

CHEMISTRY

PREPARED BY

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Course Outcomes

- CO-1: Apply Schrodinger wave equation to hydrogen atom , Illustrate the molecular orbital energy level diagram of different molecular species , Explain the calculation of bond order of O₂ and Co molecules .
- CO-2: Apply the principle of Band diagrams in application of conductors and semiconductors .
- CO-3: Compare the materials of construction for battery and electrochemical sensors
- CO-4: Explain the preparation, properties, and applications of thermoplastics & thermosetting, elastomers & conducting polymers.
- CO-5: Explain the principles of spectrometry, slc in separation of solid and liquid mixtures



CHEMISTRY

Unit- I: Structure and Bonding Models:

Planck's quantum theory, dual nature of matter, Schrodinger equation, significance of Ψ and Ψ^2 , applications to hydrogen, molecular orbital theory - bonding in homo- and heteronuclear diatomic molecules - energy level diagrams of O_2 and CO , etc. π -molecular orbitals of butadiene and benzene, calculation of bond order.

Unit-II: Modern Engineering materials:

Coordination compounds: Crystal field theory - salient features - splitting in octahedral and tetrahedral geometry. Properties of coordination compounds-Oxidation state, coordination, magnetic and colour.

Semiconductor materials, super conductors- basic concept, band diagrams for conductors, semiconductors and insulators, Effect of doping on band structures.

Supercapacitors: Introduction, Basic Concept-Classification - Applications.

Nano chemistry: Introduction, classification of nanomaterials, properties and applications of Fullerenes, carbon nano tubes and Graphines nanoparticles.

Unit-III: Electrochemistry and Applications:

Electrodes - concepts, reference electrodes (Calomel electrode, $Ag/AgCl$ electrode and glass electrode); Electrochemical cell, Nernst equation, cell potential calculations and numerical problems.

Potentiometry- potentiometric titrations (redox titrations), concept of conductivity, conductivity



potentiometry- potentiometric titrations (redox titrations), concept of conductivity, conductivity cell, conductometric titrations (acid-base titrations).

Electrochemical sensors - potentiometric sensors with examples, amperometric sensors with examples.

Primary cells - Zinc-air battery, Secondary cells - Nickel-Cadmium (NiCad), and lithium-ion batteries working of the batteries including cell reactions; Fuel cells, hydrogen-oxygen, methanol fuel cells - working of the cells.

Unit - IV: Polymer Chemistry:

Advanced Engineering Materials Composites: Definition, Constituents, Classification- Particle, Fiber and Structural reinforced composites, properties and Engineering applications Refractories- Classification, Properties, Factors affecting the refractory materials and Applications. Lubricants- Classification, Functions of lubricants, Mechanism, Properties of lubricating oils - Viscosity, Viscosity Index, Flash point, Fire point, Cloud point, saponification and Applications. Building materials- Portland Cement, constituents, phases and reactivity of clinker, Setting and Hardening of cement

Unit-V: Instrumental Methods and Applications

Electromagnetic spectrum. Absorption of radiation: Beer-Lambert's law. Principle and applications of pH metry, UV-Visible, IR Spectroscopies. Solid-Liquid Chromatography-TLC, retention time.



Textbooks:
1. Jain and Jain, Engineering Chemistry, 16/e, Dhan Patrai, 2013. 2. Peter Atkins, Julio de Paula and James Keeler, Atkins' Physical Chemistry, 10/e, Oxford University Press, 2010
Reference Books:
1. G.V. Subba Reddy, K.N. Jayaveera and C. Ramachandra, Engineering Chemistry, Mc Graw Hill, 2020. 2. Skoog and West, Principles of Instrumental Analysis, 6/e, Thomson, 2007. 3. D. Lee, Concise Inorganic Chemistry, 5/e, Oxford University Press, 2008. 4. J.M. Lehn, Supra Molecular Chemistry, VCH Publications

UNIT- I

STRUCTURE AND BONDING MODELS

PLANCKS QUANTUM THEORY

Planck's Quantum Postulate

- Radiating body consists of large number of atomic oscillators. atomic oscillators have energy in the form of discrete unit of energy $E = hv$.
- where, h is a new fundamental constant called as Planck's constant : $h = 6.63 \times 10^{-34}$ Joules sec
- Atomic oscillators can absorb or emit energy in discrete unit known as quanta



3.6 Wave Particle duality

The dual nature of light:

The diffraction of light provides evidence of light being wavelike in nature

The photo electric effect provides evidence of light being particle-like in nature

The dual nature of matter:

The diffraction of an electron beam directed at a thin metal film provides evidence of matter being wavelike in nature (also electron deflection in electric and magnetic fields)

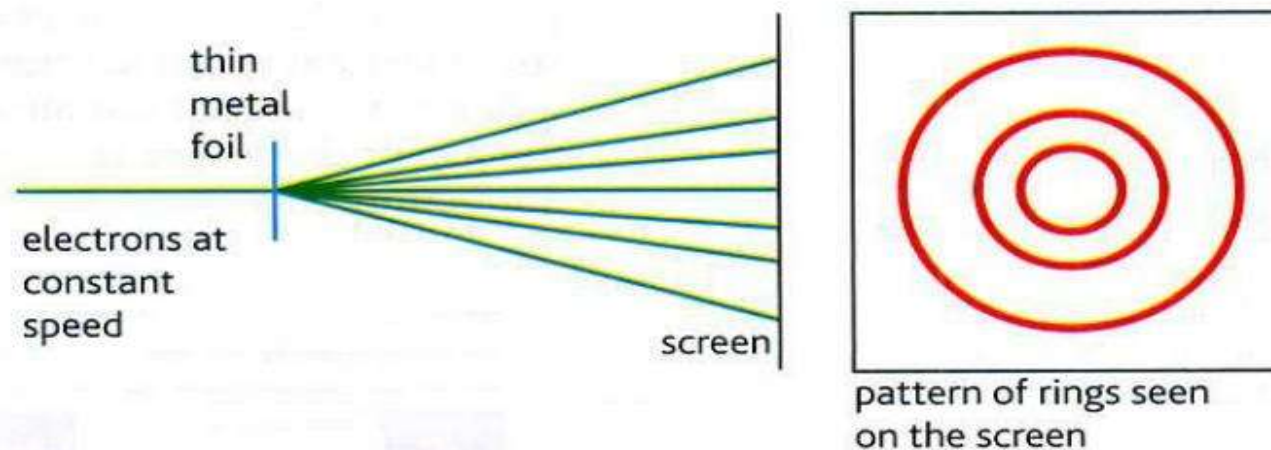


Figure 2 *Diffraction of electrons*

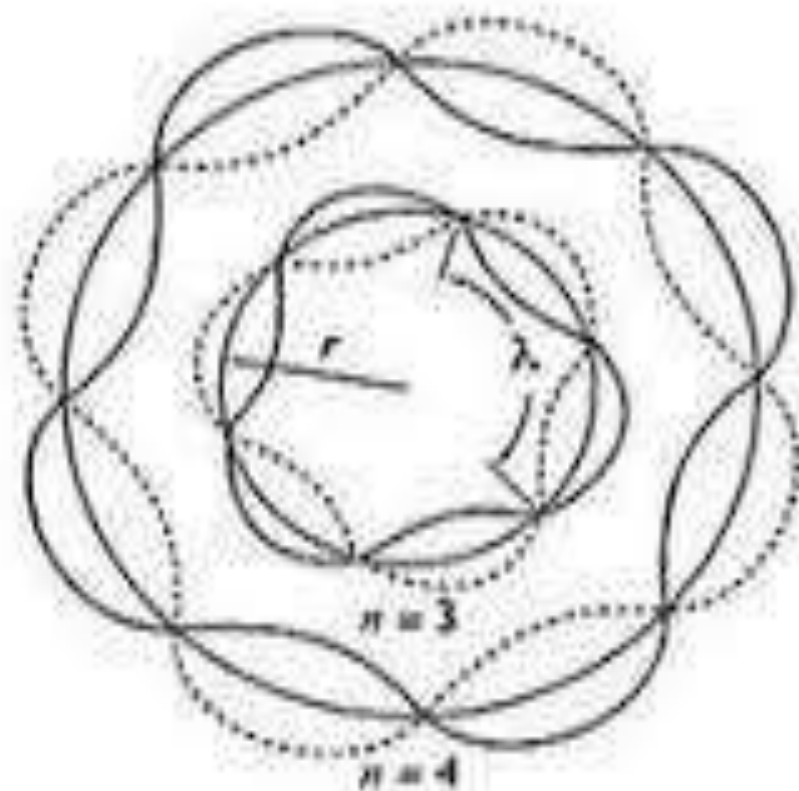
The rows of atoms in the metal crystals behave like light passing through slits

DE BROGLIE EQUATION

The De Broglie Wavelength

$$\lambda = \frac{h}{p} = \frac{h}{mv}$$

- λ = wavelength
- h = Planck's constant ($6.63 \times 10^{-34} \text{ J} \cdot \text{s}$)
- p = momentum
- m = mass
- v = speed



Heisenberg's Uncertainty Principle

uncertainty
in momentum

↓

$$\Delta x \Delta p \geq \frac{h}{4\pi} = \frac{\hbar}{2}$$

↑

uncertainty
in position

The more accurately you know the position (i.e., the smaller Δx is), the less accurately you know the momentum (i.e., the larger Δp is); and vice versa

Schrodinger Wave Equation

$$\frac{\partial^2 \Psi}{\partial x^2} + \frac{\partial^2 \Psi}{\partial y^2} + \frac{\partial^2 \Psi}{\partial z^2} + \frac{8\pi^2 m}{h^2} (E - V) \Psi = 0$$

$$\nabla^2 \Psi + \frac{8\pi^2 m}{h^2} (E - V) \Psi = 0$$

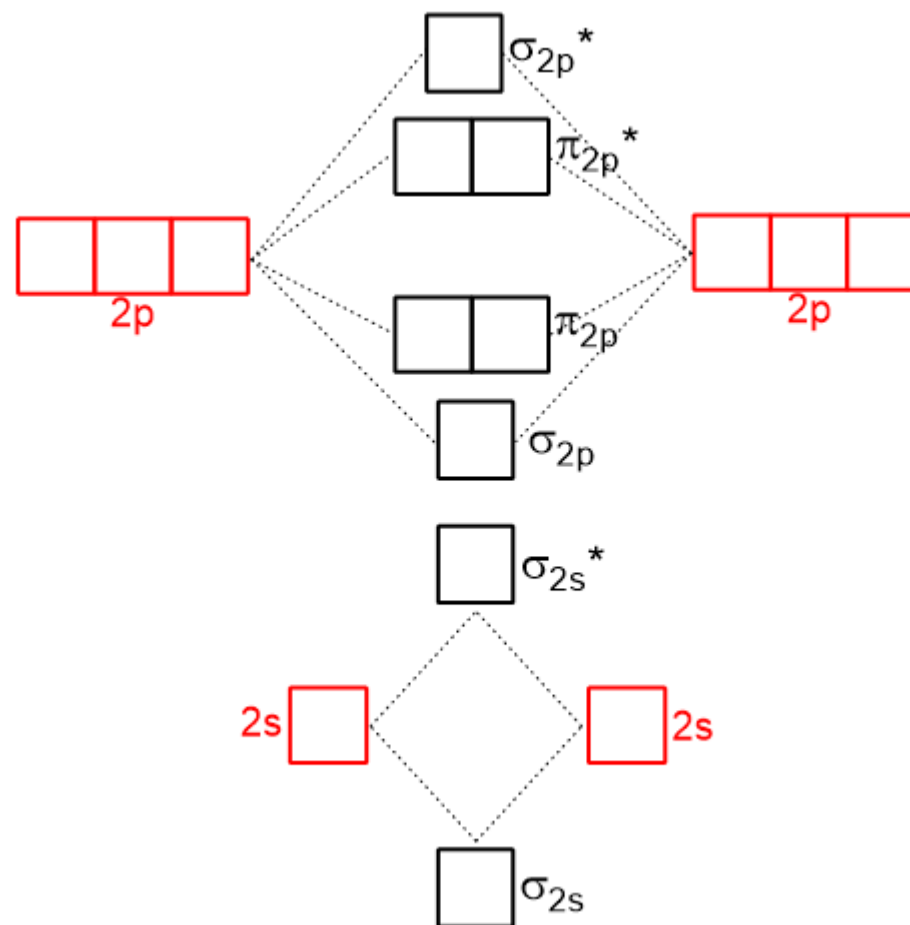


significance of Ψ and Ψ^2 :

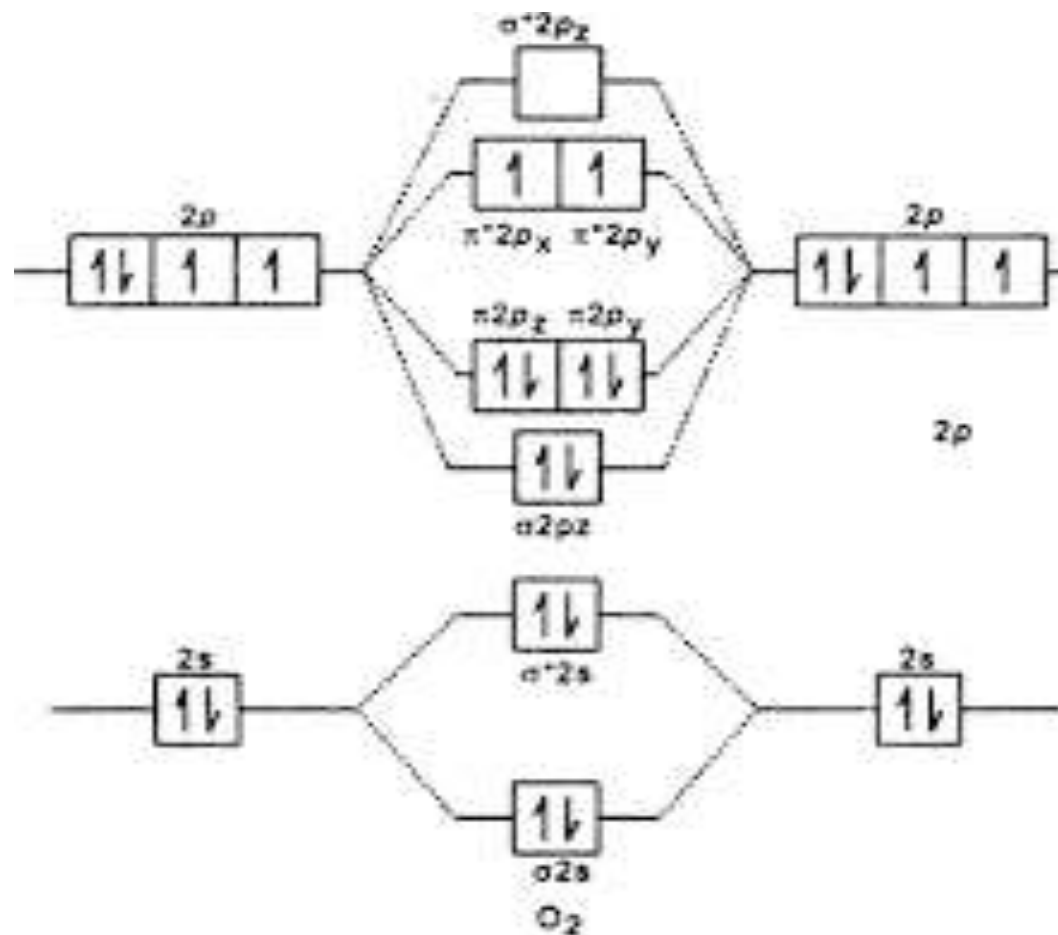
- ▶ ψ is a wave function and refers to the amplitude of electron wave i.e. probability amplitude. It has got no physical significance. The wave function ψ may be positive, negative or imaginary.
- ▶ $[\psi]^2$ is known as probability density and determines the probability of finding an electron at a point within the atom. This means that if:
 - ▶ (i) is zero, the probability of finding an electron at that point is negligible.
 - ▶ (ii) $[\psi]^2$ is high, the probability of finding an electron is high i.e. electron is present at that place for a long time.
 - ▶ (iii) $[\psi]^2$ is low. the probability of finding an electron is low i.e. electron is present at that place for a shorter time.

Molecular Orbital Theory

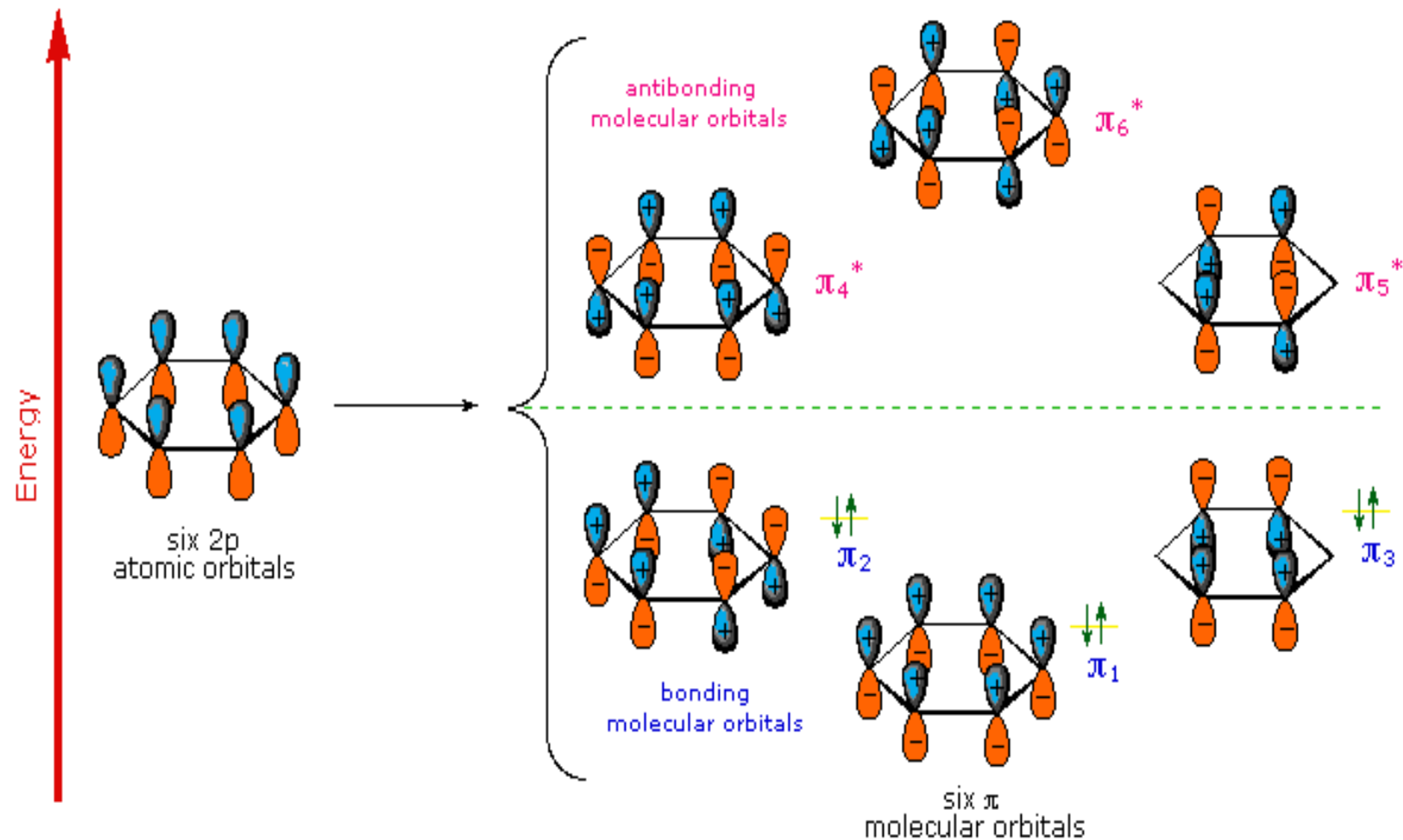
Molecular orbital theory approximation of the molecular orbitals as linear combinations of atomic orbitals can be illustrated as follows.



