen. In 1812, Berzelius proposed that all atoms can be electrified. Later on, Sir Humphrey Davey used current to separate compounds into their individual components and electrolyzed molten sodium hydroxide to get sodium. Michael Faraday studied the relationship between electricity and magnetism and invented the first electric motor in 1821. His laws of electrochemistry quantified the relation between the amount of electric charge and the electrolysis product.

Basic Principles of Electrochemistry

Electrochemistry is a branch of chemistry dealing with chemical reactions that involve electrical currents and potentials. Electrochemical reactions are invariably oxidation/reduction reactions carried out under special circumstances.

Redox Reactions

Oxidation is a process, which involves loss of electrons by a substance while reduction involves gain of electrons by a substance. Oxidation and reduction usually occur simultaneously and the simplest example is the precipitation of copper when zinc metal is placed in a solution of copper sulphate.



Here, zinc is oxidized to zinc ion since it loses electrons whilst copper ion is reduced to copper since it gains electrons.



The overall reaction is called a redox or oxidation-reduction reaction. Each of these reactions is known as a half-reaction. The oxidation reaction is called an oxidation half-reaction and the reduction reaction is called a reduction half-reaction.

Electrode Potential

A metal (M) consists of metal ions (Mⁿ⁺) with the valence electrons binding them together. If the metal is in contact with a solution of its own salt, the positive ions in the metal come into equilibrium with those in the solution. Thus, the metal acquires a negative charge since it is

now left with excess number of electrons and a number of positive metal ions are formed in the solution. E.g. zinc in zinc sulphate solution. However, if the positive metal ions from the solution enter the metal, the metal gets a positive charge. E.g. copper in copper sulphate. Thus, the following two reactions can take place when a metal is in contact with its salt solution.

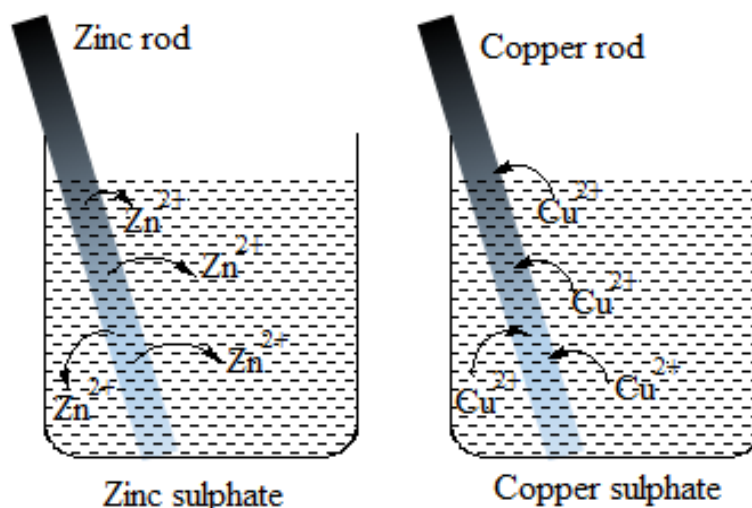
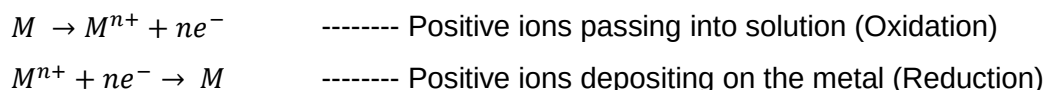


Fig. 1 Redox reactions and Electrode potential

This creates a dynamic equilibrium since positive or negative charge developed on the metal attracts the oppositely charged ions in the solution. Thus, a double layer of positive and negative ions are formed which is called the **Helmholtz electrical double layer**. Thus a difference in potential is created which becomes a constant value at equilibrium. This potential difference is called the **electrode potential**. Thus, electrode potential of a metal is defined as

"The measure of tendency of a metallic electrode to lose or gain electrons, when it is in contact with a solution of its own salt of unit molar concentration at 25°C."

If the tendency is to lose electrons, it is called oxidation potential and if the tendency is to gain electrons, it is called reduction potential.

Measurement of electrode potential

It is not possible to calculate the absolute value of a single electrode potential. However, the difference in potential between two electrodes can be measured potentiometrically by combining them to form a complete cell. The standard hydrogen electrode (SHE) is generally used for this purpose.

Galvanic Cell or Electrochemical Cell

An electrochemical cell is a device in which a redox reaction is utilized to get electrical energy. It is also called as galvanic or voltaic cell. Oxidation occurs at the anode and reduction occurs at the cathode.

The galvanic cell consists of a zinc metal in zinc sulphate solution and copper metal in copper sulphate solution. The two solutions are separated by means of a salt bridge such as sodium nitrate. Each electrode is considered as a half cell. When the two electrodes are electrically connected, a voltage of 1.1 volts is observed. A **voltmeter** can be used to measure the potential of the galvanic cell. This is called the **cell potential** or **electromotive force (EMF)**. This potential results from zinc metal getting oxidized at the Zn anode and Cu^{2+} being reduced at the cathode. A practical application of this is also called a Daniel cell.

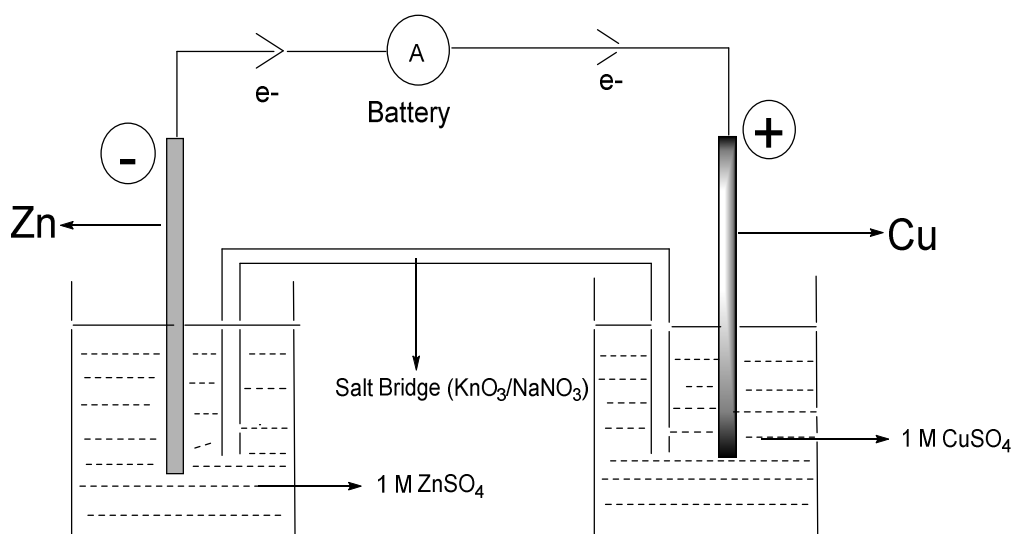


Fig. 2 Electrochemical Cell

At the anode (negative) $\text{Zn} \rightarrow \text{Zn}^{2+} + 2e^-$ ----- Oxidation

At the cathode (positive) $\text{Cu}^{2+} + 2e^- \rightarrow \text{Cu}$ ----- Reduction

Cell reaction $\text{Zn} + \text{Cu}^{2+} \rightarrow \text{Zn}^{2+} + \text{Cu}$

Representation of a galvanic cell

A galvanic cell can be represented as follows.

1. Anode is written on the left hand side whilst the cathode is written on the right hand side.
2. The metal is written first followed by the electrolyte for the anode and vice versa for the cathode.
3. The metal and the electrolyte are separated by a single vertical line or a semi colon.

4. If the concentration of the electrolyte is known, that may be represented within brackets next to the electrolyte.
5. A salt bridge is represented by two vertical lines separating the two half cells.
6. Thus the galvanic cell may be represented as



E.g. $\text{Zinc} | \text{ZnSO}_4(1M) || \text{CuSO}_4(1M) | \text{Copper}$

Standard Reduction Potential

The standard reduction potential of a substance can be determined by connecting the half-cell of the substance to the standard hydrogen electrode as the reference half-cell and measuring the resulting cell potential.

EMF of an electrochemical cell

The EMF of an electrochemical or galvanic cell is the algebraic sum of the single electrode potentials. The cell is written with the anode to the left and the cathode to the right. Hence, it can be calculated using the following equation

$$E_{\text{cell}} = E_{\text{right}} - E_{\text{left}}$$

Where E_{cell} – EMF of a cell, E_{right} – reduction potential of the cathode and E_{left} – reduction potential of the anode.

A positive value for E_{cell} indicates that the reaction is feasible. For the above galvanic cell, the Nernst's equation at 298 K can be written as

$$E_{\text{cell}} = (E_{\text{cathode}}^0 - E_{\text{anode}}^0) - \frac{0.0592}{n} \log \frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]}$$

Electrochemical Series

When elements are arranged in increasing order of their standard reduction electrode potential, it is called the electrochemical series.

Significance of the Electrochemical Series

The electrochemical series provides valuable and pertinent information such as

1. Relative ease of oxidation and reduction – A positive value indicates greater tendency to undergo reduction. A negative value indicates greater tendency to undergo oxidation. Hence, F_2/F^- system is very easily reduced whilst Li^+/Li system is very easily oxidized.

2. Relative tendency of metals towards displacement – The lesser the reduction potential of a metal, the more easily will it displace metals with greater reduction potential. For e.g., zinc will easily displace copper from copper sulphate solution. However, the reverse will not take place.

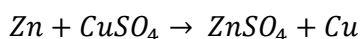


Table 1: Electrochemical series

Metal ion	Potential in volts
$\text{Li}^+ + \text{e}^- \rightarrow \text{Li}$	-3.05
$\text{K}^+ + \text{e}^- \rightarrow \text{K}$	-2.93
$\text{Ca}^{2+} + 2\text{e}^- \rightarrow \text{Ca}$	-2.90
$\text{Na}^+ + \text{e}^- \rightarrow \text{Na}$	-2.71
$\text{Mg}^{2+} + 2\text{e}^- \rightarrow \text{Mg}$	-2.37
$\text{Al}^{3+} + 3\text{e}^- \rightarrow \text{Al}$	-1.66
$\text{Zn}^{2+} + 2\text{e}^- \rightarrow \text{Zn}$	-0.76
$\text{Cr}^{3+} + 3\text{e}^- \rightarrow \text{Cr}$	-0.74
$\text{Fe}^{2+} + 2\text{e}^- \rightarrow \text{Fe}$	-0.44
$\text{Ni}^{2+} + 2\text{e}^- \rightarrow \text{Ni}$	-0.23
$\text{Sn}^{2+} + 2\text{e}^- \rightarrow \text{Sn}$	-0.14
$\text{Pb}^{2+} + 2\text{e}^- \rightarrow \text{Pb}$	-0.13
$\text{Fe}^{3+} + 3\text{e}^- \rightarrow \text{Fe}$	-0.04
$2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$	0.00
$\text{Cu}^{2+} + 2\text{e}^- \rightarrow \text{Cu}$	+0.34
$\text{Ag}^+ + \text{e}^- \rightarrow \text{Ag}$	+0.80
$\text{Pt}^{4+} + 4\text{e}^- \rightarrow \text{Pt}$	+0.86
$\text{Au}^+ + \text{e}^- \rightarrow \text{Au}$	+1.69
$\text{F}_2 + \text{e}^- \rightarrow 2\text{F}^-$	+2.87

3. Calculation of EMF of a cell—The EMF of a cell can be determined by the following equation.

$$E_{\text{cell}} = E_{\text{right}} - E_{\text{left}} \quad (\text{OR}) \quad E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}}$$

For a Zn/Cu system, the EMF can be calculated as follows.

$$\begin{aligned} E_{\text{cell}} &= E_{\text{Copper}} - E_{\text{Zinc}} \\ &= +0.34 - 0.76 \\ &= +1.10\text{V} \end{aligned}$$

4. Predicting spontaneity of a redox reaction - The EMF of the cell must be positive for a spontaneous redox reaction. If it is negative, the reaction is not feasible.

5. Calculation of equilibrium constant—The equilibrium constant K_{eq} can be calculated as follows.

$$\begin{aligned}
 E^0 &= \frac{RT}{nF} \ln K_{eq} \\
 &= \frac{2.303RT}{nF} \log K_{eq} \\
 \log K_{eq} &= \frac{nFE^0}{2.303RT} \\
 &= \frac{nE^0}{0.0592V}
 \end{aligned}$$

Batteries

One of the most practical applications of electrochemistry is the battery. In 1800, Volta discovered that certain liquids could be used as conductors to generate electrical power. Further experimentation led to the invention of the first voltaic cell also called a battery. Cruickshank, in 1802, invented the first electric battery which was later improved upon by John F. Daniel in 1836. Gaston Planté designed the first rechargeable battery in 1859. A battery is a self-contained electrical device that can produce electrical energy. Since electricity cannot be stored directly, an indirect form of storage is used. The advantage of batteries is in their versatility. They come in various sizes and shapes, can be assembled into packs, are portable and capable of supplying instant electricity.

An electrochemical cell is a device for generating electrical power. It consists of a positive and a negative electrode separated by an electrolyte which is capable of electrical conduction between the two electrodes. Most of the electrolytes used in batteries are aqueous solutions of acids, bases or salts. The latest technology uses polymers, ceramics, etc. as electrolytes. When two or more of such cells are electrically connected in series or parallel, it is called a battery. The essential parts of a battery include the electrodes, electrolyte, separator and the container. The electrodes must be very close to each other to minimize the internal resistance of the cell. Each electrode in the battery undergoes a half-cell reaction. The chemicals which undergo the reaction are called the active materials.

Glossary of Battery terms

1. **Battery** – A battery is an electrochemical device that can convert chemical energy obtained from its active materials into electrical energy by means of a redox reaction.
2. **Anode** – It is the negative electrode at which oxidation occurs involving loss of electrons.
3. **Cathode** – It is the positive electrode at which reduction occurs involving gain of electrons.
4. **Active materials** – The material in the electrodes that take part in the redox reaction generating electrical energy are called active materials.
5. **Electrolyte** – It is the medium that provides ionic conductivity between the two electrodes.

6. **Separator** – It is a thin, porous, insulating material that prevents electrical contact between two electrodes and hence short circuiting.
7. **Container** – It is a fully insulated plastic case that holds the various components of the battery inside it.
8. **Voltage** – It is the difference in potential between the two electrodes of a cell or the two terminals of a battery. Its unit is volts.
9. **Current** – It is the flow of electrical charges. Its unit is amperes.
10. **Primary battery** – These are cells that are designed to discharge current only once after which they must be discarded.
11. **Secondary battery** – These are batteries that can discharge current and be charged multiple times.
12. **Fuel cell** – A fuel cell is an electrochemical device that combines hydrogen fuel with oxygen to produce electricity, heat and water.
13. **Discharging** – It is an electrochemical process in a battery that generates current from the active materials when connected to an external load.
14. **Charging** – It is an electrolytic process in a battery in which external current is applied to regenerate the active materials.
15. **Capacity** – It is the amount of charge that can be withdrawn from a fully charged battery. It is usually expressed in ampere hours (Ah).
16. **Cycle life** – A cycle is a single charge-discharge of a battery. Cycle life is the number of cycles that can be obtained from a battery before it fails permanently.
17. **Shelf life** – It is the period over which a battery can be stored and yet retain its performance and use.
18. **Self-discharge** – It is the loss of capacity of a battery as a result of internal chemical reactions and short-circuit.
19. **Internal resistance** – It is the opposition to current flow that results from the various electronic and ionic resistances within the battery.
20. **Load** – It relates to energy consuming devices to which electric power is delivered.
21. **Load voltage** – It is the voltage of a battery when delivering a current.
22. **Open circuit voltage (OCV)** – An open circuit is a discontinuous circuit through which no current can flow. OCV is the voltage of a battery when there is no net current flow.
23. **Closed circuit voltage (CCV)** – A closed circuit is a circuit without interruption, providing a continuous path through which the current can flow. CCV is the voltage of a charged battery.
24. **Series connection** – It is the combination of opposite terminals of a cell to form a battery of greater voltage.

25. **Short-circuit** – It is the direct connection of positive and negative electrodes either internal or external to the battery.
26. **Power** – It is the product of voltage and current. Its unit is Watt.
27. **Energy** – It is the product of voltage and capacity. Its unit is Watt hour.
28. **Specific power/Power density**–It is the amount of power generated per unit weight or volume of the battery. Its unit is Watt/kg or Watt/m³.
29. **Specific Energy/Energy density** – It is the amount of energy generated per unit weight or volume of a battery. Its unit is Watt hour/kg or Watt hour/m³.

Lead Acid batteries

Lead acid batteries are the most common electrochemical energy storage devices. They are used in a variety of applications and have been in use since their invention by Gaston Planté in 1859. It is considered as the most successful secondary battery of all ages. They are reliable and cost effective for all types of vehicles. Lead acid batteries are affected by temperature and proper maintenance is required to maintain maximum life expectancy.

Chemistry of a lead acid battery

A lead acid battery consists of six two-volt batteries connected in series.

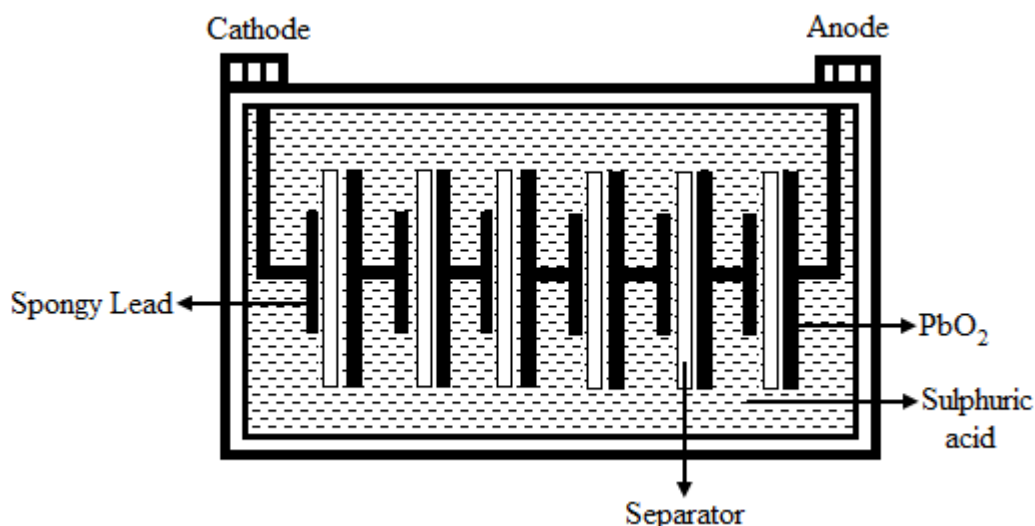


Fig. 3 Lead Acid Battery

Components

Anode – Spongy lead in a grid made up of lead antimony alloy

Cathode – Lead dioxide in a lead antimony grid

Electrolyte – Dilute H₂SO₄ (~25%, specific gravity – 1.265)

Separator – A thin sheet of insulating material such as wood, plastic, etc.

Cell Representation - $Pb|H_2SO_4(25\%)|PbO_2$

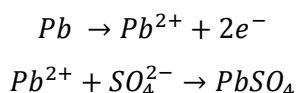
Cell voltage – 2.1 V

Specific energy density – 30-50 Wh/kg

Discharging

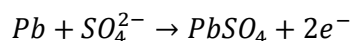
When the battery is connected to an external load, it discharges current which is a spontaneous redox reaction. The reactions involved are

At the anode during discharging



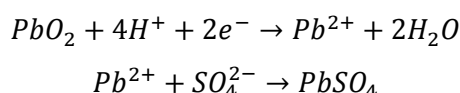
Lead sulphate sticks to the frame of the anode.

The overall reaction at the anode is



Electrons migrate from anode to the cathode.

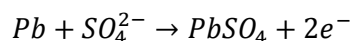
At the cathode during discharging



Lead sulphate sticks to the frame of the cathode. Electrons are consumed at the cathode.

Overall discharging reaction is

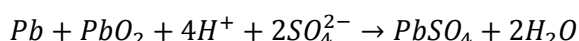
Anode reaction



Cathode reaction



Overall reaction



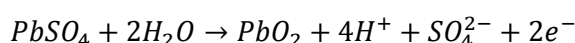
As the lead acid undergoes discharging, lead sulphate precipitates out and water is produced at the cathode. Consequently, the pH of the electrolyte increases and the specific gravity decreases.

Charging

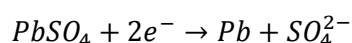
It is a non-spontaneous electrolytic process. The battery is connected to an external circuit and current is passed through the battery to regenerate the active materials.

At the anode during charging

Lead sulphate is oxidized by water to form lead dioxide

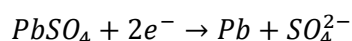


At the cathode during charging

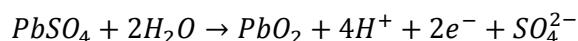


Overall charging reaction is

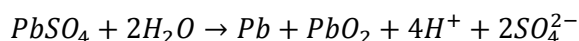
Cathode reaction



Anode reaction



Overall reaction



As the lead acid charges up, the lead sulphate on each electrode is removed and the pH of the electrolyte decreases. A minimum of 2V is required to recharge a lead acid battery.

