MALLA REDDY COLLEGE OF ENGINEERING & TECHNOLOGY

(An Autonomous Institution – UGC, Govt. of India)

Recognizes under 2(f) and 12(B) of UGC ACT 1956

(Affiliated to JNTUH, Hyderabad, Approved by AICTE –Accredited by NBA & NAAC-"A" Grade-ISO 9001:2015 Certified)

MRCET

ADVANCED MATERIAL CHEMISTRY

B.Tech – I Year – I Semester

DEPARTMENT OF HUMANITIES AND SCIENCES



Preface

Chemistry as a basic science plays a vital role in making a foundation for engineering students and ensuring security by shaping a fruitful superstructure for their entire career. Chemistry is the back bone in designing an understanding the nature of various engineering materials. Moreover, thorough knowledge of chemistry provides the requisite expertise to deal with challenges in disciplines of engineering related to design an development of new materials.

Material Science and Engineering is a key aspect of most companies the world over. In the race to make things stronger, cheaper, lighter, more functional and more sustainable, the manipulation of materials, their properties and processes is key. The field of materials science and engineering is important both from a scientific perspective, as well as towards applications. Materials are of the utmost importance for engineers (or other applied fields), as the usage of the appropriate materials is crucial when designing systems.

Advanced material Chemistry is a textbook exclusively designed for the needs of undergraduate students of all disciplines of engineering and technology. The scope of the subject is very wide and writing a book for a heterogeneous variety of students across the country was a challenging assignment. The needs of the students are diversified and incorporate a combination of the both traditional topics and the latest trends in the subject including emerging areas like functional materials, smart materials and nanomaterials.

This book has been organized to meet syllabi requirements of both JNTUH and AICTE. It serves as an introductory text to first year students, enabling them to understand basic principles and updating them on the advancements in the ever-growing field of chemistry. The aim of this text is to enable the student to develop capabilities in self learning and understanding.

Keeping these objectives in mind the book has been written in very simple language. All chapters are provided with highly descriptive and well labeled figures. A simple look at a figure will enable the student to grasp the underlying description.

Organization of the book

The book has been organized into Five Units. This text book emphasizes on the basic concepts an engineering applications of advanced materials It begins with topics of common interest like electrochemistry, batteries, corrosion, photochemistry followed by functional and advanced materials like polymers, fiber reinforced plastics, nanomaterials and smart materials.

- Unit I-Electrochemistry provides through understanding of electrochemical cells, batteries and fuel cells.
- Unit II-Corrosion provides sufficient knowledge on fundamentals of corrosion and development of different techniques in corrosion control.
- Unit III-Functional materials includes various polymeric materials and composites which have increasing applications in all fields of engineering due to their low cost and ease of manufacture.

- Unit IV-Advanced Materials includes nano and smart materials which represents a fast growing set of advanced materials that have excellent engineering applications.

- Unit V-Photochemistry explains the principles and applications of photochemistry in engineering field.

We would like to extend our sincere gratitude to Dr. VSK Reddy, Principal, Malla Reddy College of Engineering and Technology (autonomous) under whose patronage we were able to write this book. We are also indebted to our Dr. V. Madhusudhana Reddy, Head of the Department, Humanities & Sciences for his constant support and motivation for our academic growth. With great pleasure we acknowledge the compatible environment shared by our colleagues.

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MALLAREDDY COLLEGE OF ENGINEERING AND TECHNOLOGY (UGC AUTONOMOUS)

B.TECH I YEAR – I SEM (MECH & ANE)

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ADVANCED MATERIAL CHEMISTRY

COURSE OBJECTIVES: The students will be able to

1. Apply the electrochemical principles for construction of batteries and fuel cells.
2. Analyze engineering problems related to corrosion and develop different corrosion control techniques.
3. Identify different types of polymers, composites and their applications in various engineering fields.
4. Gain knowledge on wide variety of advanced materials like nano and smart materials which have excellent engineering properties.
5. Explain the principles and applications of photochemistry in engineering field.

Unit I Electrochemistry: (8 hours)

Introduction- Electrochemical cells - electrode potentials, construction and working of a galvanic cell, EMF and its applications - potentiometric titration; Nernst equation and its applications; electrochemical series and its applications. Batteries -classification of batteries, primary cell - lithium cells; secondary cells - lead acid battery and lithium ion battery; Fuel cells - H_2-O_2 fuel cell; applications and advantages of fuel cells.

Unit II Corrosion: (8 hours)

Introduction- Causes and effects of corrosion; Theories of corrosion- chemical (oxidation corrosion) and electrochemical corrosion, Corrosion control methods - cathodic protection - sacrificial anodic protection and impressed current cathodic protection; protective coatings - galvanizing and tinning, electroplating (Cu plating) and electroless plating (Ni plating) - advantages and applications of electroplating/electroless plating.

Unit III Functional Materials: (10 hours)

Polymers: Introduction- thermoplastic and thermosetting resins, preparation, properties and engineering applications of Polyvinylchloride (PVC), Teflon (PTFE), Polymethyl methacrylate (PMMA), Polycarbonate, Bakelite. Conducting polymers-classification of conducting polymers-conduction mechanism in polyacetylene and applications of conducting polymers.

Composite materials: Introduction-Fibre reinforced plastics (FRPs) - Glass fibre reinforced, Carbon fibre reinforced plastics and their applications.

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Unit IV Advanced Materials: **(8 hours)**

Nanomaterials: Introduction and classification of nanomaterials; preparation of nanomaterials - Sol-gel and Chemical vapour deposition method; applications of nanomaterials (industrial and medicinal). Carbon nanotubes (CNTs) - applications.

Smart materials: Introduction- types of smart materials - examples and applications of piezoelectric materials, shape memory alloys, magnetostrictive materials and electrostrictive materials.

Unit V Photochemistry: **(8 hours)**

Introduction- Laws of photochemistry- Stark-Einstein law, Beer-Lambert's law; Photochemical processes – Photosensitization; Photophysical processes - Fluorescence and Phosphorescence - Jablonski diagram, applications of fluorescence and phosphorescence.

Suggested Text Books:

1. Engineering Chemsitry by P.C. Jain & M. Jain: Dhanpat Rai Publishing Company (P) Ltd, New Delhi. 16thEdition.
2. Engineering Chemistry by Prasanta Rath, B. Rama Devi, C. H. Venkata Ramana Reddy, Subhendu Chakroborty, Cengage Learning Publication, India Private Limited, 2018.
3. Principles and Applications of Photochemistry by Brian Wardle Manchester Metropolitan University, Manchester, UK, A John Wiley & Sons, Ltd., Publication, 2009.
4. Engineering Analysis of Smart Material Systems by Donald J. Leo, Wiley, 2007.

Reference Books:

1. Engineering Chemistry by Shashi Chawla, Dhanpat Rai Publishing Company (P) Ltd, New Delhi.
2. Engineering Chemistry, by S. S. Dara, S. Chand & Company Ltd, New Delhi.
3. P.W. Atkins, J.D. Paula, "Physical Chemistry", Oxford, 8th edition (2006).
4. B.R. Puri, L.R. Sharma and M.S. Pathania, "Principles of Physical Chemistry", S. Nagin Chand & Company Ltd.,46th edition(2013).

COURSE OUTCOMES: The student will be able to

1. Relate the knowledge of operating principles of various types of electrochemical cells, including fuel cells and batteries, to optimize the need for sustainable development.
2. Analyze and develop technically sound, economic and sustainable solutions for complex engineering problems related to corrosion and its effects.
3. Identify, formulate and develop polymeric compounds used in various engineering materials for futuristic engineering applications.
4. Apply the knowledge of nanotechnology and smart materials to find solutions for various engineering problems.
5. Evaluate the photochemical and photophysical processes to reach substantiated conclusions in the technological arena.

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UNIT I: ELECTROCHEMISTRY

Introduction:

Electrochemistry is the branch of chemistry which deals with the transformation of electrical energy to chemical energy and vice versa. In brief it deals with the chemical applications of electricity.

Electrical Energy ⟷ Chemical Energy

Electric current is a flow of electrons generated by a battery, when the circuit is completed. Electrolysis is one process where electrical energy causes chemical changes. It is carried out in an apparatus called electrolytic cell. The cell contains electrolyte and electrodes. The electrode connected to the positive pole of the current source is called anode. The electrode connected to the negative pole of the current source is called cathode. When an electric current is passed through the electrolytic solution, cations move towards cathode (-ve electrode and anions move towards anode (+ve electrode)

Ex: Electrolysis of water yields H_2 and O_2

In other process, certain chemical reactions takes place in a vessel and produce electric energy. The device is called electrochemical cell. Eg. Galvanic cell, batteries and fuel cells

Broadly we can classify the cells as electrolytic cells and electrochemical cells.

Electrolytic cell: A device which converts electrical energy to chemical energy

Electrochemical cell: A device which converts chemical energy to electrical energy

Types of Conductors:

Electrical Conductors: Substances which allow electric current to pass through them are known as electrical conductors. Eg. All metals, graphite, fused salts, aqueous solutions of acids and bases and salts.

Semi conductors: The substances which partially conduct electricity are called semi-conductors. The conducting properties of semi-conducting properties are increased by the addition of certain impurities called "dopping".

Ex: 'Si' and Ge on addition of V group elements like P produces n-type semi-conductor.

On addition of III group element like B, Al, produces p-type of semi-conductor.

Non-conductors or Insulators: The substances which do not allow electricity are called non-conductors. . Eg. Rubber, wood, paper, all non-metals except carbon.

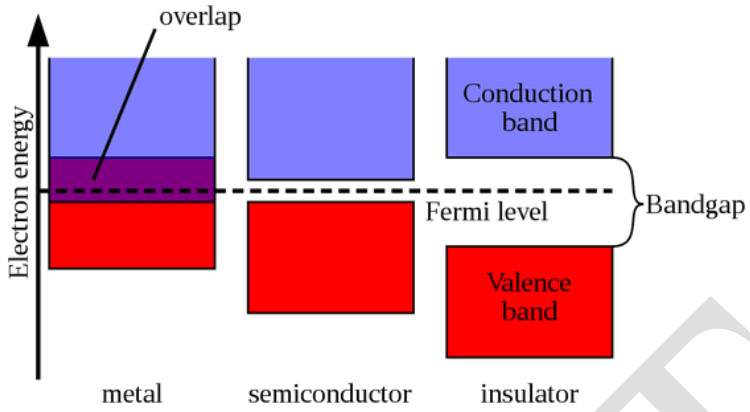
Conductance: The capacity of a conductor to allow the passage of current through it called conductance. It is a property of conductor which facilitates flow of electricity through it.

$$\text{Conductance (C)} = \frac{1}{R}$$

i.e. The reciprocal of resistance is called conductance. **Units:** Ohm.^{-1}

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Conductor: The substance which allows the passage of electric current through it is called conductors. **E.g.:-** all metals, graphite, aqueous solution of acids and bases.



Band Theory of Electrical Conductivity

Electric conductors are two types

Metallic conductor	Electrolytic conductors
Conductance due to the migration of electrons**.** **E.g.**: metals, graphite.	Conductance due to the migration of ions in a solution of fused electrolyte. **E.g.:** Acids and bases
Passage of current due to electron flow. No chemical reaction takes place.	Passage of current due to movement of ions. Some chemical reaction takes place.
Free electrons are responsible for electrical conduction.	Free ions are responsible for electrical conduction.
Mass is not transferred	Mass is transferred.
With increase of temp resistance increases and conductance decreases	With increase of temperature resistance decreases and conductance increases.

Electrolytes are classified into two types:
Strong electrolytes: The electrolytes which completely dissociates in solution at all concentrations. Their conductance is very high**.** Eg. NaCl, HCl, NaOH.

Weak Electrolytes: The electrolyte which partially dissociates at moderate concentration. Their conductance is low as they dissociate only to a small extent even at very high dilutions. Eg: CH_3COOH, NH_4OH, sparingly soluble salts like AgCl, AgBr, AgI, $BaSO_4$, $PbSO_4$ etc

CONDUCTANCE:

Ohm's Law: Ohm's law states that the current (I) flowing through a conductor is directly proportional to potential difference (E) applied across the conductor and is inversely proportional to the resistance of conductor.

Thus,

$$E \alpha I$$

Where I is the current in amperes, and E is potential difference applied across the conductor in volts.

Thus $E = IR$

or $R = \frac{E}{I}$



Where R is the proportionality constant and is known as the resistance of conductor in ohms. Thus, the resistance of a conductor is directly proportional to the potential difference applied across the conductor and inversely proportional to the current carried by the conductor.

SPECIFIC RESISTANCE: The resistance of a uniform conductor is directly proportional to its length (l) and inversely proportional to the area of the cross- section (a). Thus

$$R \alpha l/a$$

$$R = \rho\, l/a$$

The proportionality constant (ρ) is called as the specific resistance of an electrolytic solution of 1cm in length and $1cm^2$ area of cross section. i.e. resistance of $1cm^3$ of the electrolytic solution.

UNITS: specific resistance units: Ohm cm

Cell constant:

It is a constant, characteristic of the cell in which the electrolyte is taken and its value depends on the distance between the electrodes and area of cross-section of the electrodes.

$$\text{Cell constant} = \frac{\text{Distance between the electrodes}}{\text{Area of cross} - \text{section of each electrode}}$$

$$x = \frac{l}{a}$$

And specific conductance, $K = \frac{1}{R} \times \frac{l}{a}$

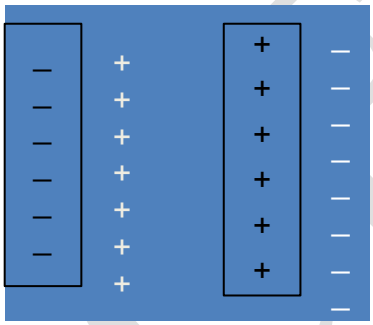
$$\therefore \text{Specific conductance} = \frac{\text{Cell constant}}{R}$$

$$\text{or } x = K \times R; \quad \text{or } x = \frac{K}{C} \ (\because c = 1/R)$$

If area of cross-section is in cm^2 and distance between the electrodes is in cm, the unit of cell constant is cm^{-1}.

ELECTRODE POTENTIAL:

- When a metal rod is dipped in its salt solution (electrolyte), the metal atom tends either to lose electrons (oxidation) or to accept electrons (reduction).
- The process of oxidation or reduction depends on the nature of metal.
- In this process, there develops a potential between the metal atom and its corresponding ion called the electrode potential.
- It is a measure of tendency of a metallic electrode to lose or gain electrons when it is in contact with its own ions in solution.
- **Reduction potential:** The tendency of an electrode to gain electrons and to get reduced is called *reduction potential, i*ts value is +x volts.
- **Oxidation potential:** Similarly the tendency of an electrode to lose electrons and to get oxidized is called *oxidation potential,* its value is –x volts
- The potential develop between electrode and electrolyte by the formation of charges and these charges are formed Helmholtz electrical double layer, through which potential develop between electrode and electrolyte.



Anode Cathode

Helmholtz Electrical Double LayeR

Single electrode potential:

Each electrochemical cell is made up of two electrodes, at one electrode electrons are evolved and at other electrode electrodes used up. Each electrode which is dipped in its salt solution is called Half Cell. The potential of half-cell i.e. the potential difference between the metal and its salt solution in which it is dipped is called single electrode potential. It cannot be measured directly.

$Zn/ZnSO_4// CuSO_4/Cu$

←Half-cell→ ←half cell→

← Single electrode→ ← single electrode→

The total cell E.M.F is equal to the sum of the single electrode potentials. Each electrode is affixed with a symbol corresponding to the reaction that takes place near the electrode.

$$E_{cell} = E_{(anode)} + E_{(Cathode)}$$

The half-cell reactions are as follows; the half-cell reaction which corresponds oxidation is

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

The electrode is called oxidation electrode and potential of the electrode is oxidation potential or the potential of left hand electrode which is represented as E_{OX} or E_L. The cell reaction of the electrode where reduction takes place is given below

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

The electrode is called reduction electrode or right hand electrode and the potential of this electrode is reduction potential and represented as $E_{(Red)}$ or $E_{(R)}$.

The total cell reaction is $Zn + Cu^{2+} \rightarrow Zn^{2+} + Cu$.

$$E_{(cell)} = E_{(OX)} + E_{(Red)}$$

E.M.F of the cell is equal to the sum of the oxidation potential and reduction potential, also expressed as the reduction potential of the right hand electrode minus reduction potential of the left hand electrode.

GALVANIC CELL: A galvanic cell is a system in which a spontaneous oxidation and reduction reaction occurs and generates electrical energy. Eg. Daniel cell

Construction of Galvanic Cell

A galvanic cell is made up of two half cells. One is oxidation or anodic half- cell and other one is reduction or cathodic half cell. Daniel cell is an example of galvanic cell having zinc and copper electrodes. The first half cell consists of zinc electrode dipped in $ZnSO_4$ solution and the second half is made of copper electrode dipped in copper sulphate solution. Both half cells are connected externally by metallic conductor and internally by a bent glass tube having saturated solution of a strong electrolyte (KCl) called salt bridge. It acts as a bridge between the two half cells.

Working of Galvanic cell:

When two half cells are connected externally by a wire through a voltmeter, spontaneous redox reaction takes place at the electrode.

At anode: Oxidation takes place with the liberation of two electrons.

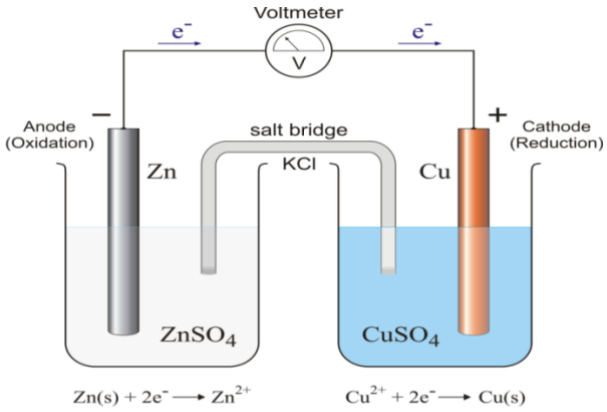
$$Zn \rightarrow Zn^{+2} + 2e^- \text{ (oxidation or de-electronation)}$$

At cathode: Reduction occurs and cuprous ion is reduced to metallic copper.

$$Cu^{+2} + 2e^- \rightarrow Cu \text{ (reduction or electronation)}$$

The overall reaction is $Zn + Cu^{+2} \rightleftharpoons Zn^{+2} + Cu$

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$Zn(s) \mid ZnSO_4(aq) \mid\mid CuSO_4(aq) \mid Cu(s)$

As the connection is complete, the flow of electrons will be externally from anode to cathode and internally from cathode to anode through the salt bridge. The flow of current is due to the difference in electrode potentials of both the electrodes. The potential difference in the cell is called the EMF and is measured in volts. It can be measured by the potentiometer. The flow of current becomes slow after using the electrodes for a long time because of the polarization of the electrodes.

At this stage, the salt bridge comes to the aid and restores the electrical neutrality of the solution in the two half cells. When the concentration of Zn^{2+} ions around the anode increases, sufficient number of Cl^- ions migrate from the salt bridge to the anode half cell. Similarly, sufficient number of K^+ ions migrate from the salt bridge to cathode half cell for neutralizing excess negative charge due to the additional SO_4^{2-} ions in the cathodic half cell. Thus it maintans the electrical neutrality of the two solutions in the half cells.

Representation of a galvanic cell:

1. The electrode showing oxidation reaction is anode and the other electrode where reduction occurs is cathode.
2. As per IUPAC convention, the anode is always represented on the left and cathode always represented on the right side of the cell.

Anode Half-Cell || Cathode Half-Cell

Electrode | Anode Soln || Cathode Soln | Electrode

$Zn(s) \mid Zn^{2+}$ (1 M) || Cu^{2+} (1 M) | $Cu(s)$

3. The electrode on left (i.e, anode) is written by writing the metal first and then the electrolyte. The two are separated by a vertical line or a semicolon. The electrolyte may be represented by the formula of the whole compound or by ionic species and concentration may also be mentioned in bracket.

Examples of representing anode half-cell as:

Eg: Zn/Zn^{2+} or $Zn;Zn^{2+}$ or $Zn/ZnSO_4$(1M).

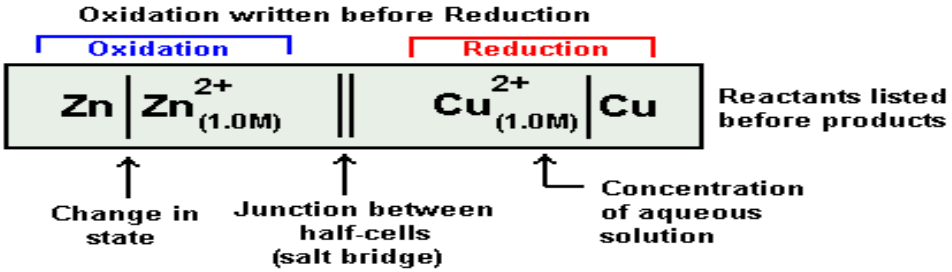
4. The cathode of the cell (at which reduction takes place) is written on the right hand side. In this case, the electrolyte is represented first and then the metal. The two are separated by a vertical line or a semicolon.

Examples of representing cathode half-cell as:

Cu^{2+}/Cu or Cu^{2+}; Cu or $CuSO_4(1M)/Cu$.

5. A salt bridge is indicated by two vertical lines, separating the two half-cells.

$Zn;Zn^{2+}(1M)$ // $Cu^{2+}(1M)$; Cu.



Electromotive Force or Cell Potential (EMF):

The flow of electricity from one electrode to another electrode in a galvanic cell indicates that the two electrodes have different potentials. The difference of potentials between the electrodes of a cell which causes flow of current from an electrode at higher potential to other electrode at lower potential is known as electromotive force or cell potential.

The EMF of the cell depends on (a) temperature (b) nature of reactants and (c) concentration of solutions in two half cells.