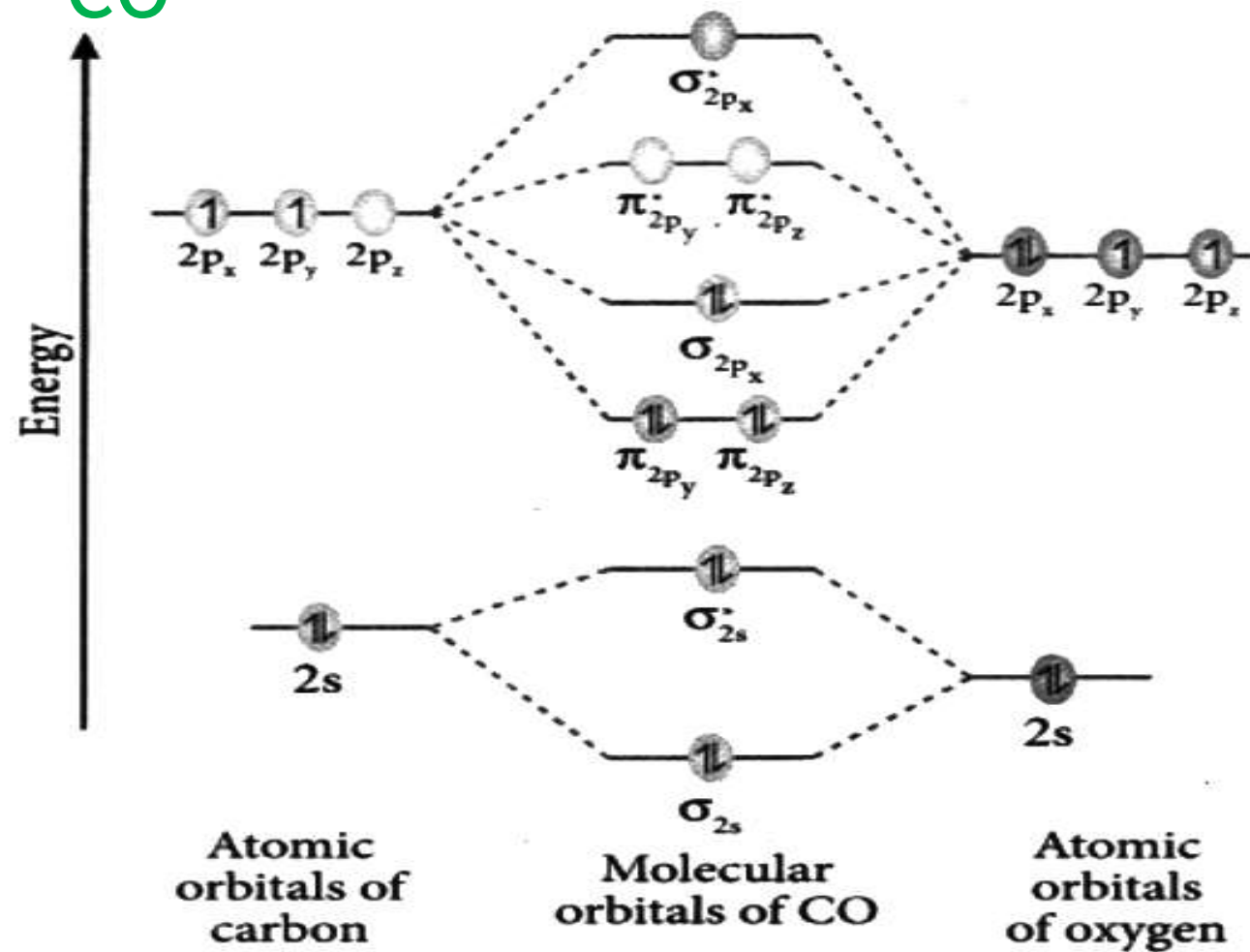
MOLECULAR ORBITAL DIAGRAM OF O₂



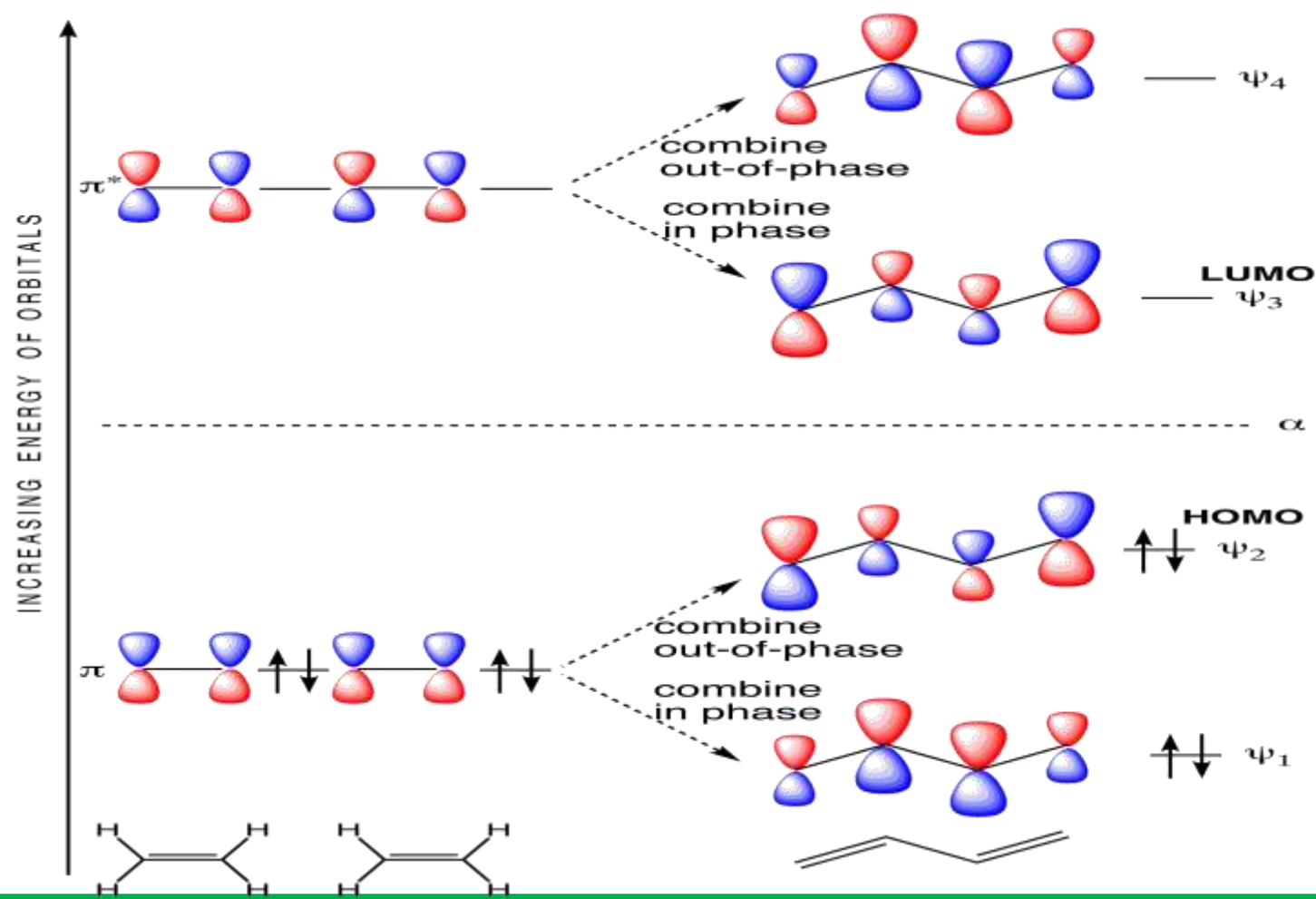
MOLECLAR ORBITAL DIAGRAM OF BENZENE



MOLECLAR ORBITAL DIAGRAM OF CO



MOLECLAR ORBITAL DIAGRAM OF BUTADIENE





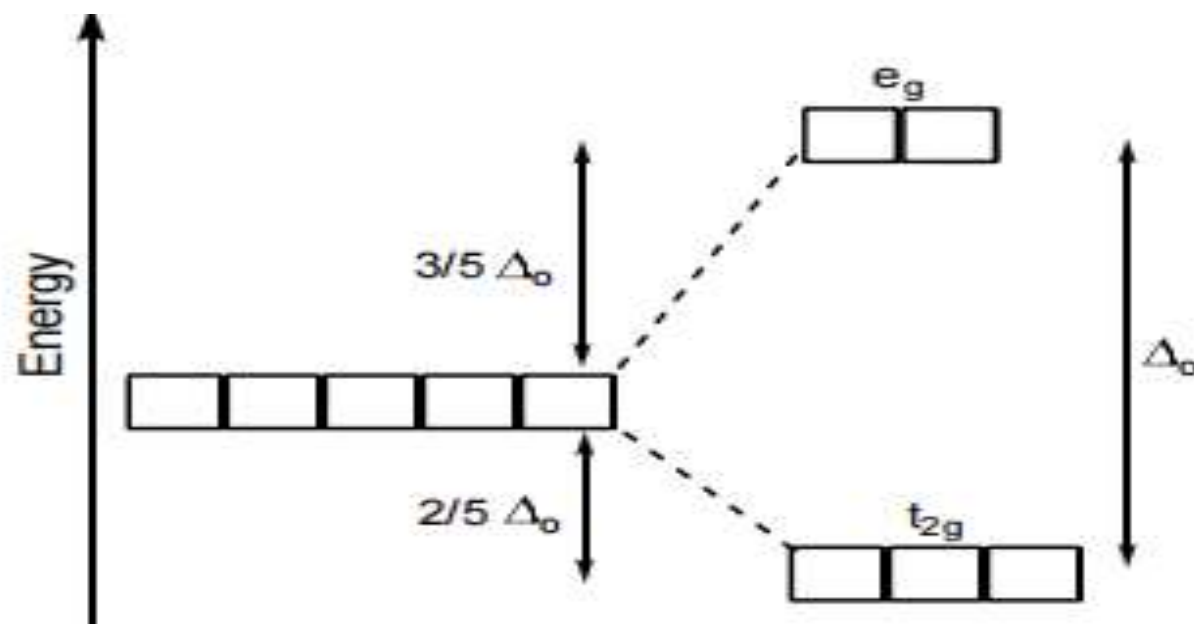
UNIT-II

MODERN ENGINEERING MATERIALS



Coordination compounds

Crystal Field Splitting in an Octahedral Field



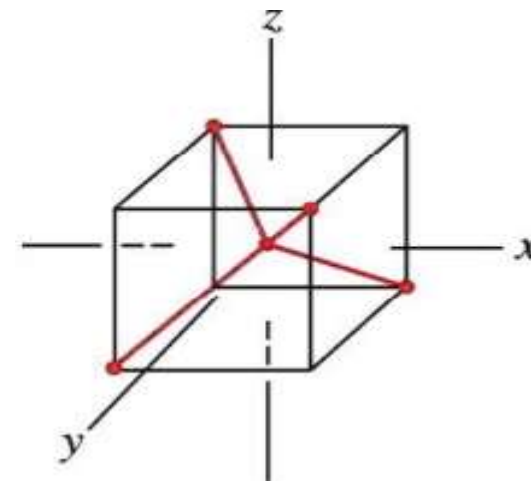
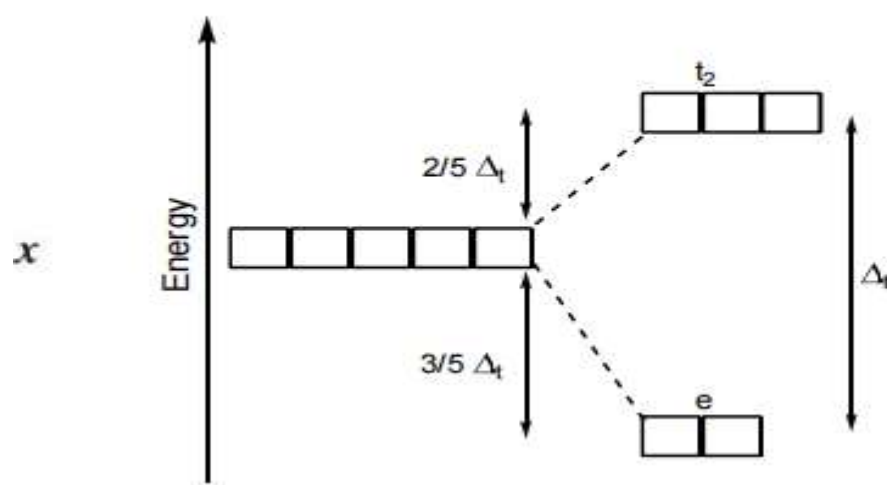


CFSE

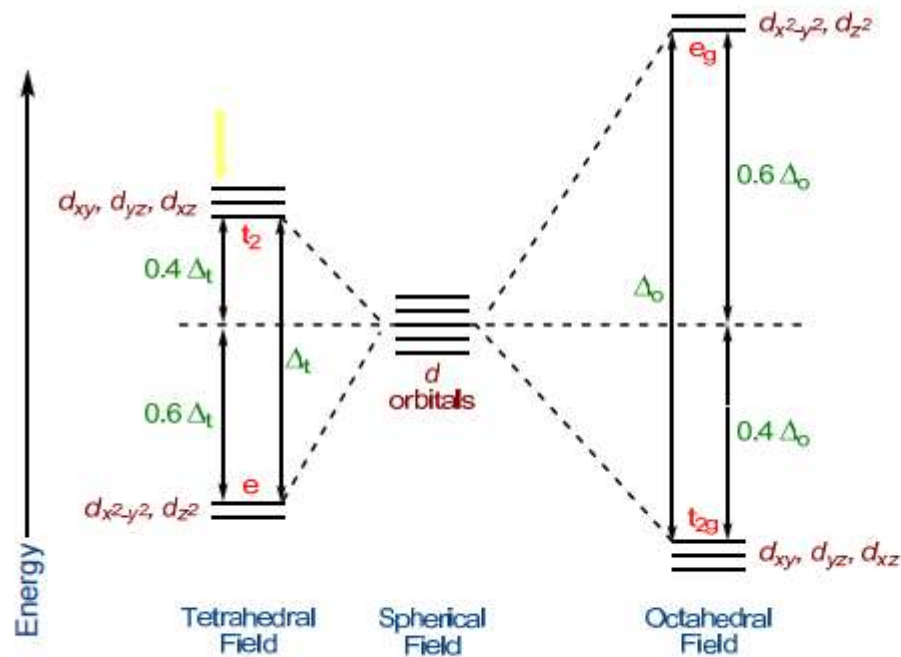
- eg - The higher energy set of orbitals (d_{z^2} and $d_{x^2-y^2}$)
- t_{2g} - The lower energy set of orbitals (d_{xy} , d_{yz} and d_{xz})
- Δ_o or $10 Dq$ - The energy separation between the two levels
- The eg orbitals are repelled by an amount of $0.6 \Delta_o$
- The t_{2g} orbitals to be stabilized to the extent of $0.4 \Delta_o$

CFSE OF Tetrahedral Field

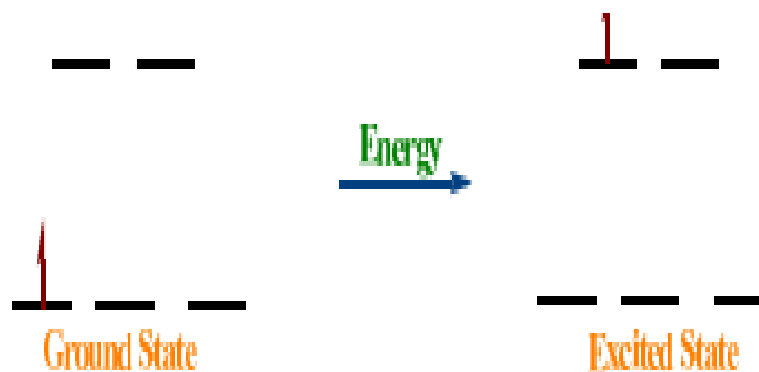
Tetrahedral Field



Octahedral Vs Tetrahedral



[Ti(H₂O)₆]³⁺ – a *d*1 system

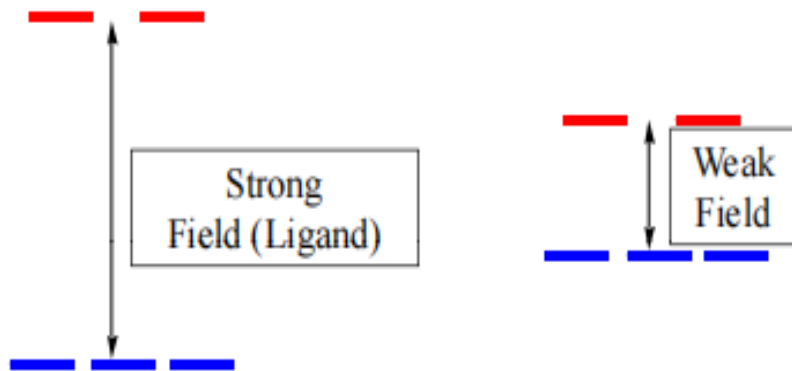


The single electron in the t_{2g} orbital's absorb energy in the form of light and gets excited to the e_g orbital's.

In case of [Ti(H₂O)₆]³⁺, this corresponds to 520 nm (20,300 cm⁻¹)

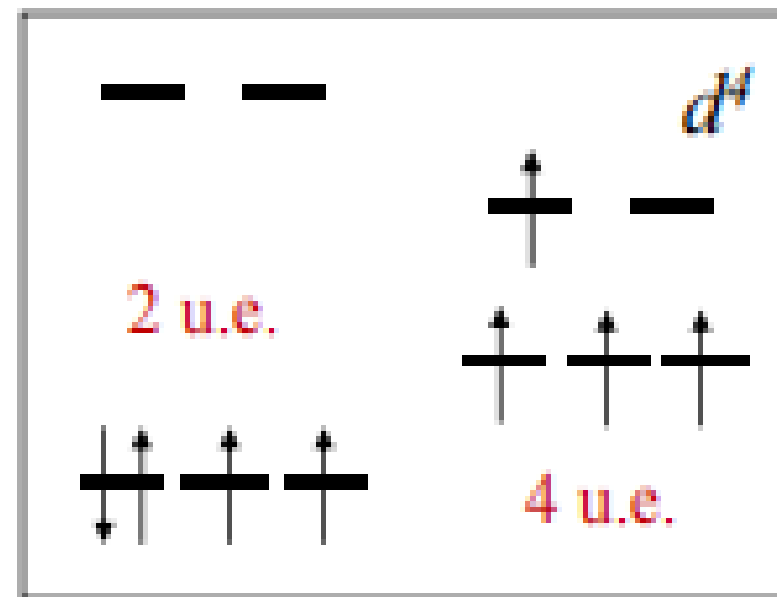
Spectrochemical Series

- An arrangement of ligands according to their ability to increase Δ for a given metal center
- Weak – I^- , Br^- , SCN^- , Cl^- , N_3^- , F^- , $H_2NC(O)NH_2$, OH^- , ox^{2-} , O^{2-} , H_2O , NCS^- , py , NH_3 , en , bpy , $phen$, NO_2^- , CH_3^- , $C_6H_5^-$, CN^- , CO – Strong



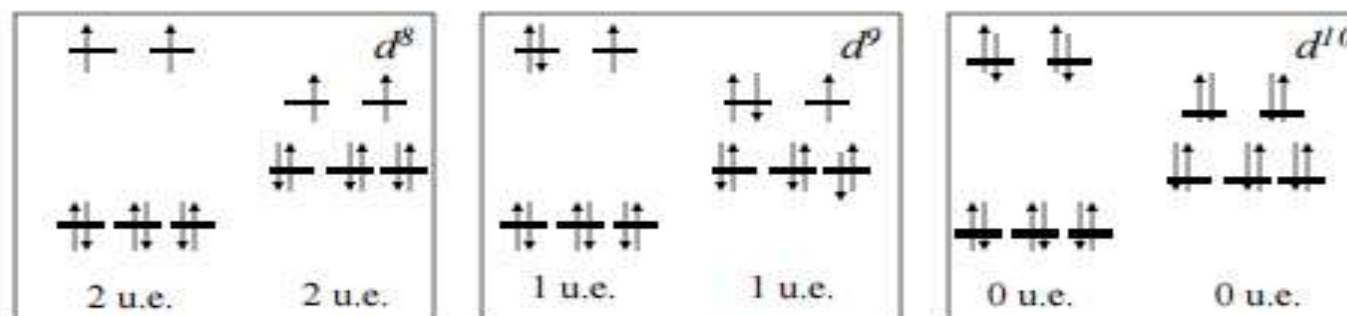
Distribution of Electrons in an Octahedral Complex

There are two possibilities for metal ions having $d4-d7$ electronic configuration. Depending on the nature of the ligands and the metal they could be **high-spin complexes**



Distribution of electrons in octahedral complex

Distribution of Electrons in an Octahedral Complex



$$\text{For } d^8, \text{CFSE} = (6 \times 0.4) - (2 \times 0.6) = 1.2 \Delta_o$$

$$\text{For } d^9, \text{CFSE} = (6 \times 0.4) - (3 \times 0.6) = 0.6 \Delta_o$$

$$\text{For } d^{10}, \text{CFSE} = (6 \times 0.4) - (4 \times 0.6) = 0.0 \Delta_o$$

In all electronic configurations involving two electrons in the same orbital, the actual CFSE is reduced by the energy spent on pairing the electrons.

Metal ions with 4 – 7 electrons in the d orbital can exist as high-spin or low-spin complexes. Weaker ligands tend to give high-spin complexes, whereas stronger ligands tend to give low-spin complexes.



NANOMATERIALS



ABOUT NANO

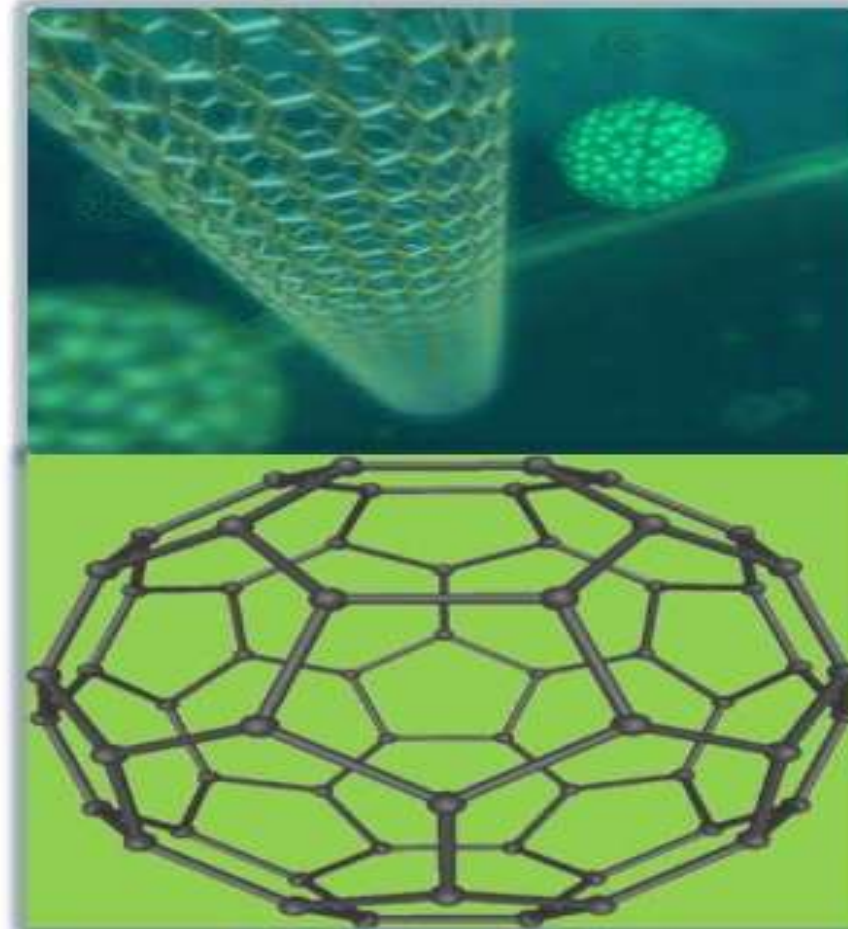
- Nano = 10^{-9} or one billionth in size
- Materials with dimensions and tolerances in the range of 100 nm to 0.1 nm
- Metals, ceramics, polymeric materials, or composite materials One nanometer spans 3-5 atoms lined up in a row
- Human hair is five orders of magnitude larger than nanomaterials

NANO & TECHNOLOGY

- A **Nanometre** is a unit of length in the metric system, equal to one billionth of a metre(10^{-9}).
- **Technology** is the making, usage, and knowledge of tools, machines and techniques, in order to solve a problem or perform a specific function.

Defination

- **Nanotechnology** is the study of manipulating matter on an atomic scale.
- **Nanotechnology** refers to the constructing and engineering of the functional systems at very micro level or we can say at atomic level.
- A **Nanometer** is one billionth of a meter, roughly the width of three or four atoms. The average human hair is about 25,000 nanometers wide.