Applications

- Used in automotive and traction applications
- Used as standby or emergency power for electrical installations
- Used as uninterrupted power supplies

Nickel-Cadmium batteries (NICAD)

The nickel cadmium battery was designed by Waldemar Jungner in 1899. It was the preferred battery as it had several advantages over the lead acid battery. For almost half a century, portable devices relied on this battery for working. Now, due to environmental regulations, it is limited to specialty applications.

Components

Anode – Cadmium

Cathode – Nickel (III) oxide hydroxide [NiO(OH)]

Electrolyte – KOH (~30%, specific gravity – 1.24)

Separator – A thin sheet of insulating polymer

Cell Representation - $Cd|KOH(30\%)|NiO(OH)$

Cell voltage – 1.2 V

Specific energy density – 45-80 Wh/kg

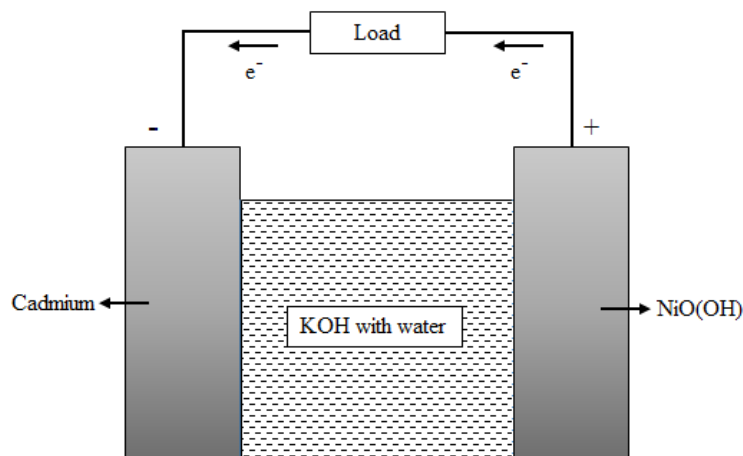
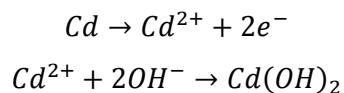


Fig. 4 Nickel-Cadmium battery

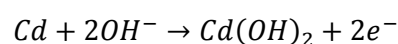
Discharging

When the battery is connected to an external load, oxidation occurs at the anode and reduction at the cathode to generate electric current.

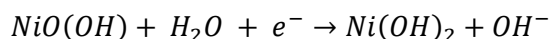
At the anode during discharging



The overall reaction at the anode is

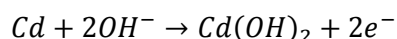


At the cathode during discharging

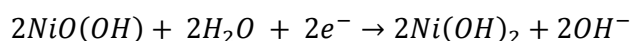


Overall discharging reaction is

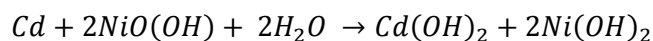
Anode reaction



Cathode reaction



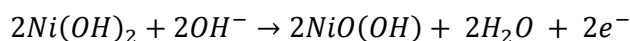
Overall reaction



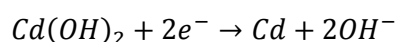
Charging

During the charging process, the active materials are regenerated through a non-spontaneous electrolytic process. The average charging voltage of a Nickel-Cadmium battery is 1.45 V.

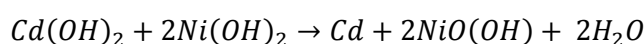
At the anode during charging



At the cathode during charging



Overall reaction is



No appreciable change occurs in KOH during charging or discharging and hence, the battery charge cannot be determined by checking the specific gravity of the electrolyte.

Applications

- Used in video cameras, cordless drills, laptops, phones, etc.
- Used as aircraft batteries, electric vehicles and stand by power supply.

Fabrication of Nickel-Cadmium batteries

There are generally two types of nickel-cadmium batteries each with their own characteristics.

1. **Pocket plate cells**– These have the active materials, positive and negative, pressed into individual pockets of perforated nickel plated steel plates or tubes. They are then connected in series. Plate designs vary depending on the requirements. Pocket plate cells are generally encased in a metal or plastic shell case.

Features

- Long and reliable service life
 - Quick recharge capability
 - Vent protection
 - Long shelf life
2. **Sintered plate cells**–Sintered metal is a type of metal in which the powdered metal is heated below its melting point, molded and compacted. The active materials are

impregnated onto a sintered nickel screen. Nickel nitrate or cadmium nitrate is taken in the sintered nickel screen and processed to give nickel hydroxide and cadmium hydroxide respectively.

Features

- High energy density
- Lower internal resistance
- Reliable and requires little maintenance
- Good cycle life

Lithium batteries

The first primary Lithium battery was made available commercially in the 1970s. The instability of the Lithium metal led to battery design using non-metallic lithium ions. The first lithium ion battery was commercialized in 1991 and soon it became the most popular and fastest growing in the market. The reasons for the choice of Lithium over other metals are

- It is the lightest of all metals with a density of 0.543 g/cc
- It has the greatest electrochemical potential
- It is a good reducing agent
- It is highly electropositive so higher voltage can be obtained depending on the cathode
- Good mechanical stability
- Can be easily fabricated

Advantages of Lithium batteries over other types of batteries

- They have a high cell voltage of 3.60V
- High cell voltage allows battery packs with only one cell
- Requires little maintenance
- Can operate at very low temperatures
- They pollute less than other batteries
- They have high energy density
- Rate of self-discharge is less than other batteries
- Different types are available.

Disadvantages of Lithium batteries

- They need to be protected from overcharging and discharging.
- They should never be discharged completely.
- They get heated up very quickly.
- Transportation of bulk Lithium batteries by air is restricted.
- They are expensive.
- It is still a developing field and is prone to changing technology.

Lithium Primary Cells

Primary lithium batteries are the most energy-dense electrochemical cells made for various electronic, medical and military applications. These cells have an energy density of around 250 Wh/kg which is much higher than that of Li-ion batteries. They are generally classified based on the type of electrolyte and cathode used.

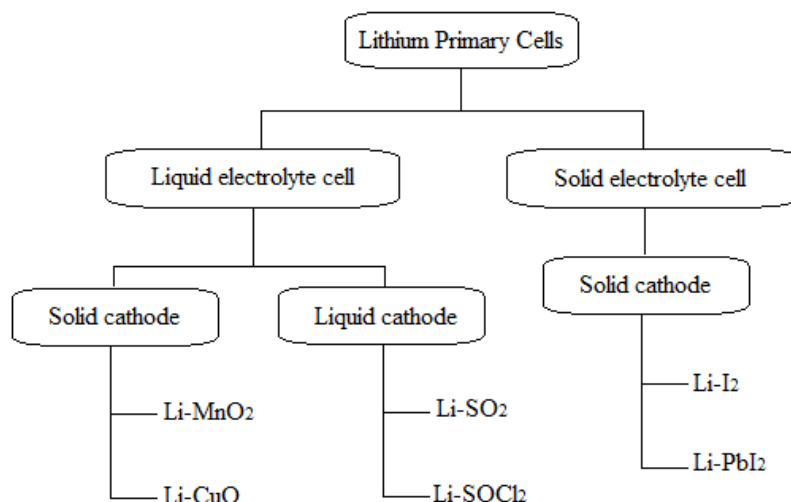


Fig. 5 Classification of Lithium Primary Cells

Lithium-Thionyl chloride cell

Components

Anode: Lithium foil

Cathode: Porous carbon filled with thionyl chloride

Electrolyte: Neutral solution of Lithium tetra chloroaluminate(LiAlCl_4) in thionyl chloride

Separator: Porous glass fibre

Cell Representation: $\text{Li}|\text{LiAlCl}_4, \text{SOCl}_2|\text{C}$

Energy density: 650 Wh/kg

Cell Voltage: 3.6 V

Operating Temperature: -55 to 85°C

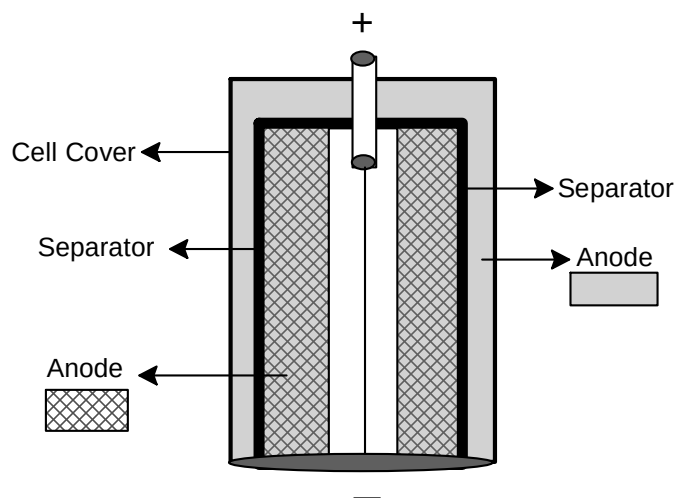


Fig. 6 Lithium-Thionyl chloride cell

Discharging

During discharge, the SOCl_2 is reduced at the cathode. Oxidation of Lithium at the anode results in the formation of LiCl at the anode.



Applications

- Used in automated meter reading (AMR)
- Used in alarms and security wireless devices
- Used in military radio communication

Lithium-Iodine cell

Components

Anode: Lithium

Cathode: Polyvinyl pyridine (PVP) with iodine (90% by weight)

Electrolyte: Thin film of Lithium iodide (LiI)

Separator: LiI acts as the separator as well as the electrolyte

Cell Representation: $\text{Li}|\text{LiI}|\text{I}_2(\text{PVP})$

Cell voltage: 2.8 V

Energy density: 100-200 Wh/kg

Operating temperature: Optimized at 37°C

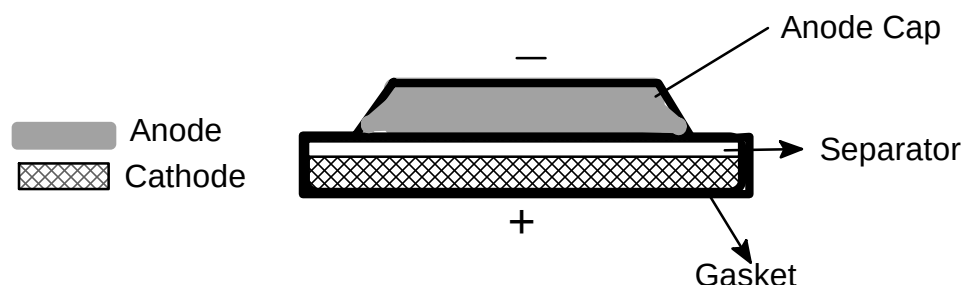


Fig. 7 Lithium-Iodine cell

Discharging

Lithium undergoes oxidation at the anode whilst Iodine undergoes reduction forming lithium iodide which acts as the electrolyte as well as the separator.



Applications

- Used in cardiac pacemakers.
- Used for random access memory (RAM) power supplies in electronics

Lithium-ion secondary battery

The Lithium ion battery was first designed by Gilbert Lewis in 1912. However, they have been commercially available only since the 1990s with a technology that is well proven for powering small electronic devices. A lithium ion battery does not contain lithium metal, only charged lithium ions. These ions shuttle back and forth between the two electrodes through the separator.

Components

Anode: Graphite (C_6)

Cathode: Lithium cobalt oxide ($LiCoO_2$)

Electrolyte: Lithium hexafluorophosphate ($LiPF_6$)

Separator: Micro perforated polymer (e.g. Polyethylene, polypropylene, etc.)

Cell Representation: $C_6 | LiPF_6 | LiCoO_2$

Cell Voltage: 3.7 V

Energy density: 160 Wh/kg

Operating temperature: $-20^{\circ}C$ to $60^{\circ}C$

Intercalation is the inclusion of a guest molecule or ion into the crystal lattice of a host molecule. This process is reversible and does not lead to any significant alteration in the structure of the host molecule. Graphite and $LiCoO_2$ are good intercalation compounds since they act as hosts to the Li^+ ion and hence are used in Lithium ion batteries.

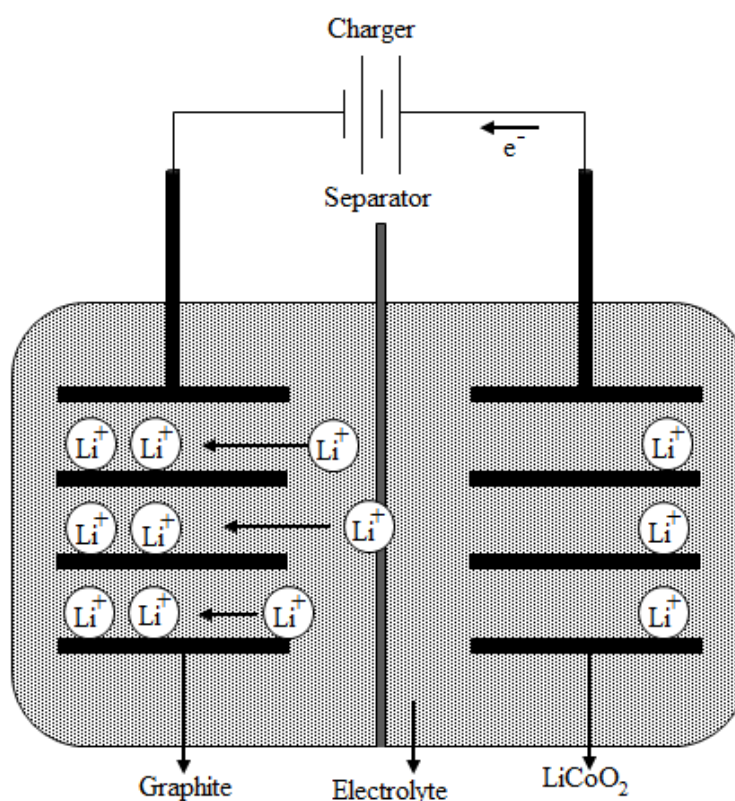
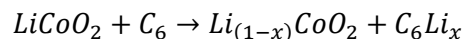
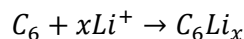
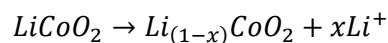


Fig. 8 Charging Mechanism in Lithium ion battery

Charging

During the charging process, the LiCoO_2 gives up some of its lithium ions which move through the electrolyte and are intercalated between the layers of graphite. The electrons move through the external circuit and reach the graphite electrode.



Discharging

During the discharging process, the lithium ions are extracted from graphite, travel through the electrolyte and are intercalated between the layers of LiCoO_2 . The electrons move through the external circuit and reach the LiCoO_2 electrode.

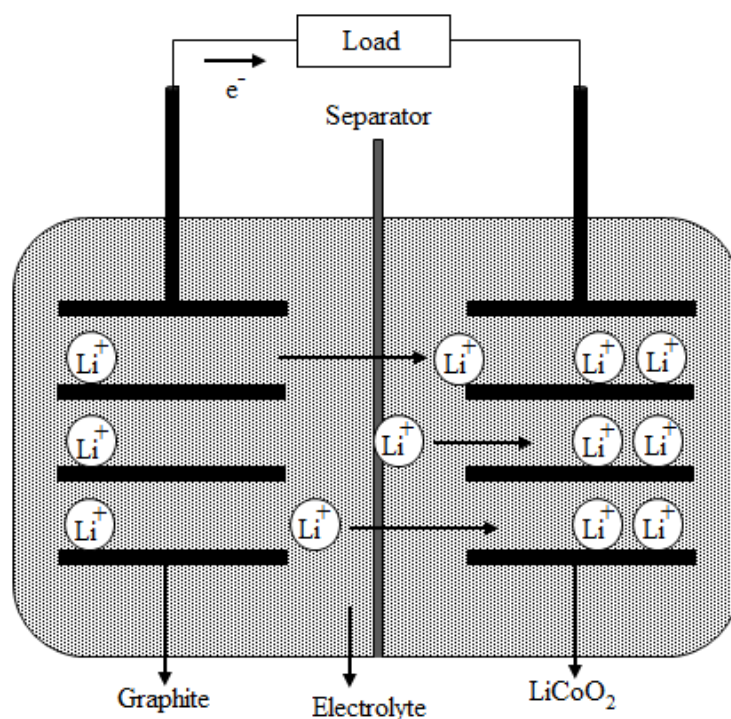
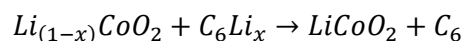
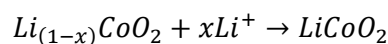
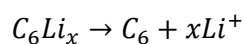


Fig. 9 Discharging Mechanism in Lithium ion battery

Applications

- Used as emergency power backup
- Used for electric vehicle powering
- Used for solar power storage

- Used for surveillance or alarm systems
- Used in portable electronic equipment

Fuel Cells

The first fuel cell was developed in 1839 by Sir William Grove. However, due to various technical problems, further research was not done on fuel cells until the 1930s when Francis Bacon produced the first practical fuel cell. They have many advantages over batteries as they produce more energy and are more environmentally friendly. The fuel cell for the Apollo spacecraft was designed in the 1960s and it was capable of producing 1.5 kW of electrical power. In addition to this, the fuel cell could also supply drinking water aboard the spacecraft. They are also being developed for military applications.

Advantages of fuel cells over batteries

- Since no combustion is involved, fuel cells have higher efficiency
- They are environmentally friendly since the by product is water
- They are reliable
- Fuel cell reactions do not degrade over time
- They can be located anywhere across the globe
- They offer a good alternative to power lines

Disadvantages of Fuel Cells

- They are expensive
- If fuels other than hydrogen are used, the efficiency decreases
- A continuous supply of fuel and oxygen is required

Classification of Fuel Cells

Fuel cells are classified based on the type of electrolyte used.

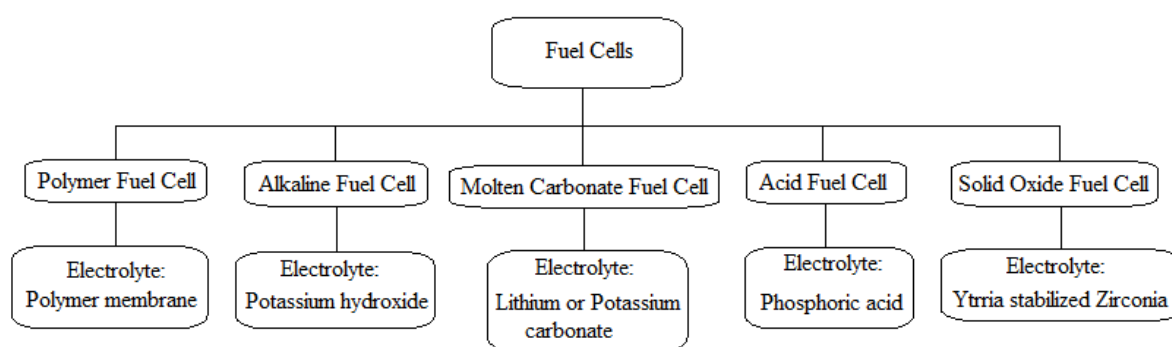


Fig. 10 Classification of Fuel Cells

Components of a Fuel Cell

Fuel cells consist of an anode and a cathode along with an electrolyte. Fuel cell reactants are called the fuel and the oxidant due to their electron donating and accepting properties respectively. Hydrogen is used as the fuel, but oxygen is also required for the redox reaction to take place and produce electricity. A single fuel cell produces a small amount of current

but when many are connected together, the output increases. A **fuel stack** is an arrangement of many individual fuel cells connected in series to generate electric current. Separators are used to separate individual fuel cells in a stack. If fuels other than hydrogen are used, a fuel reformer is generally required to convert the fuel to hydrogen. Thus a **fuel reformer** is a device that transforms a hydrocarbon fuel into pure hydrogen inside the fuel cell.