Mathematically:

EMF or $E_{cell} = E_{cathode} - E_{anode}$ or

$E_{(cell)} = E_{(right)} - E_{(left)}$

Where

E(cell) = e.m.f of cell
E(right) = reduction potential of right hand side electrode (cathode)
E(left) = reduction potential of left hand side electrode (anode)

$E_{cell} = E_{ox}$ (anode) + E_{Red} (cathode)
$E_{cell} = E_R - E_L$ (both are reduction potentials)
$E_{cell} = E_L$ (anode) - E_R (cathode) (both are oxidation potentials)

Salt bridge: Salt bridge is a U shaped glass tube containing concentrated solution of an inert electrolyte such as KCl, KNO_3 and K_2SO_4 or paste of inert electrolyte (whose ions do not take part in redox reaction and do not react with the electrolyte) in agar–agar medium or gelatin.

Functions of salt bridge:

1. Salt bridge helps to complete the circuit by allowing the ions to flow from one solution to the other without mixing the two solutions.
2. It helps to maintain electrical neutrality of the solution in the half cells.

Applications of EMF

Potentiometric Titration:

A potentiometric titration is one in which the end point is detected by measuring changes in the potential of a suitable electrode (after coupling it with a standard reference electrode) during the course of reaction. No indicator is used in this titration. The electrode whose potential varies during the reaction and which depends upon the concentration of ionic species is called the indicator electrode.

The potentiometric titrations are subdivided in terms of the type of chemical reaction involved in the titration, e. g. acid-base titration, redox titration, precipitation titration and complexometric titration.

Acid-Base titration*:* The acid solution whose strength has to be determined is taken in a beaker and the hydrogen electrode and calomel electrode were dipped in the solution. The electrodes were connected to the potentiometer and the e.m.f. is measured.

Reference Electrode: Saturated Calomel Electrode (SRP = 0.242 V) [Anode]

Indicator Electrode: Quinhydrone Electrode [Cathode].

Cell Notation:

(-) Pt / Hg, Hg_2Cl_2 / KCl (sat) // H^+ Test Sol. / Q, QH_2 / Pt (+) Cell Reactions:

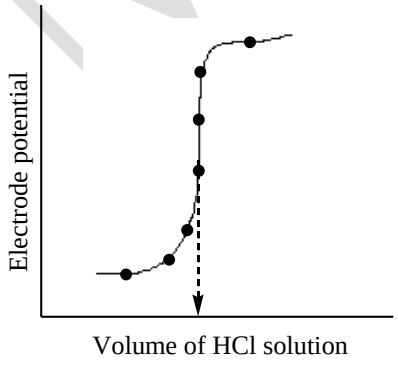
Anode: $2Hg + 2Cl^- \rightarrow Hg_2Cl_2 + 2e^-$

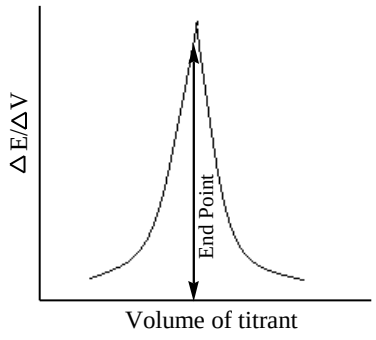
Cathode: $Q + 2H^+ + 2e^- \rightarrow QH_2$

$E_{cell} = E_{cathode} - E_{anode} = [0.0990 - 0.0591\ pH] - 0.242$ i.e. E_{Cell} is a function of pH.

During titration, as base is added to the acid, the H^+ ion concentration in the half cell containing Quinhydrone will decrease. Correspondingly, there will be a decrease in the E_{QE} and E_{Cell} values also. E_{Cell} values are noted, graph is plotted, where equivalence point is located and concentration of test solution is calculated.

The steepest portion of the curve indicates the equivalent point of the titration. Instead $\Delta E/\Delta V$ is plotted against the volume of the base.





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Nernst equation:

Derivation of Nernst equation: Nernst found that the single electrode potential varies with the change in concentration of ions and temperature and hence the EMF of the cell also varies. He derived a mathematical relationship between the standard electrode potential, temperature and the concentration of ions. This relationship is known as the Nernst equation.

Consider the redox reaction: $M^{n+} + ne^- \rightleftarrows M$

In the above reversible reaction the free energy change (G) and its equilibrium constant (K) are related by the following equation which is popularly known as Van't Hoff reaction isotherm.

$$\Delta G = RT \ln K + RT\ln \frac{\text{product}}{\text{reactant}}$$

$$\Delta G = \Delta G^0 + RT\ln \frac{\text{product}}{\text{reactant}}$$

When ΔG^0 is the standard free energy change

The free energy change is equivalent to the electrical energy –nFE

Where n = valency

F = Faraday (96500 coloumbs)

E = Electrode potential

R = 8.314 Joules K^{-1} $mole^{-1}$(Gas constant)

T = Temperature (K)

$-nFE = -nFE^0 + RT\ln([M])/([M^{n+}])$ (Concentration of M is unity)

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

$= -nFE^0 - RT2.303 \log_{10} [M^{n+}]$

Dividing the equation by – nF

$$E = E^{0+} + \frac{2.303RT}{nF} \log_{10} [M^{n+}]$$

Put the values of R, T and F then

$$\frac{2.303RT}{nF} = \frac{0.0591}{n}$$

$$E = E^0 + \frac{0.0591}{n} \log_{10} [M^{n+}]$$

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APPLICATIONS OF NERNST EQUATION:

1. It can be used to study the effect of electrolyte concentration on electrode potential.
   $E = E^o - RT/nF \ln[1/M^{n+}]$
2. It can also be used for the calculation of the potential of a cell under non-standard conditions.
   For example,
   $Cu(s)/Cu^{2+}(aq)(0.50M)//H^+(0.01)/H_2(0.95atm)$
   $E_{cell} = E^o_{cell} - \frac{0.0591}{2}\log(Cu^{2+})P_{H2}/[H^+]^2$
3. Determination of unknown concentration of one of the ionic species in a cell is possible with the help of Nernst equation, provided E_{cell} and concentration of other ionic species are known.
4. The pH of a solution can be calculated from the measurement of EMF and Nernst equation.
5. Nernst equation can also used for finding the valence of an ion or the number of electrons involved in the electrode reaction.

ELECTROCHEMICAL SERIES:

A series in which various metals and elements have been arranged in increasing order of their standard reduction potential or decreasing order of their standard oxidation potential as compared to that of standard hydrogen electrode is called electrochemical series. These standard electrode potentials are measured at 25^0C

Electrode	Oxidation reaction	Standard potential (volts)	Nature
$Li \mid Li^+$	$Li \longrightarrow Li^+ + e^-$	+3.040	reducing agents
$K \mid K^+$	$K \longrightarrow K^+ + e^-$	+2.924	
$Ca \mid Ca^{2+}$	$Ca \longrightarrow Ca^{2+} + 2e^-$	+2.870	
$Na \mid Na^+$	$Na \longrightarrow Na^+ + e^-$	+2.710	
$Al \mid Al^{3+}$	$Al \longrightarrow Al^{3+} + 3e^-$	+1.660	
$Zn \mid Zn^{2+}$	$Zn \longrightarrow Zn^{2+} + 2e^-$	+0.762	
$Fe \mid Fe^{2+}$	$Fe \longrightarrow Fe^{2+} + 2e^-$	+0.441	
$Cd \mid Cd^{2+}$	$Cd \longrightarrow Cd^{2+} + 2e^-$	+0.403	
$Ni \mid Ni^{2+}$	$Ni \longrightarrow Ni^{2+} + 2e^-$	+0.236	
$Sn \mid Sn^{2+}$	$Sn \longrightarrow Sn^{2+} + 2e^-$	+0.140	
$Pb \mid Pb^{2+}$	$Pb \longrightarrow Pb^{2+} + 2e^-$	+0.126	
$Pt \mid H_2\ H^+$	$H_2 \longrightarrow 2H^+ + 2e^-$	0.000	
$Cu \mid Cu^{2+}$	$Cu \longrightarrow Cu^{2+} + 2e^-$	-0.337	oxidising agents
$Ag \mid Ag^+$	$Ag(s) \longrightarrow Ag + e^-$	-0.799	
$Hg \mid Hg^+$	$Hg(l) \longrightarrow Hg^{2+} + 2e^-$	-0.920	
$Cl_2 \mid Cl^-$	$2Cl^- \longrightarrow Cl_2(g) + e^-$	-1.359	

In this series, iron lies above hydrogen and copper lies below it. Hence, if an iron rod is dipped in $CuSO_4$ solution a layer of copper metal will get deposited on the surface of the iron rod.

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

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

$Fe + Cu^{++} \rightarrow Fe^{++} + Cu.$

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The reverse of this reaction is not possible, i.e. a copper rod dipped in $FeSO_4$ solution will not show redox reaction.

Applications of Electrochemical Series:

1) **Comparison of oxidizing and reducing power:** It gives information about the relative ease with which oxidation and reduction of metal occurs. Based on the electrochemical series the element with higher reduction potential have a greater tendency to get reduced and act as good oxidizing agents. Whereas the elements with lower reduction potential have a tendency to get oxidized and act as good reducing agents.

Ex: F_2 can be reduced easily than Li^+ ions. So it is a good oxidizing agent.

2) **Relative activities of metal:** Provides information about the replacement tendencies of metals. The greater the O.P of a metal, more easily it can lose electrons and greater is its reactivity, i.e. the metal with higher O.P can displace the metal with lower O.P. in their salt solution.

Ex: Mg > Zn > Fe > Cu > Ag. Zn has lower reduction potential than Cu. Hence Zn can displace copper from $CuSO_4$ solution.

3) Any metal above hydrogen will displace hydrogen from dil. acid solution. For example, Na reacts with water to liberate hydrogen because

E^0 (Na^+/Na) = -2.714 V is less than E^0(H^+ / H_2 = 0).

$$2Na + H_2SO_4 \rightarrow Na_2SO_4 + H_2$$

$$2K + H_2SO_4 \rightarrow K_2SO_4 + H_2$$

$$Ca + H_2SO_4 \rightarrow CaSO_4 + H_2$$

4) Provides information about the relative corrosion tendencies of metals. Metals above hydrogen undergo corrosion easily as they have higher oxidation potentials.

5) Predicts spontaneity of redox reaction. Spontaneity of a redox reaction can be predicted from EMF of the cell reaction. If EMF of a cell is –ve, the reaction is non spontaneous and if EMF is +ve then the reaction is spontaneous.

6) When a cell is constructed anode should be a metal higher in the series and cathode should be a metal lower in the series. Eg. When a cell is constructed using Zn and Cu, Zn higher in the series will be the anode and Cu will be the cathode.

7) This series is also helpful in direct calculation of the EMF of cell formed between electrodes.

E^0= -0.76V (reduction potential)

E^0= 0.34V (reduction potential)

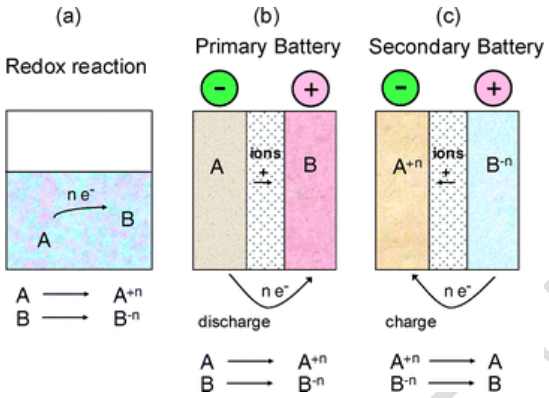
$E^0 = E_R - E_L$

= 0.34 - (0.76) = 1.10V

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BATTERIES

Battery is an electrochemical cell or often several electrochemical cells connected in series that can be used as a source of direct electric current at constant voltages. A device which converts chemical energy to electrical energy is called battery cells, connected together electrically in series. Batteries are commercial electrochemical cells.



ADVANTAGES OF BATTERIES:

(1) Batteries act as a portable source of electrochemical energy.

(2) The portability of electronic equipment in the form of handsets has been made possible by batteries.

(3) A variety of electronic gadgets have been made more useful and popular with the introduction of rechargeable storage batteries having reliability, better shelf life and tolerance to service.

(4) For all commercial applications, batteries are constructed for their service. For example batteries for automotives and aircrafts, stand by batteries etc.

Requirements of Battery:

A useful battery should fulfill the following requirements

1. It should be light and compact for easy transport.

2. It should have long life both when it is being used and when it is not used.

3. The voltage of the battery should not vary appreciably during its use.

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Differences between Primary, Secondary and Fuel cells:

Primary cell	Secondary cells	Fuel Cell
It acts as a simple galvanic cell.	It acts as a galvanic cell while discharging and electrolytic cell while charging.	It acts as a simple galvanic cell.
Cell reaction is not reversible.	Cell reaction can be reversed.	Cell reaction is not reversible
Cannot be recharged.	Can be recharged	Do not store energy
Can be used as long as the materials are active in their composition. **E.g:** Leclanche or dry cell. Zn/NH_4Cl (20%), $ZnCl_2/MnO_2/C$. emf =1.5V. Applications: Radios, torches, transistors, hearing aids.	Can be used again and again by recharging the cell **E.g:** 1. Lead storage cell 2. Nicol or Nickel cadmium battery emf =1.4 Applications: Electronic calculators, electronic flash units & cordless electronic shavers etc.	Energy can be withdrawn indefinitely as long as outside supply of fuel is maintained **E.g:** H_2-O_2, CH_3OH-O_2 Applications: Space vehicles due to their light weight and the bi product H_2O produced is a valuable source of fresh water for astronauts.

PRIMARY CELLS:

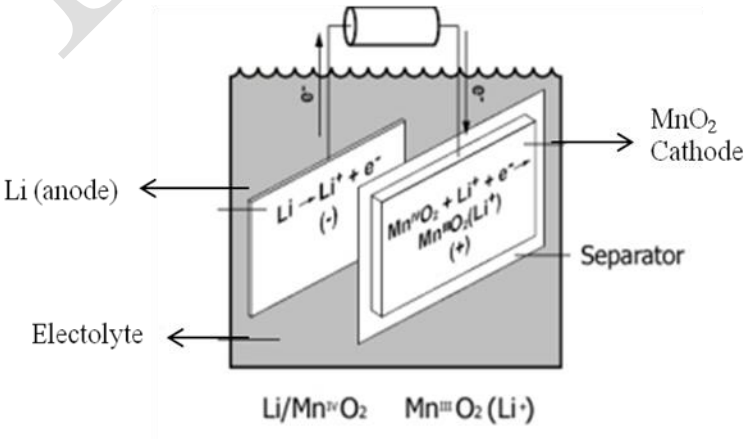
Lithium cells:

Lithium cells are primary cells in which lithium acts as anode and the cathode may differ. Lithium metal **is** used as anode because of its light weight, high standard oxidation potential (≥3V) and good conductivity. As the reactivity of lithium in aqueous solution is more, lithium cells use non-aqueous solvents as electrolyte.

Lithium cells are classified into two categories:

(a) Lithium cells with solid cathode:

The electrolyte in this system is a solid electrolyte. The most widely used cell is lithium – manganese dioxide cell (3V). MnO_2 should be heated to over 300^0C to remove water before keeping it in the cathode, thereby increasing the efficiency of the cell.



Anode: Lithium Metal,

Cathode: MnO_2 as an active material.

Electrolyte: $LiBF_4$ salt in a solution of propylene carbonate and dimethoxy ethane.

Reactions:

At anode: $Li \longrightarrow Li^+ + e^-$

At cathode: $e^- + MnO_2 \longrightarrow MnO_2^-$

Net reaction: $Li + MnO_2 \longrightarrow LiMnO_2$

Applications:

1. The coin type cells are used in watches and calculators.
2. Cylindrical cells are used in fully automatic cameras.

(b) Lithium cells with liquid cathode: Lithium–sulphur dioxide cell is an example of liquid cathode. The co-solvents used are acrylonitrile or propylene carbonate (or) mixture of the two with SO_2 in 50% by volume.

Cell reaction: $2Li + 2SO_2 \longrightarrow Li_2S_2O_4$.

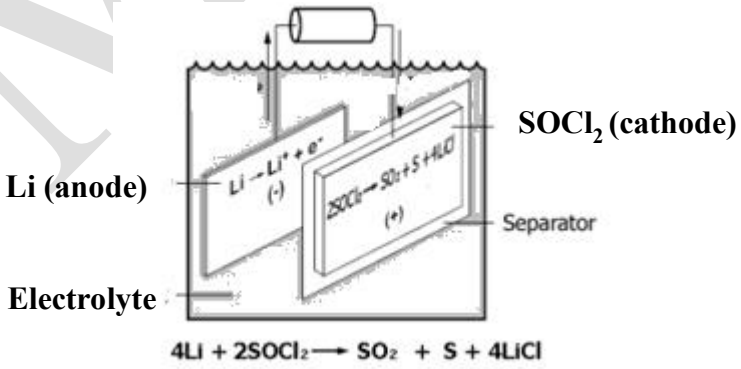
Lithium thionyl chloride cell is another example of liquid cathode. It consists of high surface area carbon cathode, a non – woven glass separator. Thionyl chloride acts as an electrolyte and as a cathode.

Cell reaction:

At anode: $Li \longrightarrow Li^+ + e^-$

At cathode: $4Li + 4e^- + 2SOCl_2 \longrightarrow 4LiCl + SO_2 + S$

Net reaction: $4Li + 2SOCl_2 \longrightarrow 4LiCl + SO_2 + S$



In this cell no co-solvent is required as $SOCl_2$ is a liquid with moderate vapor pressure. The discharging voltage is 3.3 -3.5V.

USES:

1. They are used for military and space applications.
2. In medicinal devices such as neuro-stimulators, drugdelivery system, lithium batteries are widely used.
3. They are also used in electric circuit boards for supplying fixed voltage for memory protection and standby functions.

Advantages:

1. The energy output of a lithium cell is 2-4 times better than that of conventional zinc anode batteries.
2. Lithium batteries can work over temperature range of 40-70^{0}C.
3. They have higher voltages of about 4V when compared to other primary cells with 1.5 V only.

Secondary cell: E.g.: Lead – Acid cell:

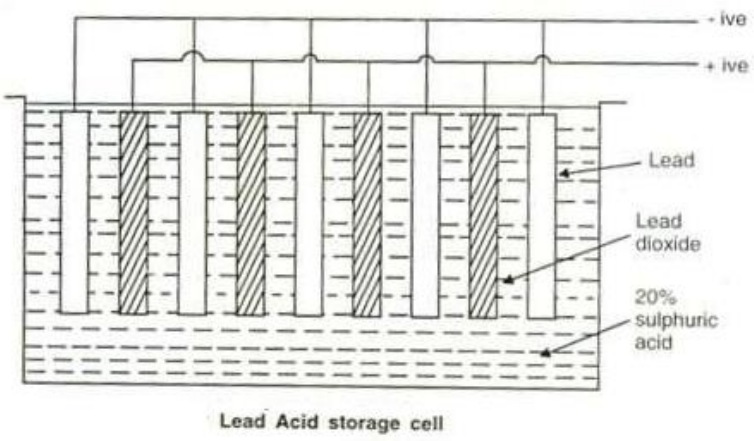
If a number of cells are connected in series, the arrangement is called a battery. The lead storage battery is one of the most common batteries that are used in the automobiles. A 12 V lead storage battery is generally used, which consists of six cells, each providing 2V. Each cell consists of a lead anode and a grid of lead packed with lead oxide as the cathode. These electrodes are arranged alternately, separated by a thin wooden piece and suspended in dil. H_2SO_4 (38%), which acts as an electrolyte. Hence, it is called lead acid battery.

Anode: Pb

Cathode: PbO_2

Electrolyte: H_2SO_4 (20-22%)

EMF = 2 V



Lead Acid storage cell



Lead storage cells: To increase the current output of each cell, the cathode and the anode plates are joined together, keeping them in alternate positions. The cells are connected parallel to each other.

The cell is represented as

$$Pb/PbSO_4(s), H_2SO_4/PbSO_4(s),Pb$$

In the process of discharging, i.e., when the battery produces current, the reactions at the electrodes are as follows:

Discharging reactions:

At anode: $Pb \rightarrow Pb^{2+} + 2e^-$

$Pb^{2+} + SO_4^{2-} \rightarrow PbSO_4\downarrow$

At cathode: $PbO_2(s) + 4H^+ + 2e^- \rightarrow Pb^{2+} + 2H_2O$

$Pb^{2+} + SO_4^{2-} \rightarrow PbSO_4$

Therefore, the overall reaction is:

$$Pb(s) + PbO_2 + 4H_2SO_4(aq) \rightarrow 2PbSO_4(s) + 2H_2O + Energy$$

During discharging the battery, H_2SO_4 is consumed, and as a result, the density of H_2SO_4 falls. When it falls below 1.20 g/cm^3, the battery needs recharging. In discharging, the cell acts as a voltaic cell where oxidation of lead occurs.

Recharging:

During recharging, the cell is operated like an electrolytic cell, i.e. electrical energy is supplied to it from an external source. The electrode reactions are the reverse of those that occur during discharge.

$PbSO_4 + 2e^- \rightarrow Pb + SO_4^{2-}$ (Reaction at cathode)

$PbSO_4 + 2H_2O \rightarrow PbO_2 + 2H_2SO_4 + 2e^-$ (Reaction at anode)

$2PbSO_4 + 2H_2O + Energy \rightarrow Pb + PbO_2 + 2H_2SO_4$

During this process, lead is deposited at the cathode, PbO_2 is formed at the anode and H_2SO_4 is regenerated in the cell.

Applications and Advantages:

Lead-acid batteries are used for supplying current to railways, mines, laboratories, hospitals, automobiles, power stations, telephone exchange, gas engine ignition, UPS. Other advantages are its recharge ability, portability, and relatively constant potential and low cost.

Disadvantages: Use of conc. H_2SO_4 is dangerous. Use of lead battery is fragile.

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Lithium-ion batteries (or) Lithium-ion cells:

Lithium-ion battery is a secondary battery. As in lithium cell, it does not contain metallic lithium as anode. As the name suggests, the movement of lithium ions are charging '& discharging. Lithium-ion cell has the following three components.