Classification of Nanomaterials

- **Nanomaterials as those which have structured components with atleast one dimension less than 100nm.**
- **One dimension in nanoscale (Other two dimensions are extended)**

Thin films

Surface Coatings

Computer chips

- **Two dimensions in nanoscale (Other one dimension is extended)**

Nanowires

Nanotubes

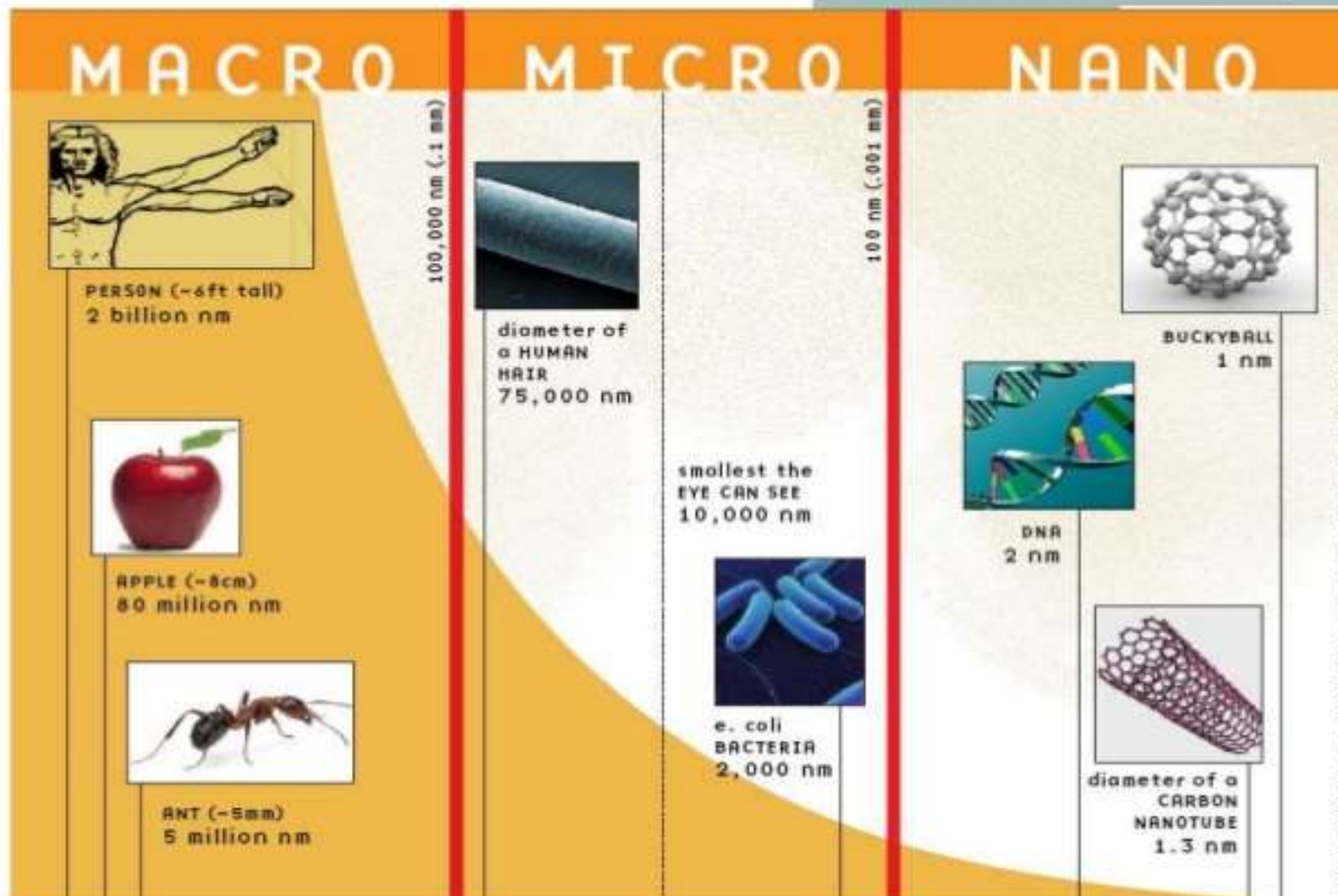
- **Three dimensions in nanoscale**

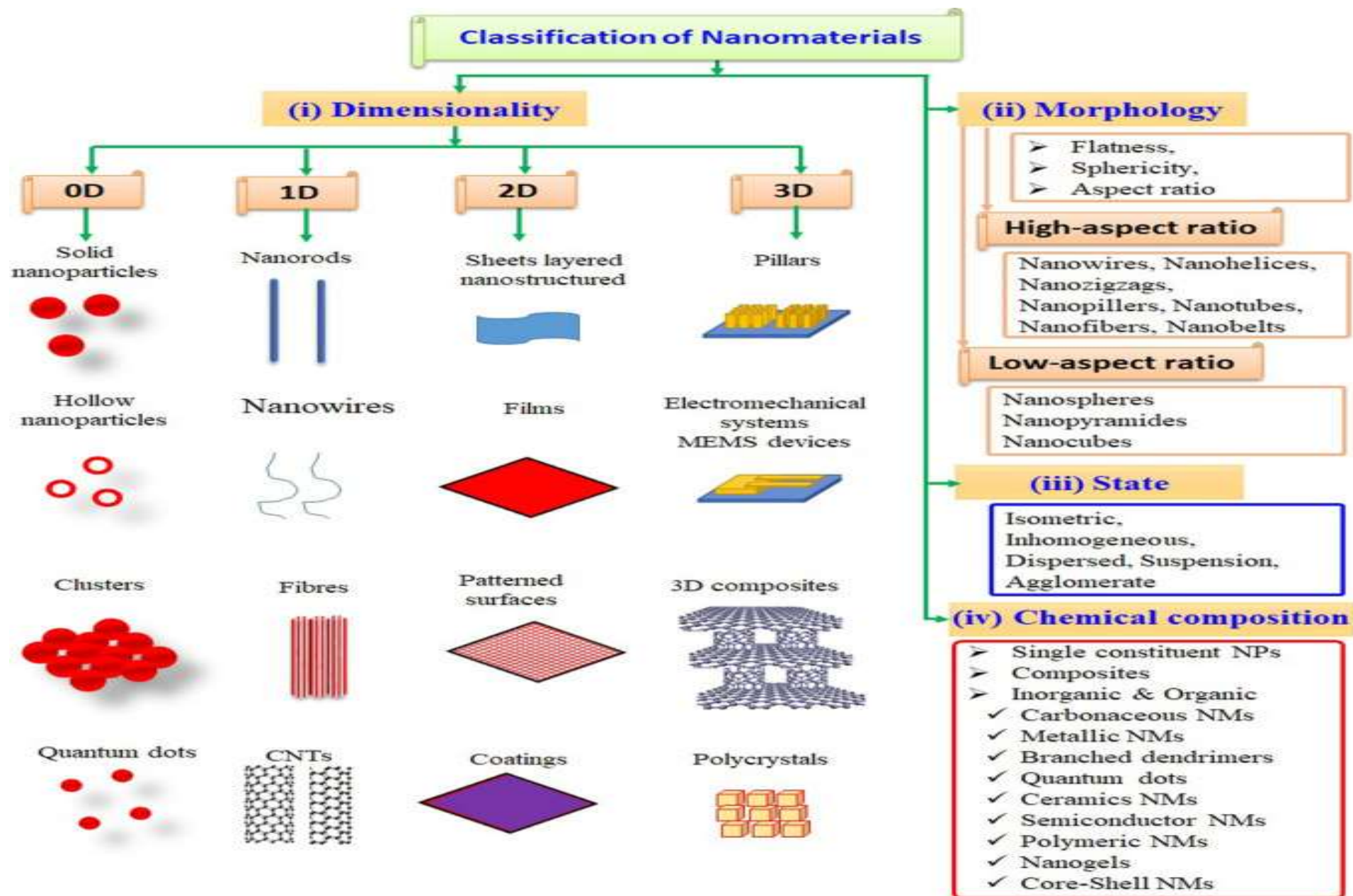
Nanoparticles

Precipitates

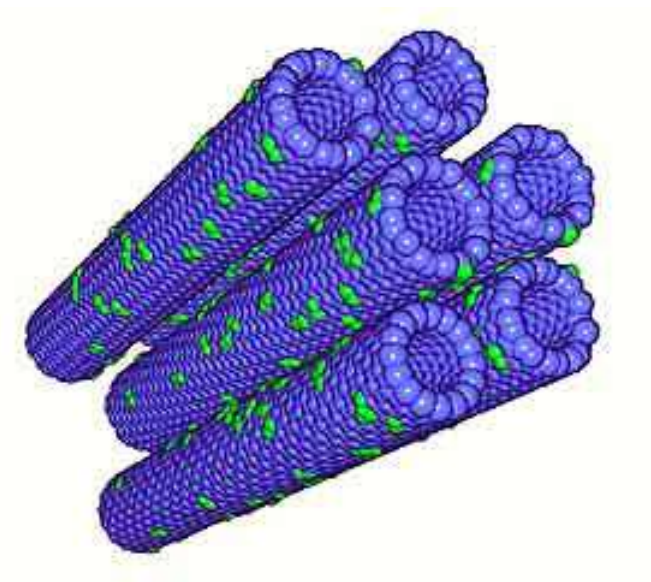
Colloids

Quantum dots (tiny particles of semiconductor material)

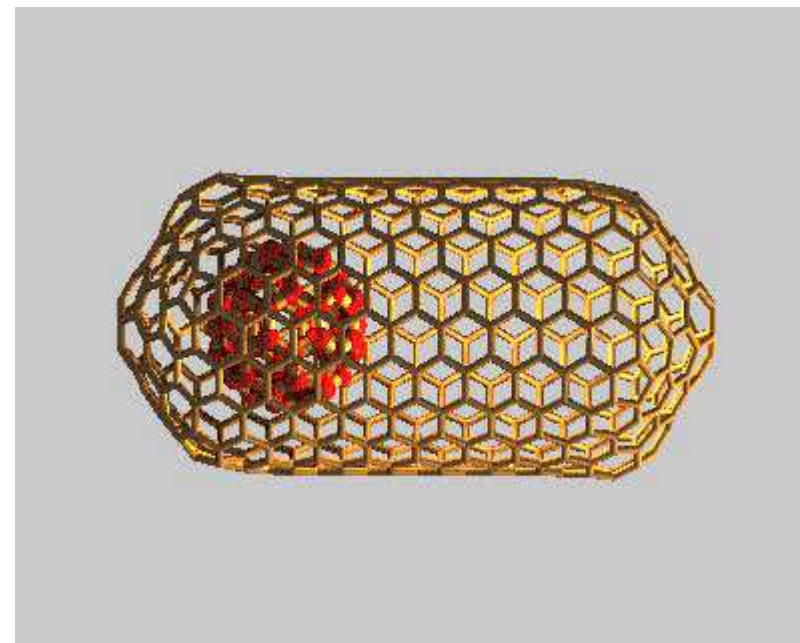




Nanotubes

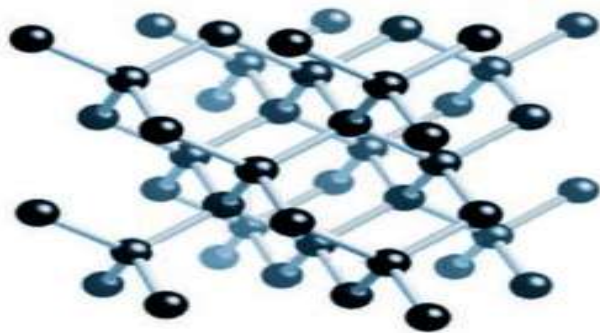


Carbon based nanotubes

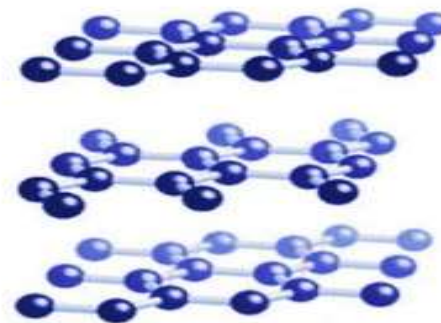


Switching nanotube-based memory

GRAPHENE AND FULLERENE



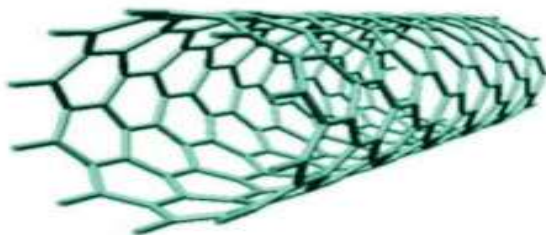
Diamond
(sp^3 hybridized carbon
3D structure)



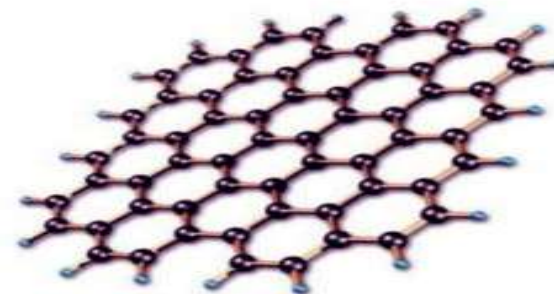
Graphite
(sp^2 hybridized carbon)



Fullerenes
(0D structure)



Nanotubes
(2D structure)

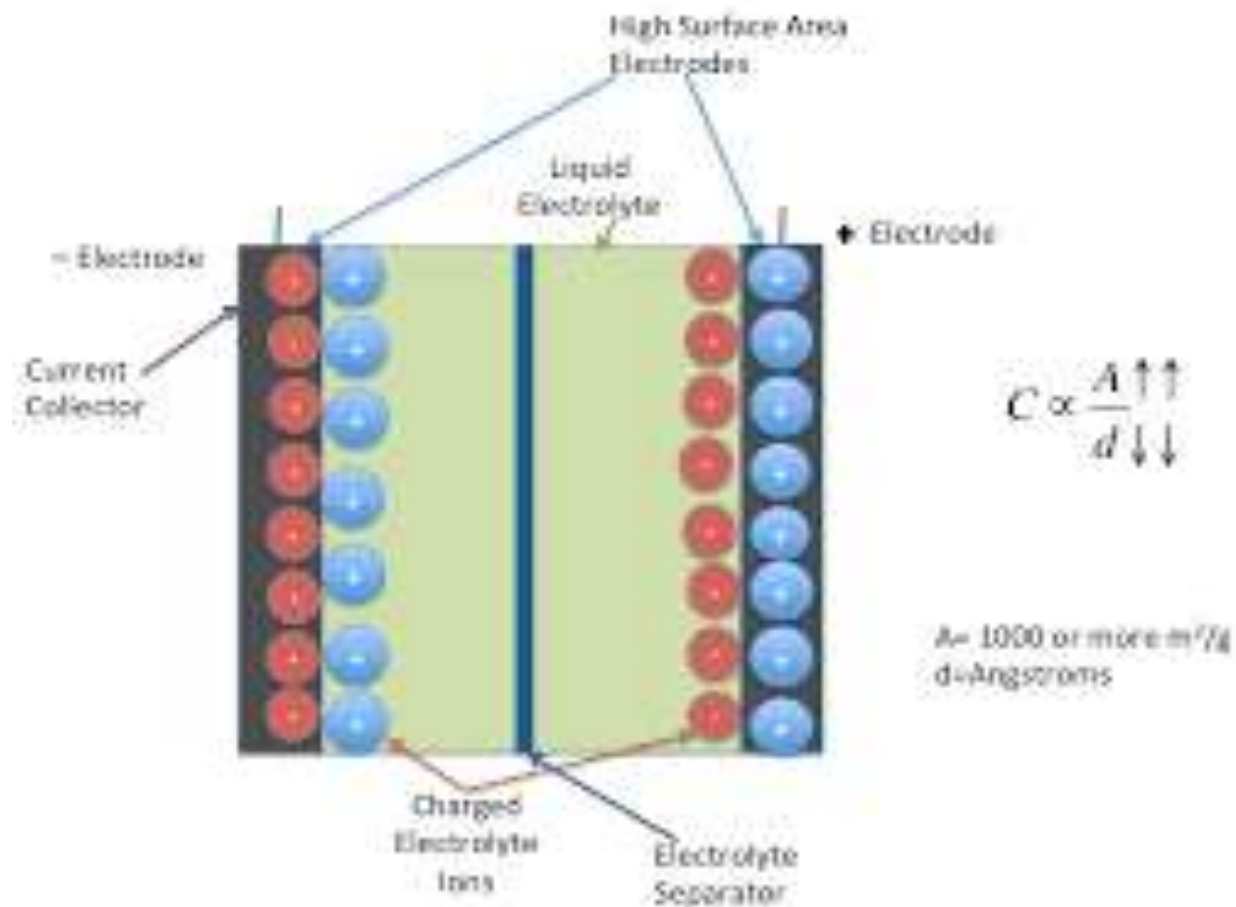


Graphene
(1D structure)