Hydrogen-Oxygen Fuel Cell (HOFC)

Components

Anode: Porous carbon impregnated with Platinum

Cathode: Porous carbon impregnated with Platinum

Electrolyte: 30-50% KOH in water

Cell Representation: $C, Pt | KOH(30\%) | C, Pt$

Charge carrier: OH^-

Fuel: Hydrogen

Oxidant: Oxygen

Operating Temperature: 70 – 120°C

Efficiency: 70%

Cell Output: 300 W to 5 kW

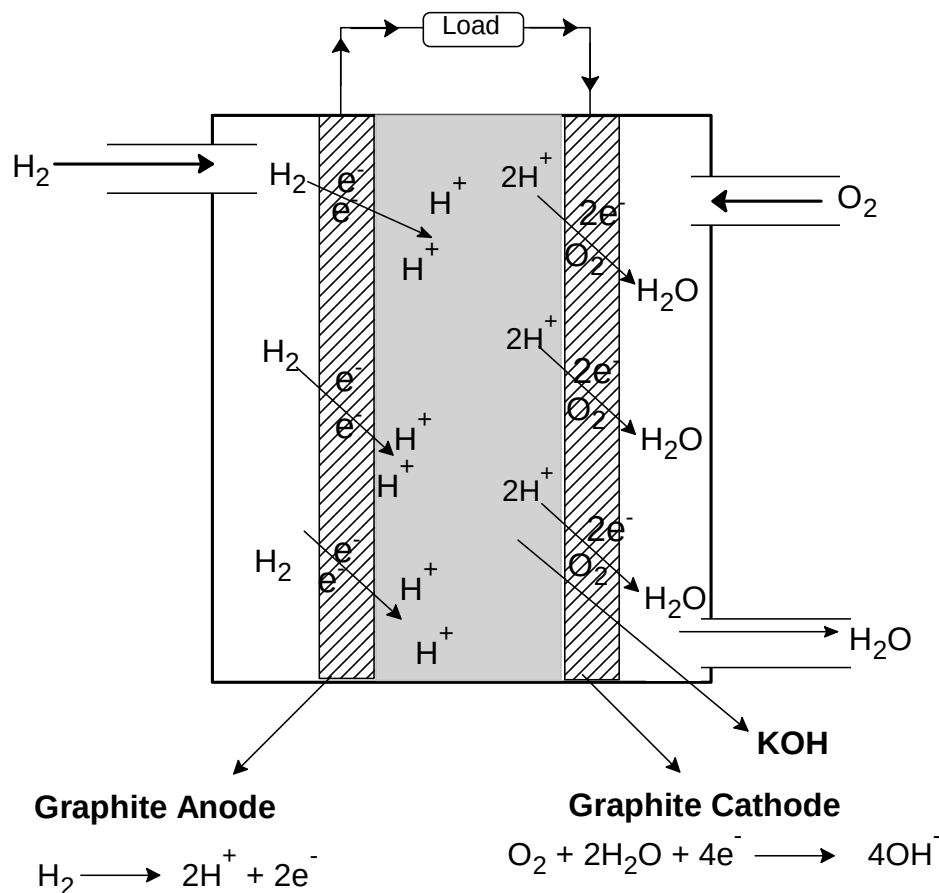
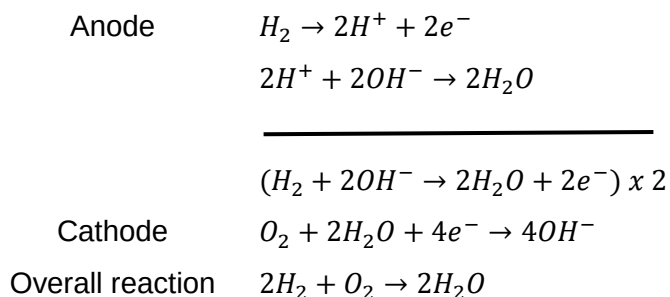


Fig. 11 Hydrogen-Oxygen Fuel Cell

This is a type of alkaline fuel that uses compressed hydrogen and oxygen as the fuel and oxidant respectively. A solution of potassium hydroxide in water is used as the electrolyte. The fuel is sent in from the side of the anode and the oxidant from the side of the cathode. They undergo oxidation and reduction respectively to produce electricity, water and heat.



Advantages

- It is environmentally friendly
- Potable water is produced as the by product
- It is highly efficient

Disadvantages

- Fossil fuels are necessary to produce hydrogen gas.
- It is flammable.
- Platinum electrodes are expensive.

Applications

- It provides electrical power in the space industry
- Drinking water is produced

Solid Oxide Fuel Cell (SOFC)

Components

Anode: Ni-ZrO₂ cermet

Cathode: Strontium doped Lanthanum Manganate (LaMnO₃)

Electrolyte: Ytria(Y₂O₃) stabilized zirconia (YSZ)

Cell Representation: $Ni - ZrO_2 | YSZ | LaMnO_3$

Charge carrier: O²⁻

Fuel: Hydrogen, Hydrocarbons, etc.

Oxidant: Oxygen

Operating Temperature: 650-1000°C

Efficiency: ~60%

Cell Output: up to 100 kW

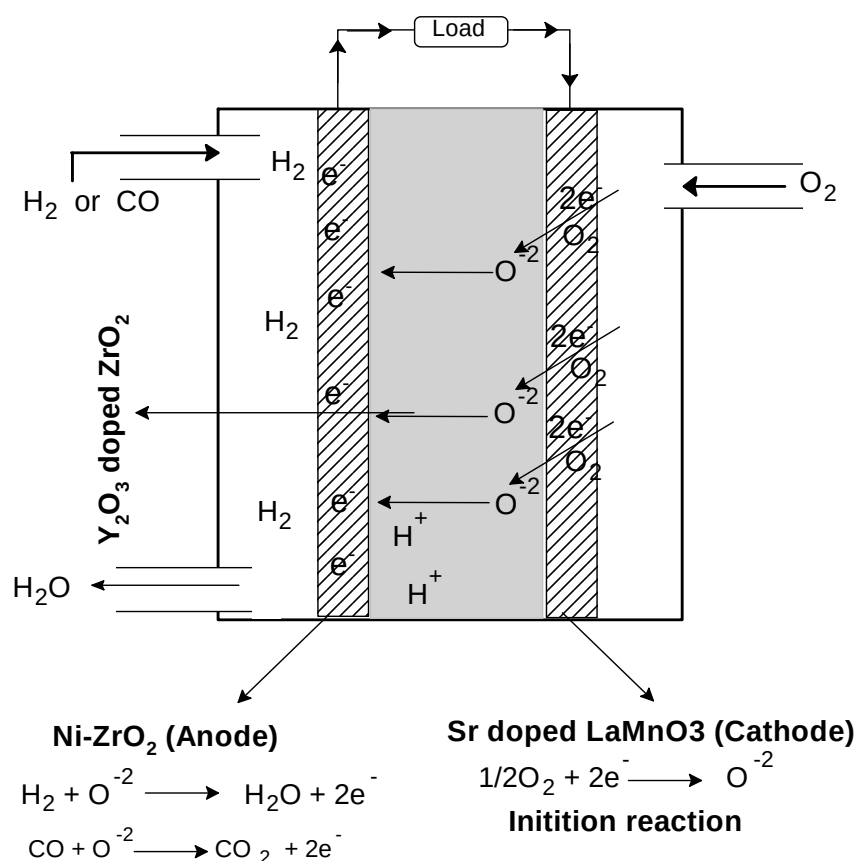
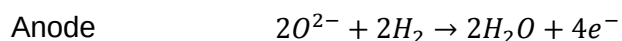


Fig. 12 Solid Oxide Fuel Cell

These fuel cells use a hard, ceramic compound as the electrolyte and operate at temperatures around 1000°C. At this high temperature, the ceramic becomes porous. When the fuel is passed through the anode, there is a flow of negatively charged oxygen ions through the electrolyte to oxidize the fuel. The oxygen is sent in from the side of the cathode.



Advantages

- Due to the high temperature involved, a fuel reformer is not required
- A catalyst is not required
- Fuels other than hydrogen can be used

Disadvantages

- The start-up takes a long time
- The solid electrolyte can crack due to the high temperature
- Thermal shielding is required to retain heat

Applications

- The waste heat can be used to make additional electricity
- They are used for mobile power generation
- They are used for powering urban cities

Questions:

1. Explain the charging and discharging reactions in a lead acid battery.
2. Explain the chemistry of charging and discharging in a nickel-cadmium battery.
3. What are the advantages of lithium cells over other conventional batteries? Explain the working of a lithium-iodine cell.
4. Explain the discharging reactions in a lithium-thionyl chloride cell.
5. Describe the charging and discharging reactions in lithium-ion batteries.
6. What is a fuel cell? Discuss the construction and working of the hydrogen-oxygen fuel cell with a neat diagram.
7. Explain the working of a solid oxide fuel cell with a suitable diagram.

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Introduction: Definition. Types: Dry corrosion: Mechanism – Pilling – Bedworth rule – Wet corrosion: Mechanism. Types: Galvanic corrosion and differential aeration cell corrosion. Galvanic series and its significance. Factors influencing corrosion. Corrosion prevention: Material selection and design – Cathodic protection. Protective coatings: Paints – Constituents. Mechanism of drying of drying oils.

Introduction

Metals and alloys are used in residential and commercial structures such as bridges and trusses, automobiles, passenger trains, railroad cars, ships, piers, docks, bulkheads, pipelines and storage tanks and construction of motors. Aluminum alloys find a variety of uses ranging from aircraft frames to canned food containers to electronic applications. Copper is used in water pipes, in electrical connectors, and in decorative roofs. Chromium and nickel, to name just two more metals, are used in the production of stainless steels and other corrosion-resistant alloys. In addition, metals are also used in various electronic applications, such as computer discs, printed circuits, connectors, and switches. Metals are even used in the human body as hip or knee replacements, as arterial stents, and as surgical plates, screws, and wires. All common metals tend to react with their environment to different extent and at different rate. Thus, corrosion is a natural phenomenon and is the destructive attack of a metal by its environment so as to cause a deterioration of the properties of the metal.

Definition

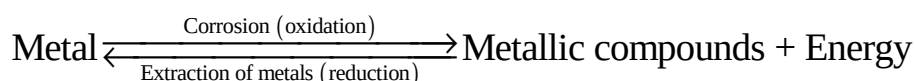
Corrosion is defined as, “the deterioration or destruction of metal by chemical or electrochemical attack by its environment”. The term corrosion is usually applied to the degradation of plastics, concrete and wood, but however typically refers to metals.

Examples of corrosion:

- (i) Rusting of iron – a reddish brown scale formation on iron and steel objects due to the formation of hydrated ferric oxide.
- (ii) Green scale formed on copper vessels – it is due to the formation of basic cupric carbonate ($\text{CuCO}_3 + \text{Cu(OH)}_2$).

Chemistry of Corrosion

Metals are extracted from their ores or naturally occurring compounds by applying enormous amount of energy. These metals can therefore be regarded as being in a metastable state and will tend to lose their energy by reverting to compounds more or less similar to their original states. Since most metallic compounds, and especially corrosion products, have little mechanical strength a severely corroded piece of metal is quite useless for its original purpose.



Gravity of Corrosion

The process of corrosion is slow and occurs only on surfaces of metals and the losses incurred, due to corrosion are enormous waste of machines, equipments and different types of metallic products. The severity of the problem may be made clear by the approximate estimate of loss of metal due to corrosion as 2.5 billion dollars per annum all over the world.

Types of Corrosion

Corrosion can be broadly classified into two types.

1. Dry or Chemical corrosion
2. Wet or Electrochemical corrosion

1. Dry or Chemical Corrosion

Dry or Chemical corrosion is defined as “the deterioration or destruction of metal by chemical attack of gases such as oxygen, halogens, hydrogen sulphide, sulphur dioxide, oxides of nitrogen in absence of moisture”.

When a metal is exposed to a gas, it adsorbs the gas and slowly reacts with it and forms the corrosion product. The corrosion product may be insoluble or soluble or a liquid. In the first case when it is insoluble, a solid film of the corrosion product is usually formed on the surface of the metal which protects the metal from further corrosion. However, if a soluble or a liquid corrosion product is formed, then the metal is exposed to further attack. There are three main types of chemical corrosion.

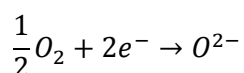
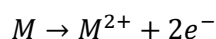
a. Oxidation Corrosion

Oxidation corrosion is defined as “the deterioration or destruction of metal by chemical attack of oxygen in absence of moisture”.

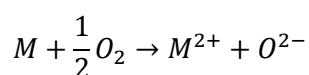
Oxygen is mainly responsible for the corrosion of most metallic structures as compared to other gases and chemicals. Alkali and alkaline earth metals (e.g., Na, Ca, Mg etc.) suffer extensive oxidation even at low temperatures, whereas at high temperatures, practically all metals except Ag, Au and Pt are oxidized.

Mechanism

When a metal surface is exposed to a gas such as oxygen at room temperature the gas gets adsorbed physically. The gas molecules are attracted to the metal surface by Vander waals forces of attraction. When the temperature is increased, electrons are transferred from the metal to oxygen resulting in the formation of metal ions and oxide ions simultaneously. The metal ions and the oxide ions combine together to form the metal oxide.



The overall reaction may be represented as,



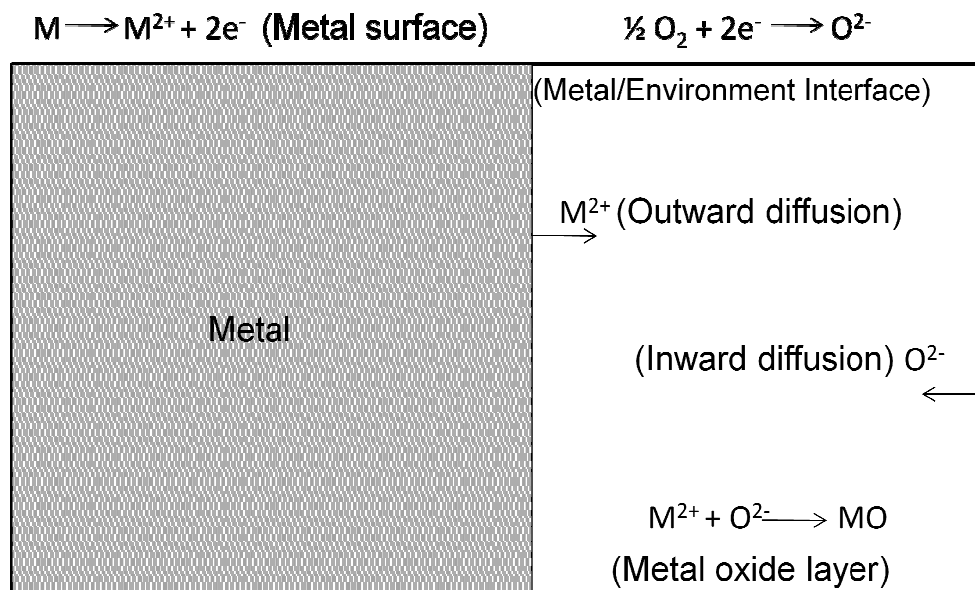


Fig. 1 Schematic representation of Oxidation Mechanism

The formation of metal oxide film at the surface actually tends to restrict further oxidation. For oxidation to continue either the metal ions must diffuse outwards through the scale to the surface or the oxide ions must diffuse inwards through the scale to the underlying metal. Both transfers occur (Fig. 1) but the outward diffusion of metal ions is likely to be more rapid due to the fact that cations are smaller in size compared to the oxide ions.

Nature of the Oxide

The nature of metal oxide layer formed on the surface of the metal during oxidation decides the further corrosion takes place or not. This oxide layer may be

- (i) **Unstable** – If the metal oxide layer formed is unstable then it decomposes back into the metal and oxygen. Therefore further corrosion will not take place on these metals. Eg: Ag, Au, Pt.

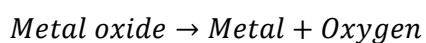


Fig. 2 Unstable oxide layer

- (ii) **Volatile** – If the metal oxide layer formed is volatile it volatilizes as soon as it is formed, thus leaving the underlying metal surface exposed for further attack. This

causes rapid and continuous corrosion. E.g. Molybdenum oxide (MoO_3) is volatile in nature.

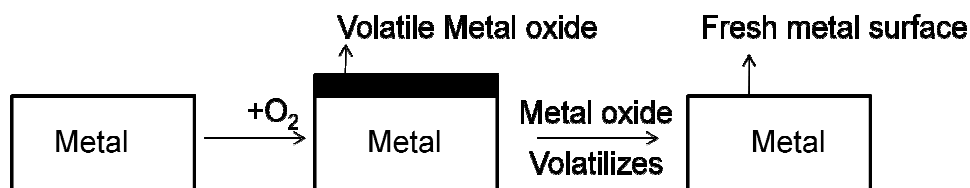


Fig. 3 Volatile oxide layer

- (iii) **Porous** – If the metal oxide layer formed has pores or cracks the atmospheric oxygen can attack the exposed surface of metal and cause further corrosion until the entire metal is completely converted into its oxide. Eg. Li, K, Na, Ca, Mg etc.

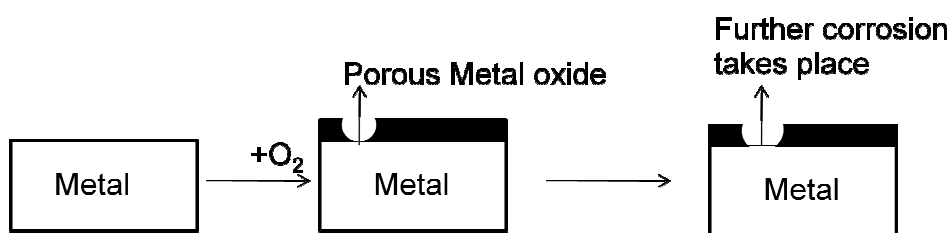


Fig. 4 Porous oxide layer

- (iv) **Stable** – A stable layer is fine grained structure and can adhere tightly to the parent metal surface. Such a layer may be protective or non-protective and therefore can expose or shield the metal surface from oxygen attack. Eg: Al, Sn, Pb, Cu, Cr etc. form stable metal oxide layers.

Pilling and Bedworth Rule

The protective and non-protective nature of the oxide layer can be predicted on the basis of Pilling – Bedworth rule. According to this rule an oxide layer is protective or non – porous, “if the volume of the oxide is at least as great as the volume of the metal from which it is formed” and the oxide layer is porous or non – protective “if the volume of the oxide is less than the volume of the metal from which it is formed.” For example, heavy metals such as Al, Cr, Pb, Sn etc. form a protective oxide film and prevent further corrosion. Whereas metals like alkali (Li, Na, K etc.) and alkaline earth metals (Be, Ca, Sr etc.) form porous oxide films, which allow further diffusion of oxygen to come in contact with the fresh metal surface and results in severe corrosion.

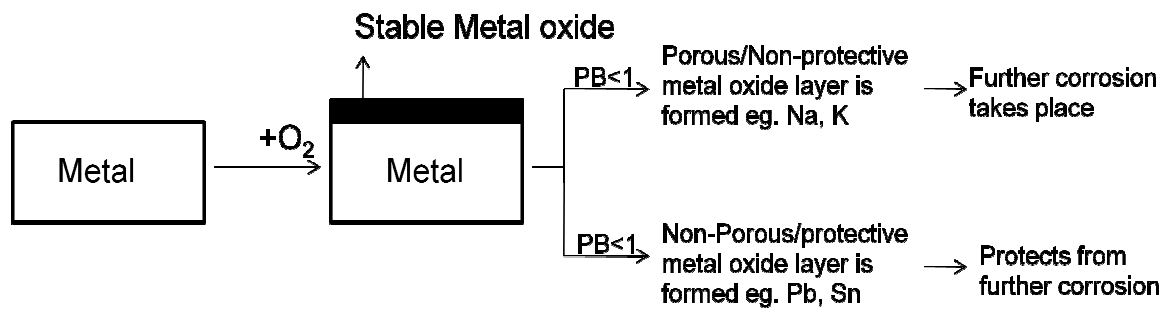


Fig. 5 Protective and Non-protective layer

$$\text{Pilling Bedworth Ratio} = \frac{\text{Volume of oxide layer formed on metal}}{\text{Volume of metal consumed during oxidation}}$$

B. Corrosion by Other gases

In dry atmosphere, gases like Cl₂, SO₂, H₂S, NO_x react with metals and form corrosion products which may be protective or non-protective. When dry Chlorine reacts with Ag it forms a protective AgCl layer, while with Sn it forms a volatile SnCl₄. The extent of corrosion of a particular metal depends on the chemical affinity of the metal and the gas involved.

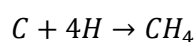
Hydrogen sulphide attacks metals forming corresponding metal sulphide and release atomic hydrogen. The hydrogen attacks the metal in two ways:

(I) Hydrogen Embrittlement

At room temperature the atomic hydrogen diffuse readily into the metal and collects at the void spaces, where the atomic hydrogen combines to form hydrogen gas. The accumulation of the gas develops a high pressure causing cracks and blisters in the metal. This condition is known as hydrogen embrittlement.

(II) Decarburization

At higher temperatures molecular hydrogen undergoes dissociation to form atomic hydrogen. The active atomic hydrogen attacks the steel and combines with the carbon present in the steel to form methane gas which collects in the voids. As the pressure increases due to the accumulation of the gas, cracks occur in steel, a condition known as decarburization. As a result of decarburization the metal loses some of its strength and ductility.



C. Liquid Metal Corrosion

In several industries, molten metal passes through metallic pipes and causes corrosion due to dissolution or internal penetration. For example liquid metal mercury dissolves most metals by forming amalgams, thereby corroding them. This type of corrosion occurs in devices used for nuclear power.

2. Wet or Electrochemical Corrosion

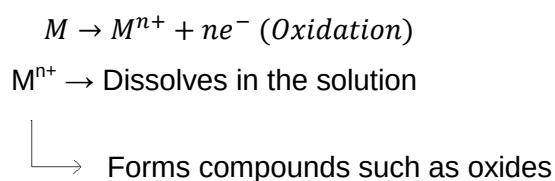
Wet or Electrochemical corrosion is defined as “the deterioration or destruction of metal by electrochemical attack of reactive liquids such as acids, bases, electrolytes in presence of moisture”.

The conditions for wet corrosion to occur are

- (i) When a metal is partially immersed in an electrolyte and metal is exposed to varying amount of oxygen
- (ii) When two dissimilar metals or alloys are in contact with each other and immersed in an electrolyte.