1. A positive electrode (Layers of lithium-metal oxide) (cathode).
2. A negative electrode (Layers of porous carbon) (anode).
3. An electrolyte (Polymer gel) (separator)

Construction:

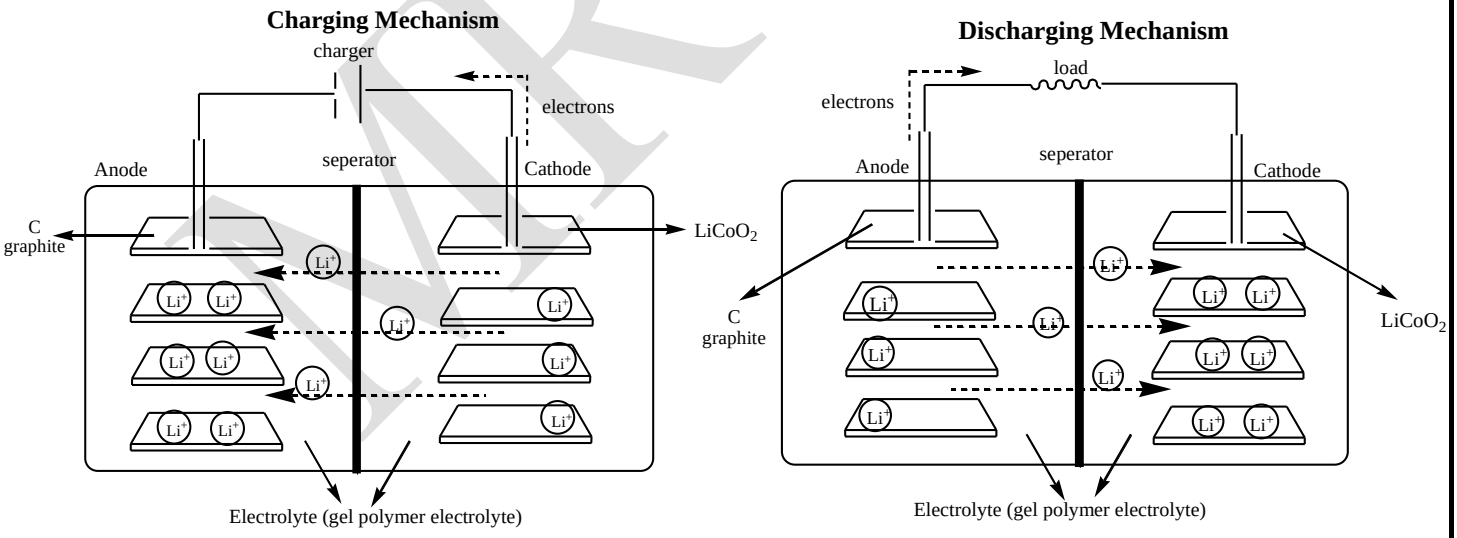
The positive electrode is typically made from a layers of chemical compound called lithium-cobalt oxide ($LiCoO_2$). The negative electrode is made from layers of porous carbon (C) (graphite).Both the electrodes are dipped in a polymer gel electrolyte (organic solvent) and separated by a separator, which is a perforated plastic and allows the Li^+ ions to pass through.

Working

Charging Reaction:

During charging, Li^+ ions flow from the positive electrode ($LiCoO_2$) to the negative electrode (graphite) through the electrolyte. Electrons also flow from the positive electrode to the negative electrode. The electrons and Li^+ ions combine at the negative electrode and deposit there as Li.

$$LiCoO_2 + C \rightarrow Li_{1-x}CoO_2 + CLi_x$$



Discharging Reaction:

During discharging, the Li^+ ions flow back through the electrolyte form negative electrode to the positive electrode. Electrons flow from the negative electrode to the positive electrode. The Li^+ ions and electrons combine at the positive electrode and deposit there as Li.

$$Li_{1-x}CoO_2 + CLi_x \rightarrow LiCoO_2 + C$$

Advantages (or) Characteristics:

1. Lithium-ion batteries are high voltage and light weight batteries.
2. It is smaller in size.
3. It produces three time the voltage of Ni-Cd batteries.
4. It has none of the memory effect seen in Ni-Cd batteries.

Uses:

It is used in cell phone, note PC, portable LCD TV, semiconductor driven audio, etc.

FUEL CELLS

Definition: A fuel cell is an electrochemical which converts chemical energy contained in readily available fuel oxidant system into electrical energy.

Principle: The basic principle of fuel cell is as same as that of an electrochemical cell. The fuel cell operates like a galvanic cell. The only difference is that the fuel and the oxidant are stored outside the cell. Fuel and oxidant are supplied continuously and separately to the electrodes at which they undergo redox reaction. Fuel cells are capable of supplying current as long as reactants are replenished.

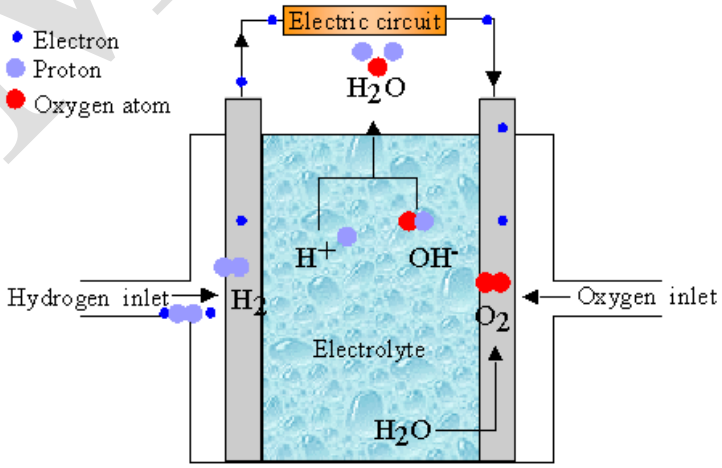
Fuel + Oxidant → Oxidation products + Electric Energy

Examples: 1. H_2-O_2 fuel cell

2. CH_3OH-O_2 fuel cell

Hydrogen Oxygen Fuel Cell:

This cell is a common type of fuel cell. Similar to a galvanic cell, fuel cell also have two half cells. Both half cells have porous graphite electrode with a catalyst (platinum, silver or a metal oxide). The electrodes are placed in the aqueous solution of NaOH or KOH which acts as an electrolyte. Hydrogen and oxygen are supplied at anode and cathode respectively at about 50 atmospheric pressure, the gases diffuse at respective electrodes. The two half-cell reactions are as follows.



At anode: $2H_2\,(g) + 4OH^-\,(aq) \rightarrow 4H_2O\,(l) + 4e^-$

At cathode: $O_2\,(g) + 2H_2O\,(l) + 4e^- \rightarrow 4OH^-\,(aq)$

The net reaction: $2H_2\,(g) + O_2\,(g) \rightarrow 2H_2O\,(l)$

The EMF of this cell is measured to be 1.23V. A number of such fuel cell are stacked together in series to make a battery.

Advantages:

1. The energy conversion is very high (75-82%).
2. Fuel cell minimizes expensive transmission lines and transmission losses.
3. It has high reliability in electricity generation.
4. The byproducts are environmentally acceptable.
5. Maintenance cost is low for these fuels.
6. They save fossil fuels.
7. Noise and thermal pollution are very low.
8. They have low maintenance cost.
9. They have quick start system.

Disadvantages:

1. The major disadvantage of the fuel cell is the high cost and the problems of durability and storage of large amount of hydrogen.
2. The accurate life time is also not known.

APPLICATIONS:

1. The most important application of a fuel cell is its use in space vehicles, submarine or military vehicles.
2. The product H_2O is valuable source of fresh water by the astronauts.
3. It is hoped that fuel cell technology will bring a revolution in the area of energy production.
4. Fuel cell batteries for automotive will be a great boom for the future.

Limitations:

1. The life time of fuel cells is not accurately known
2. It cannot store electricity
3. Electrodes are expensive ad short lived.
4. Storage and handling of H_2 gas is dangerous because it is inflammable.

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UNIT II: CORROSION

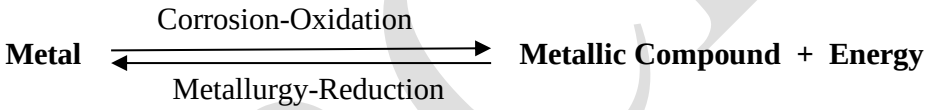
Introduction:

Metals and alloys are used as fabrication or construction materials in engineering. If the metals or alloy structures are not properly maintained, they deteriorate slowly by the action of atmospheric gases, moisture and other chemicals. This phenomenon of destruction of metals and alloys is known as corrosion.

The surface of almost all the metals begin to decay more or less rapidly when exposed to atmospheric gases, water or other reactive liquid medium.

Corrosion

- *The process of decay of metal by environmental attack is known as corrosion.*
- Metals undergo corrosion and convert to their oxides, hydroxides, carbonates, sulphides, etc.
- Examples:-
- i) Rusting of iron – when iron is exposed to the atmospheric conditions, a layer of reddish scale and powder of Fe_3O_4 is formed.
- ii) Formation of green film of basic carbonate- [$CuCO_3$ + $Cu(OH)_2$] on the surface of copper when exposed to moist air containing CO_2.
- The corrosion of metals is measured in the units of *milli/inches/year or mm/year*.



Corrosion is an oxidation process and it is reverse of metal extraction.

Causes of corrosion:

1. The metals exist in nature in the form of their minerals or ores in the stable combined forms as oxides, chlorides, silicates, carbonates and sulphides.
2. During the extraction of metals, these ores are reduced to metallic state by supplying considerable amount of energy.
3. Hence the isolated pure metals are in excited states than their corresponding ores.
4. So metals have natural tendency to go back to their combined state (minerals/ores).
5. When metal is exposed to atmospheric gases, moisture, liquids etc, the metal surface reacts and forms more thermodynamically stable compounds.

Effects of corrosion:

1. Wastage of metal in the form of its compounds.
2. The valuable metallic properties like conductivity, malleability, ductility etc. are lost due to corrosion.
3. Life span and efficiency of metallic parts of machinery and fabrications is reduced

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Theories of corrosion:

1. Dry corrosion
2. Wet corrosion

Dry corrosion or Chemical corrosion: The direct chemical action of environment on the surface of metal in absence of moisture is known as dry corrosion.

This type of corrosion occurs mainly through the direct chemical action of atmospheric gases like O_2, halogens, H_2S, SO_2, N_2 or anhydrous inorganic liquid with the metal surface.

Example: (i) Silver materials undergo chemical corrosion by Atmospheric H_2S gas.

(ii) Iron metal undergo chemical corrosion by HCl gas.

There are three types of chemical Corrosion:

1. Oxidation corrosion
2. Corrosion due to other gases
3. Liquid metal corrosion

Oxidation Corrosion:

Direct action of oxygen at low or high temperatures on surface of metals in absence of moisture is known as oxidation corrosion. Alkali metals and Alkaline earth metals are rapidly oxidized at lower temperatures. At high temperature all metals are oxidized (except Ag, Au, Pt).

Mechanism:

1) Oxidation takes place at the surface of the metal forming metal ions M^{2+}

2) Oxygen is converted to oxide ion (O^{2-}) due to the transfer of electrons from metal.

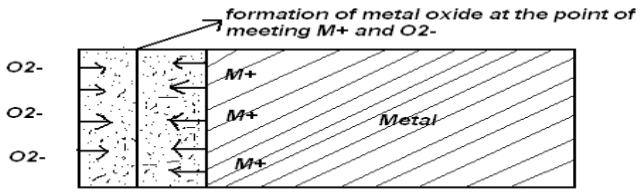
3) The overall reaction is of oxide ion reacts with the metal ions to form metal oxide film.

Reactions in oxidation corrosion

$$M \longrightarrow M^{2+} + 2e^- \quad \text{(Oxidation)}$$

$$1/2O_2 + 2e^- \longrightarrow O^{2-} \quad \text{(Reduction)}$$

$$M + O_2 \longrightarrow M^{2+} + O^{2-} \text{ (Metal oxide)}$$



Oxidation mechanism of metals

Mechanism: Initially the surface of metal undergoes oxidation and the resulting metal oxide scale forms a barrier which restricts further oxidation. The extent of corrosion depends upon the nature of metal oxide.

***Nature of the oxide formed**:* It plays an important role in further oxidation corrosion process.

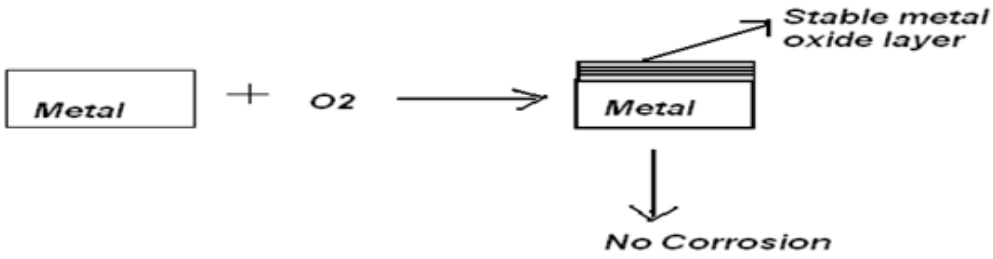
Metal + oxygen $\longrightarrow$ metal oxide (corrosion product)

When the oxide film formed is:

(a) Stable metal oxide layer

A stable layer is fine grained in structure and can get adhered tightly to the parent metal surface. Such a layer will be impervious in nature and hence behaves as protective coating, thereby shielding the metal surface. Consequently further oxidation corrosion is prevented.

E.g.: Al, Sn. Pb, Cu, etc. form stable oxide layers on surface thus preventing further oxidation.



Example:



Unstable metal oxide layer

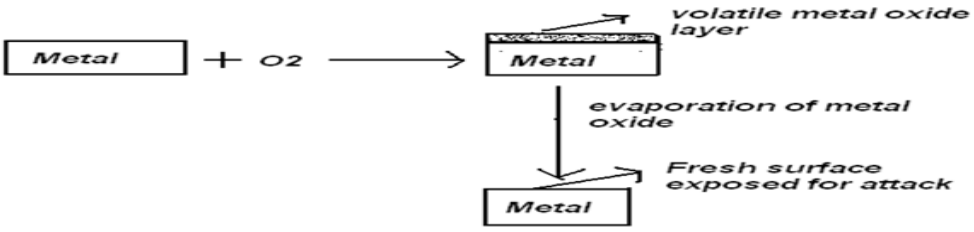
The oxide layer formed decomposes back into metal and oxygen. Consequently oxidation corrosion is not possible in such cases.

Eg: Ag, Au and Pt do not undergo oxidation corrosion.

Metal oxide ⟶ Metal + oxygen

(c) Volatile Metal oxide layer

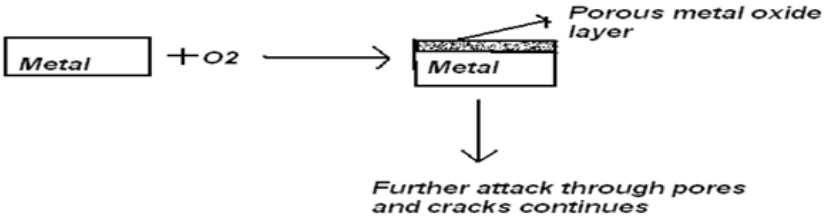
The oxide layer formed is volatile in nature and evaporates as soon as it is formed. There by leaving the under lying metal surface exposed for further attack. This causes rapid continuous corrosion, leading to excessive corrosion eg: Mo- molybdenum forms volatile MoO_3 layer.



(d) Porous Metal oxide layer

If the metal oxide layer is porous, the oxide layer formed has pores or cracks. In this case the atmospheric oxygen penetrates through the pores or cracks and corrode the underlying

metal surface. This cause continuous corrosion till conversion of metal into its oxide is completed. **Eg:** Alkali and alkaline earth metals (Li, Na, K, Mg, Fe etc.)



Example:



After corrosion **Before corrosion**

Pilling Bedworth rule:

- To express the extent of protection given by the corrosion layer to the underlying metal Pilling Bedworth rule was postulated.
- It is expressed in terms of specific volume ratio.

- **Specific Volume ratio** $= \frac{\textbf{Volume of metal oxide layer}}{\textbf{Volume of parent metal}}$

- Smaller the specific volume ratio, greater is the oxidation corrosion
- Eg. The specific volume ratio of W, Cr, and Ni are 3.6, 2.0 and 1.6 respectively. Consequently the rate of corrosion is least in Tungsten(W)

- If the volume of the corrosion film formed is more than the underlying metal, it is strongly adherent, non-porous and does not allow the penetration of corrosive gases. No further corrosion.
- If the volume of the corrosion film formed is less than the underlying metal, it forms pores/cracks and allow the penetration of corrosive gases leading to corrosion of the underlying metal.

Wet Corrosion or Electrochemical Corrosion

- The direct chemical action of environment on the surface of metal in presence of conducting liquid with the formation of electrochemical cells.
- It a common type of corrosion which occurs usually in aqueous corrosive environment
- Occurs when metal comes in contact with a conducting liquid.
- Formation of galvanic cell on the surface of metal generating anodic and cathodic areas

- At anode oxidation takes place liberating electrons.
- Electrons at anode are transported to cathodic area where H^+ or O_2 and H_2O consumes the electrons generating non-metallic ions like OH^- or O^{2-}
- Metallic (M^+) and non metallic (OH^- or O^{2-}) diffuse towards each other and results in the formation of corrosion product in between the anodic and cathodic area.

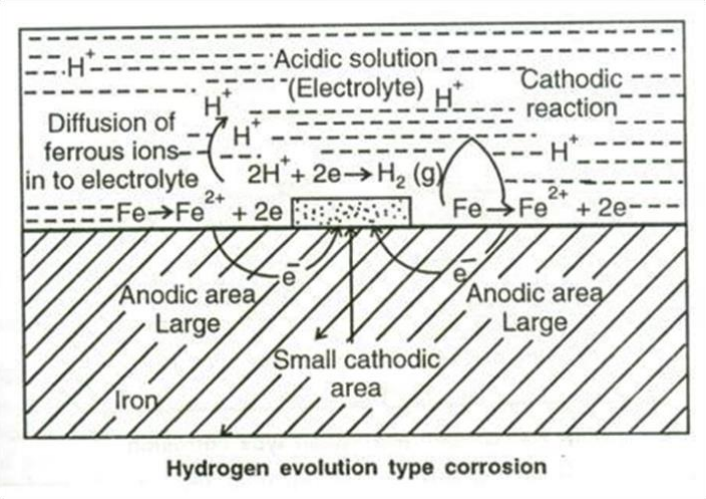
Mechanism*:* Electrochemical corrosion involves flow of electrons between anode and cathode. The anodic reaction involves dissolution of metal liberating free electrons.

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

The cathodic reaction consumes electrons with either evolution of hydrogen or absorption of oxygen which depends on the nature of corrosive environment.

Wet corrosion takes place in two ways.
1. Evolution of Hydrogen
2. Absorption of Oxygen

Evolution of Hydrogen*:*
This type of corrosion occurs in acidic medium.
Eg: Rusting of iron metal in acidic environment takes place in the following way:



Hydrogen evolution type corrosion

At Anode dissolution of iron to ferrous ion takes place with the liberation of electrons

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

The electrons released at anode flow through the metal from anode to cathode, where as H+ ions of acidic solution take up these electrons and eliminated as hydrogen gas.

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

The overall reaction is: $Fe + 2H^+ \longrightarrow Fe^{2+} + H_2\uparrow$

This type of corrosion causes "displacement of hydrogen ions from the acidic solution by metal ions.
In hydrogen evolution type corrosion, the anodic areas are large and cathodic areas are small.

Absorption of Oxygen:

- This type of corrosion takes place in basic or neutral medium in presence of oxygen.
- For example, rusting of iron in neutral or basic aqueous solution of electrolyte in presence of atmospheric oxygen.
- Usually the surface of iron is coated with a thin film of iron oxide.
- If the film develops cracks, anodic areas are created on the surface and the rest of the metal surface acts as cathodes.
- It shows that anodic areas are small and the cathodic areas are large.

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

The released electrons flow from anode to cathode through iron metal.

At cathode: $\frac{1}{2} O_2 + H_2O \longrightarrow 2OH^- + 2e^-$ (Reduction)

Overall reaction: $Fe_2^{+} + 2OH^- \longrightarrow Fe(OH)_2$

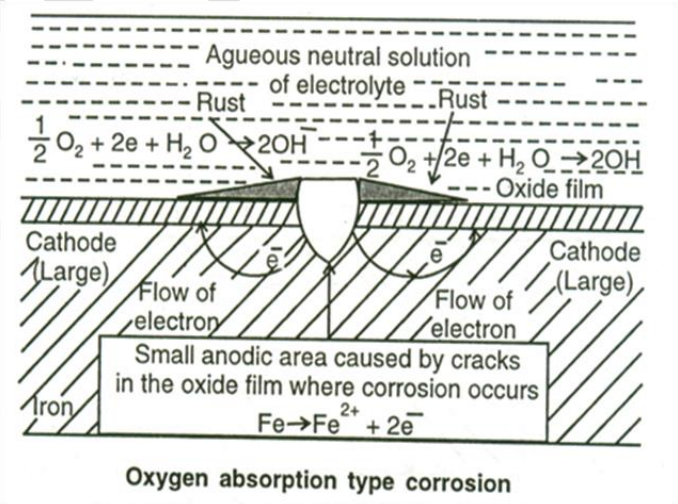
If enough oxygen is present, ferrous hydroxide is easily oxidized to ferric hydroxide and then to hydrated ferric oxide which is known as rust.

$$4Fe(OH)_2 + O_2 + 2H_2O \rightarrow 4Fe(OH)_3$$

$$4Fe(OH)_2 + O_2 + 2H_2O \xrightarrow{oxidation} 4Fe(OH)_3 \xrightarrow{oxidation} Fe_2O_3.3H_2O$$

Rust (hydrated ferric oxide)

The product called rust corresponds to **$Fe_2O_3.3H_2O$.**



Oxygen absorption type corrosion

Corrosion control methods:

1. Proper designing
2. Using Pure metals
3. Using metal alloys
4. Use of inhibitors
5. Modifying Environment
6. Cathodic protection
7. Application of protective coatings

Cathodic Protection:

The method of protecting the base metal by forcibly making it to behave like a cathode there by corrosion does not occur is called as cathodic protection.