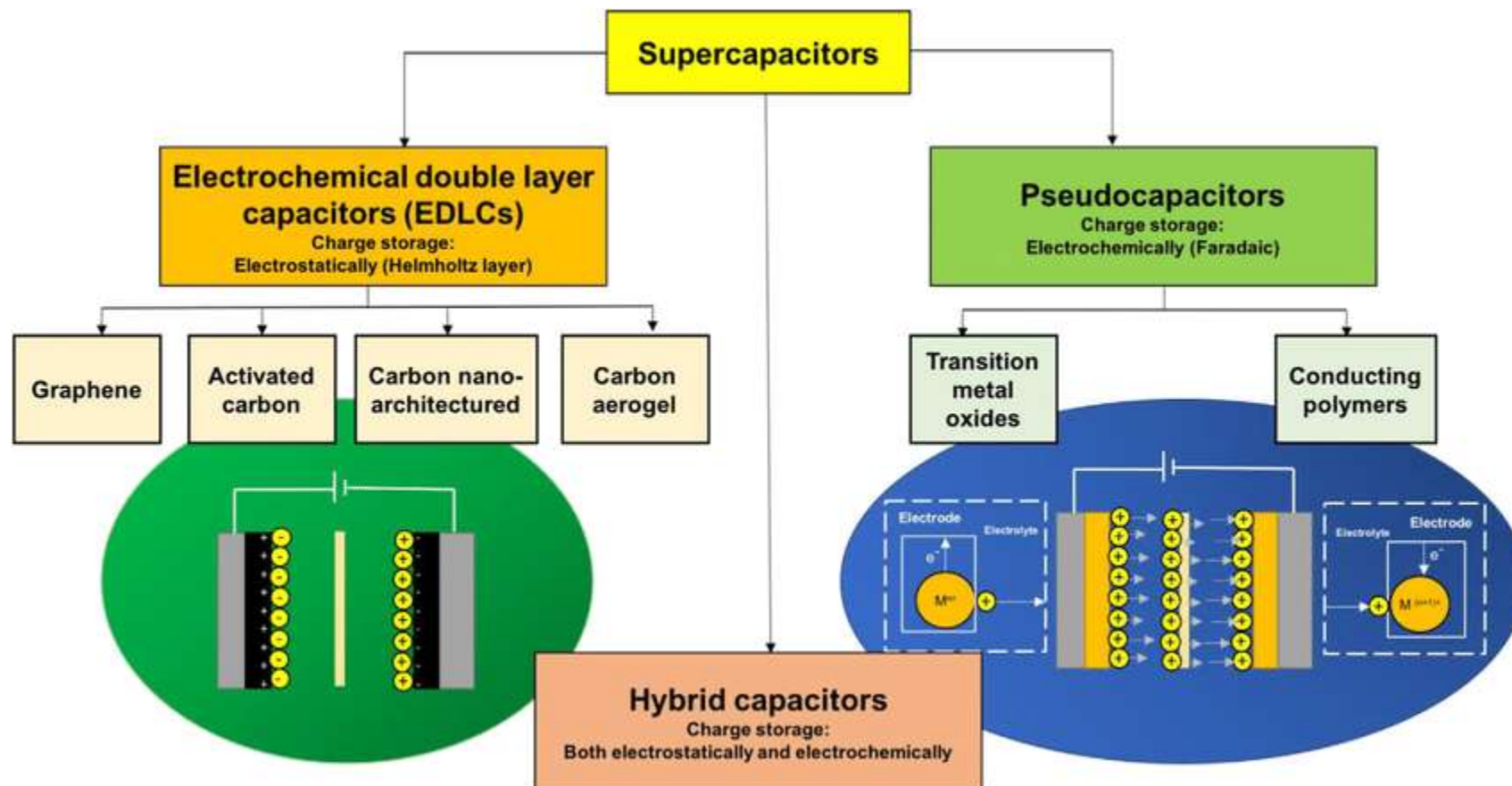
Application Of Nanotechnology



SUPERCAPACITOR



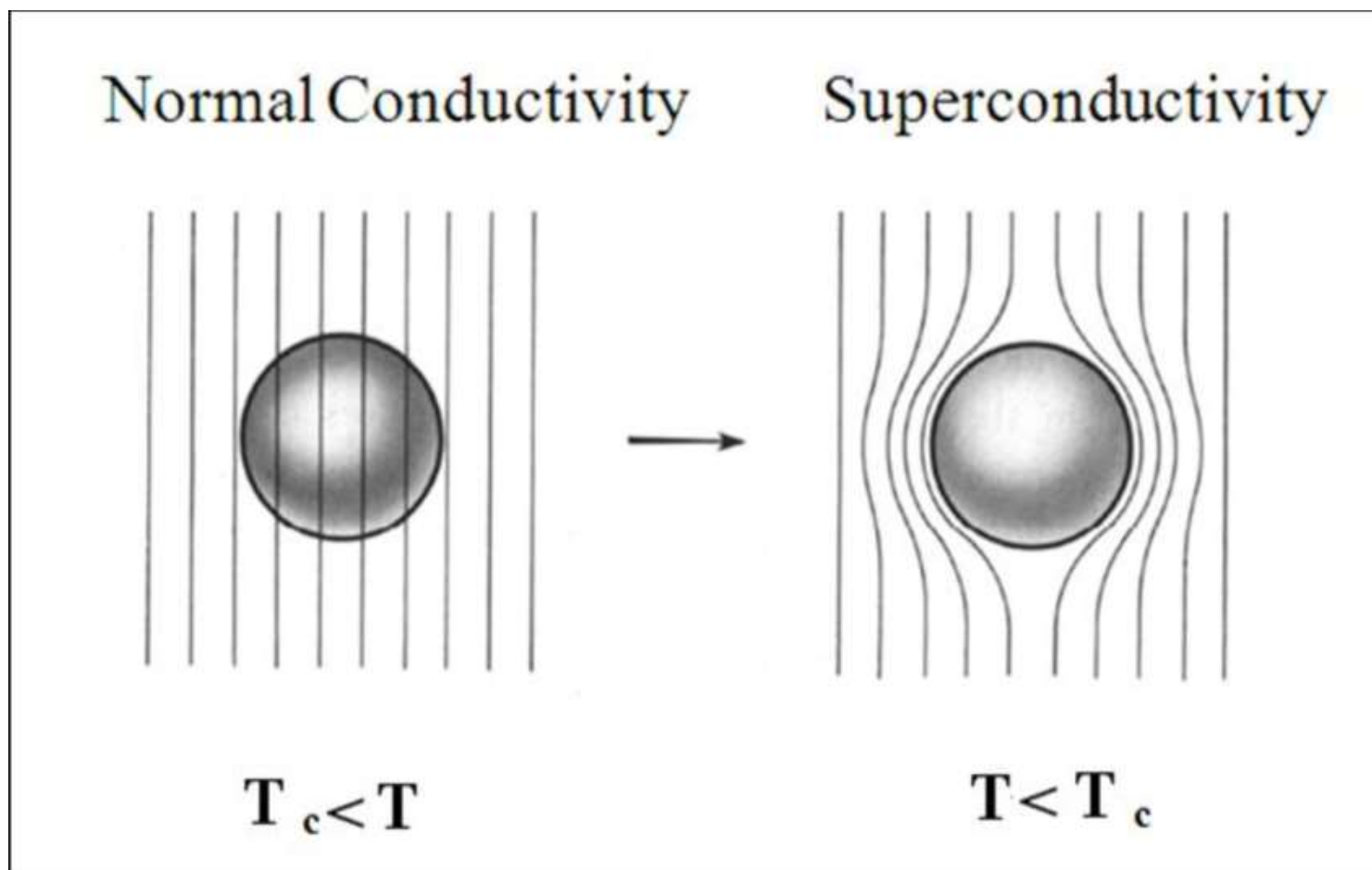
CLASSIFICATION OF SUPERCAPACITORS



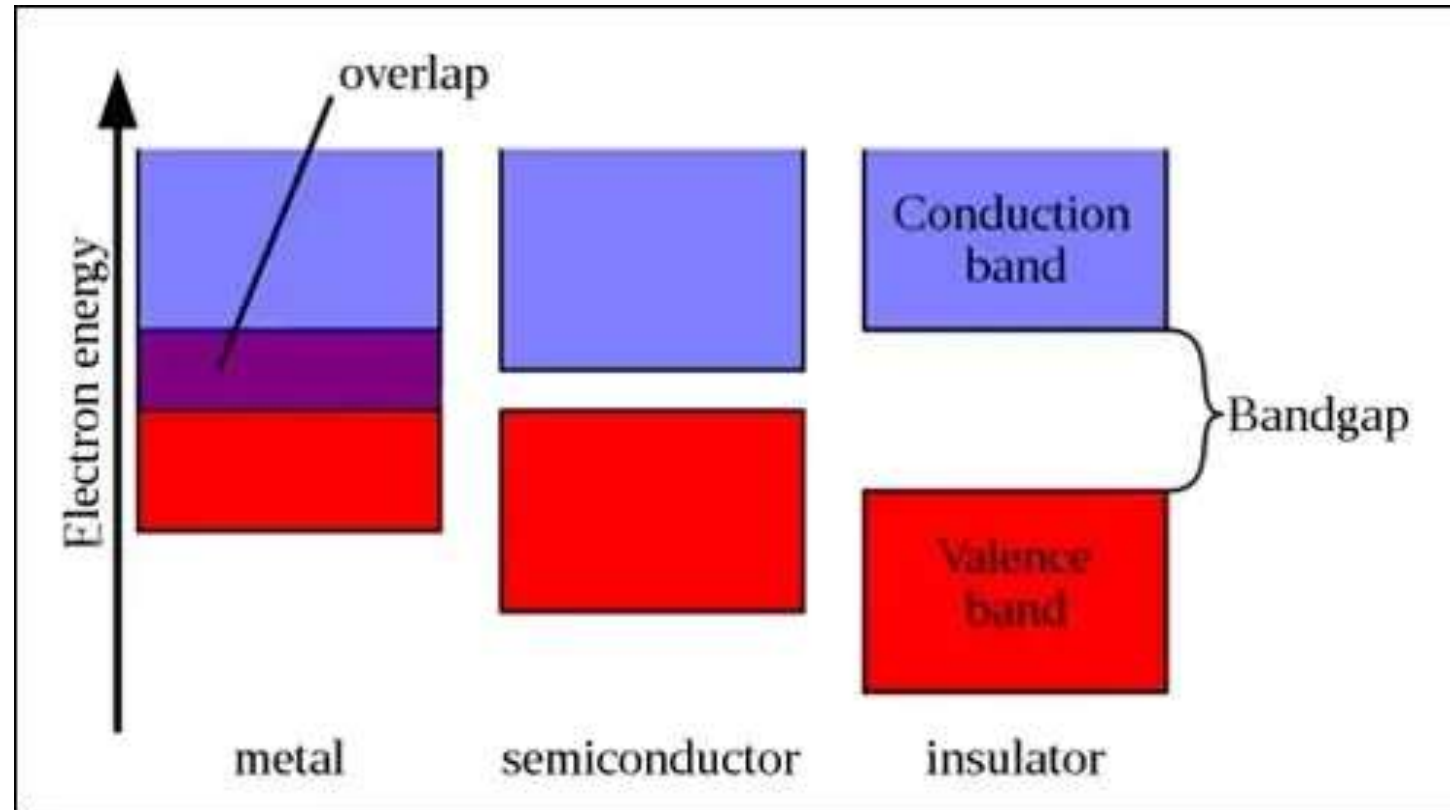


SEMICONDUCTOR MATERIALS

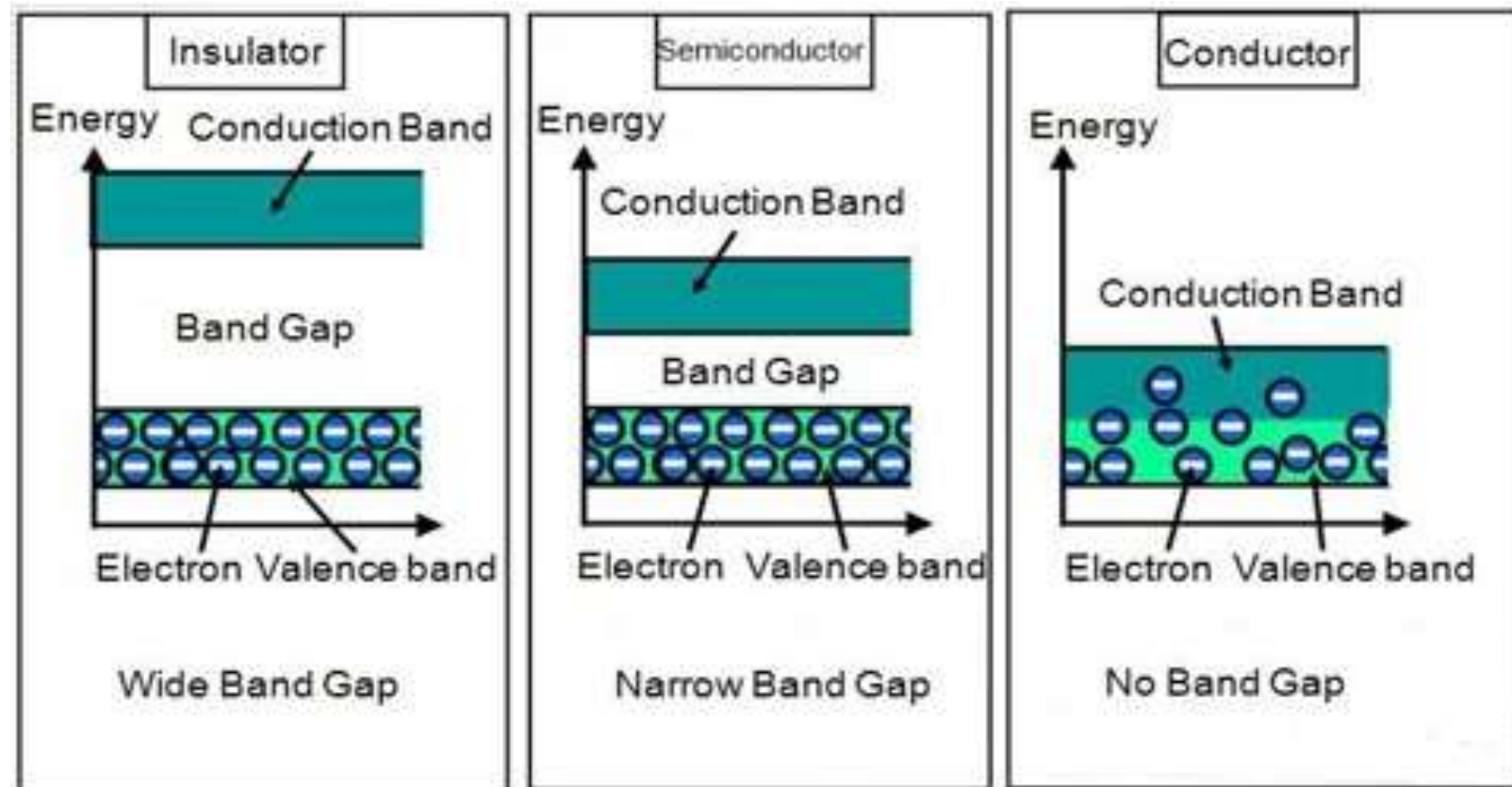
SUPERCONDUCTORS



Effect of doping on band structures



band diagrams for conductors, semiconductors and insulators





UNIT-III

ELECTROCHEMISTRY



Electrochemistry

Electrochemistry is defined as the branch of chemistry which deals with interconversion of chemical energy to electrical energy and vice versa”.

For example, in a battery, chemical energy is converted to electrical energy whereas in electrolysis electrical energy is converted to chemical energy.



Types

Electrochemical Cells are of two types:

1. Galvanic Cells

Converts chemical energy into electrical energy

2. Electrolytic Cells

Converts electrical energy into chemical energy

Galvanic cell

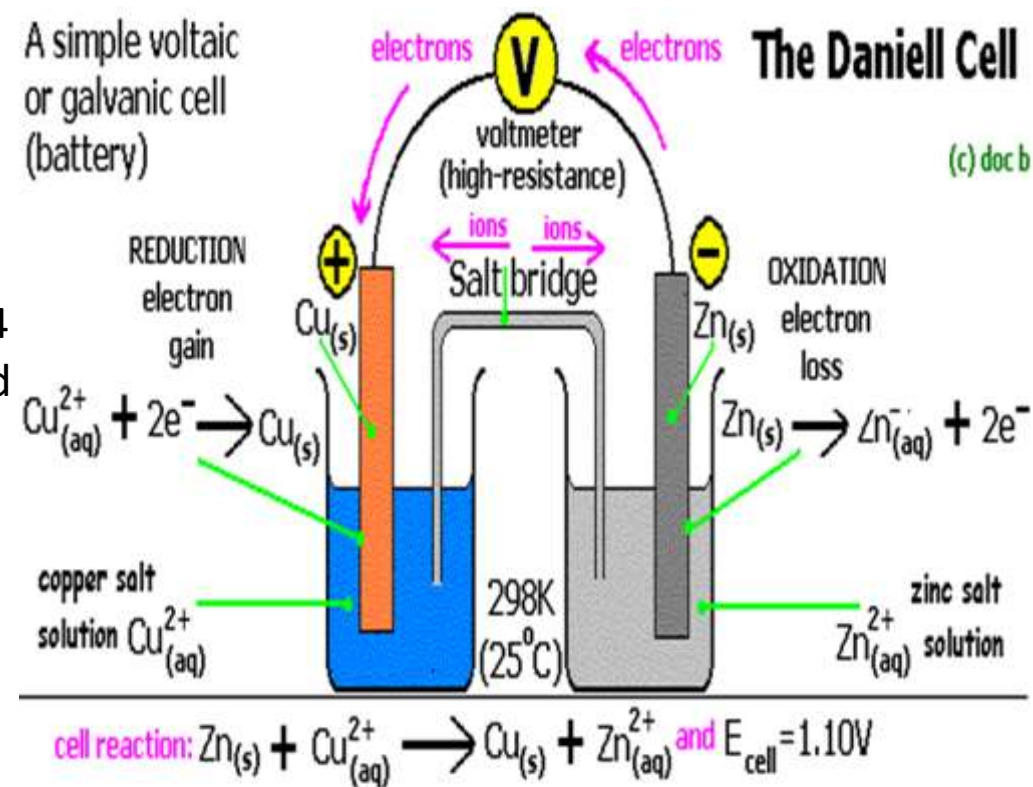
Chemical energy is converted into electrical energy by Galvanic cell. These cells are known as electrochemical cells or voltaic cells.

The best example of galvanic cell is Daniel cell.

This cell is formed by combination of two half cells. One is oxidation half cell or anodic half cell and other one is reduction half cell or cathodic half cell.

The oxidation half cell consists of 'Zn' electrode dipped in ZnSO₄ solution and reduction half cell consists of 'Cu' electrode dipped in CuSO₄ solution. Both the half cells are externally connected by metallic wire and internally connected by 'salt bridge'.

Salt bridge is a U shaped tube containing solution of K₂SO₄, KNO₃, KCl or NH₄NO₃ in agar-agar gel contained porous site. It maintains the electrical neutrality between two solutions.





The following reactions take place in the cell.

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

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

The movement of electrons from Zn electrode to Cu electrode produces a current in the reverse direction.

The overall cell reaction is:



The galvanic cell can be represented by



Presentation of galvanic cell:



Electrochemical series:

The half cell potential values are standard values and are represented as the standard reduction potential values as shown in the table at the end which is also called Electrochemical Series. Series in which elements are arranged in increasing order of their standard electrode potential is known as electrochemical series.

Stronger
oxidizing
agent



Weaker
oxidizing
agent

$F_2(g) + 2 e^-$	$\longrightarrow 2 F (aq)$	2.87
$H_2O_2(aq) + 2 H^+(aq) + 2 e^-$	$\longrightarrow 2 H_2O(l)$	1.78
$MnO_4^-(aq) + 8 H^+(aq) + 5 e^-$	$\longrightarrow Mn^{2+}(aq) + 4 H_2O(l)$	1.51
$Cl_2(g) + 2 e^-$	$\longrightarrow 2 Cl^-(aq)$	1.36
$Cr_2O_7^{2-}(aq) + 14 H^+(aq) + 6 e^-$	$\longrightarrow 2 Cr^{3+}(aq) + 7 H_2O(l)$	1.33
$O_2(g) + 4 H^+(aq) + 4 e^-$	$\longrightarrow 2 H_2O(l)$	1.23
$Br_2(l) + 2 e^-$	$\longrightarrow 2 Br^-(aq)$	1.09
$Ag^+(aq) + e^-$	$\longrightarrow Ag(s)$	0.80
$Fe^{3+}(aq) + e^-$	$\longrightarrow Fe^{2+}(aq)$	0.77
$O_2(g) + 2 H^+(aq) + 2 e^-$	$\longrightarrow H_2O_2(aq)$	0.70
$I_2(s) + 2 e^-$	$\longrightarrow 2 I^-(aq)$	0.54
$O_2(g) + 2 H_2O(l) + 4 e^-$	$\longrightarrow 4 OH^-(aq)$	0.40
$Cu^{2+}(aq) + 2 e^-$	$\longrightarrow Cu(s)$	0.34
$Sn^{4+}(aq) + 2 e^-$	$\longrightarrow Sn^{2+}(aq)$	0.15
$2 H^+(aq) + 2 e^-$	$\longrightarrow H_2(g)$	0
$Pb^{2+}(aq) + 2 e^-$	$\longrightarrow Pb(s)$	-0.13
$Ni^{2+}(aq) + 2 e^-$	$\longrightarrow Ni(s)$	-0.26
$Cd^{2+}(aq) + 2 e^-$	$\longrightarrow Cd(s)$	-0.40
$Fe^{2+}(aq) + 2 e^-$	$\longrightarrow Fe(s)$	-0.45
$Zn^{2+}(aq) + 2 e^-$	$\longrightarrow Zn(s)$	-0.76
$2 H_2O(l) + 2 e^-$	$\longrightarrow H_2(g) + 2 OH^-(aq)$	-0.83
$Al^{3+}(aq) + 3 e^-$	$\longrightarrow Al(s)$	-1.66
$Mg^{2+}(aq) + 2 e^-$	$\longrightarrow Mg(s)$	-2.37
$Na^+(aq) + e^-$	$\longrightarrow Na(s)$	-2.71
$Li^+(aq) + e^-$	$\longrightarrow Li(s)$	-3.04

Weaker
reducing
agent



Stronger
reducing
agent



Cell potential or emf of a cell

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.

$$E_{\text{cell}} = E_{\text{cathode}} + E_{\text{anode}}$$

For this equation we take oxidation potential of anode and reduction potential of cathode.

Since anode is put on left and cathode on right, it follows therefore,

$$E_{\text{cell}} = E_{\text{Left}} + E_{\text{Right}}$$

For a Daniel cell, therefore

$$E^0_{\text{cell}} = E^0_{\text{Cu}^{2+}/\text{Cu}} - E^0_{\text{Zn}^{2+}/\text{Zn}} = 0.34 + 0.76 = 1.10 \text{ V}$$



Cell diagram or representation of a cell

The following conventions or notations are applied for writing the cell diagram in accordance with IUPAC recommendations.

The Daniel cell is represented as follows:



Anode half cell is written on the left hand side while cathode half cell on right hand side.

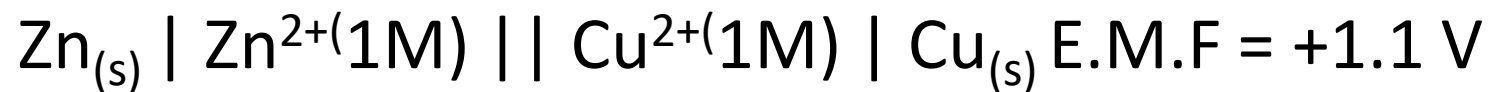


1. A single vertical line separates the metal from aqueous solution of its own ions.
2. A double vertical line represents salt bridge
3. The molar concentration (C) is placed in brackets after the formula of the corresponding ion.

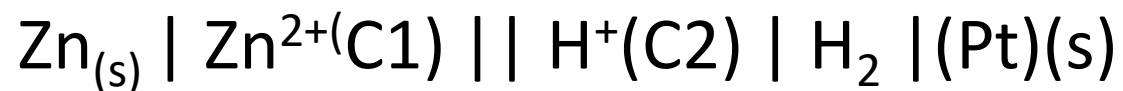


4. The value of e.m.f. of the cell is written on the extreme right of the cell.

For example,



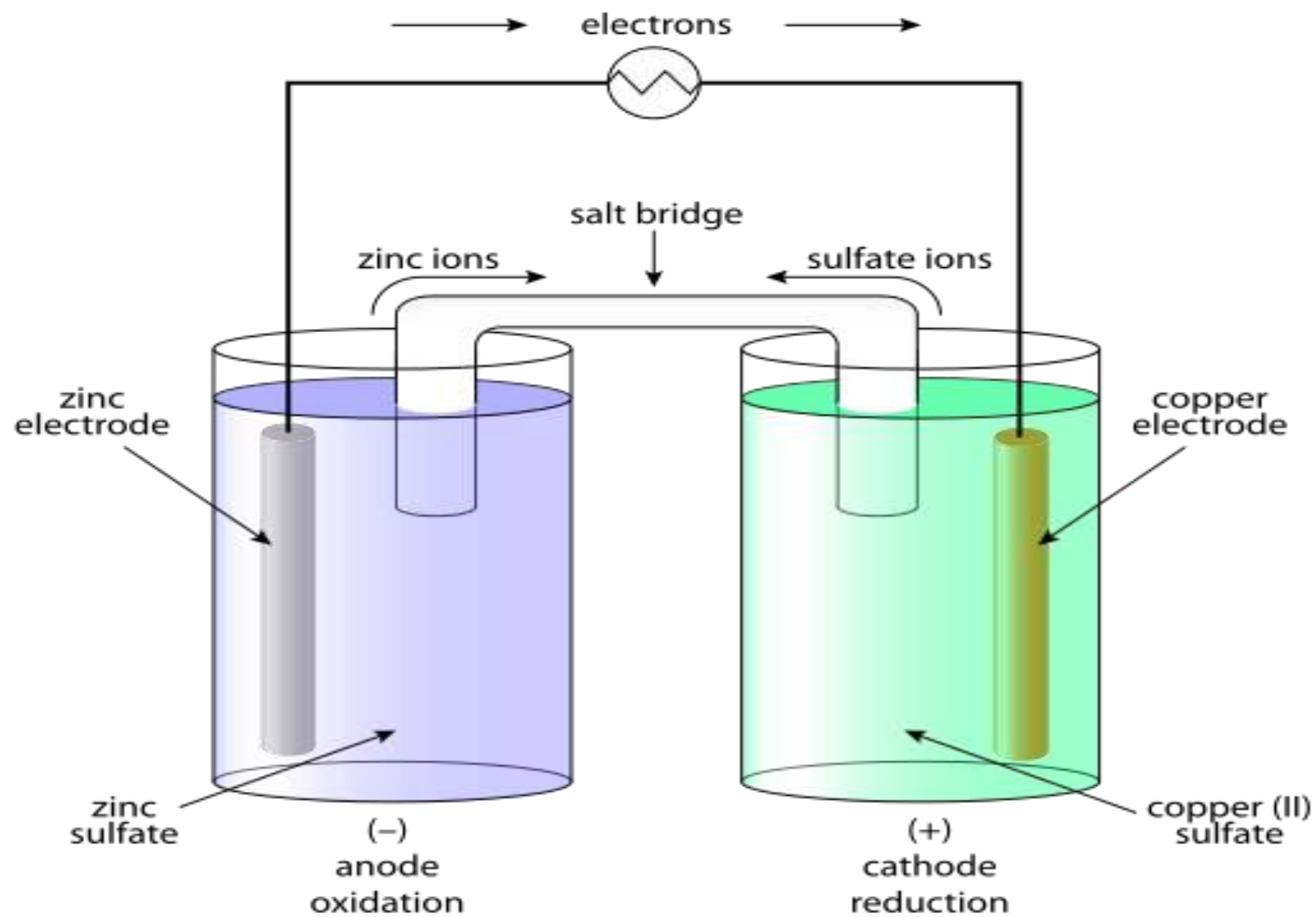
5. If an inert electrode like platinum is involved in the construction of the cell, it may be written along with the working electrode in bracket say for example, when a zinc anode is connected to a hydrogen electrode.





Salt bridge

1. Salt bridge is used to maintain the charge balance and to complete the circuit by facilitating the flow of ions through it.
2. It contains a gel in which an inert electrolyte like Na_2SO_4 or KNO_3 etc are mixed.
3. Negative ions flow to the anode and positive ions flow to the cathode through the salt bridge and charge balance is maintained and cell keeps on functioning.





Electrode potential

It may be defined as the tendency of an element, when it is placed in contact with its own ions to either lose or gain electrons and in turn become positively or negatively charged.

The electrode potential will be named as oxidation or reduction potential depending upon whether oxidation or reduction has taken place.



Characteristics

(a) Both oxidation and reduction potentials are equal in magnitude but opposite in sign.

(b) It is not a thermodynamic property, so values of E are not additive.



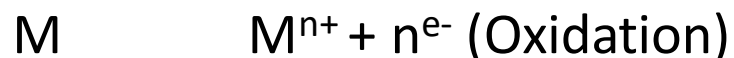
Single electrode potential:

In galvanic cell, two electrodes are presented; at one electrode oxidation takes place and at other electrode reduction takes place.

“

The tendency of an electrode (M) to get oxidized or reduced when it is contact with its own ionic (M^{n+}) solution, known as single electrode potential”. It is represented by $E(M/M^{n+})$ or $E(M^{n+}/M)$.

If metal rod or electrode (M) loses electrons and change into metal ions (M^{n+}) then metal get oxidized (oxidation potential, $E(M/M^{n+})$).



If metal ion (M^{n+}), on collection with metal rod by gain electrons and change into metal atom (M), then metal ions get reduced (Reduction potential, $E(M^{n+}/M)$)



During oxidation negative charge developed on the metal electrode and during reduction positive charge develops on the metal electrode.



Standard electrode potential (E°)

It may be defined as the electrode potential of an electrode determined relative to standard hydrogen electrode under standard conditions.

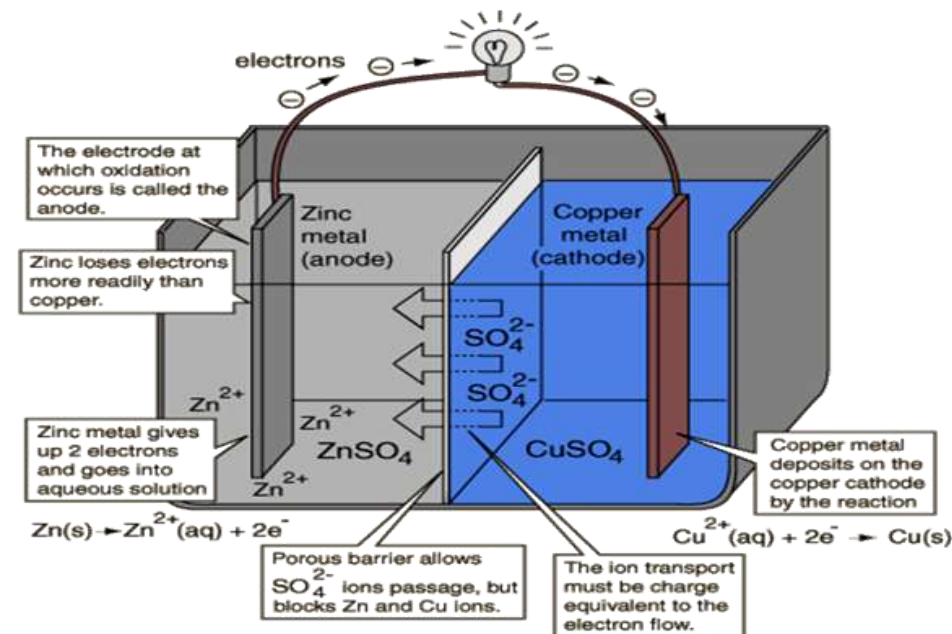
The standard conditions taken are

1. 1M concentration of each ion in the solution.
2. A temperature of 298 K.
3. 1 bar pressure for each gas.

Electrochemical cell

Electrons produced by an anode must be consumed by a cathodic reaction. Therefore an anode must be paired with a cathode. The two electrodes combine in an electrochemical cell.

An electrochemical cell can be created by placing metallic electrodes into an electrolyte where a chemical reaction either uses or generates an electric current.





Electrodes

Electrodes can be defined as conductors that are used to make electrical contact with a non-metallic part of the circuit.

Reference electrode:

Reference electrodes are of two types:

- (i) Primary reference electrode
- (ii) Secondary reference electrode

It is an electrode whose potential is arbitrarily taken as zero or is exactly known.

Standard Hydrogen Electrode (SHE), calomel electrode, silver-silver chloride electrode and glass electrode are some examples of reference electrode.