This type of corrosion occurs, due to the existence of separate anodic and cathodic areas between which current flows through the conducting solution. At anode oxidation takes place, so anode undergoes metal dissolution. Hence, corrosion always occurs at anodic areas.

At anodic area,



At cathode reduction reaction takes place. Since the metal cannot be reduced further some of the constituents present in the corrosion medium take part in the cathodic reaction to form anions like OH^- , O^{2-} . Hence the metal atoms at the cathodic areas are unaffected by the cathodic reaction.

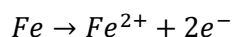
The electrons liberated at the anode migrate to the cathode constituting corrosion current. The metal ions liberated at the anode and some anions (like OH^- , O^{2-}) formed at the cathode diffuse towards each other through the conducting medium and form corrosion product somewhere between the anode and the cathode. Corrosion of metal continues as long as both anodic and cathodic reactions take place.

Mechanism of Wet or Electrochemical Corrosion

Electrochemical corrosion involves flow of electron – current between the anodic and cathodic areas. Anodic reaction is a simple oxidation reaction in which metal atoms are converted into their ions liberating electrons.



For example when iron undergoes corrosion,



The cathodic reaction takes up electrons either by (a) evolution of hydrogen or (b) absorption of oxygen depending on the nature of the corrosive environment. Correspondingly the corrosion types are known as hydrogen type corrosion and oxygen type corrosion.

a). Evolution of hydrogen

In acidic environment the anode undergoes metal dissolution with the liberation of electrons and these electrons move from anode to cathode where H^+ ions are reduced and release H_2 gas. This type of corrosion is generally considered as the displacement of hydrogen ions from the acidic solution by the metal ions. All metals above hydrogen in electrochemical series have a tendency to show this type of corrosion. In hydrogen evolution type of corrosion, anodic area is large as compared to its cathodic area.

At Anode: $Fe \rightarrow Fe^{2+} + 2e^-$ (Oxidation)

At Cathode: $2H^+ + 2e^- \rightarrow H_2 \uparrow$ (Reduction)

The overall reaction is, $Fe + 2H^+ \rightarrow Fe^{2+} + H_2 \uparrow$

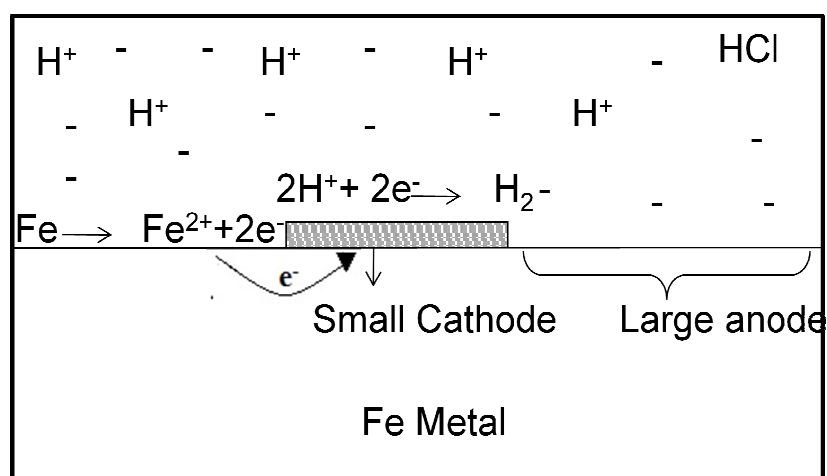


Fig. 6 Mechanism of wet corrosion by hydrogen evolution

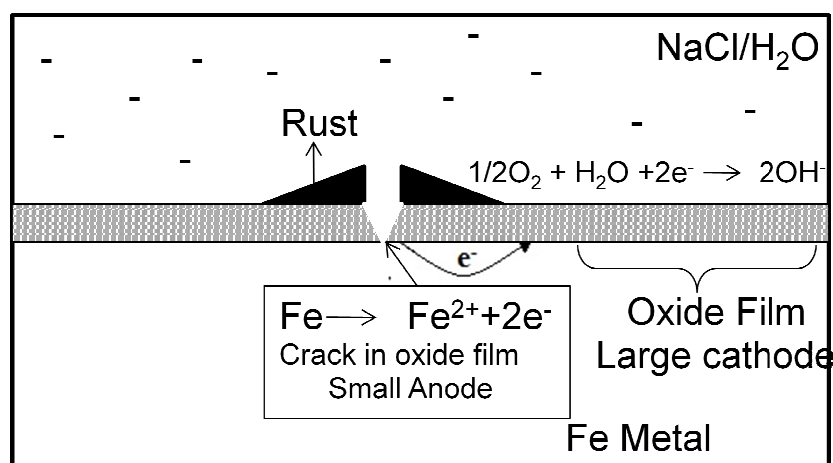


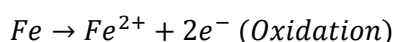
Fig. 7 Mechanism of wet corrosion by oxygen absorption

b). Absorption of oxygen

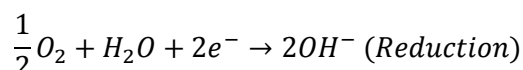
In Neutral or Alkaline environment and in the presence of oxygen this type of corrosion takes place. Due to oxidation corrosion the metal surface is covered with oxide layer. The small

cracks on oxide layer create small anode area and rest of the metal oxide layer acts as cathode area. The following chemical reactions occur at anode and cathode.

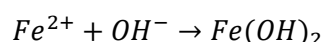
At the anode the metal (iron) undergoes metal dissolution into ferrous ions with the liberation of electrons.



The liberated electrons flow from anode to cathode through iron metal, where the dissolved oxygen takes electrons and reduced to OH^{-} ions

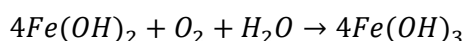


The Fe^{2+} ions (at anode) and OH^{-} ions (at cathode) diffuse and combine to form ferrous hydroxide.



Since smaller Fe^{2+} ions diffuse more rapidly than OH^{-} ions, their combination occurs more commonly near the cathodic area. The corrosion occurs near the anodic area and the corrosion product deposits near the cathodic area.

If enough oxygen is present, ferrous hydroxide is easily oxidized to ferric hydroxide.



This product is called yellow rust and it is chemically $Fe_2O_3 \cdot H_2O$.

If the supply of oxygen is limited the corrosion product may be black anhydrous magnetite, Fe_3O_4 . Generally, presence of oxygen greatly accelerates both corrosion and rust formation.

Comparison between Chemical and Electrochemical Corrosion

S. No	Chemical Corrosion	Electrochemical Corrosion
1.	It is also known as dry corrosion	It is also known as wet corrosion
2.	It occurs in the dry state	It occurs in presence of conducting medium.
3.	It involves direct attack of chemicals on the metal surface.	It involves formation of electrochemical cells.
4.	Follows adsorption mechanism	Follows electrochemical reaction mechanism
5.	The process is slow.	It is a rapid process.
6.	Corrosion products are produced at the site of corrosion	Corrosion occurs at anode but the product is deposited at cathode.
7.	The process of corrosion is uniform.	It depends on the size of the anodic part of metal.
8.	Examples Rusting of iron in dry state, reaction of dry HCl gas on Fe and tarnishing of Ag in air containing	Examples Rusting of iron in moist atmosphere and dezincification of brass



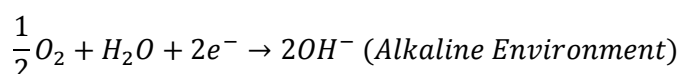
Types of Electrochemical Corrosion

1. Galvanic Corrosion

This type of electrochemical corrosion is also called bimetallic corrosion. When two dissimilar metals are connected and exposed to an electrolyte, they undergo galvanic corrosion. The anodic metal will be oxidized and it will undergo corrosion. Zinc and copper metals connected with each other in an electrolyte medium form a galvanic cell. Zinc acts as anode and undergoes corrosion while cathode will be unaffected.

At anode (Oxidation): $\text{Zn} \rightarrow \text{Zn}^{2+} + 2e^-$ Corrosion

At cathode (Reduction): $2\text{H}^+ + 2e^- \rightarrow \text{H}_2$ (Acidic Environment)



OR

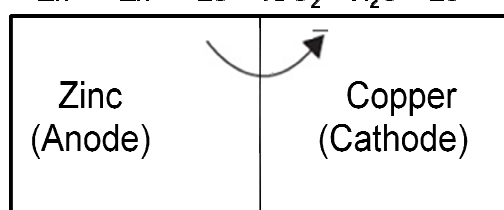
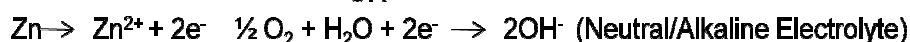


Fig. 8 Galvanic corrosion

Fig. 8 represents Zn-Fe bimetallic couple. Of the two metals, zinc (more active) dissolves at a faster rate compared to iron (less active). Here zinc act as the anode and undergo corrosion, whereas, iron act as cathode and is protected from corrosion. Similarly, a bimetallic couple can be set up with iron and copper in which, iron (more active) undergo corrosion at a faster rate whereas Cu (less active) is protected from corrosion.

1. Galvanic corrosion can be avoided by coupling metals close to each other in electrochemical series.
2. Fixing insulating material between two metals.
3. By using larger anodic metal and smaller cathodic metal.

Example of galvanic corrosion: 1. Steel screws in brass marine hardware, 2. steel pipe connected to copper plumbing, 3. steel propeller shaft in bronze bearing, 4. zinc coating on mild steel, 5. lead-tin solder around copper wires.

2. Differential aeration Corrosion or Concentration Cell Corrosion

Corrosion of metals arising as a result of the formation of an oxygen concentration cell due to the uneven supply of air on the metal surface is known as differential aeration corrosion. If

a metal rod is dipped in an electrolyte is less oxygenated and acts as anode which gets corroded easily and the portion above water acts as cathode which is protected.

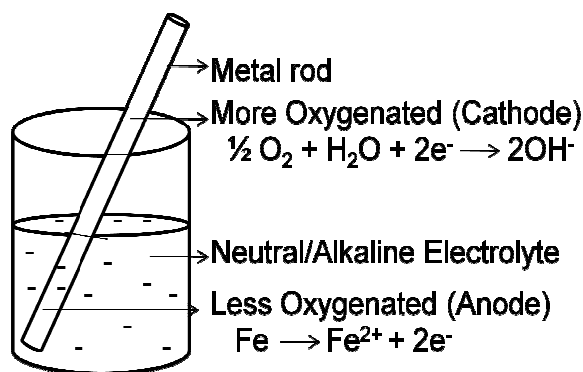


Fig. 9 Differential aeration corrosion

The system will act as a concentration cell and the metal undergoes oxidation or dissolution and oxygen reduces to hydroxide ions in presence of moisture.

At Anode (Less Oxygenated): $Zn \rightarrow Zn^{2+} + 2e^-$

At Cathode (More oxygenated): $\frac{1}{2} O_2 + H_2O + 2e^- \rightarrow 2OH^-$

There are different types of differential aeration corrosion. Some examples are pitting corrosion, pipeline corrosion, corrosion in wire fence and water line corrosion.

Pitting Corrosion

It is a localized corrosion in which a pit or hole is formed due to local straining of metal by chemical attack and leads to the formation of a local galvanic cell. The crack portion acts as anode and rest of the metal surface acts as cathode. The anodic area will be corroded and the formation of a pit is observed. This type of corrosion is called pitting corrosion (Figure 10). Metals owing to their corrosion resistance to their passive state show pitting and ultimately result in formation of passivity. Presence of external impurities such as sand, dust, scale embedded on the surface of metals lead to pitting. For example, stainless steel and aluminium show pitting corrosion in chloride solution. Pitting corrosion can be explained from the Fig. 10. When a drop of water or NaCl solution is placed on a metal surface, the area below the drop of water, which does not have much access to oxygen (less oxygenated), becomes anodic with respect to the other areas (More oxygenated), which are freely exposed to air.

The larger cathodic area demand more electrons for reduction from the smaller anodic area covered by the drop of solution. Therefore, more and more metal is removed from the smaller anodic area, which results in the formation of a hole or a pit. Pit formed is now more away from the atmosphere which act as better anode and corrosion proceeds at a very fast rate.

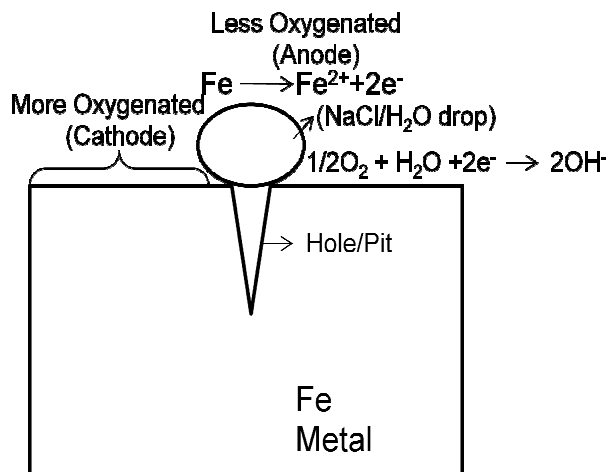
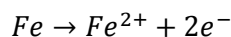
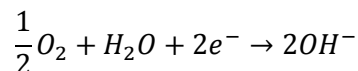


Fig. 10 Pitting corrosion

At anode the metal (iron) undergoes oxidation:



At cathode, oxygen undergoes reduction:



Pitting is initiated by,

1. Localized chemical or mechanical damage to the protective oxide film
2. Localized damage to, or poor application of, a protective coating
3. Presence of non-uniformities in the metal structure of the component, e.g. nonmetallic inclusions.

Stainless steels are sensitive to pitting corrosion, but other metals, such as passive iron, chromium, cobalt, aluminium, copper and their alloys are prone to this form of damage.

Factors Influencing the Rate of Chemical and Electrochemical Corrosion

The type, speed, cause and seriousness of corrosion depends upon the following factors that can be classified based on the

1. Nature of the metal
2. Nature of the environment

1. Nature of the Metals

a. Electrode potential or position in EMF series

Electrode potential decides the corrosion rate. A metal which is at higher position in emf series undergoes corrosion when connected to another metal below it. If the difference between the positions of the two metals in the emf series is high causes faster corrosion at anodic metal.

b. Hydrogen overvoltage

In case of zinc metal placed in a normal solution of H_2SO_4 , reaction takes place forming bubbles of hydrogen gas on zinc surface. The process is slow due to high hydrogen overvoltage of zinc (0.76 V). The addition of few drops of CuSO_4 accelerates corrosion due to decrease of hydrogen overvoltage (0.34 V). Hence corrosion rate is inversely proportional to hydrogen overvoltage.

c. Ratio of cathodic to anodic region

Smaller the area of anode compared to cathode will lead to faster corrosion of anode. It is because the corrosion current at anode and cathode will be same. Larger cathodic area will demand more electrons from small anodic area which will be fulfilled by fast reaction at anode (oxidation), i.e. rapid corrosion. Thus if the metal has small anode and large cathodic region, corrosion rate is very high.

d. Nature of oxide film

An oxide film is formed by the reaction between metal and oxygen on the surface of the metal. If this oxide film is porous or non-protective, the atmospheric oxygen can diffuse through it and corrosion takes place. If the volume of metal oxide is more than the volume of metal no further corrosion occurs.

e. Purity of metals

Pure metal resists corrosion, while impurities in a metal form a local galvanic cell (metal as anode and impurity as cathode) and result in corrosion of the metal. Corrosion rate increases with increase in impurities. For alloys the system is a homogeneous solid solution, hence no local action and no corrosion. Higher the percentage of impurity higher will be the rate of corrosion.

f. Physical state of the metal

Small granular metal will corrode faster than the larger one. Also the type of structure formed by a metal will have effect on the corrosion rate. A bent metal is rapidly corroded due to stress.

g. Volatility and solubility of corrosion product

Volatility and solubility of corrosion product also influences the corrosion rate. MoO_3 and SnCl_4 are volatile and lead to corrosion at a higher rate. In case of soluble corrosion product, corrosion will be enhanced by water and metal surface will be exposed for further corrosion.

2. Nature of the Environment*a. Temperature*

The rate of corrosion increases by rise in temperature. At higher temperature, passive metals also become active and undergo corrosion.

b. Humidity

Rate of corrosion will be high when the relative humidity of the environment is high. Presence of moisture enhances electrochemical type of corrosion.

c. Impurities in atmosphere

Pollutants like H_2S , SO_2 , CO_2 and acid vapours make the environment acidic and increases rate of corrosion.

e. pH of the corrosive environment

Acidic environment ($\text{pH} < 7$) is more corrosive than alkaline or neutral environment ($\text{pH} > 7$) and thus corrosion rate is higher. Pourbiax relation between pH of medium and potential of metal deals with the corrosion process and it gives information to reduce corrosion.

f. Nature of ions present

Cu^{2+} ions present in the vicinity of Fe, accelerate corrosion, while silicates present in the vicinity resist corrosion.

g. Polarisation of electrodes

More the polarisation at electrodes, less current will be passed and hence less corrosion.

Galvanic Series

The galvanic series is 'the arrangement of all the metals and alloys according to their relative reactivity in a given environment. The galvanic series determines the nobility of material and alloys. When two metals are submerged in an electrolyte, while electrically connected the less noble will experience the corrosion. The rate of corrosion is determined by the nature of electrolyte and the difference in nobility. The difference can be measured as a difference in voltage potential.

For example, in Zn – Al couple, zinc which is below aluminium in the electrochemical series is corroded while aluminium is protected from corrosion. This is due to the presence of protective oxide layer on Al metal surface (Al_2O_3) which protects it from corrosion. In view of this, the electrode potential of various metals and their alloys was measured using Calomel electrode as the reference electrode and immersing the metal or alloy in sea water, fresh water etc.

Significance of Galvanic series

1. Although only one Emf Series exists, there can be several Galvanic Series with various environments and differences in tendency to form surface films. In general, therefore, a specific galvanic series exists for each environment, and the relative positions of metals in such series may vary from one environment to another.
2. When two dissimilar metals are coupled together the corrosion depends not only on how far apart they are in the galvanic series (potential difference), but also on their relative areas and the extent to which they are polarized.
3. The potential difference of the polarized electrodes and the conductivity of the corrosive environment determine how much current flow between them.

Active (or Anodic) ↑ ↓ Noble (or cathodic)	1. Mg 2. Mg alloys 3. Zn 4. Al 5. Cd 6. Al alloys 7. Mild steel 8. Cast iron 9. High Ni cast iron 10. Pb – Sn solder 11. Pb 12. Sn 13. Inconel 14. Ni – Mo – Fe alloys 15. Brasses 16. Monel metal (7% Ni, 30% Cu. Rest Fe) 17. Silver solder 18. Cu 19. Ni 20. Chromium stainless steel 21. 18 – 8 stainless steel 22. 18 – 8 Mo stainless steel 23. Ag 24. Ti 25. Graphite 26. Au 27. Pt
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Corrosion Prevention

The basic methods of corrosion prevention are

1. Modification on Metal
2. Modification on Environment

1. Modification on Metal

a. Material Selection and Design

Corrosion in metals can be prevented right from the initial step of making equipments like choosing the appropriate metal which does not undergo corrosion and framing a suitable structure for the equipment.

Material Selection

The first and the foremost method of controlling corrosion is the selection of right type of material. The material selection should be made not only on its cost and structure but also on its chemical properties and its environment.

1. Noble metals are more resistant to corrosion. But they cannot be used for general purpose since they are costly.
2. The next choice is the selection of pure metal. Even the presence of minute amount of impurities cause heterogeneity which increases the rate corrosion. For example minute quantities of Fe in Mg or Pb in Zn leads to extensive corrosion.
3. Alloying improves corrosion resistance e.g. Presence of Chromium in stainless steel. It produces an exceptionally coherent oxide film which is self healing and protects steel from corrosion.
4. Heat treatment like annealing helps to reduce internal stresses and reduces corrosion.
5. If an active metal is selected, it should be insulated from more cathodic metal.

Designing

The equipment should be designed in such a way that even if corrosion occur it should be uniform and should not be intense and localized. The following conditions may be followed during designing of the equipments to reduce the rate of corrosion.

1. Two dissimilar metals should not be in contact with each other. Otherwise the more active metal gets corroded and the less active metal is protected from corrosion.
2. If the contact between two dissimilar metals is unavoidable, then the metals should be selected in such a way that their reduction potentials are as near as possible i.e. they should be as close as possible to each other in the electrochemical series.
3. If the contact between two dissimilar metals is unavoidable, then the anodic area should be very large when compared to the cathodic area.
4. Moisture should be removed whenever possible. If moisture or electrolytic solution is present, suitable inhibitors should be added.
5. When two dissimilar metals have to be in contact, then they should be separated by a suitable insulating material.
6. A proper design should not contain crevices between two adjacent parts since this causes differential aeration corrosion.

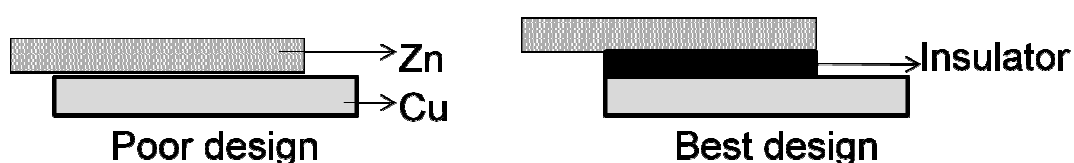


Fig. 11 Design to avoid galvanic corrosion

7. A proper design should allow the adequate cleaning of the critical parts. For example, if sharp corners or recesses are present, there may be accumulation of dirt or impurities which causes heterogeneity. Hence a proper design should have smooth joints and bends to avoid the accumulation of impurities.