There are two types of cathodic protection

(a) Sacrificial anodic protection

(b) Impressed current cathodic protection

Sacrificial anodic protection

- In this protection method, the metallic structure to be protected (base metal) is connected by a conducting wire to a more anodic metal so that all the corrosion is concentrated at this more anodic metal.
- The more anodic metal itself gets corroded slowly, while the parent structure (cathodic) is protected. The more active metal so employed is called sacrificial anode. The corroded sacrificial anode is replaced by a fresh one, when consumed completely.
- The artificially made anode thus gets corroded gradually protecting the original metallic structure. Hence the process is known as sacrificial anodic protection.
- Metals commonly employed as sacrificial anode are Mg, Zn, Al and their alloys which possess low reduction potential and occupies higher end in electrochemical series.

Eg: A ship-hull which is made up of steel is connected to sacrificial anode (Zn-blocks) which undergoes corrosion leaving the base metal protected.

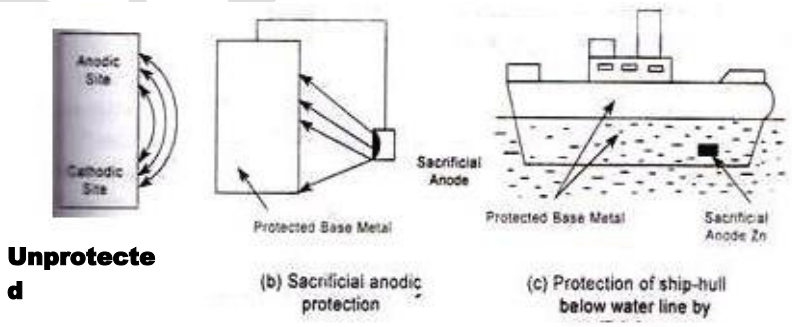
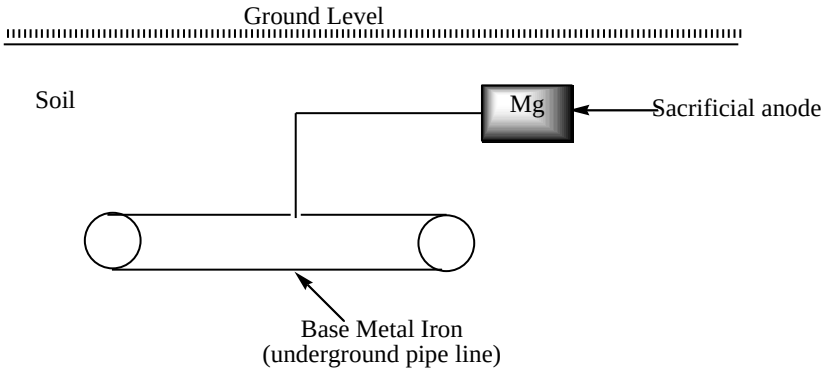


Figure1. Sacrificial anode method: Ship hull and underground water pipeline



Buried pipe line protected to Mg block

Applications of Sacrificial anodic protection:

By referring to the electrochemical series, the metal with low reduction potential is connected to the base metal which acts as anode.

1. To protect underground pipelines- Buried pipe line protected by connecting to Mg block
2. Protection of ship hulls and other marine devices.
3. Protection of water tank- by suspending Zn or Mg rods, body of the tank made cathode and protected.

Advantages:

1. It is a simple method.
2. It does not require external power.
3. It has low maintenance and installation cost
4. Cathodic interferences are minimum.

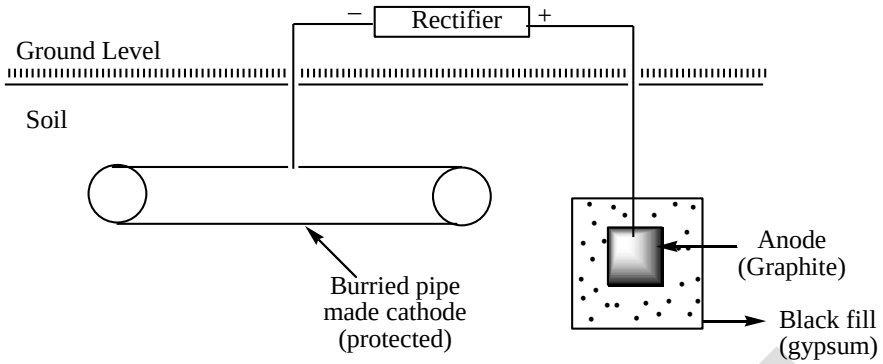
Disadvantages:

1. More than one anode is required some times.
2. It does not work properly in high corrosive environment.
3. Sacrificial anode must be replaced periodically as and when it is consumed

Impressed current cathodic protection:

- 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 impressed current is slightly higher than the corrosion current. Thus the anodic corroding metal becomes cathodic and protected from corrosion.
- The impressed current is taken from a battery or rectifier on A.C. line.
- The metal to be protected is made cathode by connecting to an external battery (-ve terminal)
- The anode is usually insoluble anode like graphite, stainless steel, or platinum connected to +ve terminal of the battery. Usually a sufficient D.C current is passed on to the insoluble anode kept in a black fill composed of coke or gypsum, so as to increase the electrical contact with the surrounding soil.
- In impressed current cathodic protection, electrons are supplied from an external cell, so that the object itself becomes cathodic and does not get oxidized.

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Applications:

1. The impressed current cathodic protection is used for the protection of water tanks, water & oil pipe lines, transmission line towers etc.

Advantages

The method is mainly employed to protect large structures for long term operations.

Disadvantages

1. The method is expensive as it requires high current
2. Capital investment and maintenance costs are more
3. It is difficult to maintain uniform current over the entire metal surface as a result localized corrosion may occur.
4. The metal should not be over protected, ie, use of much high potential is avoided otherwise problems related to cathodic reactions like evolution of H_2 and formation of OH^- Ions talks place leading to corrosion of base metal

Metallic coatings:

The surface of the base metal coated with another metal (coating metal)is called metallic coatings. Metallic coatings are broadly classified into anodic and cathodic coatings.

1. Anodic coating:

- The metal used for the surface coating is more anodic than the base metal which is to be protected.
- For example, coating of Al, Cd and Zn on steel surface are anodic because their electrode potentials are lower than that of the base metal iron. Therefore, anodic coatings protect the underlying base metal sacrificially.
- The formation of pores and cracks over the metallic coating exposes the base metal and a galvanic cell is formed between the base metal and coating metal. The coating metal dissolves anodically and the base metal is protected.

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2. Cathodic coating:

- Cathodic coatings are obtained by coating a more noble metal (i.e. metals having higher electrode potential like Sn, Au, Ag, Pt etc.) than the base metal. They protect the base metal as they have higher corrosion resistance than the base metal due to cathodic nature.
- Cathodic coating protects the base metal only when the coating is uniform and free from pores.
- The formation of pores over the cathodic coating exposes the base metal (anode) to environment and a galvanic cell is set up. This causes more damage to the base metal.

Methods of application of metallic coatings:

1. Hot dipping:

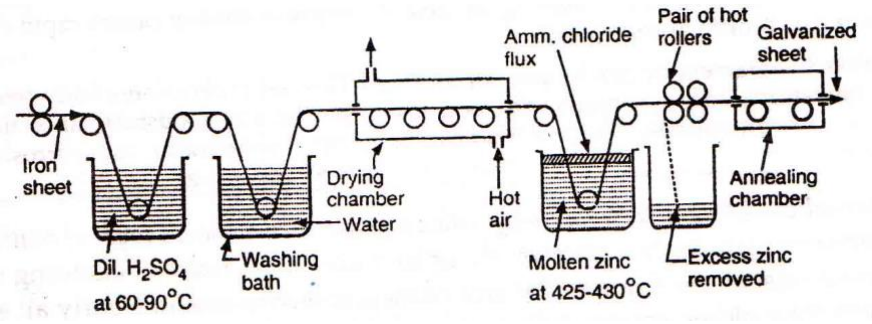
- Hot dipping process is applicable to the metals having higher melting point than the coating metal.
- It is carried out by immersing a well cleaned base metal in a bath containing molten coating metal and a flux layer.
- The flux cleans the surface of the base metal and prevents the oxidation of the molten coating metal. **Eg:** Coating of Zn, Pb, Al on iron and steel surfaces.
  The most widely used hot dipping processes are
  (a) Galvanizing
  (b) Tinning

Galvanizing:

- Galvanizing is a process in which the iron article is protected from corrosion by coating it with a thin layer of zinc.
- It is the anodic protection offered by the zinc.
- In this process, at first iron or steel is cleaned by pickling with dil.H2SO4 solution for 15-20 minutes at 60-90^{0}C. In pickling any scale, dirt, oil, grease or rust and any other impurities are removed from the metal surface.
- The article is washed well and then dried.
- It is then dipped in bath of molten zinc maintained at 425-430^{o}C.
- The surface of bath is kept covered with ammonium chloride – flux to prevent oxide formation. The article is covered with a thin layer of zinc when it is taken out of bath.
- It is then passed through a pair of hot rollers, which removes any excess of zinc and produces a thin film of uniform thickness
- Then it is annealed and finally cooled slowly.

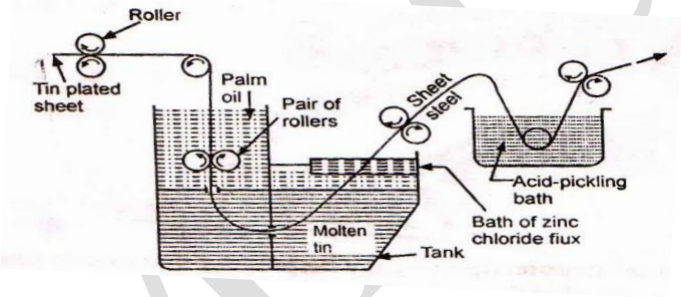
Applications: Galvanizing is widely used for protecting iron exposed to the atmosphere (roofs, wire fences, pipes etc.) Galvanized metallic sheets are not used for keeping eatables because of the solubility of zinc.

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Tinning

- The process of coating tin over the iron or steel articles to protect them from undergoing corrosion is known as tinning.
- Tin is a noble metal and therefore it possess more resistance to chemical attack. It is the cathodic protection offered by the tin. In this process, iron sheet is treated in dilute sulphuric acid (pickling) to remove any oxide film, if present.
- A cleaned iron sheet is passed through a bath of $ZnCl_2$ molten flux followed by molten tin and finally through a suitable vegetable oil. The $ZnCl_2$ flux helps the molten metal to adhere to the base metallic surface.
- Palm oil protects the tin coated surface against oxidation.
- Finally the sheet is passed through rollers to remove excess of tin and produce thin coat of tin of uniform thickness

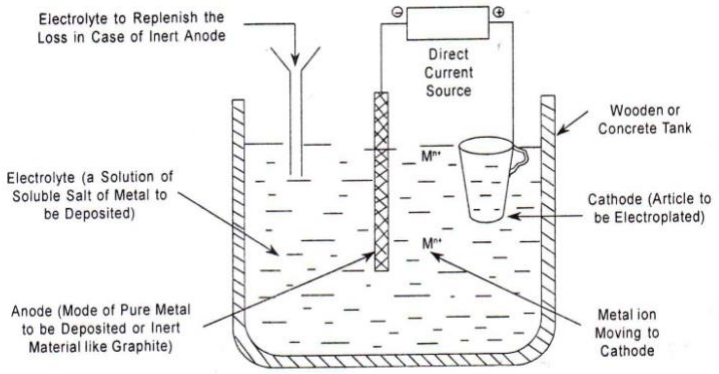


Applications:

1. Tin metal possess good resistance against atmospheric corrosion. Tin is non-toxic and widely used for coating steel, copper and brass sheets
2. The containers coated with tin are used for storing food stuffs, ghee, oil etc and packing food materials.
3. Tinned copper sheets are used for making cooking utensils and refrigeration equipment.

Electroplating:

- It is a process in which coating metal is deposited on the base metal by passing direct current through an electrolytic solution containing the soluble salt of the coating metal.



- The base metal is first subjected to acid pickling to remove any scales, oxides etc. The base metal is made as cathode of the electrolytic cell and the coating metal is made as anode.
- The two electrolytes are dipped in the electrolyte solution which contains the metal ions to be deposited on the base metal.
- When a direct current is passed from an external source, the coating metal ions migrate towards cathode and get deposited over the surface of base metal in the form of a thin layer.
- Low temperature, medium current density, low metal ion concentration conditions are maintained for better electro-plating.

Objectives of Electroplating

1. To increase resistance to corrosion, chemical attack and wear resistance of the plated metal
2. To improve physical appearance and hardness
3. To increase the decorative and commercial values of metals
4. To increase the strength of non-metals like plastics, wood and glass etc.
5. To make surface conductive by using light weight non-metallic materials like wood and plastics

Electroplating-Copper plating:

For example, for electroplating of copper on iron article the following are maintained
Electrolytic bath solution: $CuSO_4$
Anode: Pure copper
Cathode: Base metal article
Temperature: 20-40^oC (low temp for brighter and smooth surface)
Current density: 20-30 mA/cm^2
When direct current is passed, the Cu^{2+} ions migrate to the cathode and deposit on the base metal article.

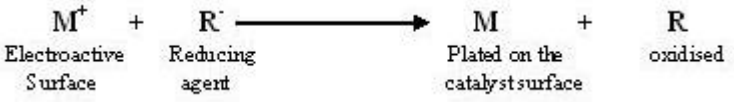
Anode: $Cu(s) \rightarrow Cu^{2+}(aq) + 2e^-$

Cathode: $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$

Electroless plating

- The method of deposition of a metal from its salt solution on a catalytically active surface by a suitable reducing agent without using electrical energy is called electroless plating.
- This process is also called chemical plating or autocatalytic plating.
- The metallic ions (M^+) are reduced to the metal with the help of reducing agents(R^{-1}). When the metal(M) is formed, it gets plated over a catalytic surface.

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Electroless-Ni plating:

It is an auto-catalytic chemical technique used to deposit a layer of nickel-phosphorus or nickel-boron alloy on a solid work piece, such as metal or plastic. The process relies on the presence of a reducing agent.

It involve the following features

Pretreatment and activation of the surface: The surface to be plated is activated by treatment with organic solvents or alkali, followed by acid treatment

Composition of Bath:

Coating solution- $NiCl_2$ solution

Reducing agent- Sodium hypophosphite ($NaH_2PO_2.H_2O$)

Buffer- Sodium acetate

Complexing agent- Sodium succinate

Optimum P^H- 4.5

Optimum temperature - 93°C

Reactions:

$$Ni^{2+} + 2e^- \longrightarrow Ni \quad \text{(Cathode)}$$

$$H_2PO_2^- + H_2O \longrightarrow H_2PO_3^- + 2H^+ + 2e^- \quad \text{(Anode)}$$

Net Rexn: $Ni^{2+} + H_2PO_2^- + H_2O \longrightarrow Ni + H_2PO_3^- + 2H^+$

Advantages of Electroless plating:

1. Electrical energy is not required.
2. Even intricate parts (of irregular shapes) can be plated uniformly
3. There is flexibility in plating volume and thickness.
5. The process can plate recesses and blind holes with stable thickness.
6. Chemical replenishment can be monitored automatically.
7. Bright finishes can be obtained.
8. Plating on articles made of insulators (like plastics) and semiconductors can easily be carried out.
9. Electroless plated Ni objects has better corrosion resistance, deposits are pore free, hard and wear resistant.

Applications:

1) They are used in electronic industry for fabricating printed circuits and diodes.
2) It is used in domestic as well as automotive fields (eg. jewelry, tops of perfume bottles).
3) Its polymers are used in decorative and functional works.
4) Its plastic cabinets are used in digital as well as electronic instruments.

UNIT III: FUNCTIONAL MATERIALS

Polymers

Introduction:

Polymers can be defined as the large molecules (macro molecules) formed by the linking together of large number of smaller molecules called monomers. (In Greek language 'poly' means "*many"* & 'mer' means "*units"*)

E.g.:- polyethylene is a polymer formed by linking together of a large number of ethylene molecules

$$n CH_2 = CH_2 \xrightarrow{\text{Polymerisation}} -(CH_2-CH_2)-_n$$

Thus the repeated unit of polymer is called monomer. The number of repeating units in a polymer chain is called degree of polymerization. For e.g. if 100 molecules of ethylene polymerize to give the polymer chain, the degree of polymerization is 100.

Polymers form very important components in our daily life. The polymers are highly useful in domestic, industrial & medical fields. The following are the reasons for the extensive use of polymers.

1) Most of the polymers are non-toxic & safe to use
2) They have low densities (light in weight), so transportation of polymers will be easy
3) They possess good mechanical strength
4) They are resistant to corrosion and will not absorb moisture when exposed to the atmosphere
5) They can function as good thermal & electrical insulators
6) They can be moulded and fabricated easily
7) They possess esthetic colors

But the limitations for the use of polymers are:

- Some polymers are combustible.
- The properties of polymers are time dependent
- Some of them cannot withstand high temperatures.
- It is also interesting to note that many carbohydrates, proteins & enzymes, DNA & RNA are natural polymers.

Plastics

Plastics are the polymers characterized by the property of plasticity (permanent deformation in structure on applying some stress/force). They can be moulded to desired shape when subjected to heat and pressure in the presence of catalyst.

Plastics as engineering materials:

Advantages of plastics over other engineering materials

1. Low fabrication cost, low thermal & electrical conductivities, high resistance to corrosion & solvents.
2. The stress – strain relationship of plastics is similar to that of the metals.
3. Plastics reduce noise & vibration in machines.

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4. Plastics are bad conductors of heat and are used to make handles for hot objects, most plastics are inflammable.
5. Plastics are electrical insulators & find large scale use in the electrical industry.
6. Plastics are resistance to chemicals.
7. Plastics are clear & transparent so they can be given beautiful colours.

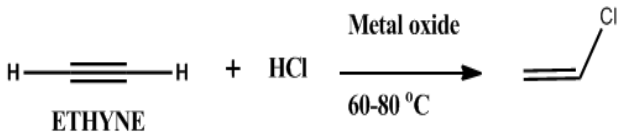
Types of Plastic: 1) Thermoplastics
2) Thermosetting plastics

Difference between Thermoplastic & Thermoset resins:

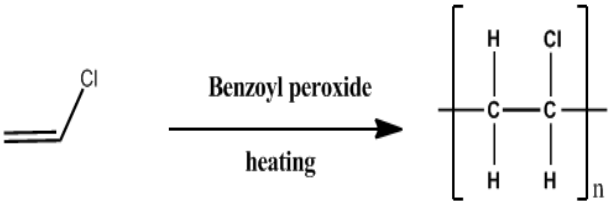
Thermoplastic Resins	Thermoset Resins
1. These resins become soft on heating and rigid on cooling by regaining original properties. These can be reshaped and used.	1. They do not soften on heating and become hard. On prolonged heating they decompose and cannot get back its structure. Hence cannot be reshaped and used.
2. The heating and cooling do not alter the chemical nature of these resins but involves changes in physical nature.	2. These resins are permanent setting resins.
3.They are formed by addition polymerization	3. They are formed by condensation polymerization.
4. Small molecular weight compounds with linear structures.	4. Large molecular weight compounds with three dimensional networks.
5. They consist of long chain linear polymer with weak secondary vandarwaal's forces of attraction in between them.	5. Highly cross-linked structure strong covalent bonds are responsible for strength.
6. They soften on heating readily because the secondary force of attraction between the individual chain can break easily by heat, pressure or both	6.The bonds retain their strength on heating, hence do not soften on heating
7. These plastic can be reclaimed from waste	7. Cannot be reclaimed from waste
8. They are soft, weak and less brittle	8. They are hard, strong and more brittle
9.These resins are usually soluble in organic solvents	9. Due to strong bonds and cross links, they are insoluble in all organic solvents.
10. Curing by cooling Eg: PE, PS, PVC, Teflon	10. By applying heat and pressure Eg: Bakelite, Polyester(Terylene)and silicones

(1) Polyvinyl chloride (PVC):

Preparation: The monomer used for the manufacture of PVC is vinyl chloride. Vinyl chloride is prepared by treating acetylene with HCl at 60-80^{0}C and in presence of a metal oxide catalyst. Polyvinyl chloride is produced by heating vinyl chloride in presence of benzyl peroxide or H_2O_2.



ETHYNE



VINYL CHLORIDE POLY VINYL CHLORIDE

Properties:

1. PVC is a colorless, non-inflammable and chemically inert powder
2. It has specific gravity 1.33 and melting point 148°C
3. Resistant to atmospheric conditions like O_2, CO_2 and moisture
4. They are rigid and flexible
5. It has resistance to light

Applications:

There are two kinds of PVC plastics

Rigid PVC (Unplasticized PVC):

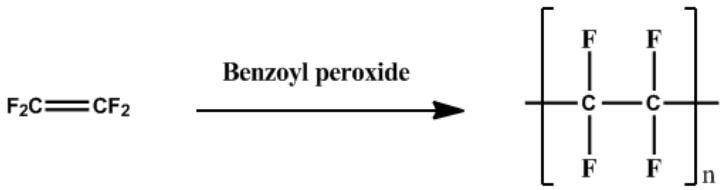
- It is chemically inert & non-inflammable powder having a high softening temperature of 148^0C.
- This PVC is used for making safety helmets, refrigerator components, tyres, cycle & motor cycle mud guards.