Standard hydrogen electrode:

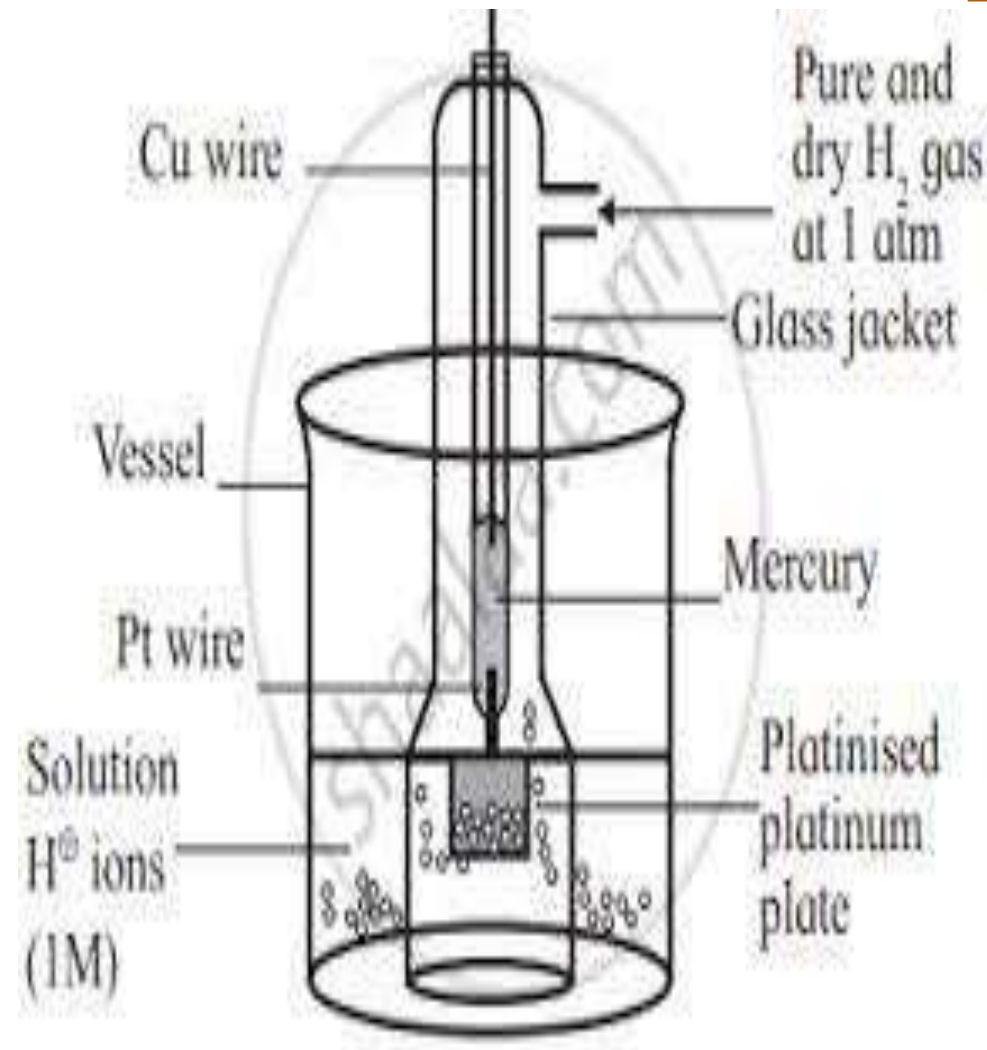
Hydrogen electrode is the primary standard electrode.

It consists of a small Platinum strip coated with Platinum black as to adsorb H_2 gas.

Platinum is welded to the Pt strip and sealed in a glass tube as to make contact with the outer circuit.

The Platinum strip and glass tube is surrounded by an outer glass tube which has an inlet for H_2 gas at top and a no. of holes at the base for the escape of excess of H_2 gas.

The Platinum strip placed in an acid solution which has H^+ ions of 1M concentration. Pure hydrogen gas passed through the inlet at 1 atmospheric pressure.



CALOMEL ELECTRODE

A solution of potassium chloride is then placed over the paste.

A platinum wire sealed in a glass tube helps in making the electrical contact.

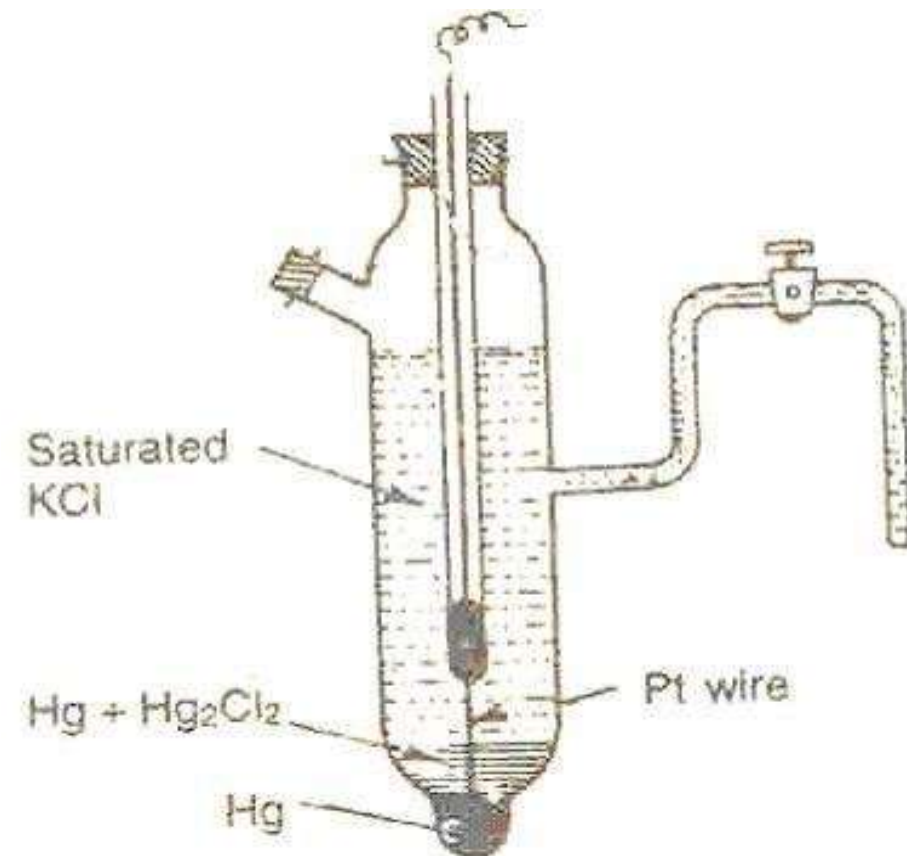
The electrode is connected with the help of the side tube on the left through a salt bridge with the other electrode to make a complete cell.

The electrode is represented as $\text{Pt, Hg/ Hg}_2\text{Cl}_2, \text{Cl}^-_{(\text{aq})}$

The potential of the calomel electrode depends upon the concentration of the potassium chloride solution.

If potassium chloride solution is saturated, the electrode is known as saturated calomel electrode (SCE)

If the potassium chloride solution is 1 N, the electrode is known as normal calomel electrode (NCE)

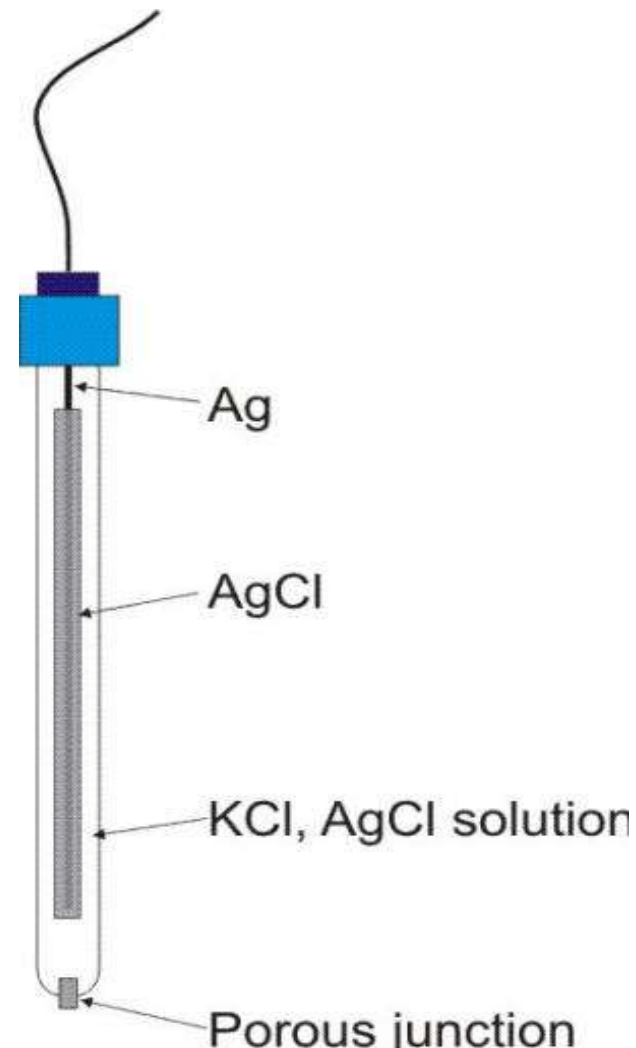


Silver/Silver Chloride Reference Electrode

The silver/silver chloride reference electrode is composed of a silver wire (Ag) that has been coated with a layer of solid silver chloride (AgCl), immersed in a solution that is saturated with KCl and AgCl. The pertinent half reaction is



with a potential of 0.197 V with respect to the SHE at 25 °C. This value differs slightly from the E^0 for the couple (0.222 V) because both KCl and AgCl contribute to the chloride activity, which is not exactly unity.

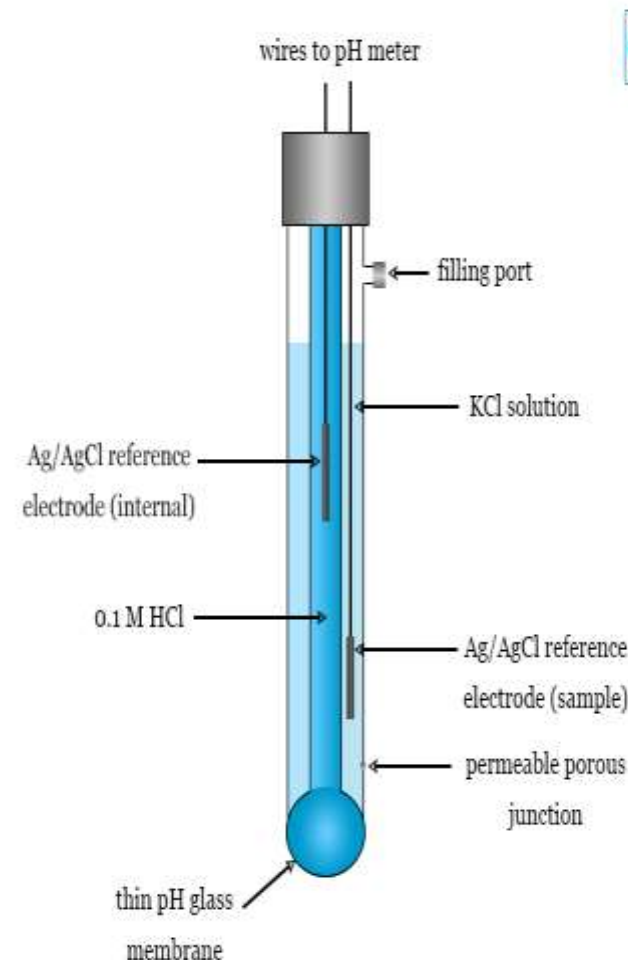


Glass Electrode

Glass electrode is a type of ion selective electrode used mainly for the measurement of the pH of a solution. A glass electrode consists of a glass tube terminating in a thin size membrane. The modern pH probe in the glass electrodes contains a hydrogen ion sensitive glass bulb.

The completed glass electrode with a reference electrode cell is represented by the electrochemical shorthand

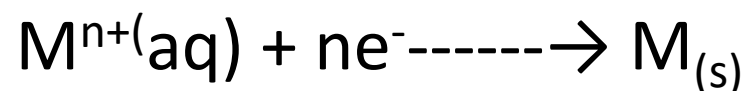
$\text{Ag/AgCl} \mid \text{HCl} \mid \text{glass} \parallel \text{probed solution} \mid \text{reference electrode (1)}$





Nernst equation:-Electrode potential

- Consider an electrode reaction,



The Nernst equation for the above reaction is given as follows:

$$E_{M^{n+}/M} = E^{\circ}_{M^{n+}/M} + \frac{RT}{nf} \times \ln [M^{n+}]$$

Where $E_{M^{n+}/M}$ = Electrode potential of given metal ion

$E^{\circ}_{M^{n+}/M}$ = Standard electrode potential

- R = Gas constant, 8314 J/K/mol/2Kcal
- T = Temperature
- n = no. of moles of electrons
- f = Faraday (f = 96500 c/mol)



Consider Daniel cell and the electrodes and ions are denoted as follows:



OHR

RHR

The electrode potential for RHR's written as

$$E_{\text{Cu}^{2+}/\text{Cu}} = E^{\circ}_{\text{Cu}^{2+}/\text{Cu}} + RT/2f \times \ln [\text{Cu}^{2+} (\text{aq})]$$

The electrode potential for OHR's written as

$$E_{\text{Zn}^{2+}/\text{Zn}} = E^{\circ}_{\text{Zn}^{2+}/\text{Zn}} + RT/2f \times \ln [\text{Zn}^{2+} (\text{aq})]$$

Total cell potential = RHR – OHR

$$\begin{aligned} E_{\text{cell}} &= \{E^{\circ}_{\text{Cu}^{2+}/\text{Cu}} + RT/2f \times \ln [\text{Cu}^{2+} (\text{aq})]\} - \{E^{\circ}_{\text{Zn}^{2+}/\text{Zn}} + RT/2f \times \ln [\text{Zn}^{2+} (\text{aq})]\} \\ &= (E^{\circ}_{\text{Cu}^{2+}/\text{Cu}} - E^{\circ}_{\text{Zn}^{2+}/\text{Zn}}) + (RT/2f \times \ln [\text{Cu}^{2+} (\text{aq})] - RT/2f \times \ln [\text{Zn}^{2+} (\text{aq})]) \\ &= (E^{\circ}_{\text{Cu}^{2+}/\text{Cu}} - E^{\circ}_{\text{Zn}^{2+}/\text{Zn}}) + RT/2f \times \ln [\text{Cu}^{2+} (\text{aq})] / [\text{Zn}^{2+} (\text{aq})] \\ &= E^{\circ}_{\text{cell}} + RT/2f \times \ln [\text{Cu}^{2+} (\text{aq})] / [\text{Zn}^{2+} (\text{aq})] \end{aligned}$$

By substituting the values of R,T and F we get

$$= E^{\circ}_{\text{cell}} + 0.0592/2 \ln [\text{Cu}^{2+} (\text{aq})] / [\text{Zn}^{2+} (\text{aq})]$$

After converting natural logarithm into log, we get

$$= E^{\circ}_{\text{cell}} + 0.0592/2 \log [\text{Cu}^{2+} (\text{aq})] / [\text{Zn}^{2+} (\text{aq})]$$

$$= E^{\circ}_{\text{cell}} - 0.0592/2 \log [\text{Zn}^{2+} (\text{aq})] / [\text{Cu}^{2+} (\text{aq})]$$

eg: consider another following cell and whose cell reaction is written as follows



Cell potential is written as

$$E_{\text{cell}} = E^{\circ}_{\text{cell}} + 0.0592/2 \log [\text{Ag}^{2+} (\text{aq})]^2 / [\text{Ni}^{2+} (\text{aq})]$$

In general it is written as $aA + bB \rightleftharpoons cC$

$$E_{cell} = E^0_{cell} - \frac{2.303}{RT} \log (C)^c (D)^d / (A)^a$$

Potentiometry

Potentiometry is based on the measurement of the potential of an electrode system (e.g. electrochemical cell).

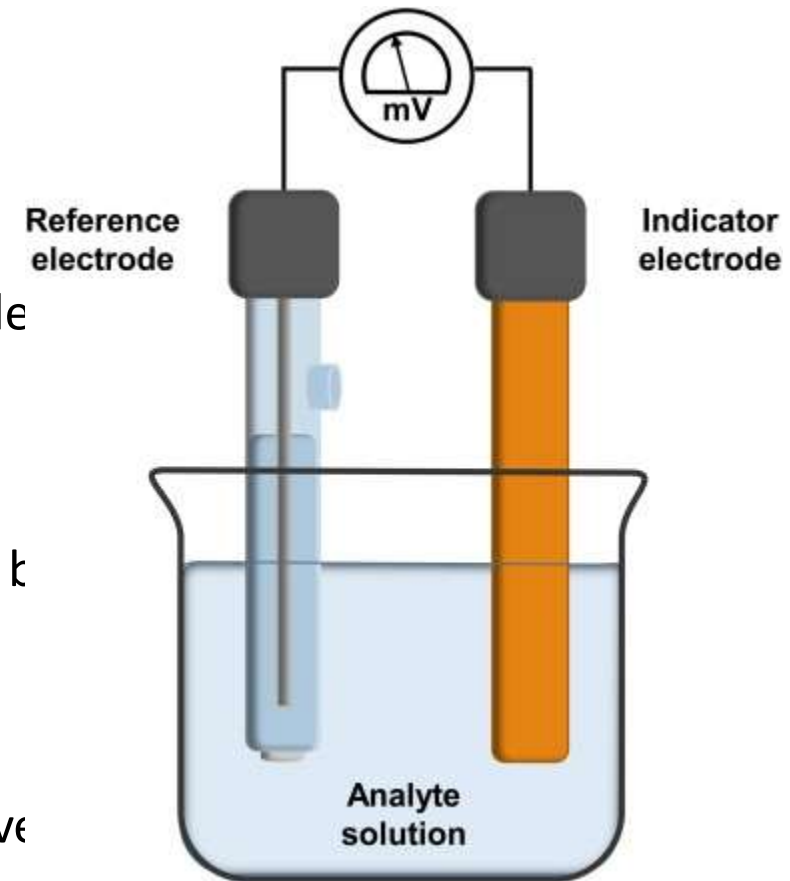
Potentiometric measurement system consists of two electrodes called reference and indicator electrode, potentiometer and a solution of analyte (figure 2).

Reference electrode is an electrode with potential which is a) independent of concentration of analyte (or other) ions in solution; b) independent of temperature.

Potential of an indicator electrode depends mainly on the concentration of the analyte ions (in this case hydrogen ions).

In case of figure 2, the potential of the indicator electrode is sensitive to hydrogen ions.

In a system like this, the potential is measured in reference to a calomel electrode, e.g. calomel electrode functions as the reference electrode.





Potentiometric titration

Potentiometric titration is a volumetric method in which the changes in the emf between two electrodes (reference and indicator electrode) on the addition of titrant of known concentration (titrant) to a solution of unknown (analyte).

- The indicator electrodes is reversible with respect to one of the ions of analyte taking part in the titration reaction but does not take part in the reaction. They are inert electrode made up of Pt or Au.
- During the course of the titration, the concentration of active ion in the analyte changes thereby electrode potential of indicator electrode changes.
- Types of potentiometric titration for the determination of analytes in solutions include acid-base, redox, precipitation, and complexometric.



1) Redox Titration: Fe^{2+} against dichromate

The concentration of an ion such as Fe^{2+} can be found by titrating with a strong oxidizing agent such as KMnO_4 (Mn^{7+}) or $\text{K}_2\text{Cr}_2\text{O}_7$ (Cr^{6+}).

The titration is carried out in one side of a cell whose other half is a reference electrode: Calomel electrode, $\text{Pt} | \text{Hg} | \text{Hg}_2^{2+} (\text{aq}) | \text{KCl} ||$

Cell configuration:



$$E_{\text{meas}} = E_{\text{ind}} - E_{\text{SCE}}$$

$$E_{\text{ind}} (E_{\text{Fe}^{3+} / \text{Fe}^{2+}}) = E_{0 \text{ Fe}^{3+} / \text{Fe}^{2+}} + 0.0591 \log \text{Fe}^{3+} / \text{Fe}^{2+}$$

$$\text{where } E_{0 \text{ Fe}^{3+} / \text{Fe}^{2+}} = 0.77\text{V}$$

Initially the left cell contains only Fe^{2+} . As the titrant is added, the ferrous ion is oxidized to Fe^{3+} according to the reaction.



Once the first drop of Cr^{6+} ($\text{K}_2\text{Cr}_2\text{O}_7$) titrant has been added, the potential of the indicator electrode is controlled by the ratio of oxidized and reduced iron which causes the potential to rise as more iron becomes oxidized.

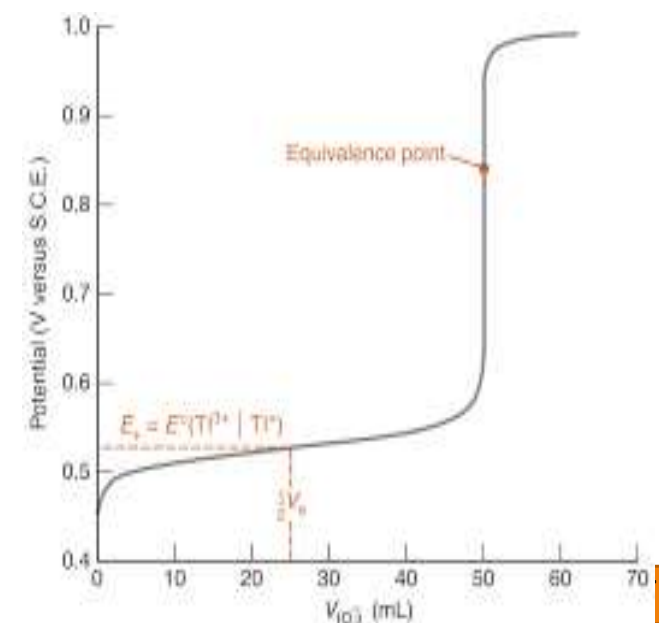
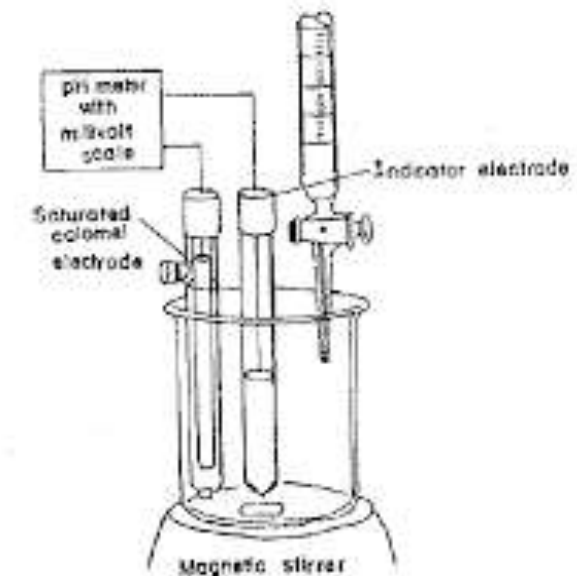
Near the end-point the ratio changes very rapidly since a small quantity of added Mn^{7+} or Cr^{6+} removes considerable proportion of the few remaining Fe^{2+} ions.

When the equivalence point is reached, the Fe^{2+} will have been totally consumed and the potential will then be controlled by the concentration ratio of cell couple $\text{Cr}^{6+} / \text{Cr}^{3+}$.

The end point is found not by measuring a particular cell voltage, but by finding what volume of titrant gives the steepest part of the curve.

A titration curve has a characteristic sigmoid curve. The part of the curve that has the maximum change marks the equivalence point of the titration.

The first derivative, $\Delta E / \Delta V$, is the slope of the curve, and the endpoint occurs at the volume, V' , where $\Delta E / \Delta V$ has the maximum value.