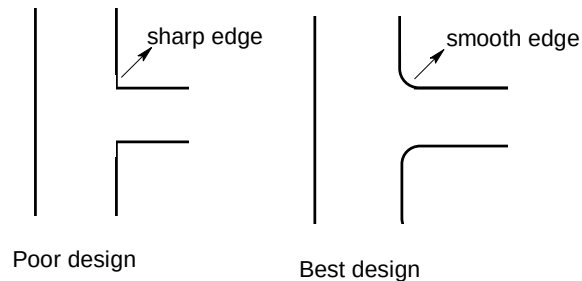


Fig. 12 Designing of materials with smooth joint and bends

8. Whenever possible, the equipment should be supported on legs to allow free circulation of air.

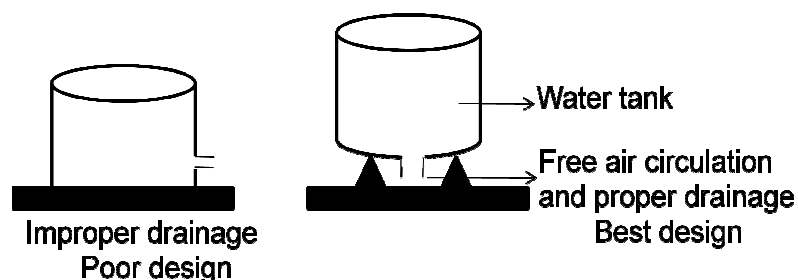


Fig. 13 Design having free circulation of air

b. Cathodic Protection

Cathodic protection is a method used to control the corrosion of a metal by making it as cathode of an electrochemical cell. When two dissimilar metals are coupled together, the more active metal acts as anode and undergoes corrosion. The less active metal acts as cathode and is protected from corrosion. Hence, anode always undergoes corrosion. There are two ways by which cathodic protection is carried out.

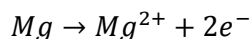
1. Sacrificial anodic protection
2. Impressed current cathodic protection

i. Sacrificial Anodic Protection

Sacrificial anodic protection involves the protection of a metal at the expense of some other more active metal. The more active metal acts as sacrificial anode and protects the less active metal. This method is generally used for the protection of underground cables or pipes.

In this method, the metallic structure to be protected is connected by a wire to a more anodic metal. Hence corrosion is concentrated at more active metal. The more active metal itself gets corroded slowly while the cathode metal is protected. The more active metal so employed is called sacrificial anode. Metals commonly used as sacrificial anodes are magnesium, zinc, aluminium and their alloys.

Magnesium has the most negative potential and is widely used in high resistivity electrolytes such as soil. Zinc is used as anode in good electrolytes like sea water.



The electrons migrate to the iron object which starts acting as cathode. At iron cathode, electrons reduce oxygen into OH^{-} ions.

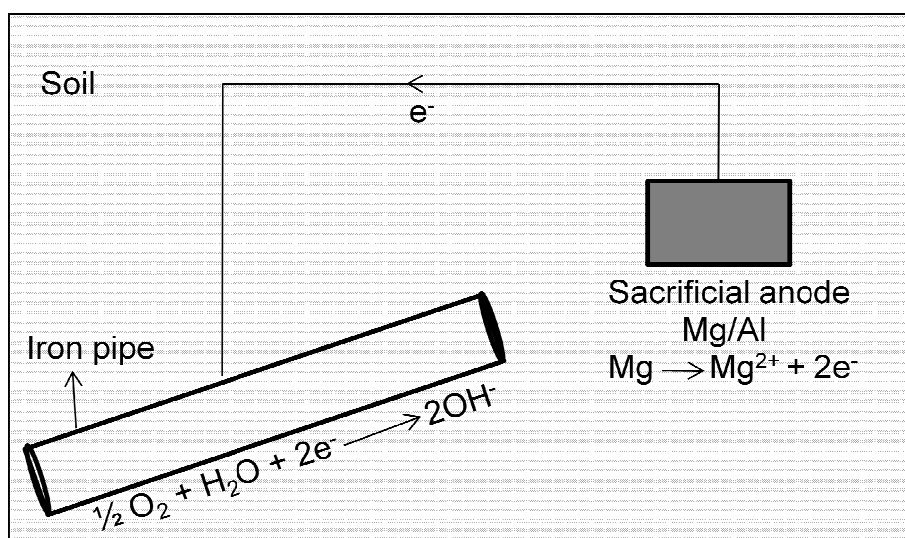
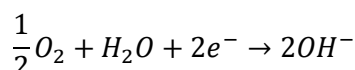


Fig. 14 Sacrificial anodic protection

The anode gradually disappears due to oxidation. The iron object remains protected as long as the sacrificial anode is present. The corroded anode block is replaced by a fresh one, when corroded completely. Important applications of sacrificial anodic method are protection of buried pipelines, underground cables, marine structures, ship hulls, water tank etc.

ii. Impressed Current Cathodic Protection

Whenever there is corrosion, because of the redox reaction (oxidation of anode and reduction at the cathode), a current is produced which is called corrosion current. In this method, an impressed current is applied in opposite direction to nullify the corrosion current and convert the corroding metal from anode to cathode.

The metal structure to be protected is connected to the negative terminal of a DC source like a battery or a rectifier. The positive terminal of the DC source is connected to an inert anode. The inert anodes used for this purpose are graphite, high silica iron, platinised titanium etc.

The anode is usually buried in a backfill composed of a mixture of gypsum, bentonite and sodium sulphate. This increases the electrical contact with the surrounding medium.

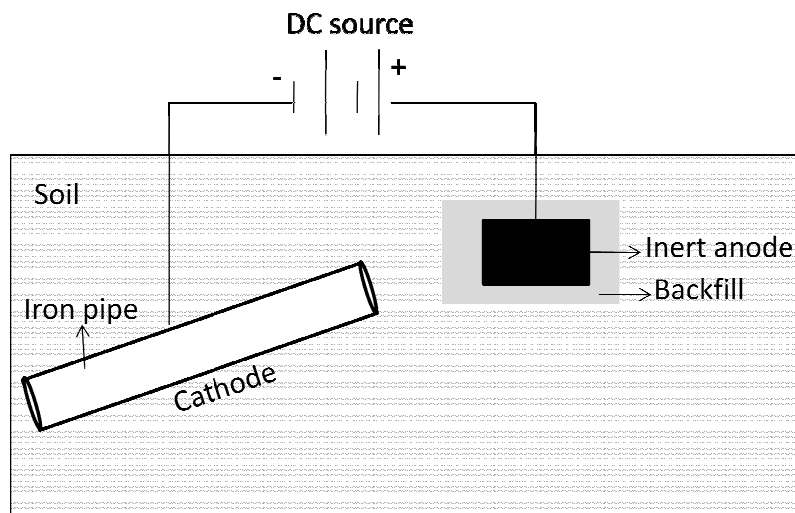


Fig. 15 Impressed current method

This method is useful for the protection of large underground structures like water tanks, buried oil or water pipes, transmission line towers, marine pipes etc. However, this method involves large installation and maintenance cost.

2. Modification on Environment

Corrosion Inhibitors

Corrosion inhibitors are 'chemical substances which when added in small quantities to the aqueous or gaseous corrosion environment, retard or slow down the corrosion processes resulting in the reduction of overall corrosion rate'. Corrosion inhibitors are broadly classified into two types.

- a. Immersion inhibitors
- b. Atmospheric inhibitors

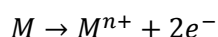
a. Immersion Inhibitors

They are used in solutions to achieve inhibition. There are two types of immersion inhibitors.

- i. Anodic inhibitors
- ii. Cathodic inhibitors

i. Anodic Inhibitors

Examples of anodic inhibitors are alkalis, chromates, phosphates, molybdates etc. The basic reaction at the anodic area is oxidation i.e. formation of metal ions.

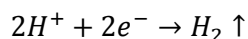


When the anodic inhibitors are added to the corrosive environment, they react with the metal ions from the anodic area and form a sparingly soluble salt which gets adsorbed at the

surface of the anodic area. This forms a protective film or barrier on the anode, which prevents the oxidation of the metals. This reduces the rate of corrosion.

ii. Cathodic Inhibitors

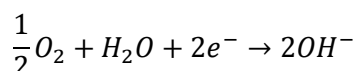
(a) In acidic medium, the basic cathodic reaction is evolution of hydrogen gas.



Rate of corrosion may be reduced either by slowing down the diffusion of hydrogen ions through the cathode or by increasing the hydrogen over voltage. The diffusion of hydrogen ions can be reduced by adding organic inhibitors like amines, pyridine, mercaptans, substituted urea and thiourea, quinoline etc. These positively charged cationic groups attach themselves to the cathodic areas through the nitrogen and provide inhibition. The efficiency of inhibition depends upon the size and the number of alkyl groups. For example, primary amyl amine ($C_5H_{11}NH_2$) has been found to be a more effective inhibitor than primary ethyl amine ($C_2H_5NH_2$).

The hydrogen over voltage can be increased by adding antimony oxide, arsenic oxide or sodium meta arsenite. These substances deposit an adherent film of metallic antimony or arsenic at the cathodic areas, thereby considerably increasing the hydrogen over voltage.

(b) In neutral aqueous medium, the cathodic reaction is,



The formation of OH^- ions is only due to the presence of oxygen. Hence, corrosion can be controlled either by removing oxygen from the environment or by preventing the diffusion of oxygen to the cathodic area. Oxygen can be removed from the solution by adding substances like sodium sulphide, sodium sulphate or hydrazine. The diffusion of oxygen towards the cathodic area is prevented by adding inhibitors like magnesium, zinc or nickel salts which react with the hydroxyl ions at the cathode to form insoluble hydroxides which deposit on the cathode. These deposits are impermeable barriers and hence retard the diffusion of oxygen at the cathode.

iii. Vapour Phase Inhibitors

These are organic inhibitors which readily vapourise and form a protective layer of the inhibitor on the metal surface. These are conveniently used to avoid corrosion in enclosed spaces and also during storage, packing, shipping etc. Cyclohexylamine carbonate, benzoate, Dicyclohexylamine nitrite most widely used vapour phase inhibitors.

Protective Coatings Protective coating is coating a metal to be prevented from corrosion with another metal or an inorganic material or an organic material. This coating forms a physical barrier between the surface of the metal and the environment thereby protecting the metal from corrosion.

Organic coating is one of the important protective coatings. Examples of organic coating are paints, varnishes and lacquers.

Paints

Paint is a mechanical dispersion of one or more pigments in a vehicle. The vehicle is a non-volatile drying oil and a highly volatile thinner. When a metallic surface is painted, the thinner evaporates while the drying oil oxidizes and forms a dry pigmented film.

Important qualities of paint

- (i) It should spread easily on the surface
- (ii) It should form a tough, uniform and adherent film
- (iii) The coating of paint should not crack after drying
- (iv) It should have high covering power
- (v) It should neither be oxidised or reduced in environment
- (vi) The colour due to paint should be shining and stable.

Ingredients of a paint

Paint essentially consists of the following ingredients.

- (i) Pigment, (ii) Vehicle or drying oil, (iii) Thinner, (iv) Drier, (v) Filler or extender, (vi) Plasticiser and (vii) Antiskinning agent.

1. Pigments

Pigment is a solid substance which provides colour to the paint. A good pigment should be (i) opaque, (ii) chemically inert, (iii) non-toxic (iv) cheap and (v) freely mixable with film forming constituent oils.

Functions: To give colour and opacity to the paint.

Examples:	Black	-	Lamp black
	Blue	-	Prussian blue
	Brown	-	Burnt umber
	Green	-	Chrome green
	Red	-	Red lead
	Yellow	-	Chrome yellow
	White	-	Zinc oxide

2. Vehicle or Drying oil

The vehicle is a non-volatile liquid and film forming material which holds all the ingredients of the paint together. They are triglycerides of higher fatty acids (saturated or unsaturated),

Functions: (i) To spread the paint evenly on the surface. (ii) To provide a binder for the ingredients of a paint so that they may stick or adhere to the surface.

Examples: Linseed oil, Tung oil.

3. Thinner

It is a highly volatile solvent which reduces the viscosity of paint and increases its elasticity. It increases the penetration power of drying oil.

Functions:

- i. To make the paint thin so that it can be easily applied on the surface.
- ii. To dissolve the vehicle.
- iii. To suspend the pigments.

Examples: Turpentine, Toluene, Xylol, Kerosene, etc.

4. Driers

These are oxygen-carrier catalyst used to accelerate the process of drying.

Functions: To accelerate the drying of drying oil through oxidation, polymerization and condensation.

Examples: Litharge, Red lead, (Resinates and linoleates of Co, Mn and Pb).

5. Extenders or Fillers

Functions: (i) To bring down the cost of paint. (ii) To improve the durability of paint. (iii) To prevent shrinkage and cracking.

Examples: Barytes (BaSO_4), Gypsum, China clay.

6. Plasticisers

Plasticisers are added to paint to provide elasticity to the film and to minimize its crack.

Examples: Triphenyl phosphate, dibutyl phosphate, dibutyltartarate etc.

7. Antiskinning Agents

They are added to the paint in order to prevent gelling and skinning of the finished product.

Examples: Poly hydroxy phenol.

Pigment Volume Concentration (PVC)

Pigment Volume Concentration (PVC) is an important property of paint. The higher the volume of P.V.C the lower will be durability, adhesion, consistency and glossy of the paint.

The following equation is used to calculate the P.V.C.

$$P.V.C. = \frac{V_1}{V_1 + V_2}$$

Where V_1 = Volume of pigment in paint

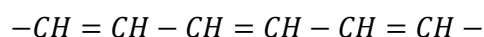
V_2 = Volume of non-volatile vehicle in the paint.

Mechanism of Drying of Drying Oils

Drying oils are glyceryl esters of high molecular weight fatty acids. They are the main film forming agent of the paint. They bind all other ingredients of paint. Examples are Linseed oil, Tung oil, etc.

The mechanism of drying of drying oils involves oxidation followed by polymerization and condensation. The structural arrangements required for drying of drying oils are

- (i) Conjugated oil structure (Example: Tung oil)



- (ii) Non-conjugated oil structure (Example: Linseed oil)



Time required for drying of oils at 25°C under standard conditions

Linseed oil (Non-conjugated)	120 Hrs (Without drier)	3 Hrs. (With drier)
Tung oil	8 – 72 Hrs.	1 ½ Hrs.
(Conjugated)	(Without drier)	(With drier)

Mechanism of drying of conjugated oils

Conjugated oils contain higher proportion of fatty acids with triple unsaturation. They have more positions (double bonds) for oxidation (O_2 attack).

The absorption of O_2 at the site of the double bond gives 1, 2- diradical. Rearrangement of double bonds in the above diradical can give 1,4- and 1,6- diradicals. Oxygen attack at these radical sites gives peroxide radical. The peroxide radicals produce polyperoxides by polymerization, which is a durable, hard, and adherent film.

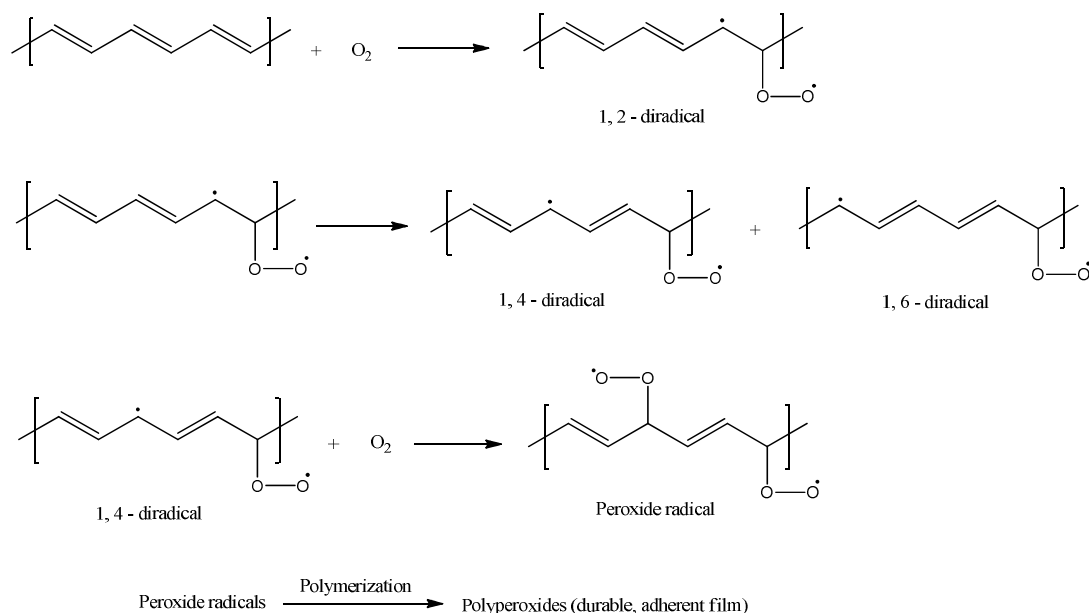


Fig.16 Schematic Representaiton of drying of conjugated oils

Mechanism of drying of non-conjugated oils

The reaction between oxygen and non-conjugated oils takes place without loss of unsaturation. That is the methylene group present between the two double bonds is prone to direct oxidation and this reaction produces hydroperoxides. This hydroperoxide decomposes to give free radicals under the influence of heat and light. The new free radical may rearrange to give a conjugated system of double bonds. Reaction between oxygen and these conjugated systems gives peroxide radicals, and then polyperoxide, a durable, adherent film similar to conjugated drying oil.

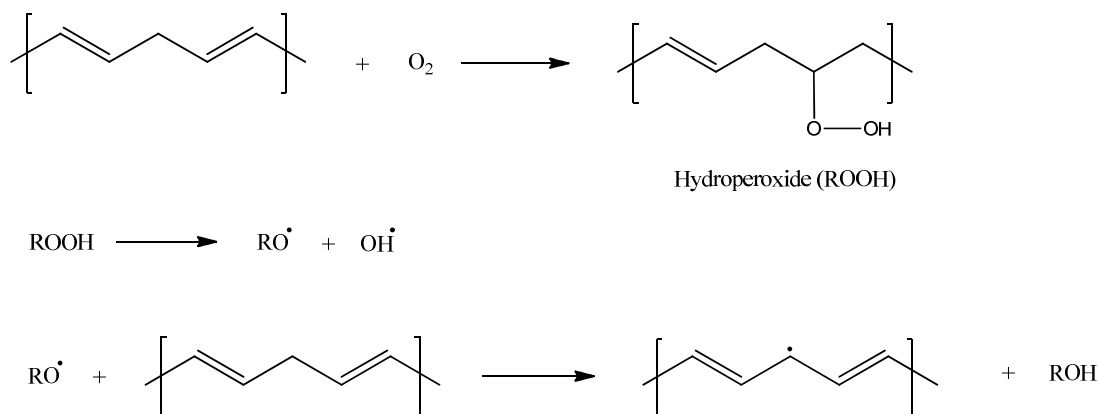


Fig. 17 Schematic Representaiton of drying of conjugated oils

Questions

1. Compare the galvanic series with the electrochemical series.
2. Explain the mechanism of oxidation corrosion.
3. Explain the mechanism of electrochemical corrosion.
4. Distinguish between chemical corrosion and electrochemical corrosion.
5. Discuss the factors influencing the rate of corrosion by the nature of the metal.
6. Discuss the factors influencing the rate of corrosion by the nature of the environment.
7. Write a short note on galvanic corrosion and microbial corrosion.
8. Write a note on corrosion control by material selection and design.
9. Describe the cathodic protection method of corrosion control.
10. What are corrosion inhibitors? Explain the various inhibitors.
11. Write a short note on differential aeration corrosion.
12. What are electrochemical cells? How are they represented?
13. What is Pilling Bedworth rule? Discuss the role of nature of oxides formed in oxidation corrosion.
14. Explain the sacrificial anodic protection method of corrosion control.
15. What is galvanic series? Explain its significance.
16. Explain in detail the various constituents present in paint.
17. Explain the mechanism of drying of drying oils in paints.

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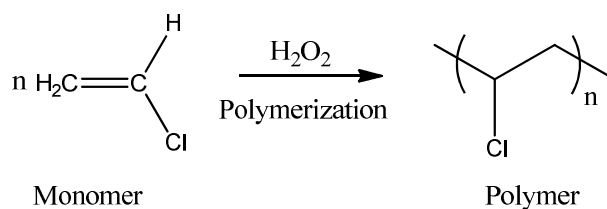
Introduction to polymers: Nomenclature – Functionality. Types of polymerization- Mechanism of polymerization: Free radical mechanism – Cationic mechanism – Anionic mechanism. Plastics: Types – Thermoplastics and Thermosetting plastics. Properties: Strength – Crystalline and amorphous state – Average molecular weight – Polydispersity. Compounding of plastics-Molding of plastics: Compression molding - Injection molding - Extrusion molding. Introduction to Conducting polymers.