Plasticized PVC:

- It is produced by mixing plasticizers like dibutyl phthalate with PVC resin uniformly.
- It is used for making rain coats, table-cloths, handbags, curtains & electrical insulators, radio,

2) Teflon (Polytetrafluoro ethylene):

Preparation: Teflon is prepared by addition polymerization of tetraflouroethylene



TETRA FLUORO ETHYLENE

POLY TETRA FLUORO ETHYLENE

Properties:

Teflon is also known as Fluon. Due to the presence of highly electronegative fluorine atoms, Teflon has got:

- High melting point (350^{o}C)
- The strong attractive force is responsible for high toughness & high chemical resistance towards all chemicals except hot alkali metal & hot fluorine.
- High density 2.1-2.3gm/cc
- It is a very good electrical insulator
- It possess very good abrasion resistance

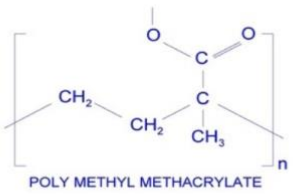
Engineering applications:

- It is used in making seals & gaskets, which have to withstand high temperature.
- It is also used for insulation of electrical items and for making non-sticky surface coating, particularly for cooking utensils.
- Teflon used as insulating material for motors, transformers, cables, wires, fitting etc.,

3) Polymethyl methacrylate:

It is also known as acrylic or plexiglass as well as by trade name Plexiglas Acrylite lucite and Perspex

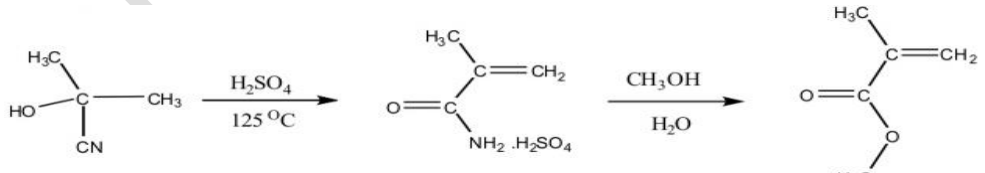
Chemical structure



POLY METHYL METHACRYLATE

Preparation

a) from cyanohydrin

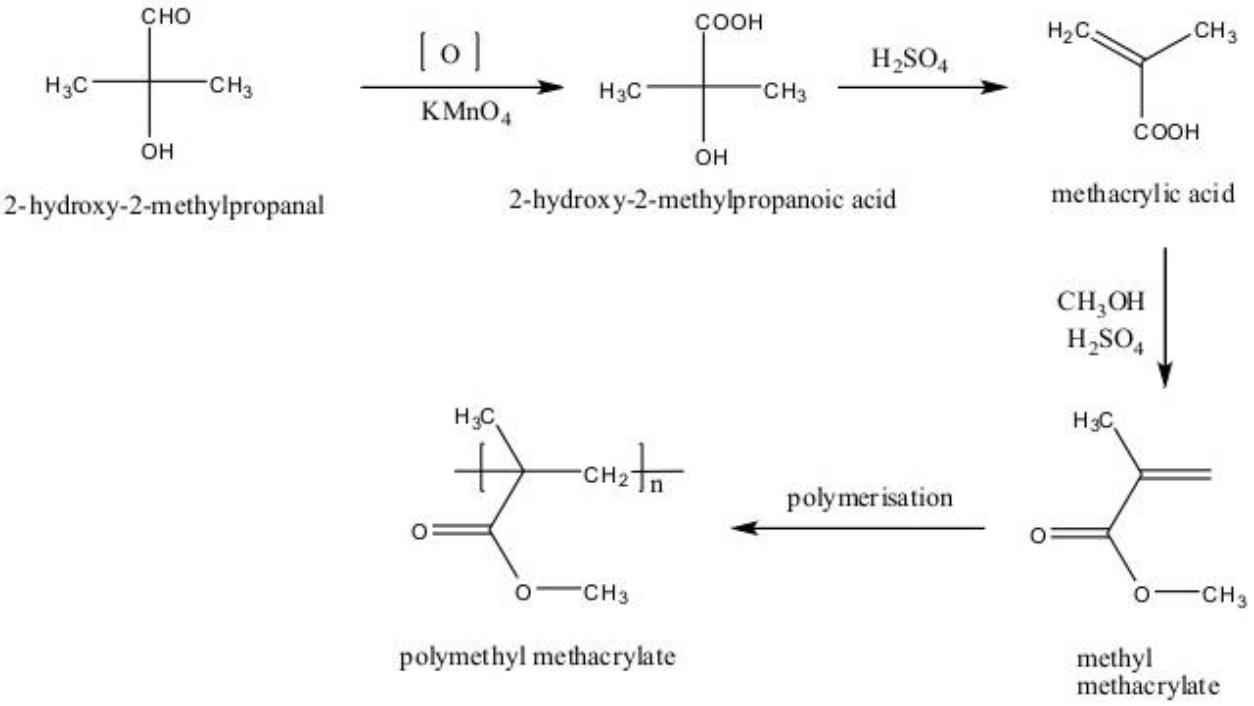


Acetone cyanohydrin

Methacrylamide sulphate

Methyl methacrylate

b) from hydroxy propanol



Properties

PMMA polymer exhibits glass-like qualities – clarity, brilliance, transparency, translucence

Transmittance – PMMA (Acrylic) polymer has a Refractive Index of 1.49 and hence offers high light transmittance. PMMA grades allow 92% of light to pass through it, which is more than glass or other plastics. These plastic materials can easily be thermoformed without any loss in optical clarity. As compared to polystyrene and polyethylene, PMMA is recommended for most outdoor application thanks to its environmental stability.

Surface Hardness – PMMA is a tough, durable and lightweight thermoplastic. The density of acrylic ranges between 1.17-1.20 g/cm^3 which is half less than that of glass. It has excellent scratch resistance when compared to other transparent polymers like Polycarbonate, however less than glass. It exhibits low moisture and water absorbing capacity, due to which products made have good dimensional stability.

UV Stability – PMMA has high resistance to UV light and weathering. Most commercial acrylic polymers are UV stabilize for good resistance to prolonged exposure to sunlight as its mechanical and optical properties fairly vary under these conditions, Hence, PMMA is suitable for outdoor applications intended for long-term open-air exposure.

Chemical Resistance – Acrylics are unaffected by aqueous solutions of most laboratory chemicals, by detergents, cleaners, dilute inorganic acids, alkalies, and aliphatic hydrocarbons. However, acrylics are not recommended for use with chlorinated or aromatic hydrocarbons, esters, or ketones.

Engineering Applications of PMMA

Architecture and Construction

PMM is widely used in window and door profiles, canopies, panels, façade design, etc. It also facilitates light transmission and provides good heat insulation, hence a suitable choice of building green houses. PMMA is also used to build aquariums and marine centers.





Lighting

PMMA sheets are used for designing LED lights where it helps maximize light emitting potential. It is also used for construction of lamps thanks to its transparency and optical properties.

Automotive and Transportation

In vehicles, PMMA sheets are used in car windows, motorcycle windshields, interior and exterior panels, fenders etc. Also colored acrylic sheets are used in car indicator light covers, interior light covers etc. It is also used for windows of a ship (Salt resistance) and aviation purposes. PMMA also open new design possibilities for car design possibilities for manufacturers thanks to its pleasant acoustic properties, outstanding formability and excellent surface hardness.





Electronics:

Due to its excellent optical clarity, high light transmission and scratch resistance, PMMA is widely used in LCD/LED tv screens, laptops, smartphones display as well as electronic equipment displays. PMMA also finds used in solar panels as cover materials thanks to its excellent UV resistance and excellent light transmission allowing high energy conversion efficiencies.

Medical and Healthcare:

PMMA is a high purity and easy-to-clean material and hence used to fabricate incubators, drug testing devices, storage cabinets in hospitals and research labs. Also, due to its high bio-

compatibility, PMMA is also applied as dental cavity fillings and bone cement.



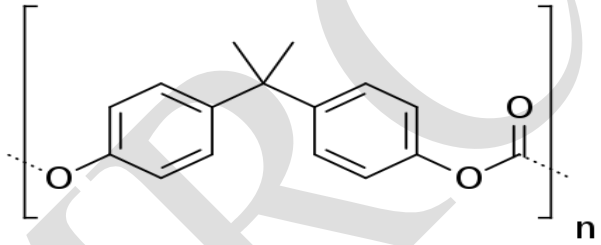


Furniture

PMMA offers exception properties such as transparency, toughness and aesthetics to produce chairs, tables, kitchen cabinets, bowls, table mats etc. in any shape, color or finishes

Polycarbonate:

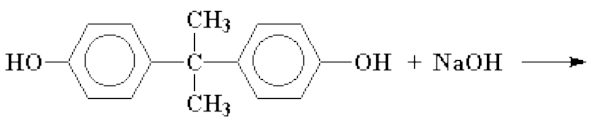
Polycarbonates (PC) are a group of thermoplastic polymers containing carbonate groups in their chemical structures. Polycarbonates used in engineering are strong, tough materials, and some grades are optically transparent. They are easily worked, molded, and thermoformed. Because of these properties, polycarbonates find many applications.



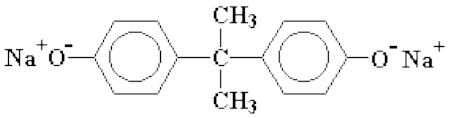
Preparation of polycarbonate

The polymer is usually formed by the reaction of bisphenol A and carbonyl chloride in a basic solution. A solution of bisphenol A in sodium hydroxide (i.e. a solution of the sodium salt of the phenol) is prepared. It is mixed with a solution of carbonyl chloride in an organic solvent (dichloromethane).

The first step in the synthesis of polycarbonates starts out with the reaction of bisphenol A with sodium hydroxide to get the sodium salt of bisphenol A

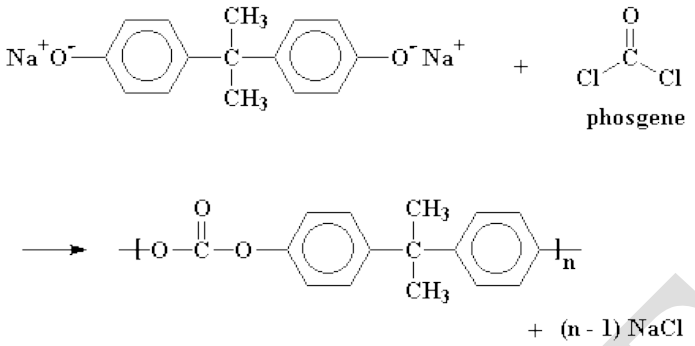


bisphenol A



sodium salt of bisphenol A

The sodium salt of bisphenol A is then reacted with phosgene a right nasty compound which was a favourite chemical weapon in World War I to produce the polycarbonate



Properties:

Polycarbonates are strong, stiff, hard, tough, transparent engineering thermoplastics that can maintain rigidity up to 140°C and toughness down to -20°C or special grades even lower.

Applications in Engineering :

Electronic components

Polycarbonate is commonly used in eye protection, as well as in other projectile-resistant viewing and lighting applications that would normally indicate the use of glass, but require much higher impact-resistance. Polycarbonate lenses also protect the eye from UV light.

Being a good electrical insulator and having heat-resistant and flame-retardant properties, it is used in various products associated with electrical and telecommunications hardware. It can also serve as a dielectric in high-stability capacitors.[

Construction materials

Polycarbonate sheeting in a greenhouse.

The second largest consumer of polycarbonates is the construction industry, e.g. for dome lights, flat or curved glazing, and sound walls.

Data storage

CDs and DVDs

A major application of polycarbonate is the production of Compact Discs, DVDs, and Blu-ray Discs. These discs are produced by injection molding polycarbonate into a mold cavity that has on one side a metal stamper containing a negative image of the disc data, while the other mold side is a mirrored surface.

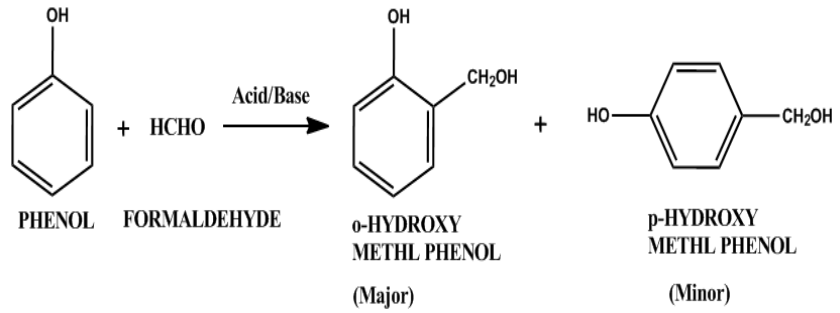
It is also used in automotive, aircraft and security components'

3. Bakelite (or) Phenol Formaldehyde Resin:

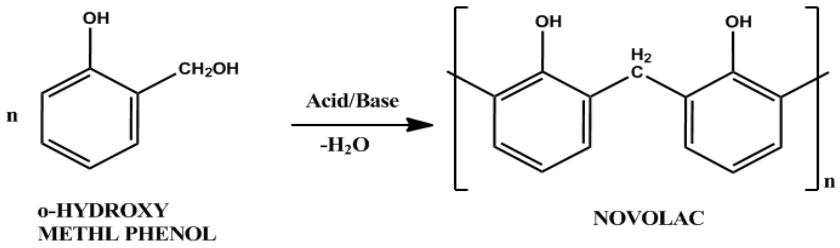
Bakelite is an important thermosetting resin named after the scientist Bakeland, who synthesized this resin in the year 1909. The condensation reaction of phenol & formaldehyde in the presence of acid or alkali catalyst and at proper temperature produces the phenol formaldehyde resin or Bakelite resin.

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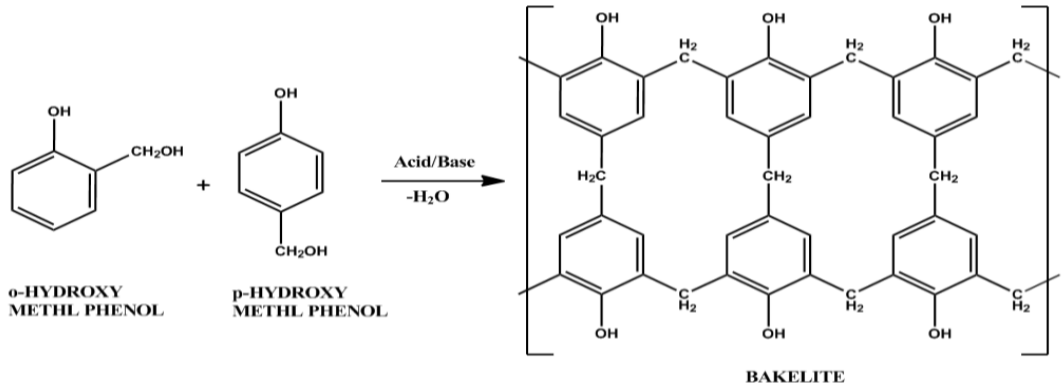
Stage-I: The initial reaction of phenol & formaldehyde in presence of acid or alkali produces *o*-hydroxy methyl phenol and *p*-hydroxy methyl phenol.



Stage-II: *o*-hydroxy methyl phenol undergoes self condensation in presence of acid or alkali and forms a linear polymeric chain called novolac.



Stage-III: On further heating, in the presence of hexamethylenetetramine both o-hydroxy methyl phenol and p-hydroxy methyl phenol undergoes self condensation and forms a 3D-cross linked thermosetting polymer which is known as "Bakelite".



Properties:

(1) Bakelites are hard, rigid and withstand very high temperatures.
(2) They have excellent heat and moisture resistance.
(3) They have good chemical resistance, resistance to acids, salts and many organic solvents, but it is attached by alkalis due the presence of –OH group.
(4) They have good abrasion resistance.
(5) They have electrical insulation characteristics.
(6) It is a good anionic exchanging resin, exchange –OH group with other anion.
(7) Low molecular weight grades have excellent bonding strength and adhesive properties.

Engineering Applications:

(1) It is used for making electric insulator parts like switches, plugs, switch boards etc.
(2) For making moulded articles like telephone parts cabinet of radio and television.
(3) As an anion exchanger in water purification by ion exchange method in boilers.
(4) As an adhesive (binder) for grinding wheels etc.,
(5) In paints and varnishes.
(6) For making bearings used in propeller shafts, paper industry and rolling mills.

Conducting Polymers:

Most polymeric materials are poor conductors of electricity because of the non-availability of large number of free electrons for the conduction process. Thus most of the polymers are used as insulators. However some polymers have electrical conductivity and can be used in place of metals due to their light weight and low cost, Polymeric materials which possess electrical conductivities on par with the metallic conductors are called conducting polymers. Special polymers with conductivities as high as 1.5 x 107 ohm-1 m-1 have been made their conductivity may be due to unsaturation or due to the presence of externally added ingredients to polymers. Those polymers which conduct electricity are called conducting polymer. The conduction of polymers is due to unsaturation or due to the presence of externally added ingredients to them. Conducting polymers are classified into two types.

a) Intrinsic conducting polymers:

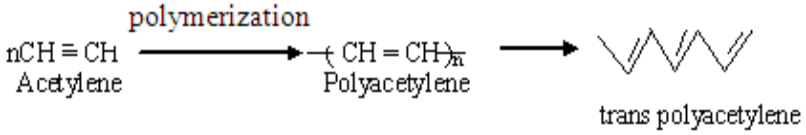
These are characterized by intensive conjugation of π-bonds in their structure. This is a polymer whose back bones or associated groups consisting of delocalized electron pair or residual charge, which increases their conductivity to a large extent. The conduction process is due to the overlapping of orbitals containing conjugated π-electrons, resulting in the formation of valence bands as well as conduction bands separated by significant Fermi energy gap. The electrical conductivity is due to thermal or photolytic activation of the electrons, which gives them sufficient energy to cross the Fermi gap and cause conduction. Important commercially produced intrinsic conducting polymers are polyacetylene, polythiophene, polyaniline.

Conducting polymers having conjugation:

Polymers have alternating double and single bond along the polymer chain and each carbon atom is in sp^2 hybridized state. One valence πe^- on carbon is in P_z orbital. The orbitals of conjugated πe^-s overlap the entire backbone of the polymer and result in the formation of valence bands & conduction bands.

The valence band is filled band and conduction band is empty. When the energy gap between these is low, the e^-s from valence band are excited to conduction band become mobile throughout the polymer and show conductivity.

E.g. trans-polyacetylene, polyaniline



Doped conducting polymers:

The conducting polymers having πe^-s in their backbone can easily be oxidized or reduced because they possess low ionization potential and high electron affinities. Hence their conductance can be increased by introducing a positive charge or negative charge on polymer backbone by oxidation or reduction. This process is similar to semiconductor technology and is called doping. Doping is again two types.

(1) Creating a positive site on polymer backbone called p-doping.

(2) Creating a negative site on the polymer backbone called n-doping.

Oxidation process is done by adding some alkali metals or e^- acceptor and conductivity is enhanced by p-doping. Reduction process is done by adding reducing agents or electron donor and conductivity is enhanced by n-doping.

p-doping:

p-doping is done by oxidation of a conducting polymer like polyacetylene with a Lewis acid or iodine vapour. This is called oxidative doping.

During oxidation process the removal of π electrons from polymer backbone lead to the formation of a delocalized radical ion called polaron having a hole in between valence band and conducting band.

The second oxidation of the polaron results in two positive charge carriers in each chain called bipolaron, which are mobile because of delocalization. These delocalized charge carriers are responsible for conductance when placed in electric field.

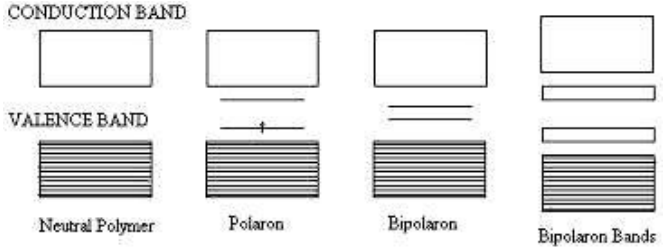
n-doping:

n-doping is carried out by reduction process by the addition of an electron to polymer backbone by using reducing agents like sodium napthalide $Na^+(C_{10}H_8)^-$. Formation of polaron, bipolaron takes place in two steps, followed by recombination of radicals, which yields two charge carriers on the polyacetylene chain responsible for conduction

The electron added to polyacetylene by reductive doping doesn't go into the conducting band but goes into an intermediate electronic state within the band gap of radical anion. Bipolaron contains electrons in the energy levels residing in the band gap.

$$[CH]_n + 3x/2\ I_2 \rightarrow [CH]_n^{x+} + xI_3^- \quad \text{oxidative doping}$$

$$[CH]_n + xNa \rightarrow [CH]_n^{x-} + xNa^+ \quad \text{reductive doping}$$



b) Extrinsic conducting polymers:

The conductivity of these polymers is due to the presence of externally added ingredients in them. These polymers are two types.

Conducting element filled polymers:

The polymers acting as a binder to hold the conducting element such as carbon black, metallic fibers, metallic oxides etc., minimum concentration of filler is added so that the polymer starts conducting. This minimum concentration of conductive filler is called percolation threshold. At this concentration of filler, a conducting path is formed in polymeric material. The most preferred filler is the special conducting grade C-black has very high surface area, more porosity and more of filamentous properties.

Advantages:

1. These polymers are low cost polymers
2. They are light in weight and mechanically durable.
3. These polymers are strong with good bulk conductivity.
4. They are fabricated very easily to any design.

Applications of conducting polymers:

- The conducting polymers are used in rechargeable batteries, small in size (bottom size), producing current density up to 50glucos Conducting polymers are also used for making analytical sensors for pH, O_2, NOx,SO_2, NH_3 and glucose
- The conducting polymers are used for making ion exchangers. These membranes made of conducting polymers show selective permeability for ions and gases hence they are used for control release of drug.
- The conducting polymers are used for making electronic displays and optical fibres
- They are used for cancer chemotherapy
- The conducting polymers are applicable in photovoltaic devices, LED's and data storage.

Composite Materials:

A composite material (also called a composition material or shortened to composite, which is the common name) is a material made from two or more constituent materials with significantly different physical or chemical properties that, when combined, produce a material with characteristics different from the individual components.