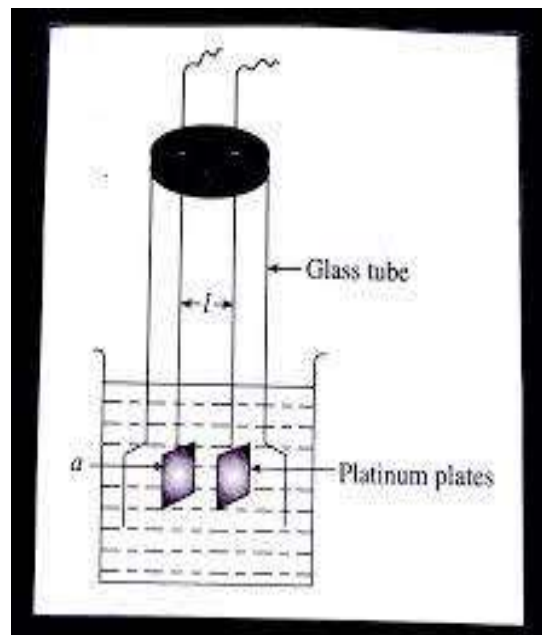


Conductivity

- Conductivity is a measurement of the ability of an aqueous solution to transfer an electrical current.
- The current is carried by ions, and therefore the conductivity increases with the concentration of ions present in solution, their mobility, and temperature of the water.

Conductivity Cell:

- Specially designed cells in which two plates of inert metal (Pt or Au) are provided to serve the flow in and flow out of electron.





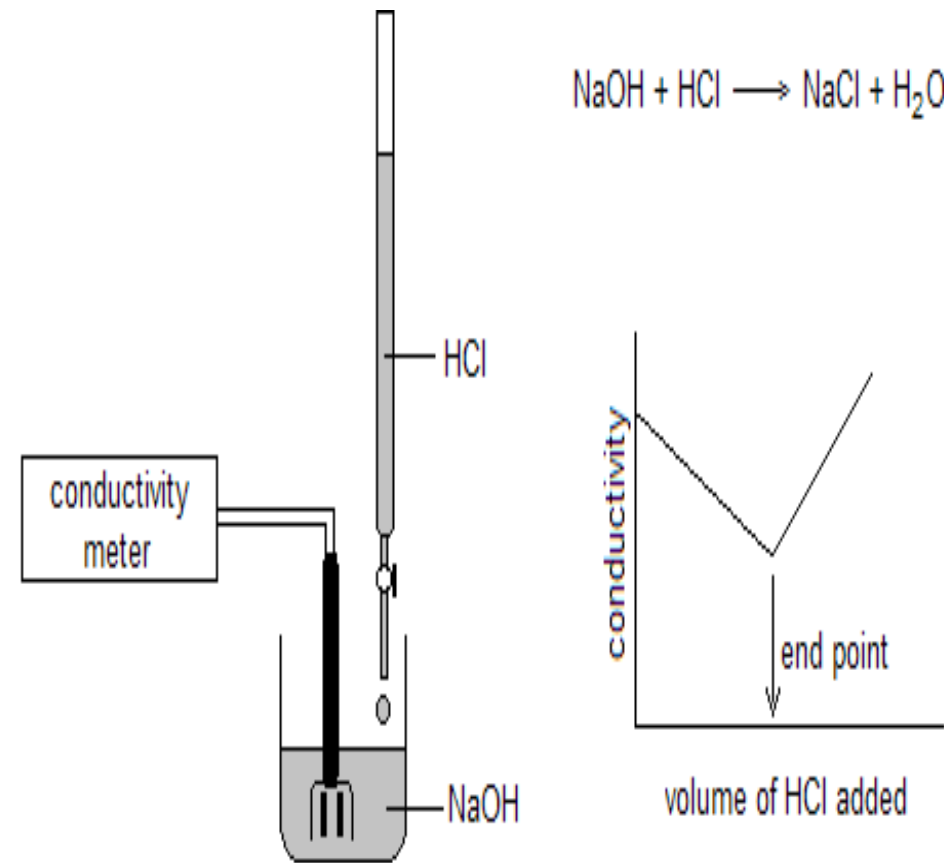
CONDUCTOMETRIC TITRATIONS

- Titrations in which conductance measurements are made use of in determining the end-point of acid-alkali reactions, some displacement reactions or precipitation reactions are called Conductometric titrations.
- In these titrations, advantage is taken of the fact that the conductance of a solution at a constant temperature depends upon the number of ions present in it and their mobility.
- For this purpose, the titrant is added from a burette into a measured volume of the solution to be titrated which is taken in a conductance cell and the conductance readings corresponding to the various additions are plotted against the volume of the titrant.
- In this way two linear curves are obtained, the point of intersection of which is the end-point.
- **actual conductance = $v+V/V$ * observed conductance**

Titration of strong acid vs strong base (hydrochloric acid with sodium hydroxide)

- The reaction that takes place in the titration vessel is $\text{H}^+ + \text{Cl}^- + \text{Na}^+ \text{OH}^- \rightarrow \text{H}_2\text{O} + \text{Na}^+ \text{Cl}^-$
- Before the end point, H^+ is removed from the solution by reaction with OH^- , and Na^+ is added to the solution.
- Since the relative conductance of H^+ is about seven times that of Na^+ , the conductance of the solution decreases prior to the end point.
- After the end point, no H^+ is available to react, and the conductance of the solution increases as a result of the addition of Na^+ and OH^- .
- Consequently the titration curve has a V-shape as shown in the figure.

$\text{Na}^+ \text{OH}^-$ – The end point of the titration corresponds to the intersection of the extrapolated linear portions of the titration curve.



Titration of weak acid vs strong base (Acetic acid with NaOH)

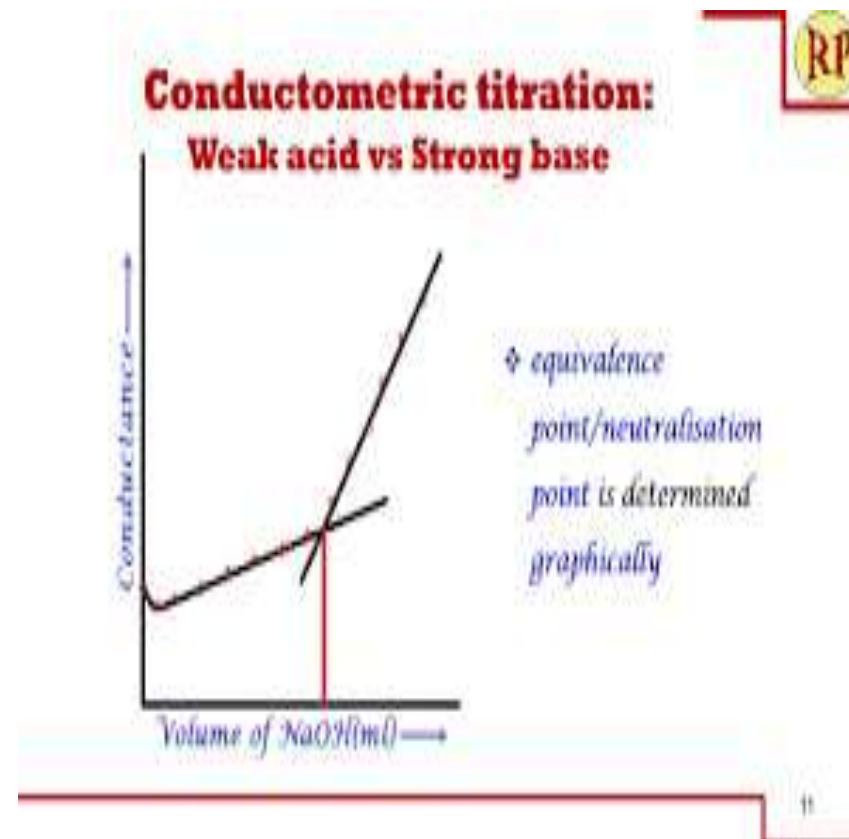
Since acetic acid is dissociated slightly ($K_a = 1.8 \times 10^{-5}$) in aqueous solution, the conductance of the acetic acid solution is initially small.

- As sodium hydroxide is added, the hydroxide reacts with the acid to form water and acetate.



- The addition of CH_3COO^- and Na^+ ions to the solution causes the conductance of the solution to increase.

After the end point, Na^+ and OH^- are added to the solution. Since the relative conductance of OH^- is nearly five times that of $\text{C}_2\text{H}_3\text{O}_2^-$, the conductance of the solution after the end point increases more rapidly than it did before the end point. • The end point corresponds to the intersection of the extrapolated linear portions of the curve



Titration of a strong acid and weak base

An example of a strong acid and weak base are HCl and NH_4OH respectively.

As the acid is a strong acid it will dissociate into H^+ and OH^- ion completely and hence number of ions will be maximum in the solution.

Furthermore as H^+ ion has very large ionic mobility and hence ionic conductance, the solution will show high conductance.

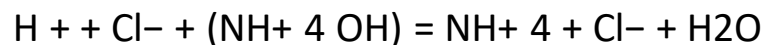
Now as we add base drop by drop from burette, acid-base reaction will take place. During the acid-base reaction, the OH^- ion will consume H^+ to form water.

So, we can say as drops of NH_4OH will be added, H^+ ion will be consumed by OH^- and NH_4^+ ion will be added in solution. So, we can say that as titration will proceed each Na^+ is being replaced by NH_4^+ .

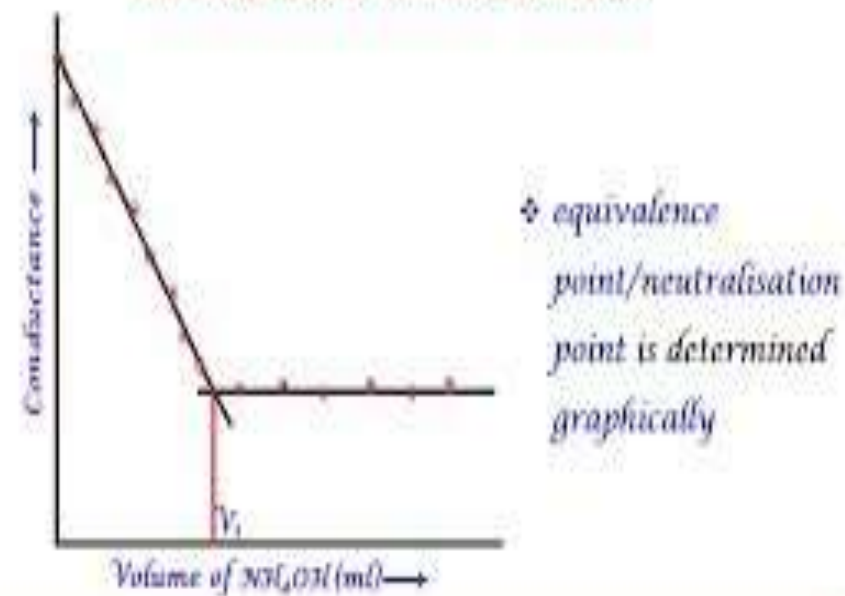
Now ionic conductance of NH_4^+ is less compared to H^+ and hence conductance will decrease as the titration will proceed. After reaching equivalent point when all the H^+ ion is consumed, additional addition of NH_4OH will have no effect.

This is due to the fact that NH_4OH will not dissociate further as it is weak base and due to common ion effect.

So, the conductance value will be unchanged or we will get a parallel line to X-axis.



Conductometric titration: Strong acid vs Weak base





A battery is a device in which number of electrochemical cell are connected in a series. It transformed chemical energy into electrical energy.

Classification of Batteries

- i) Primary battery
- ii) Secondary battery
- iii) Fuel cell

i) Primary batteries: Primary batteries are those in which only one redox reaction occurs and battery become dead after some time. These are non rechargeable and cell reaction are irreversible.

In these batteries the cell reactions are in directional i.e., chemical energy can be converted into electrical energy and cannot be reversed. These batteries once used have to be discarded or disposed.

For example: lithium cell, dry cell, mercury cell

ii) Secondary batteries: Secondary batteries are those which recharge when electric current pass through the cell. These are rechargeable and cell reactions are reversible, therefore they can be use again and again .e., chemical energy can be converted into electrical energy and vice versa. When we pass electricity in opposite direction, it is stored in the form of chemical energy

For example: lead storage battery (lead acid battery), Ni-Cd battery.

iii) Fuel cell: Fuel cell is a device, which produce electricity by the combustion of fuel.

Fuel + oxygen

oxidation products + electricity



Zinc–air batteries (non-rechargeable), and zinc–air fuel cells:

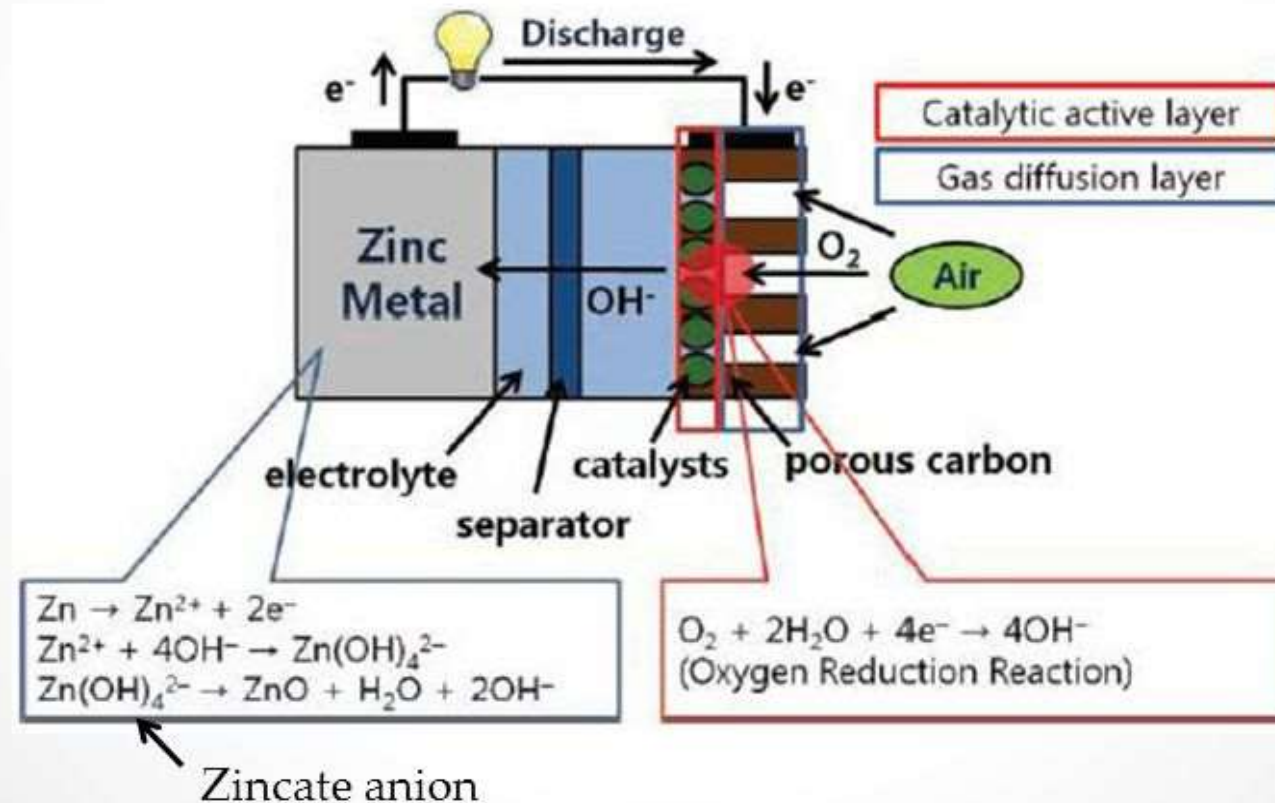
(mechanically rechargeable) are metal–air batteries powered by oxidizing zinc with oxygen from the air. These batteries have high energy densities and are relatively inexpensive to produce. Sizes range from very small button cells for hearing aids, larger batteries used in film cameras that previously used mercury batteries, to very large batteries used for electric vehicle propulsion and grid-scale energy storage.

During discharge, a mass of zinc particles forms a porous anode, which is saturated with an electrolyte. Oxygen from the air reacts at the cathode and forms hydroxyl ions which migrate into the zinc paste and form zincate ($\text{Zn}(\text{OH})_2-4$), releasing electrons to travel to the cathode. The zincate decays into zinc oxide and water returns to the electrolyte. The water and hydroxyl from the anode are recycled at the cathode, so the water is not consumed. The reactions produce a theoretical 1.65 volts, but this is reduced to 1.35–1.4 V in available cells.

Zinc–air batteries have some properties of fuel cells as well as batteries: the zinc is the fuel, the reaction rate can be controlled by varying the air flow, and oxidized zinc/electrolyte paste can be replaced with fresh paste.

Zn-Air Chemistry

- Schematic representation of Zn-air cell operation:





Lithium batteries:

From the electrochemical series, it is observed that Li has most negative Standard Reduction potential (-3.05).

Characteristics of Li:

Lot of appeal of anode material

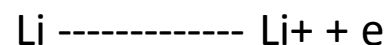
Light metal -corresponding lithium cells is also light weight.

Lithium batteries are of two types:

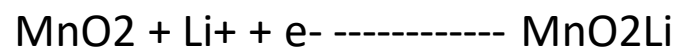
- i) Primary batteries:- It is one of the most common Lithium primary cell, it is known as Li-MnO₂ battery.
The electrodes are
 - i) Anode – Li
 - ii) Cathode – Heat treated MnO₂
 - iii) Electrolytic solution – Propylene carbonate, dimethoxy ethane in LiClO₄

The electrode reactions are

At Anode:



At Cathode:



Mn (IV) reduced to Mn (III)]



Applications:

produces a voltage of about 3.4V (double the alkaline dry cell).

It is used in things require high current drains or photo flash

i) Rechargeable batteries:

These cells contain Li^+ ions instead of metallic Li.

Instead of oxidation and reduction, Li^+ ions are transported from one electrode to other through electrolytic solution.

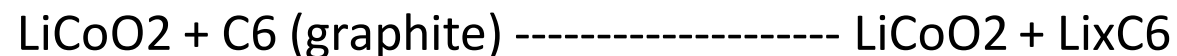
This is compensated by transport of e^- in the external circuit.

Li^+ ions are able to slip between the two layers of atoms in certain crystals such as graphite (C_6) and LiCoO_2 .

Charging:

When the cell is constructed, it is uncharged state with no Li^+ ions between the layers. An external voltage forces e^- through external circuit and causes Li^+ ions to travel from the LiCoO_2 electrode to C_6 (graphite) electrode (but e^- moves from C_6 (graphite) electrode to LiCoO_2 electrode).

Say for eg. x Li^+ ions are transported from LiCoO_2 electrode to C_6 (graphite) electrode.

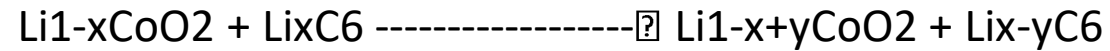


Discharging:

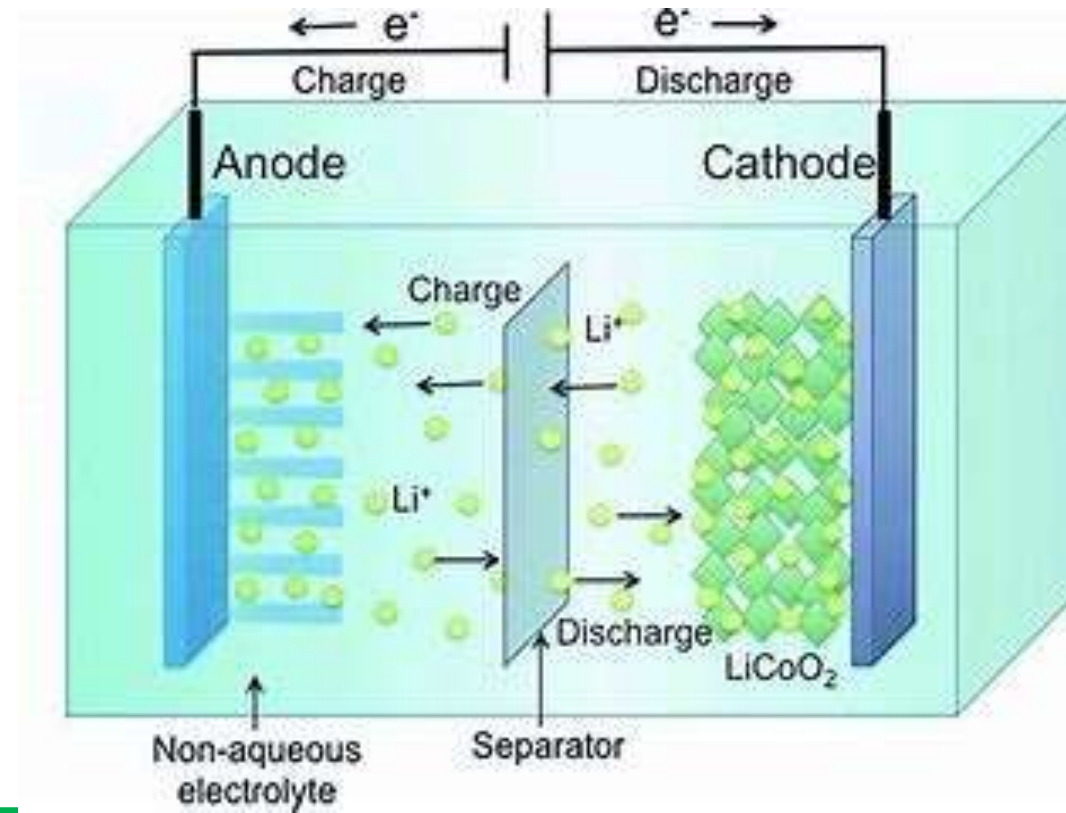
When the cell is fully charged, it is ready to discharge continuously to give electrical power.

During discharging Li^+ ions move back through the electrolyte from C6 (graphite) electrode to LiCoO_2 electrode (but e^- moves from LiCoO_2 electrode to C6 (graphite) electrode).

Say for eg. y Li^+ ions are transferred from C6 (graphite) electrode to LiCoO_2 electrode.



Thus charging and discharging cycle consists of movement of Li^+ ions from LiCoO_2 to C6 and the e^- flows in reverse to maintain balance in the external circuit





Nickel – Cadmium cells: (Ni-Cd Cell)

This has high energy density due to which it is easily discharged and charged.

Anode: Cd

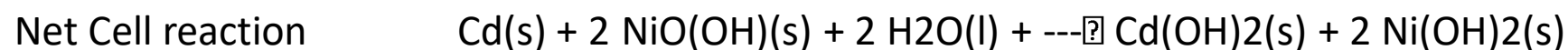
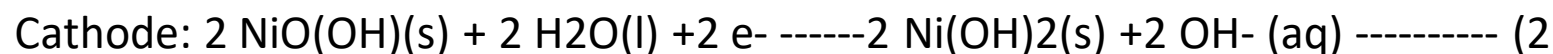
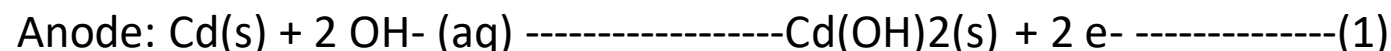
Cathode: Nickel oxy hydroxide Ni O OH

Electrolyte: Aqueous KOH, H₂O

Emf: 1.4V

Discharging: The electrode reactions are

Cell reaction:



The formed products Ni(OH)₂ & Ni(OH)₂ are adhered to the electrode surfaces.

Charging:

While charging, the above electrode reactions are reversed. Since the products are adhered to the electrode surfaces.

Applications:

Calculators, digital cameras, pagers, laptops, tape recorders, flash lights, medical devices, electrical vehicles, space applications.

Advantages: -

Good performance in low temperature long life.



Fuel Cells:-

In comparison with galvanic cell, which produces electrical energy for limited period due to depletion of reactants – fuel cells are electrochemical cells which produce energy as long as reactants are supplied. This makes fuel cells an attractive source of power.