Introduction

Polymer is a large molecule, made up of large number of small molecules often referred as repeating units. It is also known as macromolecules. The term “polymer” is derived from Greek word; poly (many) meros (part = repeating units). Polymeric materials are divided between natural and synthetic materials. The synthetic polymers are used for plastics, fibers, and elastomers. Some of the examples of naturally occurring polymers are rubber, wool and cellulose. Since the polymeric materials are indispensable in human life, it is worthy to call the current scenario, as polymeric-age.

Important Terms

Monomer: The polymers are built up by the large number repetition units, which is small and simple chemical units. The smallest repeating units, which are the building block for large polymeric structure, are called monomers.



Oligomers: The polymer with fewer repeating units (between 3 -20 number of repeating units) is often referred to as oligomers (Greek: oligo = few). So the oligomers are low molecular weight polymers, which lack the significant properties as that of the high molecular weight species (polymer).

End group: The head and tail of the polymeric chain is referred as end group. The end groups are not shown in the structural representation of the polymers, since it makes insignificant contribution to the molecular weight.

Polymerization: The process or the methods in which the monomer are converted in to polymers are called polymerization.

Degree of polymerization: The number of repeating units present in the polymeric chain is called degree of polymerization; it is often referred as DP. The relationship between the DP and molecular weight of the polymer is given by

$$M = (\text{DP}) \times M_0$$

Where M_0 is the formula weight of the monomer

Resin: The term resin is referred for the vegetable-derived organic products of relatively high molecular weight polymers. Initially the term was used for rosin and balsam from

coniferous trees. Now a day the term is broadly used for the polymeric product used in plastics, textiles and paints applications.

Plastics: The term plastic is used for a material that can be molded to the desired shape. (plasticos = fit for molding). It is a high molecular weight polymer except rubbers and fibers.

Differences between monomer and polymer:

S. No.	Monomer	Polymer
1	Single molecule	many molecules joined together
2	Unique molecular weight	Average molecular weight
3	Solids possess melting point	Solids possess melting point and glass transition temperature
4	Variable viscosity	Highly viscous

Nomenclature of Polymers

a) Vinyl polymers

Polymers are named with their monomer's name with the prefix poly-. For example, Poly(vinyl chloride).

Common names for monomers are also used. For example, the common name for ethenyl benzene is styrene, so chemists call the polymer of styrene polystyrene.

Trade name is also used for some polymers. They use the trade name Teflon® more frequently than the IUPAC name of polytetrafluoroethylene.

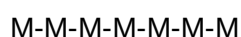
b) Non-vinyl polymers

As like the vinyl polymers, the nomenclature of these polymers is often based on their trade names. Nylon is an example of a family of compounds that chemists call by their trade names.

The numbers following the names indicates the number of carbons in the monomer(s) for that specific Nylon. Nylon 6 is a polymer made from monomers that consist of a single cyclic amide with six carbons. The monomers in Nylon 6.8 are diamines with six carbons and dicarboxylic acids with eight carbons.

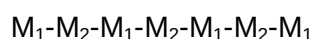
General polymer nomenclature is based upon the type of monomer residues comprising the polymer.

A. Homopolymers: Polymers with single type of repeat unit are known as homopolymers. Examples: Polystyrene is composed only of styrene monomer residues, and is therefore classified as a homopolymer. Other examples are: polyethylene, polypropylene.



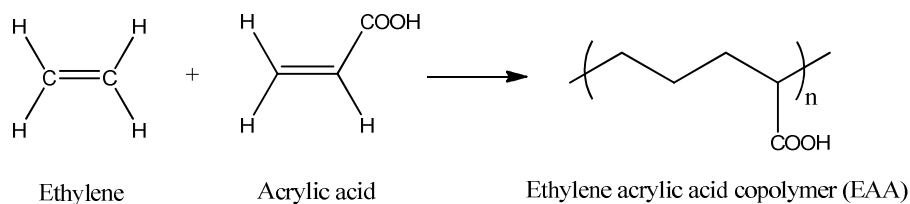
where M is a monomer unit

B. Heteropolymers or Copolymers: Polymers containing more than one kind of repeating unit are known as copolymers or heteropolymers.



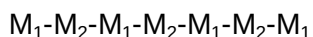
where M_1 and M_2 are the different monomer units

Example:



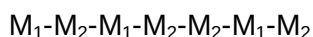
Based on the arrangement of the monomers along the backbone of a copolymer, the following types of copolymers are obtained:

Alternating Copolymers: They possess regularly alternating monomer units.



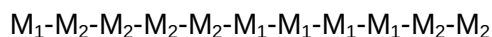
M_1 = vinyl chloride and M_2 = vinyl acetate

Statistical Copolymers: The copolymers having the monomer units arranged according to a known statistical rule is called statistical copolymer. A statistical copolymer in which the different types of monomer residue are randomly present in the polymer chain is called random copolymer.



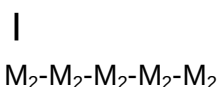
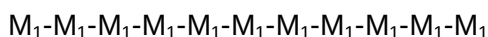
M_1 = Styrene and M_2 = Butadiene

Block copolymers: These polymers have two or more homopolymer subunits linked by covalent bonds. Polymers with two or three blocks of two distinct chemical species (e.g., M_1 and M_2) are called diblock copolymers and triblock copolymers, respectively. Polymers with three blocks, each of a different chemical species (e.g., M_1 , M_2 , and M_3) are termed triblock terpolymers.



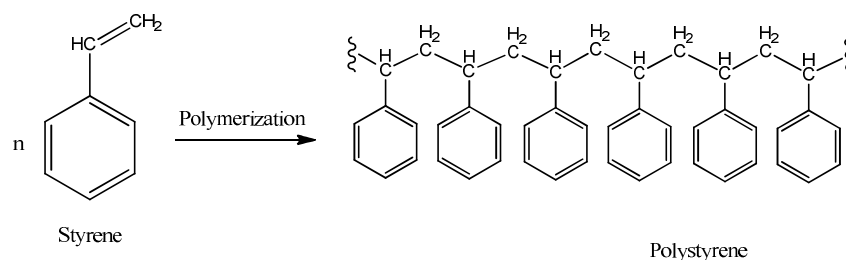
M_1 = acrylic acid and M_2 = methylmethacrylate

Graft or grafted copolymers: The polymers containing side chains that have a different composition or configuration compared to the main are called Graft copolymers.

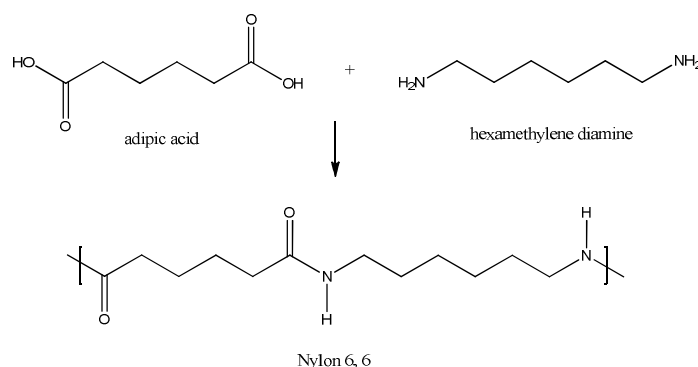


M_1 = vinyl chloride and M_2 = styrene

C. Homochain polymer: When the backbone of the polymer is made up of only one atomic species then it is called homochain polymer.



D. Heterochain polymer: When the backbone of the polymer is made up of more than one atomic species then it is called heterochain polymer.

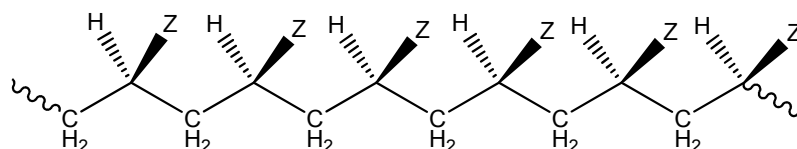


E. Stereospecific polymer or Tacticity

Tacticity or stereoisomer is the relative spatial arrangement of substitutions around the chiral centers present in the main chain of a polymer. The classification is based on the orientation of the substitution in the monomeric units with respect to the similar substitution on the alternating carbon of the backbone. Symmetrical monomer such as ethylene and tetrafluoroethylene does not possess stereo isomers, because there is only one way of spatial arrangement of substitution around the backbone carbon. Mono-substituted monomers, on the other hand, may have three different spatial orientation of substitution around the main chain (backbone).

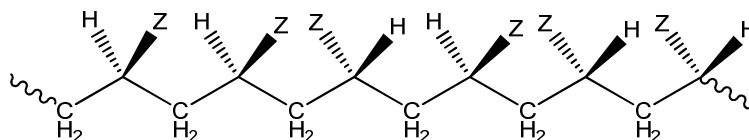
If the polymer chain is drawn in a zig-zag fashion, as shown above, each of the substituent groups (Z) will necessarily be located above or below the plane defined by the carbon chain. Consequently we can identify three configurational isomers of such polymers. If all the substituents lie on one side of the chain the configuration is called isotactic. If the substituents are alternatively present with respect to the main chain in a regular manner the configuration is termed as syndiotactic. Finally, a random arrangement of substituent groups is referred to as atactic. Examples of these configurations are shown here.

Isotactic polymer: It is a polymer with all substituents on the same side with respect to the main chain of the polymer. Example: Polypropylene, cis-polyisoprene



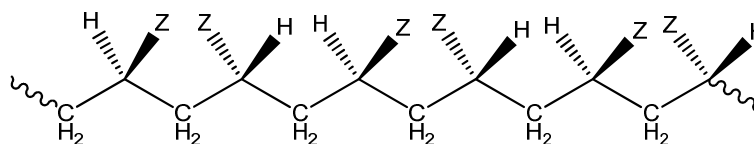
Isotactic polymer

Atactic polymer: It is a polymer with the random orientation of the substituents with respect to the main chain of the polymer. Example: Polypropylene, trans-polyisoprene



Atactic polymer

Syndiotactic polymer: It is a polymer having substituents that are alternatively placed with respect to the main chain of the polymer. Example: Polypropylene



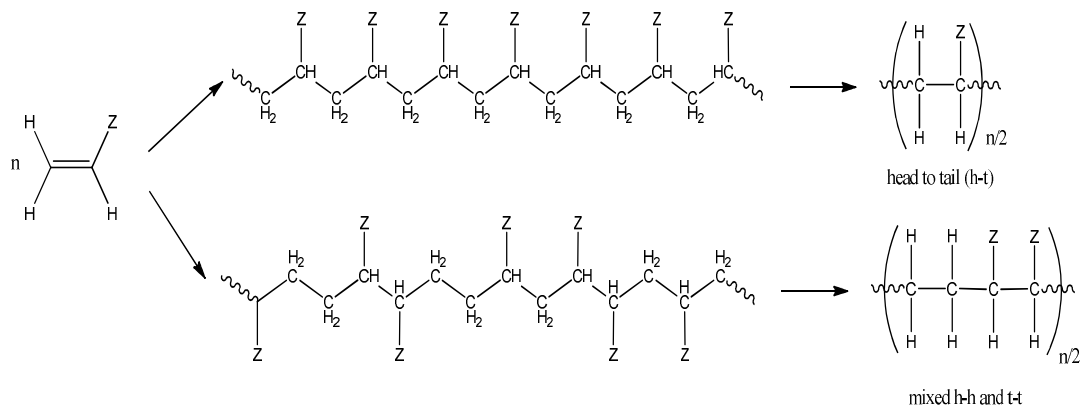
Syndiotactic polymer

Under normal conditions only atactic polymers are formed. Example polystyrene, polyacrylonitrile and poly(vinyl chloride). Catalysts are needed to obtain stereospecific polymers like isotactic and syndiotactic. The stereoregular polymers have improved properties like polymers associated with the increased crystallinity; these products have made this an important field of investigation. The following T_g (glass transition temperature) values of some polymers have been reported.

Polymer	T_g atactic	T_g isotactic	T_g syndiotactic
PP	-20 °C	0 °C	-8 °C
PMMA	100 °C	130 °C	120 °C

Tacticity plays a significant role in modifying some of the properties of a given polymer to a considerable extent. Thus, atactic polypropylene is useless as a solid construction material, and is employed mainly as a component of adhesives or as a soft matrix for composite materials. In contrast, isotactic polypropylene is a high-melting solid (ca. 170 °C) which can be molded or machined into structural components.

Symmetrical monomer such as ethylene and tetrafluoroethylene does not even possess regio isomers, because there is only one way of attachment of the carbon for the backbone main chain formation. Mono-substituted monomers, on the other hand, may have three different ways of monomer attachment with respect to each other. Most monomers of this kind, including propylene, vinyl chloride, styrene, acrylonitrile and acrylic esters, prefer to join in a head-to-tail fashion, with some randomness occurring from time to time.



Functionality

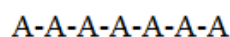
Functionality (F) denotes the number of reacting functional groups in a monomer. It can also be defined as number of reactive sites present in a monomer is called 'Functionality'. For a monomer of addition polymer (alkene) a double is considered to be bi-functional, since it can form two covalent bonds with the neighboring carbons.

Significance of Functionality:

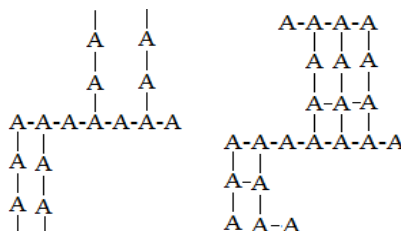
1. Substances having only one bonding or reactive site are called "mono-functional monomers". Eg. CH_3COOH

They cannot grow as a polymer chain; it can form only the dimers.

2. If $F = 2$, they form linear chain structure. (eg) Ethylene, Ethylene glycol
Since there is no covalent linkage across the chain, they are held together by only weak Vander Waal's attraction, there is no restriction for the movement of one polymer chain over another chain. They have less strength, low heat resistance, softness and flexibility.



3. If $F=3$, they form cross linked polymer with branched structure. (Eg) Polyglycerol
4. The movement of polymer chain is restricted because of the strong covalent bond across the carbon chains. They have high strength, high heat resistance and hardness.

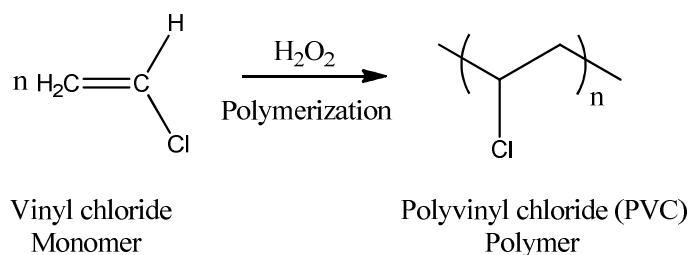


5. If $F \geq 4$, then they form network polymer with 3D structure.

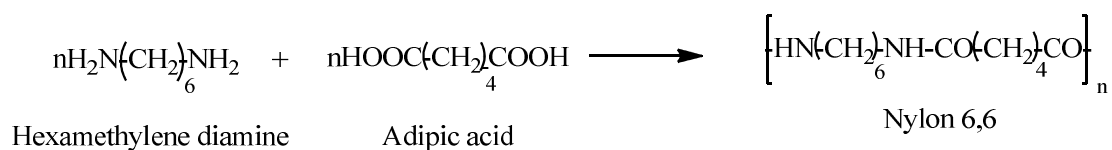
Polymerization

Basically there two broad types of polymerization reactions based on the mechanism of polymerization, 1) The addition or chain growth polymerization and 2) Condensation or step growth polymerization.

1) The addition or chain growth polymerization: In this type of polymerisation, the molecules of the same monomer or different monomers added together to form a polymer without any elimination. The molecular weight of polymer will be integral multiples of the monomeric molecular weight. The monomers must contain double bond, e.g., alkenes, alkadienes and their derivatives. This mode of polymerisation leading to an increase in chain length or chain growth can take place through the formation of either free radicals or ionic species. Among these, the free radical polymerisation is the most common mode.



2) Condensation or step growth polymerization: This type of polymerisation generally involves a repetitive condensation reaction between two bi-functional monomers. These polycondensation reactions may result in the elimination of some simple molecules like water, alcohol, etc. At the end of each step bifunctional species are produced which in turn reacts with two more monomeric units and the sequence of condensation goes on. Since, each step produces a distinct functionalized species and is independent of each other, this process is also called as step growth polymerization. The formation of nylon from the reaction between Adipic acid and 1,6 hexamethylene diamine is an example of this type of polymerization.



The differences between two major polymerization methods are tabulated as follows:

S. No	Addition Polymerization	Condensation Polymerization
1	Eg. PVC	Eg. Nylon 6,6
2	Otherwise known as "Chain growth Polymerization".	Otherwise known as "Step wise Polymerization".
3	Monomers are adding together to form polymers.	Monomers are condensed to form polymer.

4	No elimination of other molecules.	Elimination of smaller molecules occur.
5	At least one multiple bond presence is essential condition.	Monomers must have two or more functional groups.
6	Homo polymers are formed.	Hetero polymers are formed.
7	Thermoplastics are formed.	Thermosetting plastics are formed.
8	Molecular weight of the polymer is the integral multiple of the molecular weight of the monomer.	Need not be so.
9	Monomers disappear slow and steadily.	Monomers disappear after the initial stage of the reaction.
10	Longer processing time is needed to increase yield.	Longer time is essential for increasing molecular weight.

Mechanism of Polymerization

The general mechanism for the addition polymerization consists of three following steps, irrespective of the method.

- A) Initiation
- B) Propagation
- C) Termination

No such generalization for the polymerization mechanism can be written for the condensation polymerization, as it is more specific depending upon the functional group present in the monomer

Mechanism of Free Radical Addition Polymerization

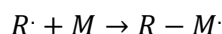
The free radical mechanism also involves 3 steps as mentioned earlier 1. Initiation, 2. Propagation and 3. Termination

Step I - Initiation:

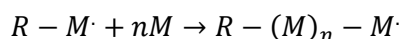
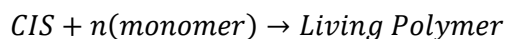
1a) *Initiator* → *Radical*



1b) *Radical + Monomer* → *Chain Initiating Species (CIS)*



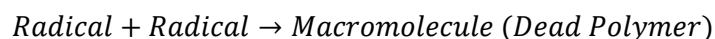
Step II - Propagation:

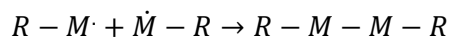


The growing chain the polymer is known as Living Polymer.

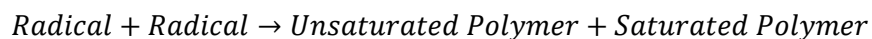
Step III – Termination:

3a) By Coupling :





3b) By disproportionation by Hydrogen transformation:



EXPLANATION OF FREE RADICAL MECHANISM (eg) PVC polymerization

1. Initiation

a) *Initiator* $\rightarrow$ *Radical*

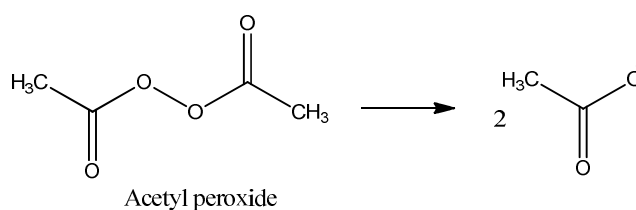
1. The substance which undergoes homolytic cleavage to form radical is called 'Initiator'.