Fiber Reinforced Plastics (FRP):

- Combination of plastic material & solid fillers give hard plastic with mechanical strength & impact resistant is known as reinforced plastic.
- The fiber polymers with solid/fillers to impart mechanical strength & hardness without losing plasticity are known as fiber reinforced plastics (FRP).
- Fillers like carborandum, quartz & mica – impart hardness & strength.
- Barium salt impervious to x-rays.
- Asbestos provide heat & corrosion resistant for FRP.

Nature of polymers used for FRP:

Composition of FRP – 50% of the mouldable mixture contain fillers.

- Addition of carbon black to natural rubber increase the 40% strength of rubber & used in the manufacture of tyres.
- China clay improves the insulation property of PVC, Teflon.
- When $CaCO_3$ is added to PVC, then they are used for insulation of tubing, seat covers, wires & cables.
- Asbestos filled FRP → for electrical appliances'.
- FRP has good shock & thermal resistances, mouldability, dimensional stability & reparability.

Applications

- Fiber reinforced plastics find extensive use in space crafts, aeroplanes, boat nulls, acid storage tanks, motor cars and building materials.
- Melamine FRP is used for insulation & making baskets

Advantages of FRP

(a) Low efficient of thermal expansion
(b) High dimensional stability
(c) Low cost of production
(d) Good tensile strength
(e) Low dielectric constant
(f) Non inflammable & non-corrode and chemical resistance

Glass Reinforced Plastics:

Glass reinforced plastic (shortened as GRP) is made of synthetic resin as main basic material and glass fiber or other product as reinforced material, processed into a solid material by molding and setting

Fiberglass is a common type of fiber reinforced plastic using glass fiber. The fibers may be randomly arranged, flattened into a sheet (called a chopped strand mat), or woven into a fabric. The plastic matrix may be a thermoset polymer matrix—most often based on thermosetting polymers such as epoxy, polyester resin or vinyl ester or a thermoplastic.

Applications:

1. Fiberglass is an immensely versatile material due to its light weight, inherent strength, weather-resistant finish and variety of surface textures
2. During World War II, fiberglass was developed as a replacement for the molded plywood used in aircraft radomes (fiberglass being transparent to microwaves).
3. fiberglass is also used in the telecommunications industry for shrouding antennas , due to its RF permeability and low signal attenuation properties.
4. Because of fiberglass's light weight and durability, it is often used in protective equipment such as helmets. Many sports use fiberglass protective gear, such as goaltenders' and catchers' masks.
5. Storage tanks can be made of fiberglass with capacities up to about 300 tones.

6. Glass-reinforced plastics are also used to produce house building components such as roofing laminate, door surrounds, over-door canopies, window canopies and dormers, chimneys, coping systems, and heads with keystones and sills
7. In rod pumping applications, fiberglass rods are often used for their high tensile strength to weight ratio. Fiberglass rods provide an advantage over steel rods because they stretch more elastically (lower young modulus) than steel for a given weight,
8. GRP and GRE pipe can be used in a variety of above- and below-ground systems.

Carbon Reinforced Fiber:

Carbon fiber reinforced polymer or carbon fiber reinforced plastic, or carbon fiber reinforced thermoplastic, is an extremely strong and light fiber-reinforced plastic which contains carbon fibers.

One method of producing CFRP parts is by layering sheets of carbon fiber cloth into a mold in the shape of the final product. The alignment and weave of the cloth fibers is chosen to optimize the strength and stiffness properties of the resulting material. The mold is then filled with epoxy and is heated or air-cured.

Carbon Fiber Reinforced Plastics are very hard to machine, and causes significant tool wear. The tool wear in CFRP machining is dependent on the fiber orientation and machining condition of the cutting process. In order to reduce tool wear various types of coated tools are used in machining CFRP and CFRP-metal stack.

Applications

Aerospace engineering

CFRP is widely used in micro air vehicles (MAVs) because of its high strength to weight ratio.

Automotive engineering

Many supercars over the past few decades have incorporated CFRP extensively in their manufacture, using it for their monocoque chassis as well as other components.

Civil engineering

CFRP has become a notable material in structural engineering applications

Carbon-fiber microelectrodes

Carbon fibers are used for fabrication of carbon-fiber microelectrodes.

Carbon-fiber microelectrodes are used either in amperometry or fast-scan cyclic voltammetry for detection of biochemical signaling.

Sports goods

CFRP is now widely used in sports equipment such as in squash, tennis, and badminton racquets, sport kite spars, high-quality arrow shafts, hockey sticks, fishing rods, surfboards, high end swim fins, and rowing shells.

UNIT IV: ADVANCED MATERIALS

NANOMATERIALS

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 and development the major sectors are energy, environment, water technology, pharmaceuticals etc. The usage of nanomaterials is enormous as energy storage devices such as fuel cells, detection of threats in defense, 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 nanoscience and nanotechnology.

The size of the material ranging from 10nm to 100nm is called as Nano Scale. Here the nanoscale is very important because many physical and chemical properties starts changing significantly when the size of the material is below 100nm and reduction of the particle size to nano level could improve the properties of the materials to high level .This resulted in the birth of "Nano Science" and "Nano Technology" which has great potential to create many new materials and devices which has great applications in many fields.

Nanotechnology deals with structures of the size 100nm or smaller and involves in developing materials or devices within that size. It plays an important role in the fields of physics, chemistry, biology, Engineering and technology. So, a nanomaterial is defined as a material if the size of material is 100nm or below it.

The science and technology which deals with the particles in size between 1 to 100nm is known as nano science and nanotechnology.

Nano Scale:

The size of the material ranging from 10nm to 100nm is called as Nano scale. Here the nanoscale is very important because many physical and chemical properties starts changing significantly when the size of the material is below 100nm and reduction of the particle size to nano level could improve the properties of the materials to high level .This resulted in the birth of "Nano Science" and "Nano Technology" which has great potential to create many new materials and devices which has great applications in many fields.

Nanotechnology is the latest technology in which the materials are used in nano size, i.e. atoms are in the order of 1 to 100nm.

Nanoscale: $1nm = 10^{-9}m = 10^{-7}cm$

Nano means 10^{-9}m i.e. a billionth part of a meter. Atoms are extremely small & the diameter of a single atom can vary from 0.1 to 0.5nm depending on the type of the element.

Ex: Carbon atom – 0.15 in diameter, water molecule – 0.3nm

Red blood cell – 7,000nm, Human hair-80,000nm wide

White blood cell-10,000nm, Virus – 100nm, Hydrogen atom - 0.1nm

Bacteria range – 1,000 to 10,000nm, proteins – 5 to 50nm

DNA – 2nm Width, Quantum dots – 8nm

Nano particles – 1 to 100nm, Fullerenes – 1nm

Nanomaterials: The materials in which the atoms are in the order of 1 to 100nm and these atoms will not move away from each other, called as nanomaterials.
Eg: C, ZnO, Cu – Fe alloys, Ni, Pd, Pt etc.

1. Materials that are nanoscale in one dimension called as nano layers [Thin films, surface coatings].
2. Two dimensional nanomaterials are called as nano tubes and nanowires.
3. Three dimensional nanomaterials are called as nanoparticles.
   Ex: Precipitates, Colloids & quantum dots, tiny particles of semi-conductor materials.

Nanomaterial is defined as a material if the size of material is 100nm or below it.

Nano materials are classified into three types. They are
1) Materials that are nanoscale in one dimension
2) Materials that are nanoscale in two dimension
3) Materials that are nanoscale in three dimension.

Examples of materials that are nanoscale in one dimension are layers, such as thin films or surface coatings.

Materials that are nanoscale in two dimensions include nanowires and nanotubes.
Materials that are nanoscale in three dimension are particles for example precipitates, colloids and quantum dots (tiny particles of Semiconductor materials)

So, based on this nano material generally fall into two categories, they are

1) Fullerenes
2) Nanoparticle

Fullerenes:

Afullereneisamoleculecomposedofcarbonintheformofahollowsphereortube.Fullerenes are also classified into spherical and cylindrical fullerenes, spherical fullerenes are also called as bucky balls and cylindrical ones are called as carbon nanotubes or bucky tubes. Fullerenes are similar in structure to graphite.

The first fullerene discovered was Buckminster fullerene C_{60} in 1985. It was named after Richard Buckminster fuller. Carbon nanotubes (CNTs) are allotropes of carbon with a cylindrical nanostructure. Carbon nanotubes are again categorized into

(1) Single-Walled nanotubes (SWNTs)
(2) Multi-Walled nanotubes (MWNTs)

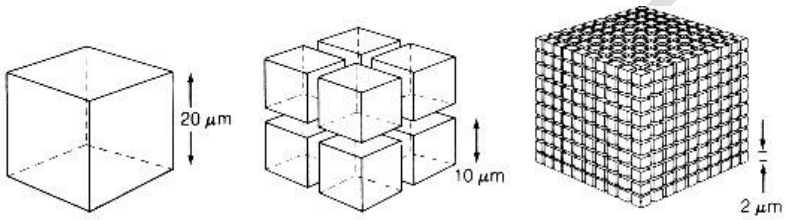
These are useful in many applications in nanotechnology, electronics, optics and material science.

Nanoparticles:
Nanoparticles are available in different forms such as clusters, metal nanoparticles, colloids, nano shells, quantum dots etc., They are made of metals, semiconductors or oxides. Nanoparticles have been used as quantum dots and as chemical catalysts.

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Surface to Volume Ratio

In chemical reactions, this surface to volume ratio plays an important role. There is an enormous change in the properties of materials due to increased surface area to volume ratio. The nanomaterials have relatively larger surface area when compared to the same volume of the material produced in larger form. So we know that material has high surface energy if it is small in size and vice versa. Therefore, nanoparticles have large surface area to volume ratio and they possess large surface energy. Due to high surface energy materials are more reactive and also nanoparticles show enhanced stability and broader scope of applications. In some cases, materials that are inert in their larger form are reactive when produced in their nanoscale form. This affects their strength or electrical properties.



Length of one side	20 μm	10 μm	2 μm
Total surface area (height × width × number of sides × number of cubes)	2400 μm^2	4800 μm^2	24,000 μm^2
Total volume (length × width × height × number of cubes)	8000 μm^3	8000 μm^3	8000 μm^3
Surface area to volume ratio (surface area ÷ volume)	0.3	0.6	3.0

Fabrication

Nanomaterials or Nanostructures can be made mainly in two ways. They are

(1) Bottom-up fabrication

(2) Top-down fabrication

Bottom-up Fabrication is one in which the nanostructure is built atom by atom from small components, whereas top-down fabrication is one in which an existing solid gradually reduced in size using some external radiation.

Bottom-up Fabrication

Preparation: Now there are many known methods to produce nanomaterials. Let us study briefly few these methods.

Sol Gel Method:

The solutions in which molecules of nanometer are dispersed appear clear. The colloids in which molecules of size ranging from 20 nm to 100 nm appear milky. A colloid suspended in a liquid is called as sol. A suspension that keeps its shape is called gel. Thus sol-gels are suspensions of colloids in liquid that keep their shape. Sol-gel formation occurs in different

stages. The sol el process can be characterized by a series of distinct steps.

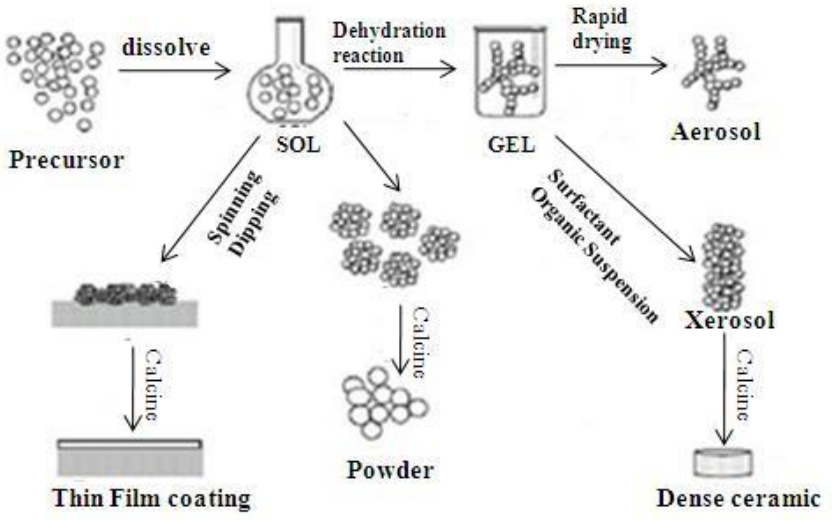


Fig: Schematic representation of Sol-Gel process for synthesis of naomaterials

Step1: Formation of different stable solutions of the alkoxide or solvated metal precursor (the sol).

Step 2: Gelation resulting from the formation of an oxide or alcohol bridged network (the gel) by a poly condensation or poly esterification reaction. This results in a dramatic increase in the viscosity of the solution.

Step 3: Aging of the gel(synthesis), during which the poly condensation reactions continue until the gel transforms into a solid mass. This is accompanied by contraction of the gel network and expulsion solvent from gel pores.

Step 4: Drying of the gel, when water and other volatile liquids are removed from the gel network. If isolated by thermal evaporation, the resulting is termed a xerosal. If the solvent (such as water) is extracted under super critical or near super critical conditions, the product is an aerogel.

Step 5: Dehydration, during which surface bound M-OH groups are removed. This is normally achieved by calcinations of the monolith at temperature's up to 800 ^{0} C.

Step 6: Densification and decomposition of the gels at high temperature (T>800 ^{0} C). The pores of the gel network are collapsed, and remaining organic species are volatilized.

The typical steps that are involved in sol gel processing are shown in fig. By different process one can get either nan film coating or nano powder or dense ceramic with nanograins.

Advantages

1. The possibility of synthesizing nonmetallic materials like glasses, glass ceramics or ceramic materials at very low temperatures.
2. One can mono sized nanoparticles.

Disadvantages

1. Controlling the growth of the particle is difficult.
2. Stopping the newly formed particles from agglomeration is also difficult.

Ex-Nanoparticles prepared by sol gel method are $Si(OR)_3$, where R is alkyl groups ay various types.

Chemical Vapour Deposition:

In this method nanoparticles are deposited from gas phase. Material is heated to form a gas and then allowed to deposit on a solid surface, usually under high vacuum. In deposition by chemical reaction new product is formed. Nanopowders of oxides and carbides of metals can be formed if vapours of carbon or oxygen are present with the metal.

It involves pyrolysis of vapours of metal organic precursors in a reduced pressure atmosphere. In the simplest form, a metal –organic precursor is introduced into the hot zone of the reactor using mass flow controller. The precursor is vapourised either by resistive or inductive heating. The carries gas such as Ar or Ne carries the hot atoms to the reaction chamber. The hot atoms collide with cold atoms and undergo condensation through nucleation and form small cluster. In side reaction chamber other reactants are added to control the reaction rate. Then these clusters are allowed to condense on a moving belt arrangement with scrapper to collect the nanoparticles. The particle size could be controlled by rate of evaporation (energy input), rate of cluster formation (energy removal rate) and rate of condensation (cluster removal from the reaction chamber).

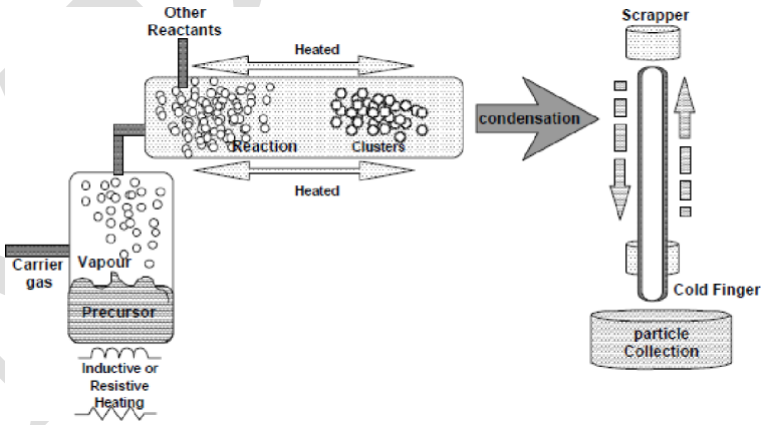


Fig: Chemical Vapour Deposition

CVD method of synthesis of nanoparticles has many advantages.

1. The increased yield of nanoparticles.
2. A wider range of ceramics including nitrides and carbides can be synthesized.
3. More complex oxides such as $BaTiO_3$ or composites structures can be formed.
4. In addition to the formation of single-phase nanoparticles by CVC of a single precursor the reactor allows the synthesis of
   a) Mixtures of nanoparticles of two phases or doped nanoparticles by supplying two precursors at the front end of the reactor, and

b) Coated nanoparticles, i.e., n-ZrO_2 coated with n-Al_2O_3 or vice versa, by supplying a second precursor at a second stage of thereactor.

Applications of Nanomaterials:

In Production Technologies

- It is important and perspective now to use nanomaterials in composites as components of various functions.
- In the production of steels and alloys adding nanopowders helps to reduce porosity and improve the range of mechanical properties.
- Manifestation of super plasticity in nano structured aluminum and titanium alloys makes their use promising in the manufacture of complex shapes details and for using as a connecting layer in welding different solid-state materials.

In Military Engineering

- Ultra-fine powders are used in a number of radars absorbing coatings for aircraft, created with the use of technology "Stealth", and promising types of explosives and incendiary.
- Carbon nanofibers are used in special ammunition intended for the scrapping of the enemy power systems (so-called "graphite bomb").

In Nuclear Power Engineering

The beginning of nuclear power engineering was given by the ultra-fine powders. These powders are commonly used in industrial processes for the separation of uranium isotopes. Prospects for the development of nuclear energy by bringing the particles to the nano state are mainly associated with a decrease in the average consumption of natural uranium. This happens mostly at the expense of increasing the depth of the nuclear fuel combustion. To do this, scientists are exploring the possibility of the creation of coarse-grained structures of nuclear materials, which can be porous. These nanomaterials will promote a high retention of fission products.

In Material Surface Protection

In some cases, for reliable operation, it is necessary to ensure the high water and oil repellency properties of material surface. Some examples of such products may be car windows, glass planes and ships, protective clothing, wall storage tanks for liquids, building construction, etc. At present the titanium oxide nanoparticles coating with sizes of 20-50 nm and a polymer binder have been developed. This coating greatly reduces the wettability of the surface with water, oil and alcohol solutions.

In Medical

- Silver nanoparticles have good antibacterial properties are used in surgical instruments, refrigerators, air-conditioners, water purifiers etc.
- Gold nanoparticles are used in catalytic synthesis of silicon nanowires, sensors carrying the drugs and in the detection of tumors.
- ZnO nanoparticles are used in electronics, ultraviolet (UV) light emitters, piezoelectric

devices and chemical sensors.

- TiO_2 nanoparticles are used as photocatalyst and sunscreen cosmetics (UV blocking pigment).
- Antimony-Tin-Oxide (ATO), Indium-Tin-Oxide (ITO) nanoparticles are used in car windows, liquid crystal displays and in solar cell preparations.
- Nanoscale structures and materials such as nanoparticles, nanowires, nanofibers, and nanotubes have been explored in many biological applications e.g., biosensing, biological separation, molecular imaging, and/or anticancer therapy because of their novel properties and functions differ drastically from their bulk counter parts.
- Their high volume/surface ratio, surface tailor ability, improved solubility, and multifunctionality open many new possibilities for biomedicine.
- The intrinsic optical, magnetic and biological properties of nanomaterials offer remarkable opportunities to study and regulate complex biological processes for biomedical applications in an unprecedented manner.

Carbon Nanotubes (CNTS):

A carbon nanotube is a tube-shaped material, made of carbon, having a diameter measuring on the nanometer scale. To understand the structure of a carbon nanotube it can be first imagined as a rolled-up sheet of graphene, which is a planar-hexagonal arrangement of carbon atoms distributed in a honeycomb lattice. A single layer of graphite sheet is called graphene.

Carbon nanotubes have many structures, differing in length, thickness, and in the type of helicity and number of layers. As a group, CNTs typically have diameters ranging from <1nm up to 50nm. Their lengths are usually several microns, but recent advancements have made the nanotubes much longer, and measured in centimeters.

There are two types of carbon nanotubes.

1. Single wall carbon nanotubes (SWCNT)

Single-wall nanotubes (SWNT) are tubes of graphite that are normally capped at the ends. They have a single cylindrical wall. The structure of a SWNT can be visualized as a layer of graphite, a single atom thick, called graphene, which is rolled into a seamless cylinder.

Most SWNT typically have a diameter of close to 1 nm. The tube length, however, can be many thousands of times longer. SWNT are more pliable yet harder to make than MWNT. They can be twisted, flattened, and bent into small circles or around sharp bends without breaking.

2. Multi wall carbon nanotubes (MWCNT)

There are two structural models of multi wall nanotubes. In the Russian Doll model, a carbon nanotube contains another nanotube inside it (the inner nanotube has a smaller diameter than the outer nanotube). In the Parchment model, a single graphene sheet is rolled around itself multiple times, resembling a rolled-up scroll of paper. The simplest representative of a MWNT is a double walled carbon nanotube (DWNT).

Multi wall carbon nanotubes have similar properties to single wall nanotubes, yet the outer walls on multi wall nanotubes can protect the inner carbon nanotubes from chemical interactions with outside materials. Multi wall nanotubes also have a higher tensile strength

than single wall nanotubes.

The diameters of MWNT are typically in the range of 5 nm to 50 nm. The interlayer distance in MWNT is close to the distance between graphene layers in graphite, around $3.39A^0$

MWNT are easier to produce than SWNT. However, the structure of MWNT is less well understood because of its greater complexity and variety. Regions of structural imperfection may diminish its desirable material properties.

Applications of Carbon Nanotubes:

1. **Catalyst supports:** CNTs can be sued a catalyst supports because they can provide higher surface areas and high chemical stability and controlled surface chemistry.
2. **Hydrogen storage:** Recently carbon nanotubes have been proposed to store hydrogen in hydrogen-oxygen fuel cell.
3. **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.
4. **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.
5. **Chemical Sensors/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.
6. **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 touchscreens.
7. **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 sued in areas such as building, structural engineering and aerospace.
8. **Aerospace Components:** CNTs have good fatigue strength over a long time which makes use of them as aircraft components.