Chemical energy -----→ Electricity (No combustion of gas & O₂)

Fuel + O₂ -----→ Oxidation product + Electricity

Two of fuel cells are discussed below:

i) H₂-O₂ Fuel cell:-

Simplest and successful

Consists of electrolyte (Con. Soln. of KOH) in the centre compartment, which is in contact with two electrodes that contain Pt catalyst to facilitate reactions.

H₂ & O₂ under pressure circulated, so as to come in contact with electrodes

The electrode reactions are:

At cathode $2 \text{H}_2(\text{g}) + 4\text{OH}^- \longrightarrow 4\text{H}_2\text{O}(\text{l}) + 4\text{e}^-$ (RHR)

At anode $\text{O}_2(\text{g}) + 2 \text{H}_2\text{O}(\text{l}) + 4 \text{e}^- \longrightarrow 4 \text{OH}^-(\text{aq})$ (OHR)

Net reaction $2 \text{H}_2(\text{g}) + \text{O}_2(\text{g}) \longrightarrow 2\text{H}_2\text{O}(\text{l})$

EMF, $E_o = 1.23\text{V}$.

But in practice the EMF, $E_o = 0.8$ to 1.0 V . Generally large numbers are connected in series to make battery

Advantages:-

Attractive alternate to gasoline powered engines

Pollution free & only by-product is H₂O.

Thermodynamically efficient – (efficiency)

(gasoline & diesel engines – 25-30% efficiency.)

**Disadvantages:-**

Energy cost of H_2 fuel generation is high.

Problem in storage & distribution of H_2 (highly inflammable).

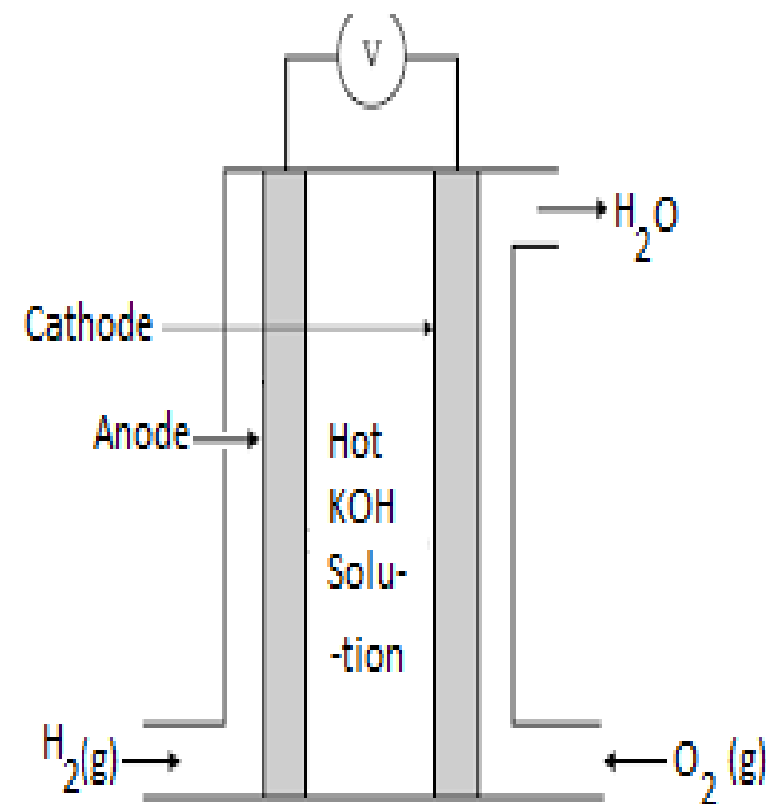
Availability of alternate fuels.

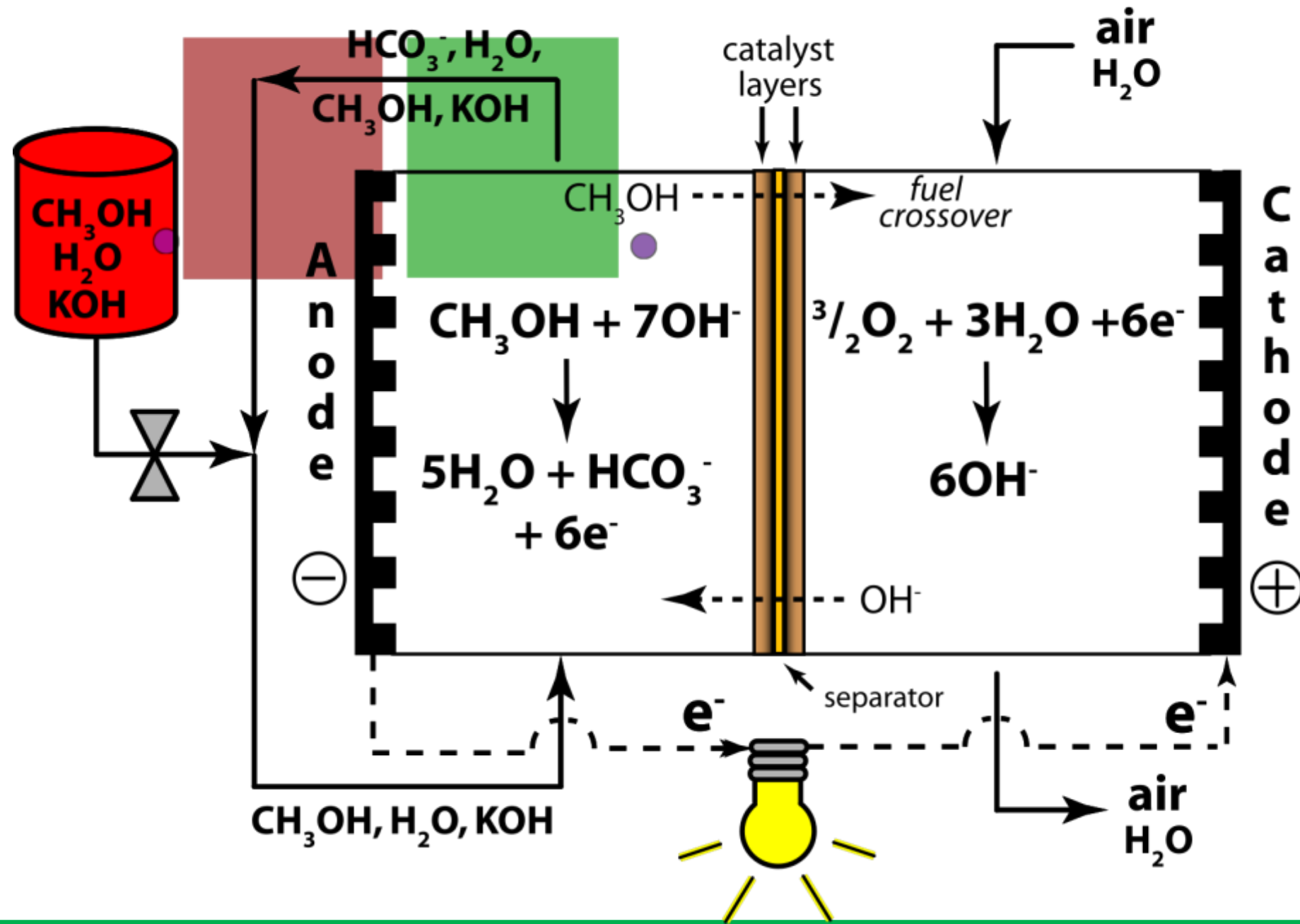
Applications:-

H_2 - O_2 fuel cells are used as auxiliary energy source in space vehicles, submarines or military vehicles.

As the by-product is H_2O , used as fresh water for astronauts.

For 15 days, weight required is 250 kg.







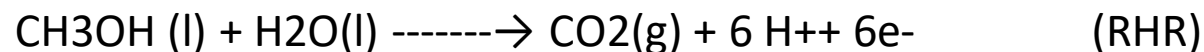
CH₃OH-O₂ fuel cell:-

- CH₃OH-O₂ is a important fuel cell.
- Oxidation of CH₃OH, takes place on catalyst (Pt) to form CO₂.
- Water consumed at anode and produced at cathode.
- H⁺ are transferred across the proton exchange membrane.
- H⁺ reacts with O₂ to form H₂O.
- e⁻s are transported through an external circuit from anode to cathode.
- CH₃OH & H₂O are absorbed on catalyst (Pt) to form CO₂ with lose of H⁺.

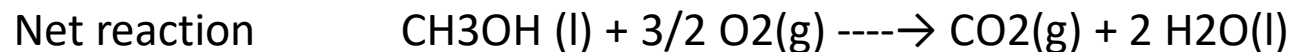
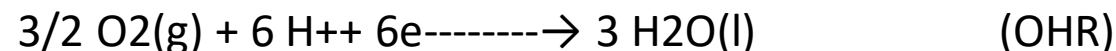
CH₃OH & H₂O – circulated through anode

O₂ -- circulated through cathode

At cathode



At anode



From the above cell reactions it is observed that...

CO₂ is formed by the addition of H₂O.

6 H⁺ reacts with 6 e⁻s.

One mole of CH₃OH reduces 3/2 O₂ to 3 H₂O (part of this is introduced at fuel compartment again).

For 6 e⁻ transfer, stranded cell voltage 1.21V is maintained.

Energy density produced is 6 KWH / kg methanol.

Advantages:-

Storage is easier, no high pressure or low temperature is required (-97.0o C to 64.7o C exists as liquid).

The energy density of the cell is comparatively higher than H₂-O₂ cell



Polymers



Introduction

INTRODUCTION:

- Matter is composed of many small units called molecules, which are in different sizes and shapes and associated with atoms.
- Polymers are giant or macro molecules which play a vital role in our daily life and provide the basic needs of our life (food, clothing and shelter).
- The word polymer was derived from Greek word
‘poly’= ‘many’ and ‘mers’ = ‘parts /units’.
- **Polymer:** A high molecular weight compound (macro molecule) made by linking together a large number of small molecules called **monomers** is called as a **Polymer**.

Ex: PVC, Polyethylene, Starch, Poly styrene, Proteins, DNA etc



Introduction

- **Monomer:** The basic repeating units present in a polymer are called monomers.

Ex: Vinyl chloride is a monomer of PVC.

Ethylene is a monomer of poly ethylene.

Glucose is a monomer of starch.

Styrene is a monomer of polystyrene.

Amino acids are the monomers of proteins.

Nucleotides are the monomers of Nucleic acids.

- **Degree of polymerization:** The number of repeating units (or) monomers present in the polymer is called as degree of polymerization. They may be hundreds (or) thousands (or) ten thousands.

- Degree of polymerization (D.P) =
$$\frac{\text{Mol.wt of polymer}}{\text{Mol.wt of monomer}}$$

$$\text{Molecular wt of polymer} = \text{D.P} \times \text{Mol. wt of monomer.}$$



Classification of Polymers

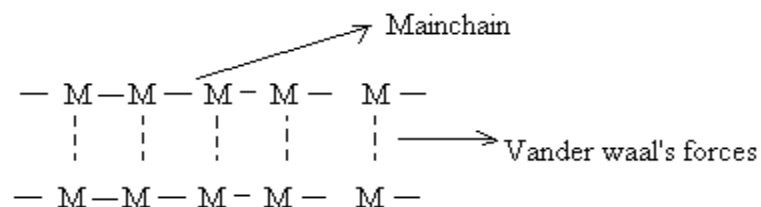
- **Based on degree of polymerization:**
 - Polymers having high DP (having of more number of monomers) are called **High polymers**. Their molecular weight range is about 10,000 to 10,00,000 Daltons.
 - Polymers with low DP are called **Oligopolymers**. Their molecular weight ranges from 5,000 to 2,00,000 Daltons.
- **Based on occurrence:**
 - Polymers may be either **Natural** (natural rubber, proteins, cellulose, starch etc) (or) **Synthetic** (PVC, PE, PS, Teflon, Nylon, Bakelite etc.....)



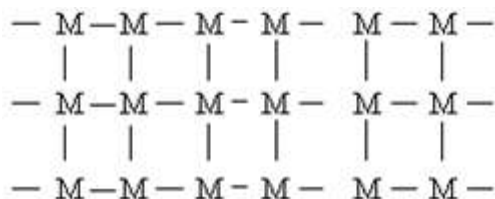
Basic Concepts

1. Functionality:

- The number of bonding sites (or) reacting sites present in a monomer is called as **functionality**.
- Each monomer should have minimum two bonding sites for polymerization.
 - a) If the functionality of monomer is 2, the resulting polymer is linear (or) straight chained. Ex: Ethylene, styrene, vinyl chloride.



- b) If the functionality of monomer is three (trifunctional), Cross linked three dimensional polymers are obtained.



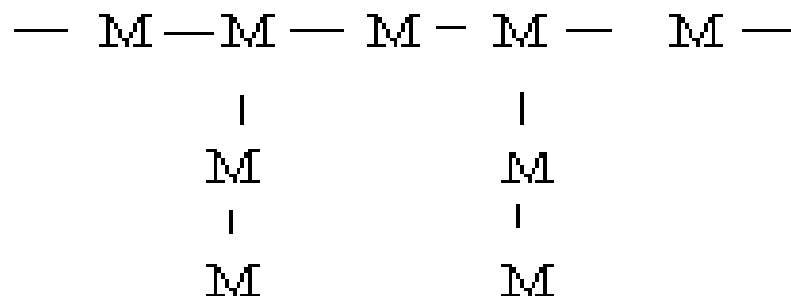


Basic Concepts

Functionality:

c) If a mixture of bi functional and tri functional monomers is present in a polymer, branched chain polymers are formed.

Ex: Buna – S – Rubber.





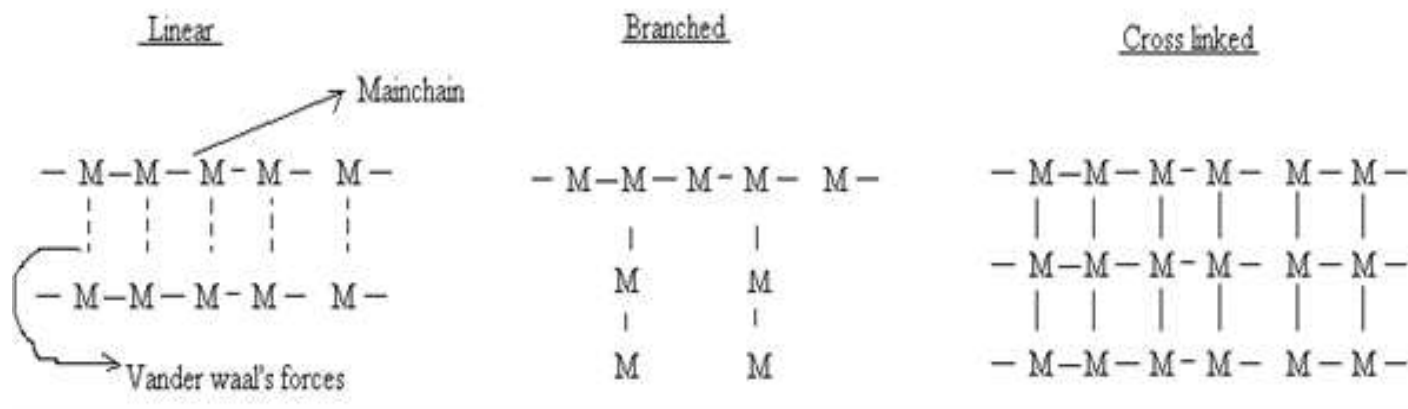
Basic Concepts

2. Nomenclature: polymers are given names based on two properties

- Type of monomers present
- Type of atoms present in back bone chain

(i) Type of monomers:

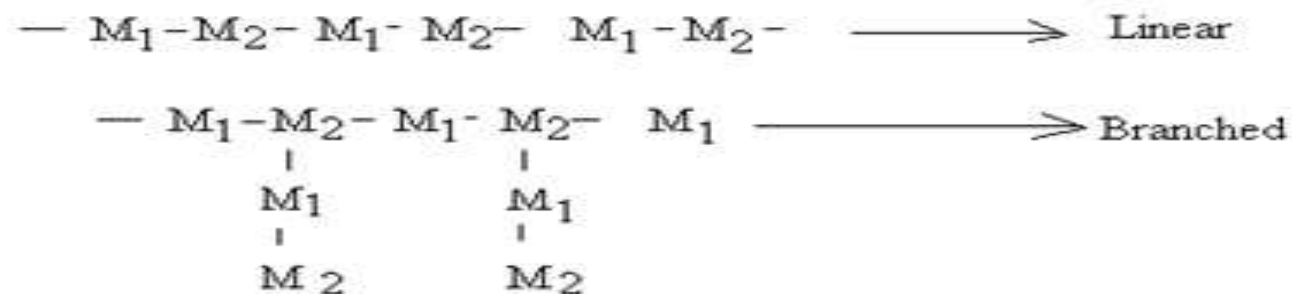
- **a) Homo polymer:** If a polymer consists of identical monomers, then that polymers are called homo polymers. They may be linear, branched (or) Cross – linked.
- Ex: PVC, Polythene, Teflon etc.....





Basic Concepts

- **b) Hetero polymers or Co-polymers:** If a polymer is composed of different types of monomers, then it is called Hetero / co – polymers. They may be generally **linear (or) Branched**.



(ii) Type of atoms present in back bone chain:

a) Homo chain polymer: If the main chain is made up of same species of atoms is called homo chain polymer.



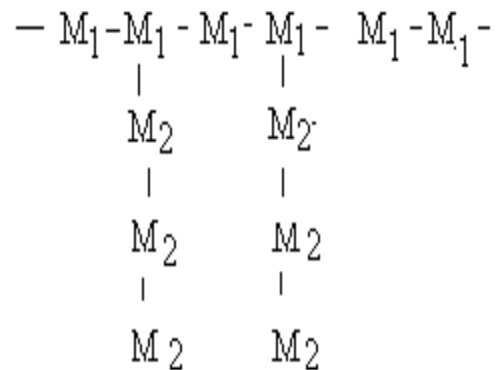
b) Hetero chain polymer: If main chain is composed of different atoms is said to be Hetero chain polymer





Basic Concepts

c) Graft co-polymers: These polymers are branched structures in which the monomer units on the branches and back bone differ.



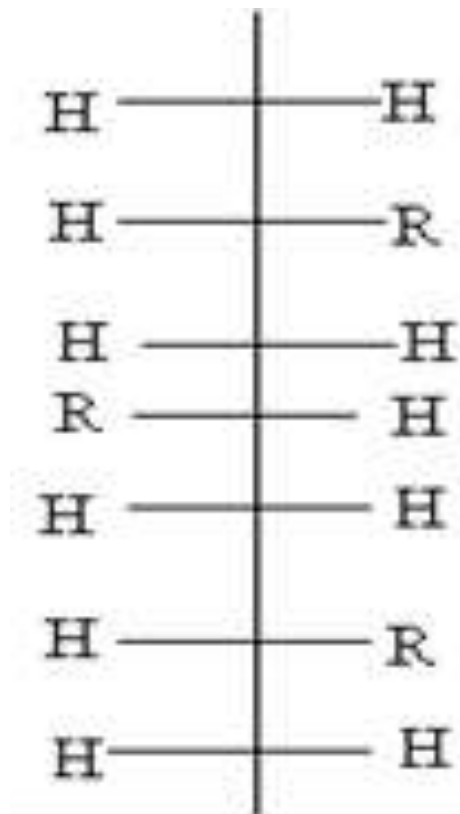
3) Tacticity: The orientation of functional groups in polymer is called as configuration. The difference in configuration of polymers because of the difference in arrangement of functional groups around main chain is called as Tacticity. Based on tacticity, polymers are of three types.

- 1. Isotactic Polymers
- 2. Syndiotactic Polymers
- 3. Atactic Polymers



Basic Concepts

c) **Syndiotactic:** If all the functional groups are arranged alternately with respect to the main chain, the polymer is called syndiotactic polymer.





Polymerization

- **Definition:** The process of combining of monomers to form polymers is called as polymerization (or) The formation of polymers from monomers is called as Polymerization.
- There are three types of polymerization. They are
 1. Addition Polymerization.
 2. Condensation Polymerization.
 3. Co-Polymerization.

1) Addition Polymerization:

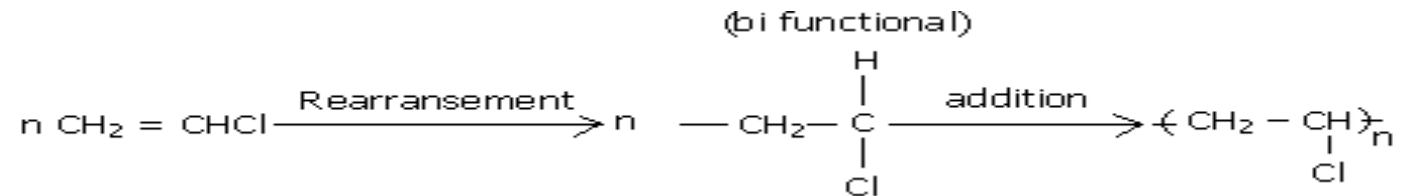
- This polymerization takes place between monomers that are **bifunctional** and contains **double bonds** in its structure.
- The process of binding of many bifunctional monomers **without elimination of byproducts by addition reactions** to form polymers is called as addition polymerization.
- This polymerization results in the formation of **linear** polymers.
- The produced polymer has **same chemical composition** as that of monomers.
- The molecular weight of polymer is an integral multiple of the mwt of monomer.



Polymerization

Examples:

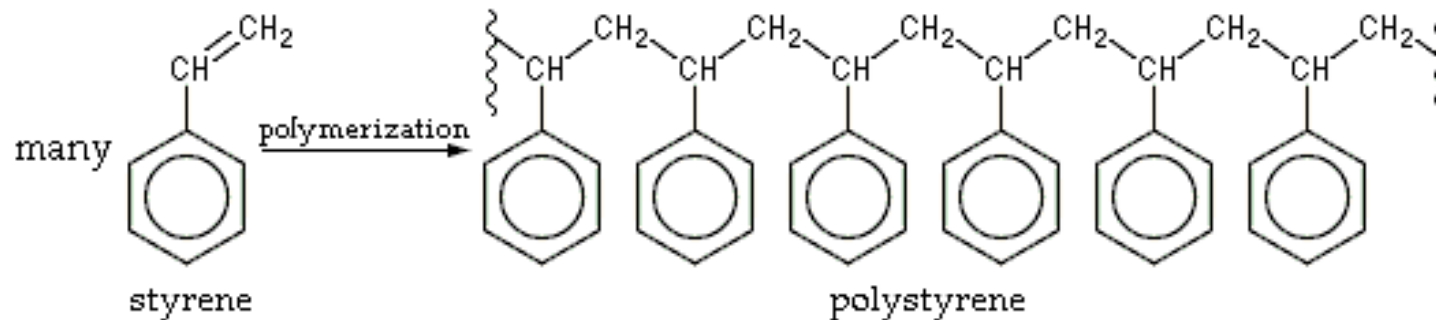
- 1. Formation of PVC:



- 2. Polymerization of ethylene:



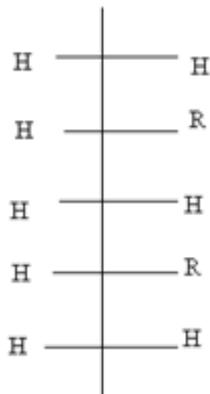
- 3. Polymerization of Styrene:



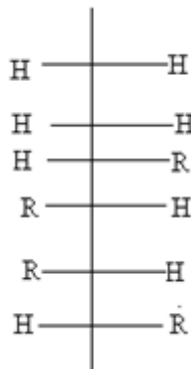


Basic Concepts

a) Isotactic: If all the functional groups are arranged on the same side of the chain, the polymer is called Isotactic polymer.



b) Atactic: If all the functional are arranged randomly around the main chain, the polymer is called Atactic polymer.