(e.g) acetyl peroxide initiator

2. The substance with single electron is called 'radical'. It is represented as R.

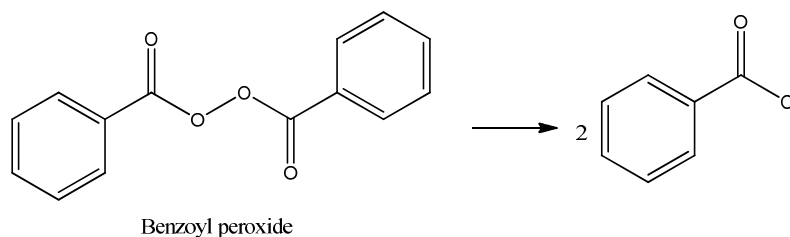
(e.g) acetyl peroxide radical

e.g Acetyl peroxide $\rightarrow$ Radicals (at 80°C)

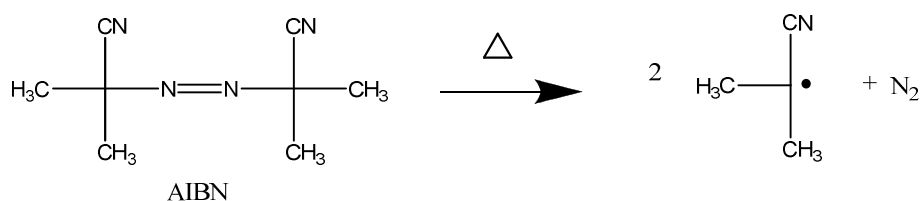


Example of Initiators

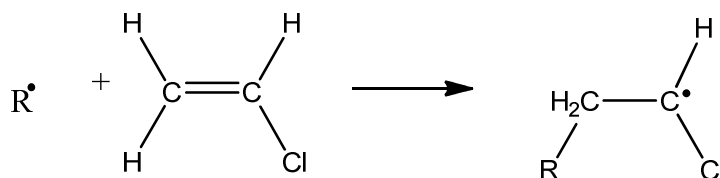
1. Benzoyl peroxide Initiator (used around 80-95°C)



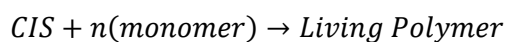
2. Azobis Isobutyro Nitrile (AIBN) Initiator (used around 50-70°C)

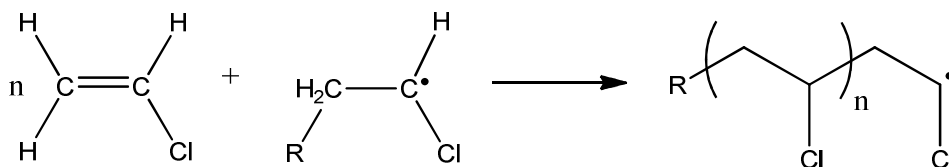


b) *Radical* + *Monomer* $\rightarrow$ *Chain Initiating Species (CIS)*

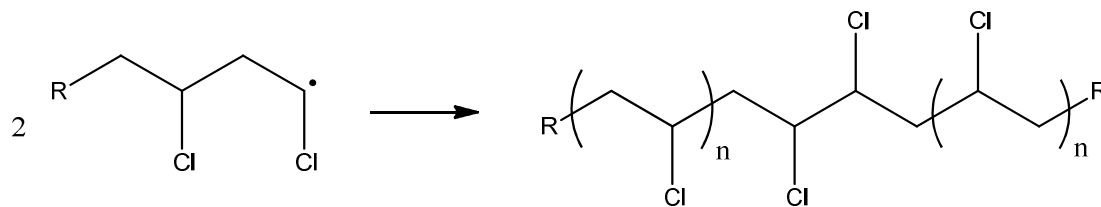
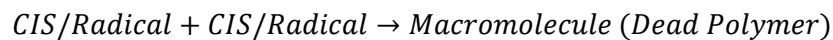


2. Propagation:



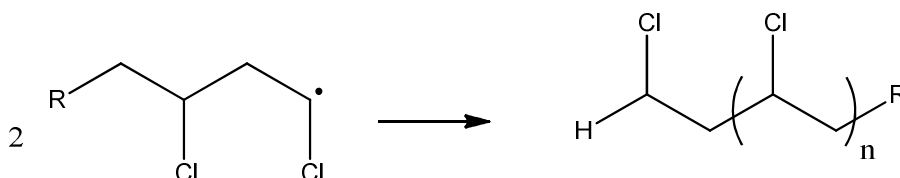
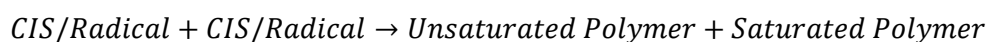
**3. Termination:**

a) Coupling



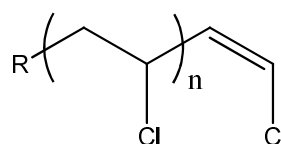
Dead Polymer

b) Disproportionation (by Hydrogen transformation)



Saturated Polymer

+



Unsaturated Polymer

The products are known as dead polymers.

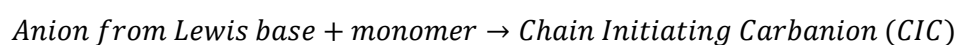
Mechanism of Anionic Addition Polymerization

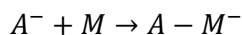
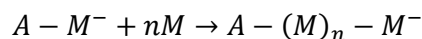
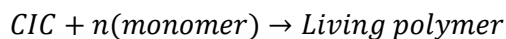
When the chain reaction is initiated and carried by negatively charged (carbanion) intermediates, the reaction is known as anionic polymerization.

- Monomers with electronegative groups like Cl^- , CN^- follow this mechanism.
- Lewis bases like KNH_2 , NaNH_2 are used as initiators.
- Eg. Vinyl chloride, Acrylonitrile polymerization

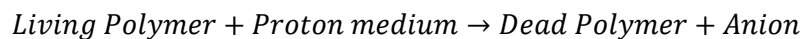
There are 3 steps involved in Anionic mechanism:

1. Initiation
2. Propagation
3. Termination

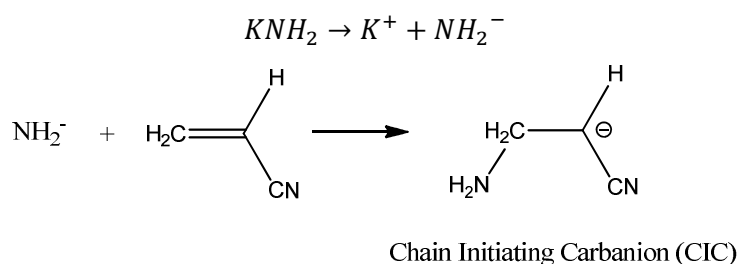
Step I - Initiation:

**Step II - Propagation;**

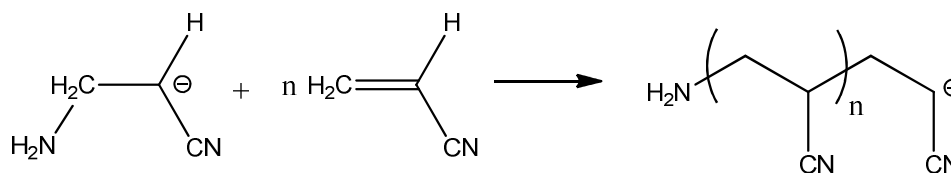
The growing chain the polymer is known as Living Polymer.

Step III - Termination;**Explanation of Anionic Polymerization (eg) Acrylonitrile****1. Initiation:**

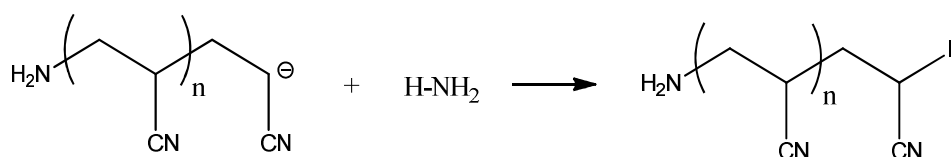
Here, Chain Initiating carbanion formation is taking place.

**2. Propagation:**

Here, the growth of the carbanion takes place. It involves the transfer of negative charge along the chain.

**3. Termination:**

The chain reaction is terminated when the carbanion reacts with the medium such as Ammonia, water, etc.

**Mechanism of Cationic Addition Polymerization**

When the chain reaction is initiated and carried by positively charged (carbocation) intermediates, the reaction is known as anionic polymerization.

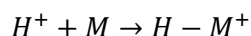
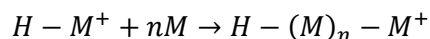
- Monomers with electropositive groups like CH_3 , C_6H_5 , etc. follow this mechanism.
- Lewis acids like $AlCl_3$, BF_3 , $TiCl_4$, etc. are generally acting as initiators.
- Examples: Isoprene, Styrene
-

The 3 steps involved in Cationic mechanism are:

1. Initiation

2. Propagation

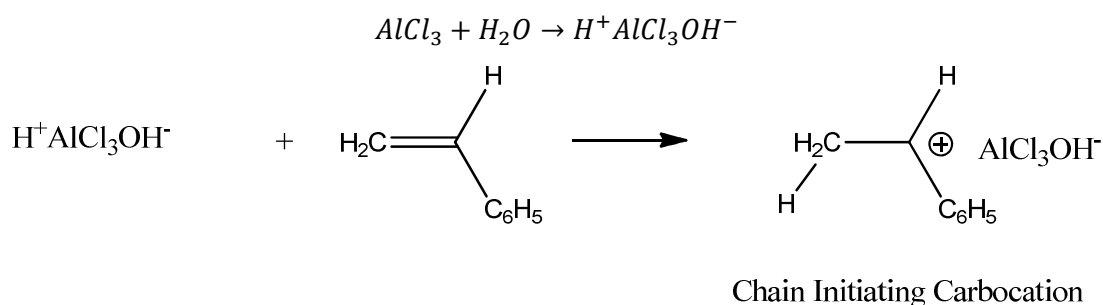
3. Termination

Step I - Initiation:*Cation from Lewis acid + monomer → Chain Initiating Carbocation (CIC)***Step II - Propagation:***CIC + n(monomer) → Living Polymer*

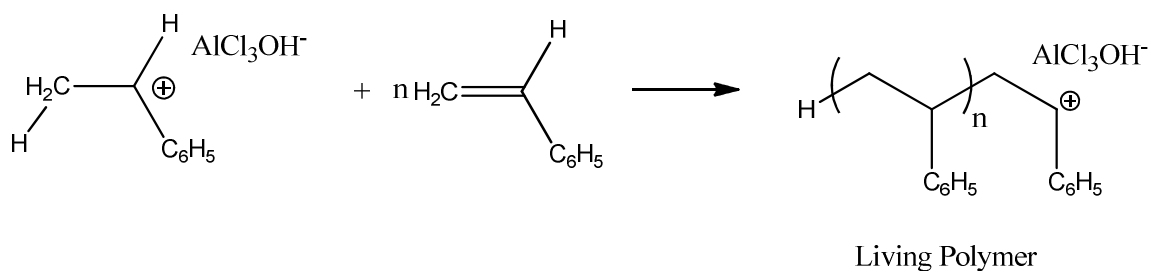
The growing chain the polymer is known as Living Polymer.

Step III - Termination;*Living Polymer → Dead Polymer + Lewis acid***Explanation of Cationic Polymerization. (eg) Polystyrene****1. Initiation:**

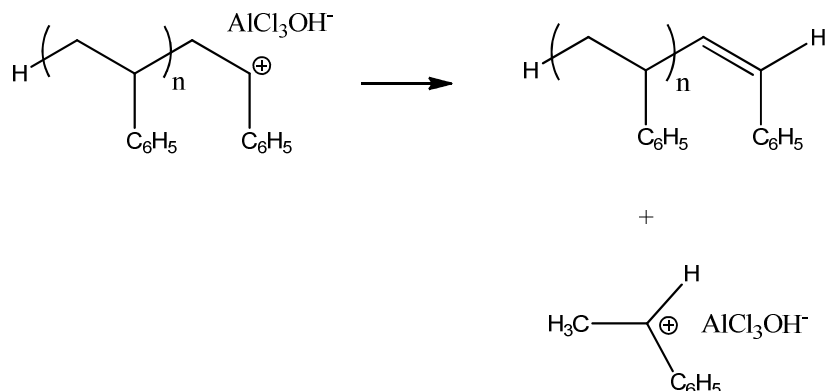
Here, Chain Initiating carbonium ion formation is taking place.

**2. Propagation:**

Here, the growth of the carbonium ion takes place. It involves the transfer of positive charge along the chain. It produces living polymer.

**3. Termination:**

When the catalyst is splitting from Living polymer, it results in Dead polymer product.



Plastics

The term plastic is used for a material that can be molded to the desired shape. (plasticos = fit for molding). It is a high molecular weight polymer except rubbers and fibers. They are made up of resins, fillers, plasticizers, lubricants etc., (e.g) PVC , PET.

Advantages of plastics are:

1. It is an Insulating material
2. It posses good corrosion resistant property
3. Easy process able and Chemical inertness
4. Has adhesive property
5. Less weight and good mechanical strength (used as a shock absorber)
6. Available in various colours

Disadvantages of low quality plastics:

1. They are soft at moderately high temperature and brittle at cold conditions.
2. Ageing (Low durability) is the major problem associated with the plastics.
3. Cannot withstand high temperatures and low Creep resistance (shape deformation due to load)

Differences between Thermoplastics and Thermosetting Plastics

S.No	Thermoplastics	Thermosetting Plastic
1	Plastics which can be remoulded i.e., melted by heating and solidified by cooling. They can be made into any desired shapes for any number of times by reheating and cooling.	They cannot be remoulded after their first usage.
2	Scrap can be used again.	Scrap cannot be used again.
3	Addition polymer	Condensation polymer
4	The bond strength is low	The bond strength is high
5	Molecular weight is low	Molecular weight is high
6	Soluble in organic solvents.	Insoluble in organic solvents.

7	Prepared by Injection moulding	Prepared by compression moulding.
8	Linear polymer	Cross linked polymer
9	Eg. PVC , Polyethylene	Polyester, Bakelite

Compounding of Plastics (or) Moulding Constituents

To overcome some of the disadvantages of the plastics when compared to other materials like metals, external substances are added during the processing stage. Compounding is the process in which the additives/modifiers are incorporated, into polymers for enhancing the desired property and achieving uniformity in the quality of the articles subsequently made from the compound. It is the first step in most plastic fabrication. Each compounding ingredient will contribute towards the particular property and makes the plastics more user friendly and adds adaptability to final product. Plastics are compounded to enhance features like:

- Mechanical/Physical and Thermal Properties
- Optical properties(color/visuals)
- Functional properties
- Cost effectiveness.

The details of the ingredients with their functions and examples of each category is listed in the chart given below

Ingredients used in Plastic Compounding

S. No	Compounding ingredients	Examples	Functions
1.	Resin	It forms the major part	It is the binder material which holds the constituents together
2.	Stabilizers	For transparent polymers: stearates of lead, cadmium or barium. For opaque polymers: Red lead or lead monoxide	They are thermal stabilizers added to improve the stability of the polymer
3.	Accelerators or Catalysts	Hydrogen peroxide, benzoyl peroxide and metals like lead, copper and oxides like zinc oxide	Added to accelerate the process of polymerization reaction during moulding process. Polymer alloys & blends: for performance plastics

4.	Lubricants	Waxes, oils and soap	It gives a shiny appearance to the polymer material and to take out the material easily from the mould.
5.	Fillers or extenders	Fillers used to increase hardness are: mica, carborundum, quartz. Asbestos powder is a filler used to improve thermal and corrosion resistance	They are inert materials added to plastics to increase bulkiness and thereby reduce the cost of production. Conductive fibers: for electrical properties
6.	Plasticizers	Vegetable oils, camphor, organic phosphates	They are added to increase softness and flexibility of the product. It neutralizes the intermolecular forces present in the material; thereby the movement of the molecular layer will become possible.
7.	Pigments	Titanium dioxide – white color Carbon black – black color Prussian blue – Blue Chromium oxide – green Ferrous oxide – red Lead chromate -- yellow	They will provide the desired color to the product. UV stabilizers: for resistance to sunlight
8.	Antioxidants	Phenylparanaphthylamine	They protect the polymer against oxidative degradation. Flame retardants and smoke suppressants

Molecular Weight of Polymers

The molecular weight of polymers is not unique like small molecules because the DP i.e., the number of monomeric unit in the polymer is not always fixed, it is an variable. Hence the molecular weight of polymer varies from each other in a given sample, so it is convenient to give the molecular weight of polymer in a range. Since the polymer molecular weights are in the range, it is always given as an average molecular weight.

Number Average Molecular Weight ($\bar{M}_n$)

The number average molecular weight of the given polymer is the statistical average molecular weight of all the polymer chains in the sample.

- It is obtained by measuring the colligative properties of the polymer.
- It is a good index of physical properties such as impact and tensile strength.

Consider, a polymer mixture containing n_1 molecules are with molecular weight M_1 , n_2 molecules with molecular weight M_2 and so on., If n_i molecules are with molecular weight M_i then the Number average weight $\bar{M}_n$ of the polymer is given by,

$$\bar{M}_n = \frac{n_1 M_1 + n_2 M_2 + \cdots + n_i M_i}{n_1 + n_2 + \cdots + n_i}$$

$$\bar{M}_n = \frac{\sum n_i M_i}{\sum n_i}$$

Weight Average Molecular Weight ($\bar{M}_w$)

It is the sum of all molecular weights multiplied by their weight fractions. It is obtained by light scattering and ultra centrifugation techniques.

Consider, in a polymer mixture w_1 is the weight of polymer with molecular weight M_1 , w_2 is the weight of polymer with molecular weight M_2 , and so on., Let w_i molecules are with molecular weight M_i . Then the weight average molecular weight ($\bar{M}_w$)

$$\bar{M}_w = \frac{w_1 M_1 + w_2 M_2 + \cdots + w_i M_i}{w_1 + w_2 + \cdots + w_i}$$

$$\bar{M}_w = \frac{\sum w_i M_i}{\sum w_i}$$

But, number of moles $n = w / M$

On rearranging, $w = nM$

Replacing the value of w from the above equation

$w_1 = n_1 M_1$, $w_2 = n_2 M_2$ and $w_i = n_i M_i$, the $\bar{M}_w$ equation becomes

$$\bar{M}_w = \frac{n_1 M_1 M_1 + n_2 M_2 M_2 + \cdots + n_i M_i M_i}{n_1 M_1 + n_2 M_2 + \cdots + n_i M_i}$$

$$\bar{M}_w = \frac{\sum n_i M_i^2}{\sum n_i M_i}$$

Polydispersity Index (PDI)

Polydispersity Index (**PDI**) is an indication that, how broadly the molecular weight of the polymer are distributed. It is given by the ratio of weight average molecular weight $\bar{M}_w$ to number average molecular weight $\bar{M}_n$.

$$\text{Polydispersity Index} = \frac{\bar{M}_w}{\bar{M}_n}$$

- If, $\bar{M}_w > \bar{M}_n$, Then the polymer is a polydisperse polymer
- When, $\bar{M}_w = \bar{M}_n$ Then it is a mono-disperse polymer
- All naturally occurring polymers are monodisperse polymer; the polymeric chains are of equal length and possess same molecular weight.
- All manmade polymers are polydisperse. They contain molecules of different molecular weight. The deviation of ratio from the unity is taken as a measure of polydispersity of the polymer sample. For all synthetic polymers, PDI is higher than 1.
- Higher values of the ratio indicate greater polydispersity. It means all the molecules of the polymers will not have identical molecular weight.

Strength of polymer

The properties of polymers which make them special when compared other materials are

- 1) Specific strength or strength / unit mass
- 2) Processability
- 3) Inexpensive
- 4) Versatile properties (Insulator, conductor, semi-conductor, transparent, non-transparent, thermal stability / lability, viscosity)

Some of these properties are dependent on the micro structure of the given polymers. For example the morphology and strength of the polymer are depends on the percentage crystallinity of the polymers.

Many of the polymers are partially crystalline. Structurally, polymers in the solid state may be amorphous or crystalline. Most of the polymers possess both the crystalline region as well as the amorphous region within its structure as shown in the diagram. But the percentage of crystallinity varies from polymer to polymer.

During solidification of molten polymers, molecular units often attracted to each other and tend to aggregate as closely as possible into a solid with the least possible potential energy. In some polymers, during the process of forming a solid, individual chains are folded and packed regularly in an orderly fashion. The resulting solid is a crystalline polymer with a long-range, three-dimensional, ordered arrangement. However, complete orderly arrangement of atoms as like small molecules are not always possible, since the polymer chains are very long, it is impossible for the chains to fit into a perfect orderly arrangement. Hence, in these polymers, there is always an associated imperfection in the crystallinity. The degree of crystallinity, i.e., the fraction of the total polymer in the crystalline regions, may vary from a few percentage points to about 90% depending on the crystallization conditions. Examples of crystalline polymers include polyethylene, polyacrylonitrile, poly(ethylene terephthalate), and polytetrafluoroethylene.

In contrast to these highly crystalline polymers, amorphous polymers does not have the ability to arrange the in an orderly manner. They are characterized in the solid state by a short-range order of repeating units. These polymers form an amorphous glassy solid in

which the molecular chains are arranged at random and even entangled. Poly(methyl methacrylate) and polycarbonate are typical examples for these category.

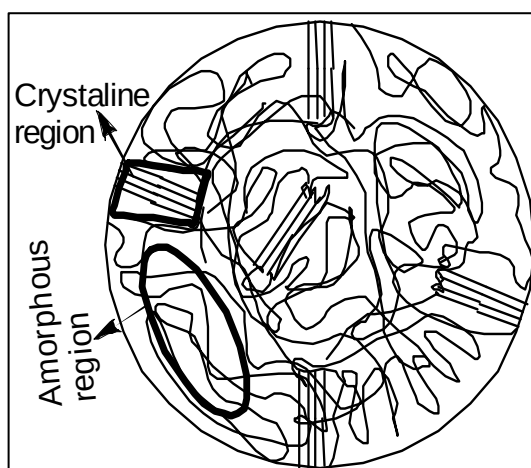


Fig. 1 Schematic Representation of amorphous and crystalline regions

Moulding of Plastics into Articles

Moulding is the process of fabrication of raw plastic material into definite and useful shapes by using a rigid framework. It is possible with both thermoplastics or thermosetting resins.

Polymer Processing

There are five fabrication techniques available to form polymer products or parts. They are injection moulding, compression moulding, transfer moulding, blow moulding, and extrusion moulding. The moulding method is selected based on the type of resin used. For thermosetting resins compression moulding or transfer moulding methods are used. For thermoplastics, injection moulding or extrusion moulding methods are used.