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SMART MATERIALS

Introduction:

The world has undergone two materials ages, the plastics age and the composite age, during the past centuries. In the midst of these two ages a new era has developed. This is the smart materials era. According to early definitions, smart materials are materials that respond to their environments in a timely manner. With the development of material science, many new, high-quality and cost-efficient materials have come into use in various field of engineering. In the last ten decades, the materials became multifunctional and required the optimization of different characterization and properties. With the last evolution, the concept has been driving towards composite materials and recently, the next evolutionary step is being contemplated with the concept of smart materials. Smart materials are new generation materials surpassing the conventional structural and functional materials. These materials possess adaptive capabilities to external stimuli, such as loads or environment, with inherent intelligence.

Smart or intelligent materials are materials that have the intrinsic and extrinsic capabilities, first, to respond to stimuli and environmental changes and, second, to activate their functions according to these changes. The stimuli could originate internally or externally. The definition of smart materials has been expanded to materials that receive, transmit, or process a stimulus and respond by producing a useful effect that may include a signal that the materials are acting upon it. Some of the stimuli that may act upon these materials are strain, stress, temperature, chemicals (including pH stimuli), electric field, magnetic field, hydrostatic pressure, different types of radiation, and other forms of stimuli

Smart materials

Smart materials, also called intelligent or responsive materials, are designed materials that have one or more properties that can be significantly changed in a controlled fashion by external stimuli, such as stress, moisture, electric or magnetic fields, light, temperature, pH, or chemical compounds.

The several external stimulus to which the smart materials sensitive are:

- Stress
- Temperature
- Moisture
- pH
- Electric Fields
- Magnetic Fields

Three basic components of a smart system are:

- Sensor
- processor
- Actuator

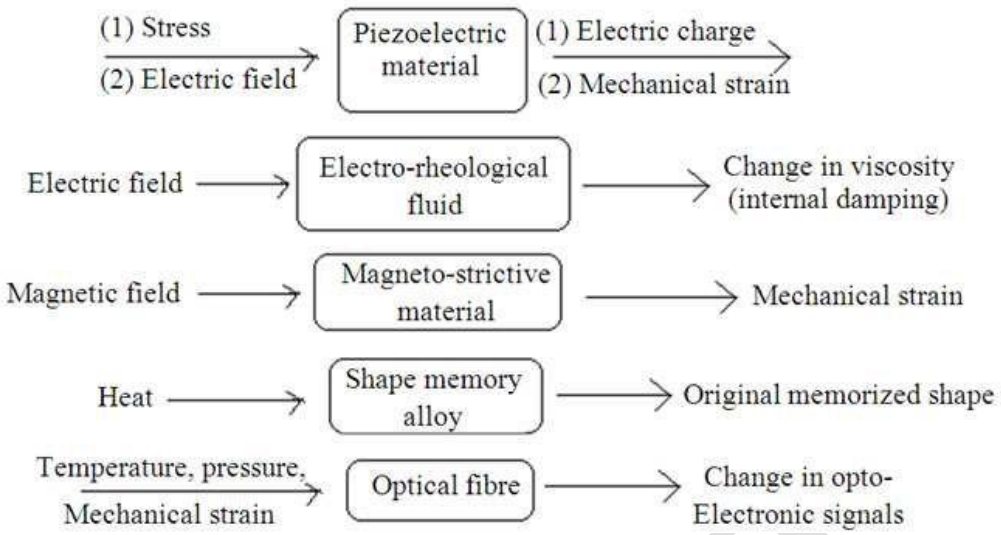


Fig: Common smart materials and associated stimulus-response.

Example: Smart concrete building (suitable to earth quake areas)
Sensor : optical fibers (embedded in concrete)
Processor: smart wires (automatic shrink/expand)
Actuator: chemically active smart materials (fillers preventing crack propagation**)**

Classification of Smart Materials

Active and Passive Smart Materials:

Smart materials can be either *active* or *passive*. Fairweather (1998) defined active smart materials as those materials which possess the capacity to modify their geometric or material properties under the application of electric, thermal or magnetic fields, thereby acquiring an inherent capacity to transduce energy. Piezoelectric materials, shape memory alloys, and magnetostrictive materials are active smart materials. Being active, they can be used as force transducers and actuators.
The smart materials, which are not active, are called passive smart materials. Although smart, these lack the inherent capability to transduce energy. Fibre optic material is a good example of a passive smart material. Such materials can act as sensors but not as actuators or transducers.

Types of Smart Materials

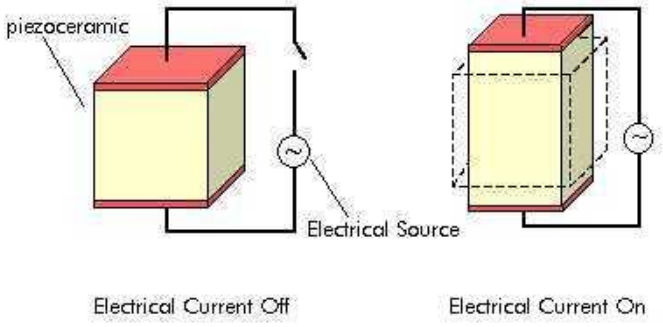
1. Piezoelectric Materials
2. Shape Memory Alloys
3. Magnetostrictive Materials
4. Electrostrictive materials

Piezoelectric Materials

- The word originates from the Greek word **"piezein"**, which means **"to press".** Discovered in 1880 by Pierre Curie in quartz crystals

- Piezoelectrics are materials that can create **electricity** when subjected to a **mechanical stress.**
- They will also work in reverse, generating a **strain** by the application of **an electric field.**
- Piezoelectric effect: When subjected to an electric charge or a variation in voltage, piezoelectric material will undergo some mechanical change, and vice versa. These events are called the direct and converse effects.

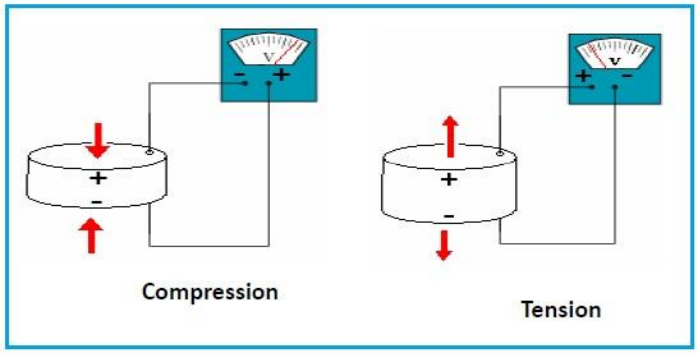
All piezoelectric materials are non-conductive in order for the piezoelectric effect to occur and work. They can be separated into two groups: crystals and ceramics.



Working Principle

Piezoelectric effect

Piezoelectric effect is the ability of certain materials to generate an electric charge in response to applied mechanical stress



Direct Piezoelectric Effect

Piezoelectric material will generate electric potential when subjected to some kind of mechanical stress.

Devices that use the direct piezoelectric effect include microphones, pressure sensors, hydrophones, and many other sensing types of devices.

Inverse Piezoelectric Effect

If piezoelectric material is exposed to an electric field (voltage) it consequently lengthens or shortens proportional to voltage.

The piezoelectric effect can be reversed, which is referred to as the inverse piezoelectric effect. This is created by applying electrical voltage to make a piezoelectric crystal shrink or expand. The inverse piezoelectric effect converts electrical energy to mechanical energy.

Using the inverse piezoelectric effect can help develop devices that generate and produce acoustic sound waves. Examples of piezoelectric acoustic devices are speakers (commonly found in handheld devices) or buzzers. The advantage of having such speakers is that they are very thin, which makes them useful in a range of phones. Even medical ultrasound and sonar transducers use reverse piezoelectric effect. Non-acoustic inverse piezoelectric devices include motors and actuators.

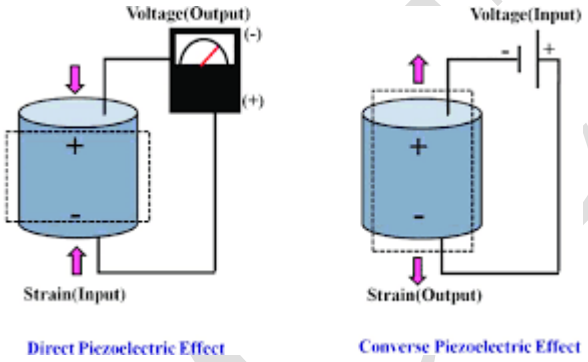
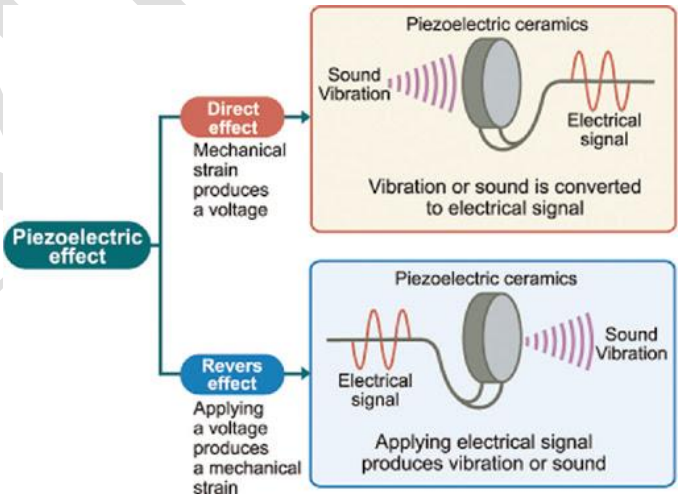


Fig: Piezoelectric effect



Examples of Piezoelectric materials

Natural	Synthetic
Quartz	Lead zirconatetitanate (PZT)
Rochelle salt	Zinc oxide (ZnO)
Topaz	Barium titanate ($BaTiO_3$)
Sucrose	Gallium orthophosphate ($GaPO_4$)
Tendon	Potassium niobite ($KNbO_3$)
Silk	Lead titanaate ($PbTiO_3$)
Enamel	Lithium tantalite ($LiTaO_3$)
DNA	Sodium tungstate ($Na2WO_3$)

Applications of Piezoelectric material

Mechanical to Electrical Conversion	Electrical to Mechanical Conversion
1. Phonograph cartridges	1. Valves
1. Microphones	2. Earphones and speakers
2. Vibration sensors	3. Ultrasonic cleaners
3. Accelerometers	4. Emulsifiers
4. Photoflash actuators	5. Sonic transducers
5. Gas igniters	6. Micro pumps
6. Fuses	-

Electrostrictive Materials:

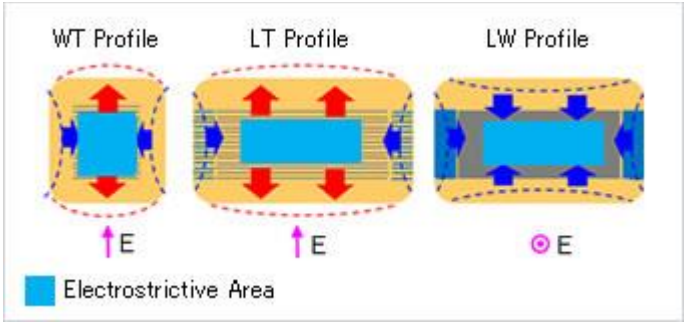
This material has the same properties as piezoelectric material, but the mechanical change is proportional to the square of the electric field. This characteristic will always produce displacements in the same direction.

Electrostrictive materials are materials that exhibit a quadratic relationship between mechanical stress and an applied electric polarization (Fig). Electrostriction can occur in any material. Whenever an electric field is applied, the induced charges in the material attract each other resulting in a compressive force. This attraction is independent of the sign of the electric field. The strain in the material lies along the axis of the induced polarization, which is preferably the direction of the applied electric field. Electrostriction is a small effect and, in contrast to piezoelectric materials, electrostrictive materials show a large effect near the Curie temperature, especially for ferroelectric substances, such as members of the perovskite family.

Examples: Lead Lanthanum Zirconate Titanate (PLZT); Lead Magnesium Niobate (PMN).

Electrostriction is used in actuators for accurate and fine positioning. Electrostrictive translators are less stable than piezoelectric devices with greater sensitivity to temperature.

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Applications of Electrostrictive Materials

- Sonar projectors for submarines and surface vessels
- Actuators for small displacements
- Lead Magnesium Niobate is a piezoelectric polycrystalline ceramic material with applications in optoelectronics and acousto-optics.
- Lead zirconate titanate is used to make ultrasound transducers and other sensors and actuators, as well as high-value ceramic capacitors and FRAM chips.
- PLZT is a piezoelectric ceramic material with applications in dielectric thin films, CMOs, ceramic capacitors and resonators, ultrasound transducers, photovoltaic cells, and energy storage.

Magnetostrictive materials:

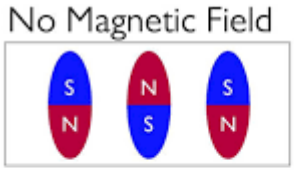
Magnetostrictive materials are similar to piezoelectric and electrostrictive materials except the change in shape is related to a magnetic field rather than an electrical field.

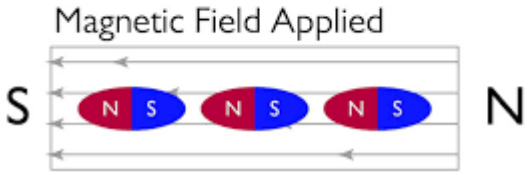
Magnetostrictive materials convert magnetic to mechanical energy or vice versa. The magnetostrictive effect was first observed in 1842 by James Joule who noticed that a sample of nickel exhibited a change in length when it was magnetised. The other ferromagnetic elements (cobalt and iron) were also found to demonstrate the effect as were alloys of these materials. During the 1960s terbium and dysprosium were also found to be magnetostrictive but only at low temperatures which limited their use, despite the fact that the size change was many times greater than that of nickel. The original observation of the magnetostrictive effect became known as the Joule effect, but other effects have also been observed. The Villari effect is the opposite of the Joule effect, that is applying a stress to the material causes a change in its magnetization.

Working Principle

When subjected to a magnetic field, and vice versa (direct and converse effects), this material will undergo an induced mechanical strain. Consequently, it can be used as sensors and/or actuators.

Magnetic materials contain domains which can be likened to tiny magnets within the material. When an external magnetic field is applied the domains rotate to align with this field and this results in a shape change as shown in Figure 6. Conversely if the material is squashed or stretched by means of an external force the domains are forced to move and this causes a change in the magnetisation.





Examples: Materials that have shown a response to a magnetic stimuli are primarily inorganic: alloys of iron, nickel, and cobalt doped with rare earths.

The most common magnetostrictive material today is called TERFENOL-D (terbium (TER), iron (FE), Naval Ordanance Laboratory (NOL) and dysprosium (D)). This alloy of terbium, iron and dysprosium shows a large magnetostrictive effect and is used in transducers and actuators.

Applications:

- Magnetostrictive materials can be used as both actuators (where a magnetic field is applied to cause a shape change) and sensors (which convert a movement into a magnetic field).
- Early applications of magnetostrictive materials included telephone receivers, hydrophones, oscillators and scanning sonar.
- The development of alloys with better properties led to the use of these materials in a wide variety of applications. Ultrasonic magnetostrictive transducers have been used in ultrasonic cleaners and surgical tools. Other applications include hearing aids, razorblade sharpeners, linear motors, damping systems, positioning equipment, and sonar

Shape Memory Alloys:

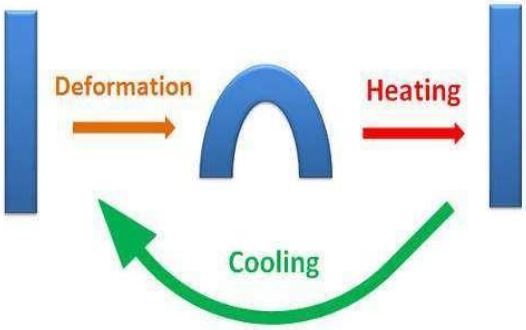
Shape Memory alloys are metals that exhibit the properties of pseudo-elasticity and the Shape Memory Effect.

- Shape memory alloys are smart materials
- A shape memory alloys (SMA) are metal alloys that can be deformed at one temperature but when heated or cooled, return to their “original shape”.
- Shape Memory Alloys are materials that “remember” their original shape.
- If deformed, they recover their original shape upon heating.
- They can take large stresses without undergoing permanent deformation.
- They can be formed into various shapes like bars, wires, plates and rings thus serving various functions.
- SMA also exhibits super elastic (Pseudoelastic) behaviour.

The high temperature causes the atoms to arrange themselves into the most compact and regular pattern possible.

Shape Memory Effect – unique ability of materials to be severely deformed and then return to their original shape through stimulus

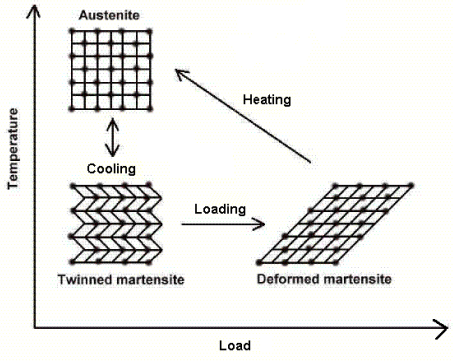
SME occurs due to the change in the crystalline structure of materials.



Working Principle

- SMAs have two stable phases are:
- Martensite: Low temperature phase, relatively weak
- Austenite: High temperature phase, relatively strong
- Martensite to Austenite transformation occurs by heating
- Austenite to Martensite occurs by cooling.
- A phase transformation which occurs between these two phases upon heating/cooling is the basis for unique properties of SMAs.

When subjected to a thermal field, this material will undergo phase transformations which will produce shape changes. It deforms to its **'martensitic'** condition with low temperature, and regains its original shape in its **'austenite'** condition when heated (high temperature).



Examples: Nickel-Titanium alloys (NiTinol)

Copper -Aluminium- Nickel alloys

Copper-Zinc-Aluminium alloys

Iron -Manganese-Silicon alloys

Nickel–titanium alloys have been the most used shape memory material. This family of nickel–titanium alloys is known as **Nitinol,** after the laboratory where this material was first observed (Nickel Titanium Naval Ordinance Laboratory).

Applications of Smart memory Alloys

Nitinol has been used in military, medical, safety, and robotics applications. Specific applications include hydraulic lines on F-14 fighter planes, medical tweezers and sutures,

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anchors for attaching tendons to bones, stents for cardiac arteries, eyeglass frames, and antiscalding valves in water faucets and showers

1) Aircraft

Alloys can be used to create flexible wings in aircrafts using Shape Memory wires.



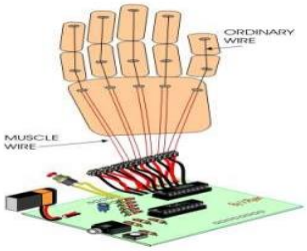
2) Automotive

To reduces engine noise, some designers installs chevrons onto engines to mix the flow of exhaust gases and reduces engine noise.



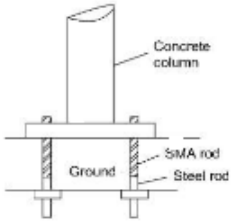
3) Robotics

Muscle Wires: SMAs are very good at mimicking human muscles and tendons so they can be used to create humanlike movements in robots.



4) Civil Structures

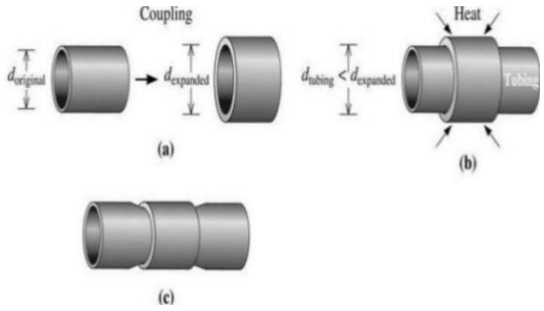
SMAs find a variety of applications in civil structures such as bridges and buildings. One such application is Intelligent Reinforced Concrete (IRC), which incorporates SMA wires embedded within the concrete.



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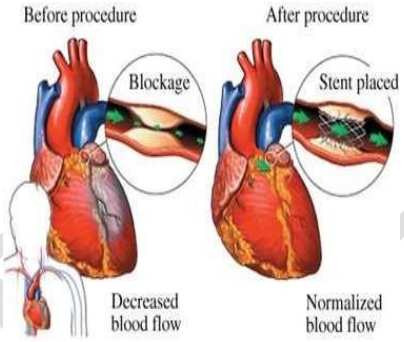
5) Piping

The first consumer commercial application was a shape-memory coupling for piping, e.g. oil line pipes for industrial applications, water pipes.



6) Medicine

Stent- A reinforced grafts for vascular application to replace or repair damaged arteries (25mm diameter)



Unit V: PHOTOCHEMISTRY

Introduction:

Photochemical reactions occur all around us, being an important feature of many of the chemical processes occurring in living systems and in the environment. The power and versatility of photochemistry is becoming increasingly important in improving the quality of our lives, through health care, energy production and the search for ' green ' solutions to some of the problems of the modern world. Many industrial and technological processes rely on applications of photochemistry, and the development of many new devices has been made possible by spin - off from photochemical research.

Photochemistry is the study of the chemical reactions and physical changes that result from interactions between matter and visible or ultraviolet light.

Photochemistry:

The branch of chemistry which deals with the absorption of light radiations and its effect (physical or chemical) on the substance is known as photochemistry.

Photochemistry is concerned with reactions which are initiated by electronically excited molecules. The light radiations which are important from the photochemistry point of view are those of visible and ultra-violet regions, i.e., those having wavelength between 2000 A^0 to 8000 A^0. It is for this reason, photochemistry has made large contributions to the fundamental and applied sciences.

Laws of Photochemistry:

Photochemistry has two basics laws, which describe the condition and efficiency of photo absorption.