Compression Moulding

It is a fabrication technique in which a specific quantity of raw, un-polymerised plastic placed in a preheated mould cavity is closed under pressure and compressed so that the molten plastic in the cavity gets converted into the desired shape of the plastic material. Pressure is applied to force the material into contact with all the mould areas with continuous application of heat and pressure until the material is cured. The process employs thermosetting resins in a partially cured stage, either in the form of granules, putty-like masses, or preforms. It is a high-volume, high-pressure method.

This type of moulding is the first method used to form plastics. The steps involved in this moulding method are:

1. Pre-formed blanks, powders or pellets are placed in the heated bottom mould or a die.
2. The other half of the mould is lowered and the pressure is applied.

3. The material softens under heat and pressure and flows to fill the mould. Excess is squeezed out of the mould. For a thermosetting plastic, cross-linking occurs in the mould.
4. The mould is opened and the polymer product is removed.

For thermoplastics, the mould is cooled before removal of the product in order to get the product in full shape. Thermosetting plastics may be ejected after complete curing while they are hot.

Compression moulding was first developed to manufacture composite parts for metal replacement applications. This method is used to make larger flat or moderately curved parts. This method is greatly useful in manufacturing automotive parts such as hoods, fenders, scoops, spoilers and smaller more intricate parts.

Advantages of compression moulding:

- It is suitable method for moulding complex, high-strength fiberglass reinforcements and advanced composite thermoplastics.
- Compression moulding is used to mould large, fairly intricate parts.
- It is one of the cheapest moulding methods compared to other methods.
- There is less wastage, giving it an advantage when working with expensive compounds.
- It is a low cost production method for samples and pilot production.

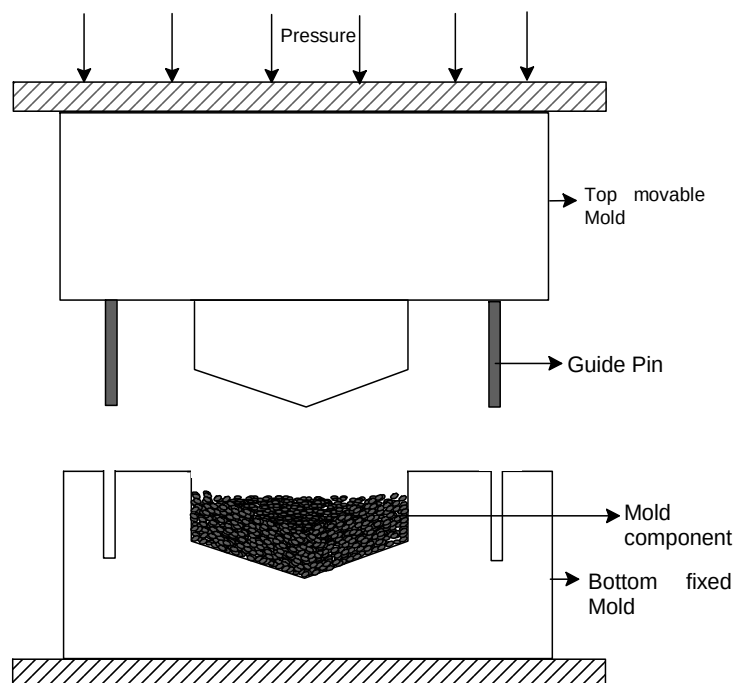


Fig. 2 Schematic Representation of Compression moulding equipment

Limitations:

- It is difficult to mould articles with complex shape.
- It has fair tolerance and flash can be a problem

Disadvantages:

- It provides poor product consistency and has difficulty in controlling flash.
- It is not suitable for certain designs.
- Fewer knit lines are produced and small fiber-length degradation is observed compared to injection moulding.

Applications

Compression moulding method is used to fabricate electrical components and fittings like electrical switches and sockets as thermosets are good electrical insulators

The process is also used for designing panels, housings, container caps, dishes and automotive parts.

Injection Moulding

Injection moulding consists of high pressure injection of raw materials into a mould during which the polymer attains the desired shape. Injection moulding can be done with metals, glasses, elastomers, most commonly with thermoplastics and thermosetting polymers.

Materials such as the polymer granules is fed into a feed hopper, mixed and heated to a molten state and then injected at high pressure into a prefabricated mould cavity where it cools and hardens to the design of the cavity. The moulds are made from metals like steel or aluminum. Injection moulding is widely used for manufacturing a variety of parts.

The injection moulding process requires very good control of the mould temperature, speed and pressure of injection, condition of the molten plastic and cooling times to ensure high quality products. It is necessary to have a sufficient clamping force proportional to the projected area of the mould to prevent creation of excess flash.

Injection blow moulding is used for the fabrication of small hollow components with more intricate designs. Injection moulding allows designing of highly complex structures. Holes, inserts, threads, bosses, minor undercuts and use of colour are all possible.

Advantages

- Injection moulding method has high production rate of 1–50 components/min and the process becomes highly economical at medium to high production volumes.
- Costs are reduced by good material utilization.
- It has the shortest cure time.
- No performs are required.
- Precise volumes of raw material can be injected into the mould.
- The product has high homogeneity in terms of cross linking.

- Wastage is minimum.
- Production automatisisation is possible.

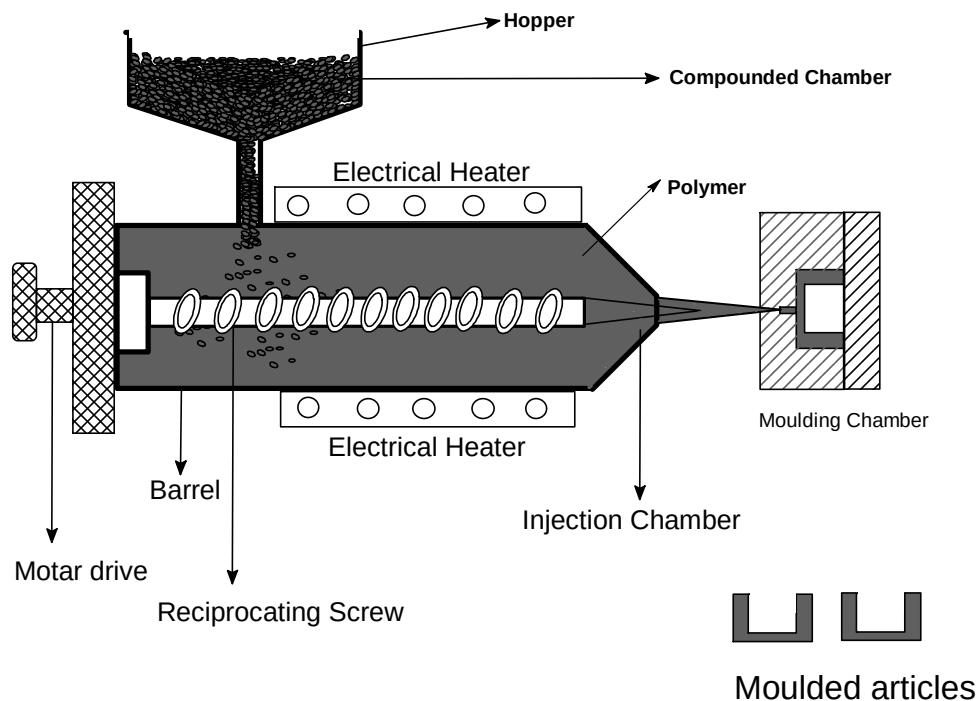


Fig. 3 Schematic Representation of Injection moulding

Disadvantages

- The capital investment required is high for injection moulding due to high equipment and tooling costs.
- Fabrication of complex die cavities made from hardened steel will result in longer lead times.
- The flexibility of the process is limited due to high cost of tool change over and machine set up times.

Applications

- Injection moulding is the common technique for plastic components.
- High precision, complex components with an excellent surface finish can be made which makes it ideal for production of automotive and aerospace components as well as electrical parts and housings e.g. computer enclosures and mobile phone cases.
- Other applications are fittings, tool handles, crates and containers.

Extrusion Moulding

In extrusion moulding method, a preheated polymer, placed in a feed hopper, is injected through an orifice having a particular cross section (the die), and a continuous shape of uniform cross section is produced.

This method is used to make parts of constant cross section like pipes and rods. Molten polymer material goes through a die to produce a final shape which involves four steps:

1. Polymer pellets are mixed with coloring agents and additives

2. The material is heated to its proper plasticity
3. The material is forced through a die
4. The material is cooled

By extrusion method, the shapes obtained are, T-sections, U-sections, square sections, I-sections, L-sections and circular sections. One of the most famous products of extrusion moulding method is optical fiber cable. Thermoplastics are extruded commonly by this method. The products that are produced by extrusion moulding method are film sheet, tubing, pipes, insulation etc. In each case the profile is determined by the die geometry and solidification is by cooling.

Advantages

- It has high production rate as continuous lengths are produced.
- It is a relatively inexpensive process.
- The final product design always has a uniform cross section.
- Open or closed profiles are possible.

Limitations

Products made by this method are prone to shrinkage and distortion

- The extruded product may increase in its size as it leaves the die and may be compensated by decreased extrusion rate or the melt temperature.
- One problem that affects the output and quality of extrusion is the possibility of trapped gases in the extrusion screw which is common with powdered raw materials.

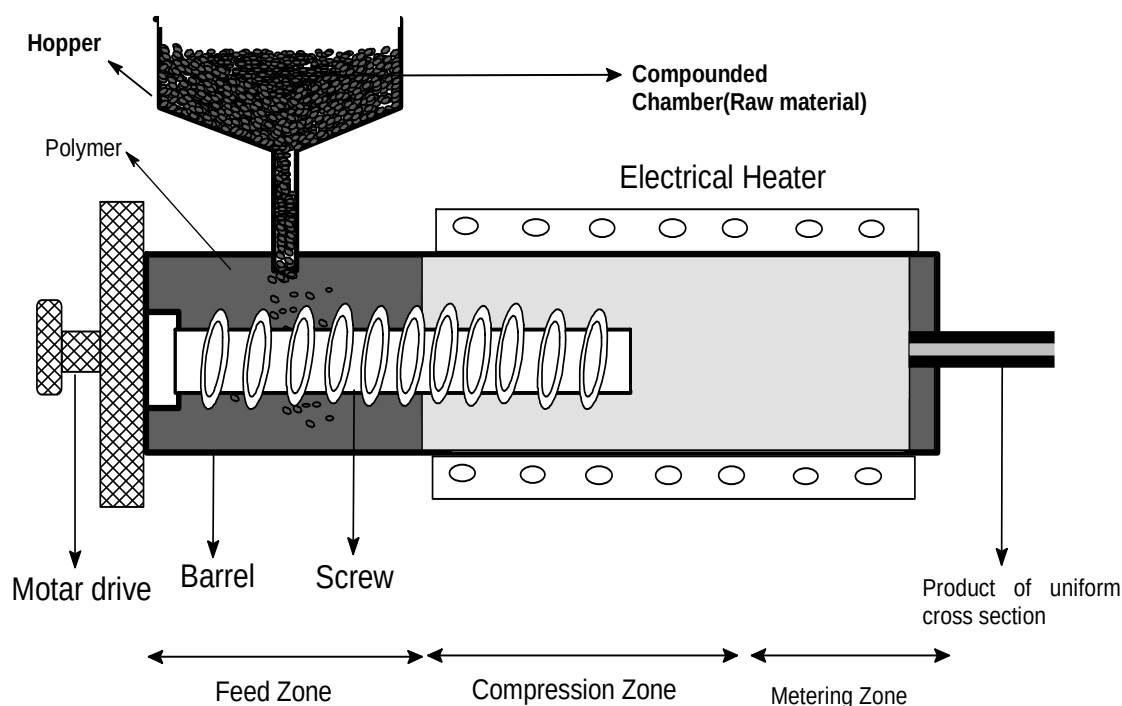


Fig. 4 Schematic Representation of Extrusion moulding

Disadvantages

- The process has high equipment costs as materials give off toxic or volatile gases during extrusion, demanding air extraction or a washing plant.

- Lead times are usually within weeks depending on the die complexity.
- The process flexibility is limited.

Applications

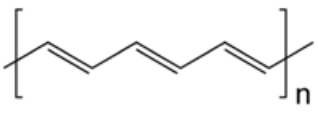
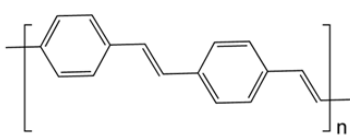
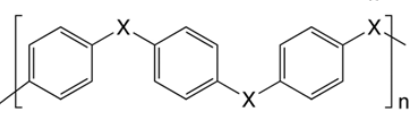
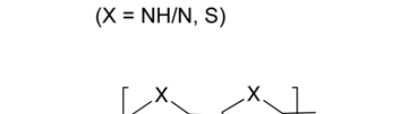
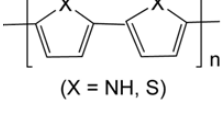
Continuous extrusion produces components having complex profiles such as rods, bar, tubing and sheets, pipes, guttering, window sills, insulation on wires, cling-film and tyre reinforcement.

Conducting Polymers

Introduction to Conducting Polymers

Conducting polymers are polyconjugated organic polymers which are able to conduct electricity due to the presence of conjugated π -bonded system. They have either metallic conductivity or can be semiconductors. The important property of conducting polymers is their processability by dispersion method. Conductive polymers are generally thermoformable but are organic materials like insulating polymers. They offer high electrical conductivity and do not show mechanical properties similar to other commercially available polymers. The electrical properties can be fine-tuned using the methods of organic synthesis and by doping processes.

Some examples of conducting polymers are:

Conducting Polymer	Structure	Conductivity (S/cm)
Polyacetylene		$10^3 - 1.7 \times 10^5$
Polyphenylene vinylene		$3 - 5 \times 10^3$
Polyaniline (X = NH/N)		30 - 200
Polyphenylene sulfide (X = S)		
Polypyrrole (X = NH), Polythiophene (X = S)		$10^2 - 7.5 \times 10^3$

The conducting polymers have low electrical conductivity and behave like an insulator or as a semiconductor in their pure or undoped (pristine state) form. The electrical conductivity of these polymers can be increased to the level of metals by treatment with suitable oxidizing or reducing agents thereby converting them to their salt form. These doped polymers having high electrical conductivities are called synthetic metals.

The undoped conjugated polymers have electrical conductivity in the range of 10^{-10} S/cm compared to insulators and in the range of 10^{-5} S/cm compared to that of semiconductors.

Molecular Basis of Electrical Conductivity

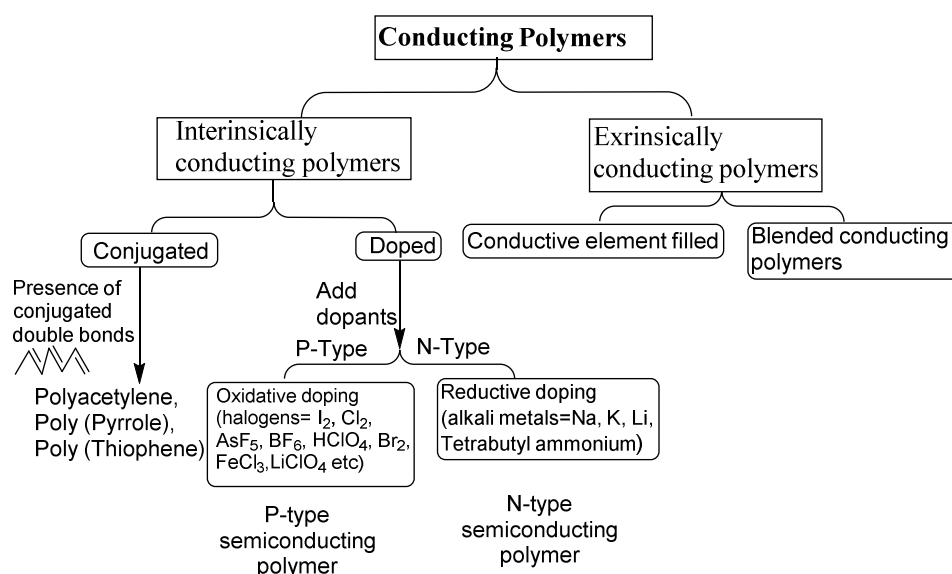
In pure polymers like polyethylenes, the covalent bonds are formed as a result of sp^3 hybridization. The electrons involved in sigma bond formation have low mobility and do not contribute to electrical conductivity of the material. In conjugated polymers, the covalent bonds are formed as a result of sp^2 hybridization. Electrons involved in sp^2 hybridisation undergo delocalization over the entire molecule rather than residing at one particular carbon atom. The electrons in these delocalized orbitals gain high mobility when the polymer is doped with oxidizing or reducing agents. Most organic conductors are doped oxidatively to give p-type materials. The redox doping of organic conductors is similar to silicon semiconductor doping, where a small fraction silicon atoms are replaced by electron-rich or electron-poor atoms to create n-type and p-type semiconductors, respectively.

Although, doping of conductive polymers involves oxidizing or reducing the material, conductive organic polymers associated with a protic solvent may be "self-doped."

Undoped conjugated polymers are either semiconductors or insulators. They have energy gap greater than 2 eV, which is too high for thermally activated conduction. Hence, undoped conjugated polymers, such as polythiophenes, polyacetylenes have low electrical conductivity of around 10^{-10} to 10^{-8} S/cm. The electrical conductivity can be increased to several orders of magnitude, up to around 0.1 S/cm, even by small level of doping (<1%). Subsequent doping will result in saturation of conductivity at values around 0.1–10 kS/cm for different polymers. Highest value is reported for the conductivity of stretch oriented polyacetylene with values of about 80 kS/cm.

Classification

Conducting polymers are classified as follows



Intrinsically Conducting Polymers**Conjugated Conducting Polymers**

Conjugated conducting polymers have alternate single and double bonds. They have sigma bonds (σ - bonds) and double bonds. The double bonds are made of one σ bond and one π -bond. The electrons involved in π -bond formation are delocalized over the entire polymer chain resulting in the formation of valence band and conduction band. When the energy gap between the two band is small, the electrons undergo excitation from the low energy valence band to the high energy conduction band and show increased conductivity.

Doped Conducting Polymers

Conjugation makes the polymer conducting and lead to a small increase in the conductivity. The electrical conductivity of conjugated polymers can be further increased by the process called 'Doping'. Doping is a process of addition of oxidizing agents or reducing agents to pristine polymers to make it more conducting. For example, the conductivities of pristine polymers (pure conjugated polymers) can be increased from insulating type ($10^{-10} - 10^5$ S/cm) to conducting type ($0.1 - 10^5$ S/cm) by the 'Doping' method. In the doping process, dopants are added to bring about partial oxidation or partial reduction of the polymer material either by the removal of the electrons from or by the addition of electrons to the π -bonds of the polymer backbone respectively. Dopants are the chemical species or agents used to increase the conductivity of the polymers. Dopants are introduced into the polymer by exposing the polymer film or powders to the vapour or solutions form of the dopants or by electrochemical oxidation and reduction.

There are two types of dopants: p-type dopants and n-type dopants.

- a) **p-type dopants:** Oxidizing agents cause the removal of electron form valence band results the hole formation or positive charge on polymer.

Examples: I_2 , Cl_2 , AsF_5 , BF_6 , $HClO_4$, Br_2 , $FeCl_3$, $LiClO_4$ etc.

- b) **n-type dopants:** Reducing agents cause the donation of electrons to the conduction band and leaving the polymer with a negative charge.

Examples: Na, K, Li, Tetrabutyl ammonium etc.

Addition of small amount of dopants to the conjugated polymer produces a drastic change in the electrical, electronic, magnetic, optical and structural properties of the polymers and by adjusting the concentration of the dopants, conductivity of the polymer can be changed anywhere between the insulating type (undoped form) and that of the highly conducting type (doped form).

Extrinsically Conducting Polymers**Conductive Element Filled Polymers**

These polymers are obtained by blending an insulating type of polymer with suitable conducting elements such as carbon black, metallic fibers, metallic oxides etc to make the

polymer conducting. The minimum amount of the conducting element required for an insulating polymer to make it conducting is called the percolation threshold.

Blended Conducting Polymers

They are obtained by blending a conventional polymer with a suitable conducting polymer. Polymers obtained by this method possess better physical, chemical, electrical and mechanical properties and can also be easily processed

Questions:

1. Write in brief on classification of polymers
2. Write notes on types of polymers.
3. Give an brief account on tacticity of polymers.
4. Explain addition and condensation polymerization reactions with one example each.
5. List out the differences between addition and condensation polymerization.
6. Explain the mechanism of addition polymerization
7. Discuss cationic polymerisation mechanism
8. Discuss free radical polymerization mechanism
9. Compare anionic and cationic polymerization mechanism.
10. Distinguish between thermoplastics and thermosetting plastics.
11. Comment on molecular weight of polymers.
12. What is compounding of plastics. What are the ingredients used and give their significance?
13. Explain compression and injection moulding methods.
14. Explain with a neat diagram the compression moulding method and compare it with the injection moulding method.
15. Explain extrusion moulding method with a neat diagram.
16. Write in detail on morphology of polymers
17. Write notes on types of conducting polymers.
18. What are conducting polymers? Give the types and explain.
19. Explain polyacetylene as a conducting polymer.
20. Describe in detail the different oxidation states of polyaniline.
21. Explain in detail the molecular basis of electrical conductivity in conducting polymers.

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