Grotthuss–Draper law:

- The first law of photochemistry called as Grotthuss-Draper law.
- This law states that radiation must be absorbed by the compounds in order for a photochemical reaction to happen.
-

Stark-Einstein law:

- The second law of photochemistry called as the Stark-Einstein law.
- This law states that for each photon of radiation absorbed by a chemical system, no more than one molecule is activated for a photochemical reaction.

Stark-Einstein Law: (Einstein law of photochemical equivalence)

"Each molecule of absorbing substance absorb one photon (or quantum) of the radiation in primary process."

Explanation:
A molecule acquire energy by absorbing photon as,

$$\mathbf{A + h\upsilon \text{ ---------> } A^*}$$

Thus energy of photon is,

$$\mathbf{E = h\upsilon}$$

Where υ = frequency of absorbing photon. h = plank's constant = 6.624 × 10–34 J.s The energy of 1 mol photon (ie. Einstein) is given by, E = N.h.υ

But, $\upsilon = C/\lambda$ $\quad E = \frac{N.h.C}{\lambda}$

N= Avogadro's no. = $6.023 \times 10^{23}\ mol^{-}$. C= velocity of light. = 3×10^8 m/s.

$$E = \frac{6.023 \times 10^{23} \times 6.624 \times 10^{-34} \times 3 \times 10^8}{\lambda \times 10^{-9}}$$

$$E = \frac{1.1962 \times 10^8}{\lambda}\ J/mol = \frac{119620}{\lambda}\ KJ/mol$$

A mole of photon can excite a mole of molecule. But if electromagnetic radiations are extremely intense, molecule may absorb two or more photons.

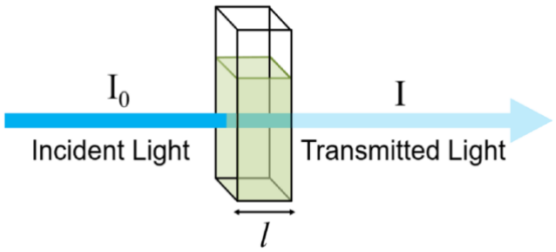
$A + 2\ h\upsilon$ ---------> A^*

Hence this law is not valid for all condition.

The Beer –Lambert's Law

The Beer–Lambert law, also known as Beer's law, the Lambert–Beer law relates the attenuation of light to the properties of the material through which the light is travelling. When a monochromatic light of initial intensity **Io** passes through a solution in a transparent vessel, some of the light is absorbed so that the intensity of the transmitted light **I** is less than **Io** .There is some loss of light intensity from scattering by particles in the solution and reflection at the interfaces, but mainly from absorption by the solution.

The relationship between **I** and **Io** depends on the path length of the absorbing medium, **l or x**, and the concentration of the absorbing solution, **c**. These factors are related in the laws of Lambert and Beer.



Lambert's Law:

When a monochromatic radiation is passed through a homogeneous absorbing medium, the rate of decrease in the intensity of radiation with thickness of absorbing medium is directly proportional to the intensity of the incident radiation.

$$\frac{-dI}{dx} \alpha I \quad \text{ie} \quad \frac{-dI}{dx} = k.I$$

$$\rightarrow \quad \frac{dI}{I} = -k.dx$$

On integrating above equation between respective limits,

$$\log_{10}\frac{I}{Io} = -a.x$$

$$\rightarrow \quad \frac{I}{Io} = 10^{-a.x}$$

Lamberts-Beer's Law (or Beer's Law):

When a monochromatic radiation is passed through a solution of absorbing medium, the rate of decrease in the intensity of radiation with thickness of absorbing medium is directly proportional to the intensity of the incident radiation and concentration of the solution.

$$\frac{-dI}{dx} \alpha I.c. \qquad \text{ie.} \quad \frac{-dI}{dx} = k'.I.c$$

$$\rightarrow \quad \frac{dI}{I} = -k'.c.d$$

On integrating equation between respective limits,

$$\log_{10}\frac{I}{Io} = -\varepsilon.c.x$$

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$$A = \frac{Io}{I} = \varepsilon c x$$

A = Absorbance or optical density (OD)

I_0 = Intensity of incident light

I = Intensity of transmitted light

ε = molar absorption coefficient (L $mol^{-1}cm^{-1}$)

c = concentration of solution (mol/lit)

x = thickness of absorbing medium(cm)

The units of e require some explanation here as they are generally expressed as non-SI units for historic reasons, having been used in spectroscopy for many years.

Concentration, c, traditionally has units of moles per litre, mol L^{-1}
Path length, l, traditionally has units of centimetres, cm.
A has no units since it is a logarithmic quantity.

Limitations of Beer – Lambert's Law

1. The law holds good only for monochromatic radiation.
2. The law governs the absorption behaviour of dilute solutions only.

Types of Photo Processes

The two main types of processes which we study under photochemistry are
1) Photophysical processes
2) Photochemical processes or Photochemical reactions

Photochemical Processes or Photochemical Reactions

Processes in which absorbed light causes some chemical change in the substance are called photochemical processes.

Types of photochemical reactions:

a) Photodissociation
b) Photosynthesis: when a larger molecule is formed from simple ones
c) Photosensitized reactions: when an excited molecule supplies activation energy for the reactants.

Processes of photochemical reactions: The overall photochemical reaction consists of

i) Primary reaction and ii) Secondary reaction.

In the primary reaction, the quantum of light is absorbed by a molecule A resulting in the formation of an excited molecule.

$$A + h\nu \rightarrow A^*$$

In the secondary reaction, the excited molecules react further to give the product of higher quantum yield.

$$A^* \rightarrow B$$

All photochemical reactions take place in two steps. In the first step, the reacting molecules are activated by absorption of light. In the second step, the activated molecules undergo a photochemical change.

Examples:

Decomposition of HI: In the primary reaction, one HI molecule absorbs a photon and dissociated to produce one H and one I. This is followed by the second reaction as shown below:

$HI + h\nu \rightarrow H + I$.....Primary reaction

$H + HI \rightarrow H_2 + I$

$I + I \rightarrow I_2$.....Secondary reaction

Overall reaction: $2HI + h\nu \rightarrow H_2 + I_2$

The overall reaction shows that the two HI are decomposed for one photon ($h\nu$).

Formation of HCl: In the primary step, one Cl_2 molecule absorbs a photon and discussed into two Cl atoms. This is followed by the secondary reaction as shown below:

$Cl_2 + h\nu \rightarrow 2Cl$.....Primary reaction

$Cl + H_2 \rightarrow HCl + H$

$H + Cl_2 \rightarrow HCl + Cl$.....Secondary reaction

Photosensitizations: In some photochemical reactions, the reactant molecules do not absorb radiation and no chemical reaction occurs. However, if a suitable foreign substance (called sensitizer), which absorbs radiation, is added to the reactant, the reaction takes place. The sensitizer gets excited during absorption of radiation and transfers its energy to the reactants and initiates the reaction.

Photosensitization: The foreign substance absorbs the radiation and transfers the absorbed energy to the reactants is called a photosensitizer. This process is called photosensitized reaction (or) photosensitization. Examples,

i) Atomic photosensitizers : mercury, cadmium and zinc.
ii) Molecular photosensitizers: benzophenone, sulphur dioxide.

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Examples:

A) Dissociation of Hydrogen: UV light does not dissociate H_2 molecule, because the molecule is unable to absorb the radiation. But, if a small amount of mercury vapour is added, dissociation of hydrogen takes place. Here Hg acts as photosensitizer.

$$Hg + h\upsilon \longrightarrow Hg^*$$

$$Hg^* + H2 \longrightarrow Hg + 2H$$

B) Photosynthesis in plants: During photosynthesis of carbohydrates in plants from CO_2 and H_2O, chlorophyll of plants acts as a photosensitizer. The energy of the light absorbed by the chlorophyll (due to the presence of conjugation in chlorophyll) is transformed to $CO_2$and H_2O molecules, which then react to form glucose.

$$6CO_2 + 6\,H_2O \xrightarrow{h\upsilon;\ \text{chlorophyll}} C_6H_{12}O_6 + 6O_2$$

Photophysical Processes

Generally atoms or molecules go to excited state by the absorption of suitable radiation. If the absorbed radiation is not used to cause a chemical reaction, it will be re-emitted as light of longer wavelength. This process is called as photophysical process.

These are processes in which a substance absorbs light and emits it without undergoing any chemical change. These processes are again classified into three types depending upon the nature of absorbed light and the manner in which it is emitted.

a) If the absorbed light is emitted instantaneously, the process is known as fluorescence.
b) If the absorbed light is emitted after time lag, the process is called phosphorescence.
c) If the absorbed light has sufficiently high energy, the electrons not only jump to the outer levels, but may leave the atom completely. This process is called photoelectric effect.

Types of Photophysical process:

Photophysical process is of two types

1) Fluorescence
2) Phosphorescence

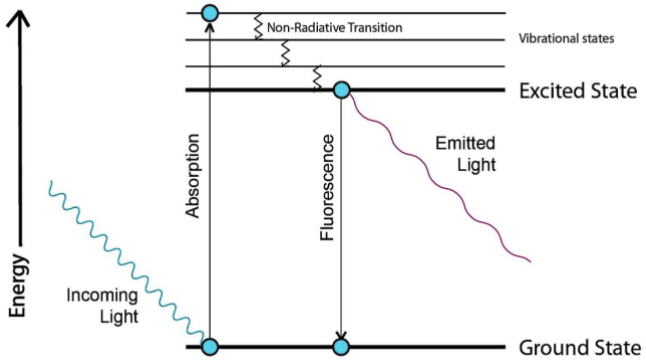
Fluorescence:

The phenomenon in which a substance absorbs light and emits a part of it instantaneously, usually at a different wavelength is called fluorescence and the substance itself is called fluorescent. Fluorescence stops as soon as light is cut off.

The phenomenon of fluorescence is explained on the basis of the fact that absorption of light energy causes excitation of the electrons of the atoms of molecules of the substance. These excited electrons immediately jump back to the lower level emitting a part of absorbed light in

the form of radiations of different wavelengths. Usually the emitted radiation has greater wavelength than that of the absorbed light. This is due to the fact that the absorbed energy raises the electron to a sufficiently higher level but the return of the excited electron to the original level takes place in steps, through the intermediate levels. The energy thus produced in every jump is smaller and hence the wavelength of the light emitted is larger than that of the absorbed light.

Mechanism of Fluorescence



However in some cases (eg: mercury vapours) the emitted light has the same wavelength as that of the absorbed light. This phenomenon is called resonance fluorescence. Further in certain cases, light of shorter wavelength (i.e., of higher energy) is emitted. This is explained by suggesting that the emitted light contains, in addition to the absorbed light, some energy is already present in the system before absorption.

If a mixture is present i.e., it mercury vapours are mixed with the vapours of silver, thallium lead or zinc, which do not absorb at the wavelength of mercury vapours, a part of the excitation energy from mercury atoms gets transferred to the atoms of the foreign substances (Silver, thallium, lead or zinc). These are then raised to higher energy states and emit, radiation when they return to their lower energy states. This is termed as sensitized fluorescence.

On the other hand the intensity of fluorescent radiation is diminished ifa photo chemically excited atom collides with another atom. This is known as quenching of fluorescence and is because of the transfer of energy from the excited atom to the colliding atoms.

A few examples of fluorescent substances are listed below:

1. Certain organic dyes eg: fluorescein and eosin. If their solutions are kept in light,they show fluorescence from green to violet color.
2. Fluorespar-fluorite (CaF_2) fluoresces with blue light.
3. Vapours of sodium, mercury, iodine, etc.
4. Uranyl sulphate UO_2SO_4 (green light).
5. Chlorophyll (green colouring matter of plants) solution in ether, fluoresces blood red, but appears green by transmitted light.
6. Petroleum
7. A solution of quinine sulphate emits blue light on irradiation with light.

Applications of Fluorescence

- Used in testing the condition of food stuffs.
- Used for detecting ring worm.
- In industry for testing and identifying material. eg: in rubber industry.
- In analysis: Concentration of riboflavin (Vitamin B2) in chloroform can be examined
- Use of fluorescent microscopes: Fluorescope used in X - ray diagnosis is helpful in testing condition of food stuff and detecting ring worms etc.
- In television: The cathode stream of the photoelectric effect is made visible in the cathode ray tube by adding ZnS to which a little Ni Is added to cut off phosphorescence which would make the picture blurred.
- For lightening purposes in fluorescence tubes.
- Using this phenomenon (fluorescence) invisible radiations like ultraviolet rays can be viewed.
- The difference in the fluorescence caused by UV rays in different types of inks enables police to detect forged documents.

Phosphorescence:

The phenomenon in which a substance absorbs light and emits it for some time even after the external light is cut off is called phosphorescence and the substances exhibiting this phenomenon are called phosphorescent. Thus phosphorescence may be regarded as slow or delayed fluorescence. This phenomenon is observed mainly in solids because in solids, molecules are tightly packed and have least freedom of motion, and thus the excited electrons keep on jumping back slowly for quite some time.

The mechanism of phosphorescence is similar to fluorescence except that the electrons are trapped in metastable excited state called triplet state with low probability of direct transition to the lower level, giving rise to a slow emission of radiation. In this phenomenon the emission of light of different wavelengths continues even after the source of light radiation has been cutoff.

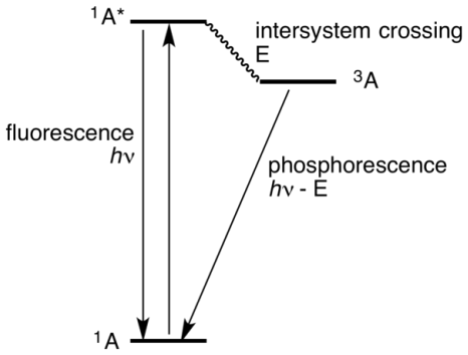


Fig: Mechanism of Phosphorescence

Sulphides of zinc and alkaline earth metals containing traces of heavy metal sulphide are best examples of phosphorescent substances. Such mixtures are generally used for luminous paints, for painting watch dials, electric switches etc. Further the fluorescent substances become

phosphorescent when fixed by suitable methods i.e., by fusion with other substances. For example, many dyes which show fluorescence, when dissolved in fused boric acid or glycerol followed by cooling, become phosphorescent.

Phosphorescence is rarely observed in gases, and almost never observed at room temperature.

Applications of Phosphorescence:

Phosphorescence finds applications in biology and medicine similar to that of fluorescence. Some interesting applications are as follows.

One can carry out the determination of aspirin (acetyl salicylic acid) in blood serum with high sensitivity by phosphorimetry at liquid nitrogen temperatures.

- Low concentration of procaine, cocaine, phenobarbital and chloropromazine in blood serum have been determined by phosphorimetry in combination with extraction procedures.
- Cocaine and atropine in urine have been determined by employing phosphorimetry in combination with extraction procedures.
- Phosphorimetry has been employed in combination with thin layer or paper chromatography for separating three tobacco alkaloids (nicotine, nor nicotine and anabasine) from crude tobacco.

Differences between Fluorescence and Phosphorescence

Fluorescence	Phosphorescence
It is the radiation emitted in a transition between states of different multiplicity	It is the radiation emitted in a transition between states of same multiplicity
Its decay period is much longer, 10^{-4}-100 s.	Its decay period is very short, 10^{-9}-10^{-4}sec.
It is not observed in solution at room temperature.	It can be observed in solution at room temperature.
Its spectrum is mirror image of the absorption spectrum.	Its spectrum is not mirror image of the absorption spectrum.
It is exhibited by some elements in vapour state.	It is rarely observed in gaseous or vapours.
Examples: uranium, petroleum, organic dyes, chlorophyll, CaF_2,etc.	Examples: ZnS, sulphides of alkaline earth metals.

Jablonski Diagram or Mechanism of Photophysical Process or Mechanism of Fluorescence and Phosphorescence:

The phenomenon of fluorescence and phosphorescence are best explained with the help of the Jablonski diagram. The Jablonski diagram is a pictorial representation of the energy transitions caused by the absorption of a UV radiation by a molecule.

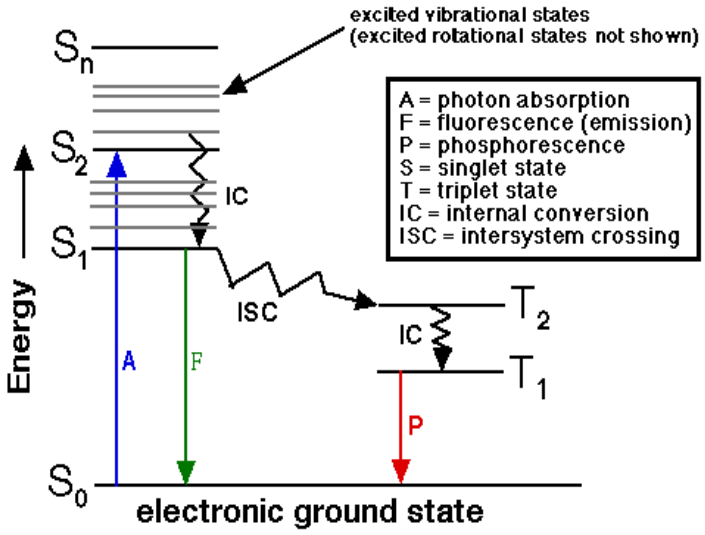


Fig: Jablonski Diagram

Modified Jablonski diagram shows transitions between excited states and the ground state. Radiative processes are shown by straight line, radiationless processes by wave lines.

Most molecules possess an even number of electrons and all the electrons are paired in ground state. The spin multiplicity of a state is given by 2S + 1, where S is the total electronic spin.

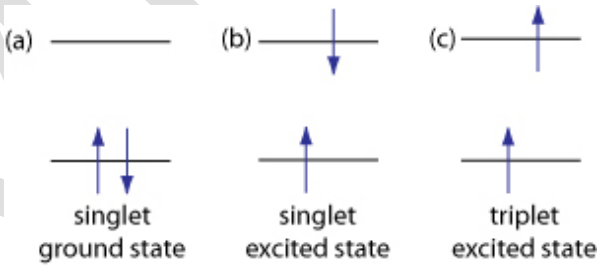


Fig: Spin orientation of absorption of light photon

i) When the spins are paired (↑↓), the clockwise orientation of one electron is cancelled by the anticlockwise orientation of other electron. Thus,

$$S = s_1 + s_2 = (1/2) - (1/2) = 0$$

2S + 1 = 1, ie., spin multiplicity is 1. The molecule is in the singlet ground state.

ii) On absorption of a suitable energy, one of the paired electrons goes to a higher energy level. The spin orientation of the two electrons may be either

a) Parallel (↑↑), then $S = s_1 + s_2 = (1/2)+(1/2) = 1$, $2S + 1 = 3$, ie., spin multiplicity is 3. The molecule is in the triplet (T) excited state.

b) or anti-parallel (↑↓), then S = s_1 + s_2 = (1/2) – (1/2) = 0, 2S + 1 = 1, ie., spin multiplicity is 1. The molecule is in the singlet (S) excited state

Since the electron can jump from the ground state to any of the higher electronic states depending upon the energy of the photon absorbed we get a series of

a) singlet excited states ie., S_1, S_2, S_3, etc., (first singlet excited state, second singlet excited state, third singlet excited state, etc.)and
b) triplet excited states ie., T_1, T_2, T_3, etc., (first triplet excited state, second triplet excited state, third triplet excited state, etc.).

Generally singlet excited state has higher energy than the corresponding triplet excited state. Thus, the energy sequence is as follows: $E_{S1} > E_{T1} > E_{S2} > E_{T2} > E_{S3} > E_{T3}$ and so on.

When a molecule absorbs light radiation, the electron may jump from S_0 to S_1, S_2 (or) S_3 singlet excited state depending upon the energy of the light radiation as shown in Jablonski diagram. For each singlet excited state there is a corresponding triplet excited state, ie.

$$S_1 \rightarrow T_1;\ S_2 \rightarrow T_2;\ S_3 \rightarrow T_3,\ \text{etc.}$$

Types of Transitions:

Absorbance

The first transition in the Jablonski diagrams is the absorbance of a photon of a particular energy by the molecule of interest. Absorbance is the method by which an electron is excited from a lower energy level to a higher energy level.

The excited species can return to the ground state by losing all of its excess energy by any one of the following absorptions

1. Non-radiative Process
2. Radiative Process

Non-radiative transition: It does not involve the emission of any radiations, so these are also known as non-radiative or radiation less transitions. It involves transition from, S2 → S1 or S3 → S1 or T2 → T1 or T3 → T1. It only involves emission of heat. Non-radiative transitions involve the following two transitions.

a) Internal Conversion (IC): These transitions involve the return of the activated molecule from the higher excited states to the first excited states, ie. It involves transition from, S3 → S2 or S2 → S1 Or T3 → T2 or T2 → T1 . In this process energy loss in the form of heat. It occurs in less than 10^{-11}second.

b) Intersystem Crossing (ISC): The molecule may also lose energy by another process called inter system crossing (ISC). These transitions involve the return of the activated molecules from the states of different spins ie. Different multiplicity ie., $S_2 \rightarrow T_2$; $S_1 \rightarrow T_1$. These transitions are forbidden, occurs relatively at slow rates.

Radiative transition: It involves the return of activated molecules from the singlet excited state S_1 and triplet state T_1 to the ground state S_0. These transitions are accompanied by the emission of radiations. It involves transition from S1→ S0 or T1→ T0. Thus, radiative transitions involve the following two radiations.

Fluorescence The emission of radiation due to the transition from singlet excited state S_1 to ground state S_0 is called fluorescence ($S_1 \rightarrow S_0$). This transition is allowed transition and occurs in about 10^{-8}second.

Phosphorescence The emission of radiation due to the transition from the triplet excited state T_1 to the ground state S_0 is called phosphorescence ($T_1 \rightarrow S_0$). This transition is slow and forbidden transition. In phosphorescence even after incident light radiation is cut off there is emission of light for some time. It is also called slow Fluorescence. The substance which shows Phosphorescence is called fluorescent substance. The name Phosphorescence is derived from phosphorous which glows in dark.

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