Polymerization

2) Condensation Polymerization:

- This is also called **Step-wise** polymerization.
- This occurs between monomers that contain **polar side groups**.
- A reaction occurring between the same (or) different polar groups containing monomers **with elimination of small molecules** like ammonia, water, HCl etc..... and forms **linear (or) Cross – linked polymers** is called Condensation Polymerization.
- The molecular weight of polymer is **not an integral multiple** of the molecular weight of monomer.
- The chemical composition of monomer and polymer are different.
- It results in the formation of **linear or cross linked polymers**.

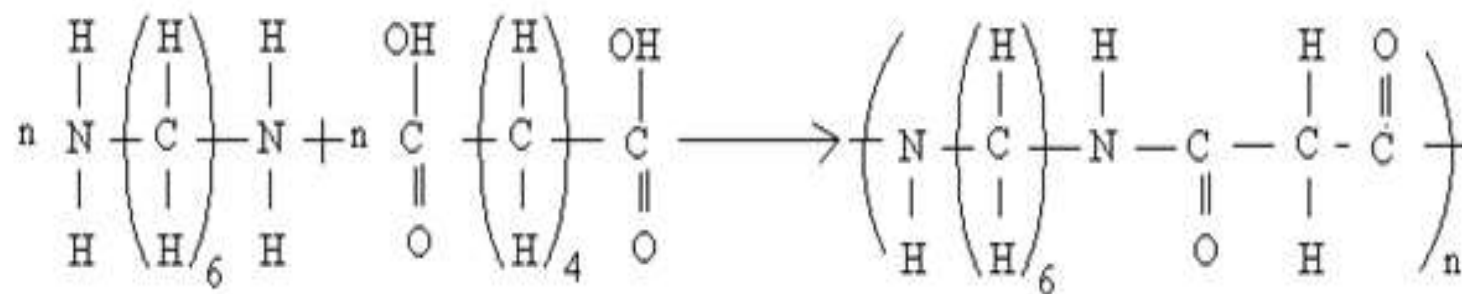


Polymerization

2) Condensation Polymerization:

Example:

- 1. Formation of Nylon-6,6:** Formed by the condensation of **Hexamethylenediamine** with **adipic acid** (Tetra methylene dicarboxylic acid).



- 2. Formation of Polyester:** Formed by the condensation between ethylene glycol and Terephthalic acid



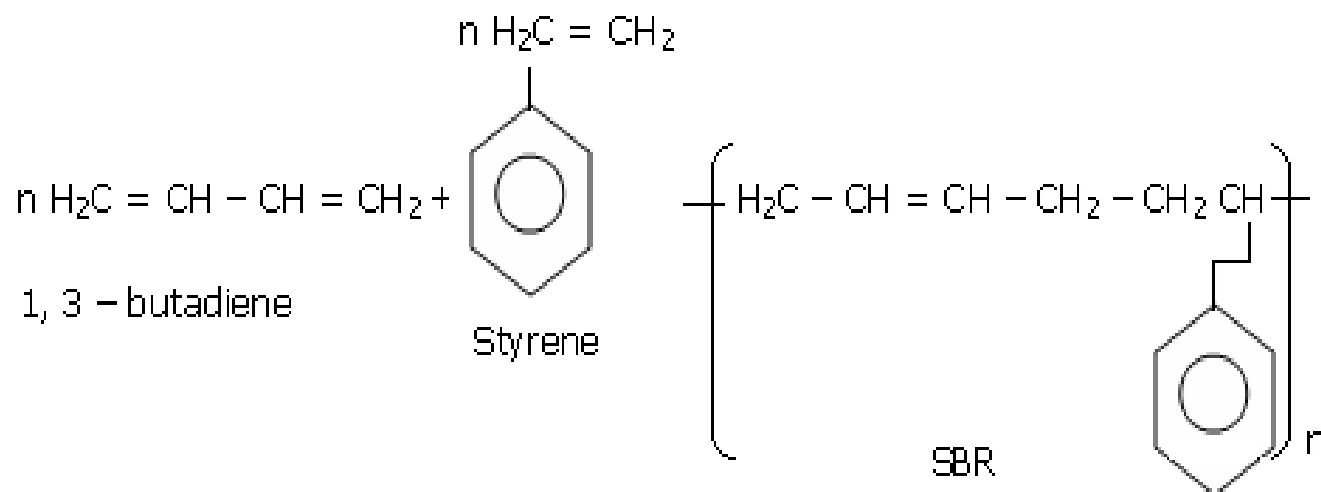


Polymerization

3) Co-polymerization:

- When two (or) more different types of monomers undergo simultaneous polymerization then it is called Co-Polymerization.
- The properties of co-polymers are different from those of individual monomers.
- The copolymers may be alternating, random, block and graft polymers.

Ex: Styrene butadiene rubber (SBR)





Plastics

Introduction:

- An organic substance with high molecular weight, which can be moulded in to any desired form when subjected to heat and pressure in the presence of a catalyst is called as plastic.

Advantages:

- Now a days plastics play a important role in daily life because of their certain unique properties.
 - Light in weight
 - Transparent
 - Low maintenance cost
 - Chemically inert
 - Corrosion resistance
 - Insect resistance
 - Easy transportability
 - Easy workability
 - Impermeable to water
 - High resistance to abrasion



Plastics

Disadvantages:

- Low heat resistance, so combustible
- High softness
- Poor ductility
- Major pollutant not degraded by soil

Uses:

- For Making many house hold articles
- For making furniture
- For making electric goods

Types of Plastics: Plastics are divided in to two types.

1. Thermo Plastics
2. Thermo setting Plastics



Plastics-PVC

Poly Vinyl Chloride (PVC):

- **Preparation:** Vinyl chloride is used as a monomer for the manufacture of polyvinyl chloride. Vinyl chloride is prepared by reacting acetylene with hydrogen chloride at 100-150°C in the presence of metal salt catalyst.



- PVC is prepared by heating a water-emulsion of vinyl chloride in presence of benzoyl Peroxide in an autoclave under pressure.



Properties:

- PVC is colorless and odorless.
- It is non-inflammable and chemically inert.
- It is soluble in chlorinated hydrocarbons like ethyl chloride, etc. and ketones.
- It has high resistance to light, inorganic acids, alkalis, and atmospheric oxygen.

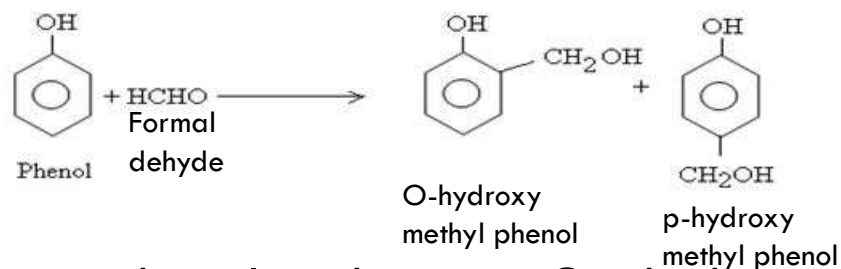
Uses:

- Plasticized PVC is used for making table cloths, rain coats, coatings for electric wire and cables, toilet articles, radio, T.V components, pipes, coupling valves, etc.
- Un-plasticized PVC or rigid PVC is used for making refrigerator components, cycle and motor cycle mudguards, tubes, pipes, etc.



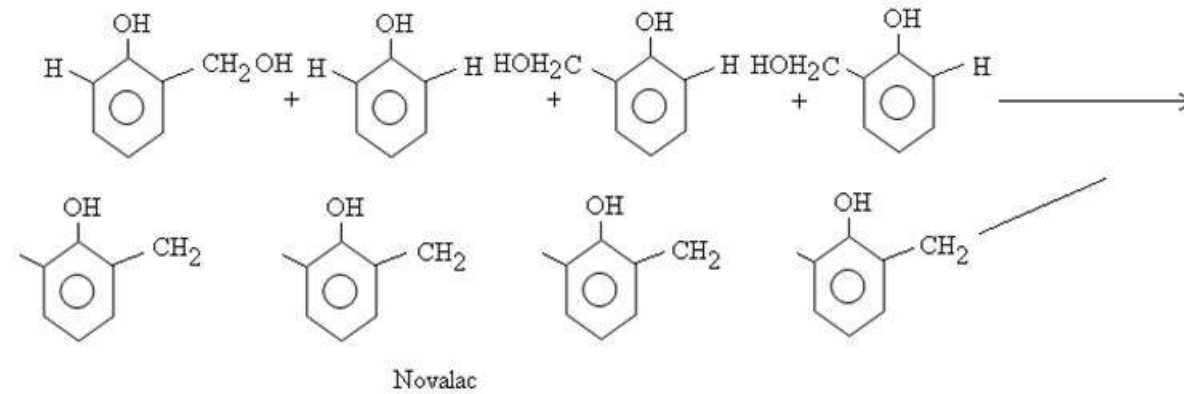
Plastics-BAKELITE

- Also called as- Phenol formaldehyde resin / phenolic resin / phenoplast.
- Bakelite is an important thermosetting plastic named after the scientist Bakeland, who synthesized this resin in the year 1909.
- It is prepared by the condensation/ stepwise polymerization of phenol with formaldehyde in the presence of an acid (or) alkali as a catalyst.
- This polymerization takes place in three steps:
- **Step I:** Phenol can condense with formaldehyde to produce O – hydroxy methyl phenol and P – hydroxy methyl phenol

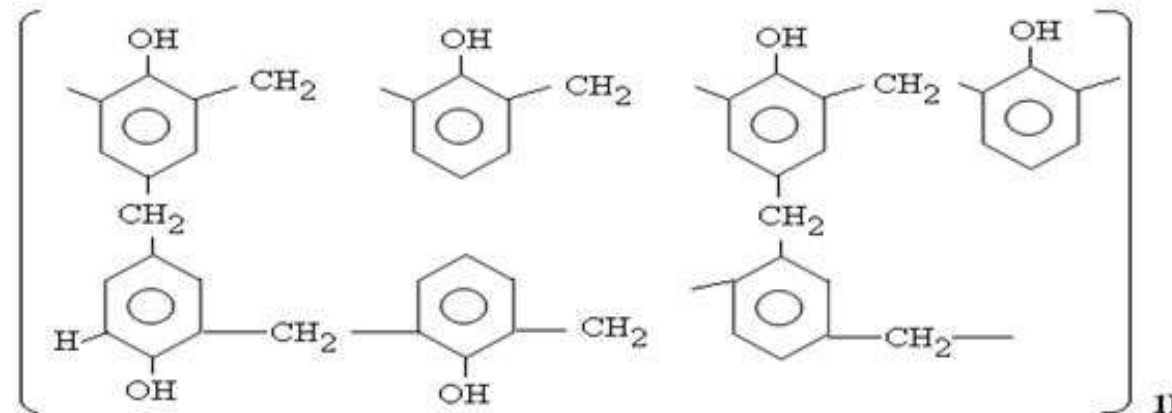


- **Step II:** condensation takes place between O – hydroxy methyl phenol and phenol to give linear polymer called Novalac.

Plastics-BAKELITE



- Step III:** During molding, Hexa methylene tetraamine $((\text{CH}_2)_6 \text{N}_4)$ is added, it produces formaldehyde and ammonia. Formaldehyde converts the soluble and fusible Novalac into a hard infusible and insoluble solid of cross-linked structure called Bakelite, whereas NH_3 neutralizes the acid.





Plastics-BAKELITE

Properties:

- Bakelites are rigid, hard, scratch resistant, infusible, water resistant, solid substance.
- Resistant to acids, salts and most organic solvents but attacked by alkali due to the presence of hydroxyl groups.
- Good electrical insulator

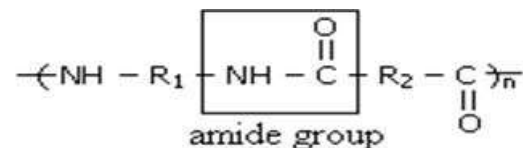
Applications:

- For making electric insulator parts like switches, plugs, holders, switch boards, heater etc.....
- For making moulded article like telephone parts, cabinets for radio and T.V.
- Used in paints and varnishes
- as adhesives for grinding and wheels.
- In the product of ion exchange resin
- For making bearings used in propeller shops, for paper industry and Rolling mills.



Plastics-Nylon-6,6

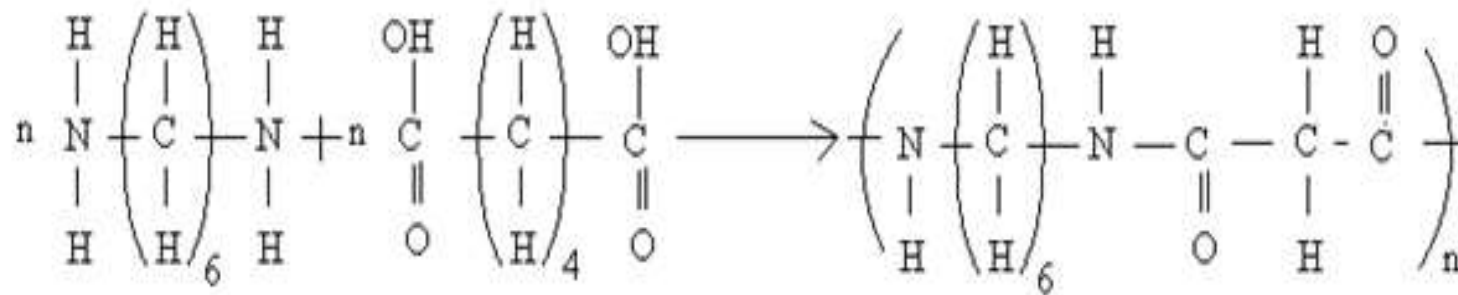
- Also called as- Poly Amid Resin
- Nylon is a poly amide resin consists of amide group produced by condensation polymerization of diamine with di-acid.



- The Nylon has been named on the basis of the number of carbon atoms in the monomer chain.

Ex: Nylon-6,6, Nylon-6,10, Nylon-6, Nylon-11 etc..... where the first number indicates that the number of carbon atoms in diamine and the second number indicates that number of carbon atoms in diacid.

- Nylon-6,6 is produced by the condensation polymerization of hexamethylene di-amine with adipic acid.





Plastics-BAKELITE

Properties:

- It show plastic and fiber property.
- Insoluble in common solvent and soluble in pharmic acid and phenol
- Posses high strength and high melting point (160 – 264⁰C)
- They absorb little moisture
- Possess resistance to environmental conditions and chemicals.
- They are good electrical insulators.

Applications:

- Nylon 6:6 is used as fiber for making socks, dresses, lady's hoses, carpets, under garments, airbags, ropes, conveyor belts etc.
- It is a light material so used to make parachutes.
- As it is water proof, it is used for making swimwear.
- It is resistant to water so it is used for making machine parts.



Thermoplastics & Thermosetting polymers

- Thermoplastics polymers: soften when heated and harden when cooled and vice versa
- Structure Example: linear, branched:
- Polyethylene, polystyrene, PVC, Poly (ethylene terephthalate)
- Thermosetting polymers: permanently hard (do not soften when heated)
- Made from network polymers: covalent bond resist motion at high temperature prevent.
- Epoxies, phenolics, and some polyester resins.



CONDUCTING POLYMERS

- Conducting polymers are of four types: 1) Intrinsically conducting 2) Doped conducting 3) Extrinsically conducting 4) Co-ordination conducting polymers
- Intrinsically conducting polymers (ICP) or conjugated Π -electrons conducting polymer is a polymer whose backbone or associated groups consist of delocalized electron-pair or residual charge. Such polymers essentially contain conjugated Π -electrons backbone which is responsible for electrical charge. In an electric field, conjugated Π -electrons of the polymer get excited, thereby can be transported through the solid polymeric material. Overlapping (of conjugated Π -electrons) over the entire backbone results in the formation of valence bands as well as conduction bands which extend over the entire polymer molecule. Presence of conjugated Π -electron in a polymer increases its conductivity to a larger extent.



CONDUCTING POLYMERS

- Important commercially produced conducting polymers : •
Polyacetylene polymers .e.g. poly-p-phenylene,
polyquinoline,polyphenylene-co-vinylene,poly-m-phenylene
sulphide ,etc.
- ii) With condensed aromatic rings ,e.g ployaniline,
polyanthrylene,polyphenanthrylene,etc.
- iii) With aromatic heteroaromatic and conjugated aliphatic
units,
e.g.polypyrrole,polythiophene,polyazomethine,polybutadienyle
ne ,etc. .



CONDUCTING POLYMERS

- B)n-doping--In this an intrinsically conducting polymer is treated with lewis base where oxidation takes place.

Common lewis acid are

Li,Na etc.

- $-\text{CH}=\text{CH}-\text{CH}=\text{CH}+\text{B}^{+} \rightarrow -\text{CH}=\text{CH}-\overset{\text{B}^{+}}{\text{C}}-\text{H}=\text{CH}$



Applications of Conducting Polymers

- 1. In rechargeable light weight batteries based on perchlorate doped polyacetylene Li system. These are 10 times stronger than conventional lead storage batteries
- 2. In wiring in aircrafts and aerospace component.
- 3. In transistors and diodes.
- 4. In electromagnetic screening materials
- 5. In photovoltaic devices.
- 6. In molecular wires and switches

UNIT-V

INSTRUMENTAL METHODS OF ANALYSIS

◆ Definition of Infrared Spectroscopy

The absorption of light, as it passes through a medium, varies linearly with the distance the light travels and with concentration of the absorbing medium. Where a is the absorbance, the Greek lower-case letter epsilon is a characteristic constant for each material at a given wavelength (known as the extinction coefficient or absorption coefficient), c is concentration, and l is the length of the light path, the absorption of light may be expressed by the simple equation $a = \epsilon \times c \times l$.



Infrared spectroscopy is the measurement of the wavelength and intensity of the absorption of mid-infrared light by a sample. Mid-infrared is energetic enough to excite molecular vibrations to higher energy levels. The wavelength of infrared absorption bands is characteristic of specific types of chemical bonds, and infrared spectroscopy finds its greatest utility for identification of organic and organometallic molecules. The high selectivity of the method makes the estimation of an analyte in a complex matrix possible.

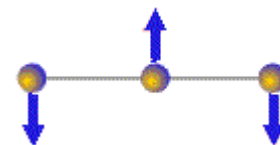
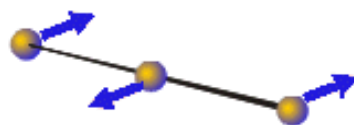
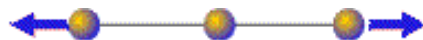


Theory of Infrared Absorption Spectroscopy

For a molecule to absorb IR, the vibrations or rotations within a molecule must cause a net change in the dipole moment of the molecule. The alternating electrical field of the radiation (remember that electromagnetic radiation consists of an oscillating electrical field and an oscillating magnetic field, perpendicular to each other) interacts with fluctuations in the dipole moment of the molecule.

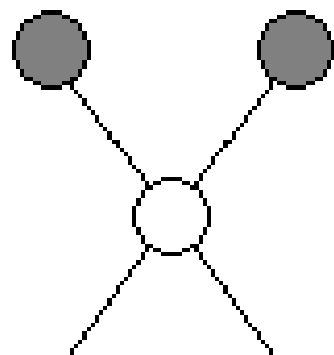
If the frequency of the radiation matches the vibrational frequency of the molecule then radiation will be absorbed, causing a change in the amplitude of molecular vibration

Stretching and Bending•

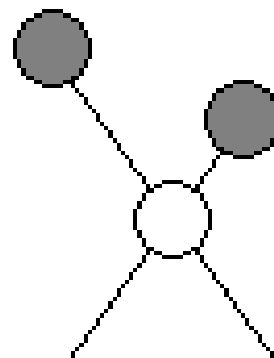


Stretching Vibrations

Stretching vibrations



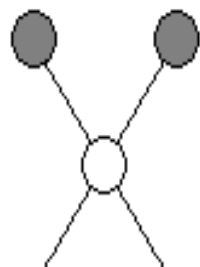
Symmetric



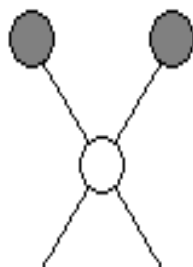
Asymmetric

Bending Vibrations

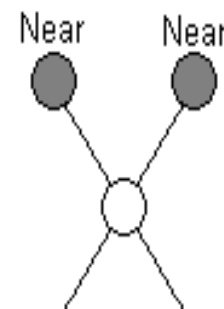
Bending vibrations



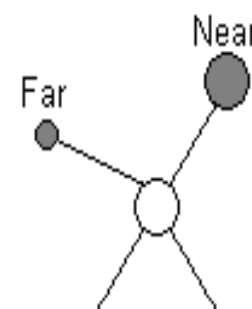
In-plane rocking



In-plane scissoring



Out-of-plane wagging



Out-of-plane twisting



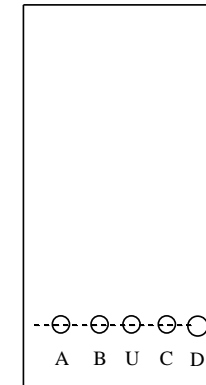
THIN LAYER CHROMATOGRAPHY

•Thin layer chromatography (TLC) is an important technique for identification and separation of mixtures of organic compounds. It is useful in:

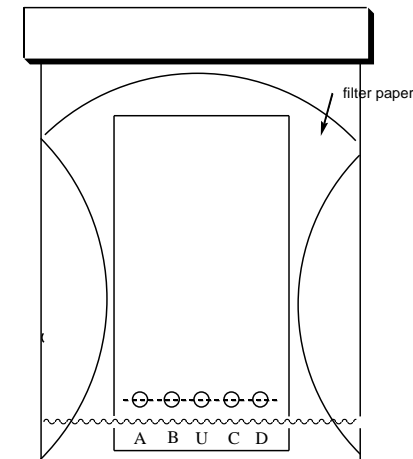
- Identification of components of a mixture (using appropriate standards)
 - following the course of a reaction,
 - analyzing fractions collected during purification,
 - analyzing the purity of a compound.
- In TLC, components of the mixture are partitioned between an adsorbent (the stationary phase, usually silica gel, SiO_2) and a solvent (the mobile phase) which flows through the adsorbent.

In TLC, a plastic, glass or aluminum sheet is coated with a thin layer of silica gel.

A very small amount of a solution of the substance to be analyzed is applied in a small spot with a capillary tube, ~1cm from the bottom of the TLC plate



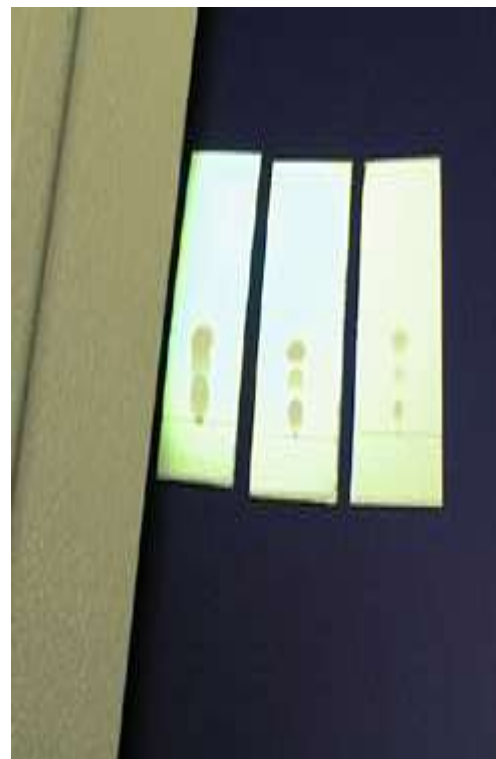
The TLC is developed in a chamber which contains the developing solvent (the mobile phase). A truncated filter paper placed in the chamber serves to saturate the chamber with mobile phase



Once the solvent is within ~1-2 cm of the top of the TLC sheet, the TLC is removed from the developing chamber and the farthest extent of the solvent (the *solvent front*) is marked with a pencil.

The solvent is allowed to evaporate from the TLC sheet in the hood.

The spots are visualized using a UV lamp.



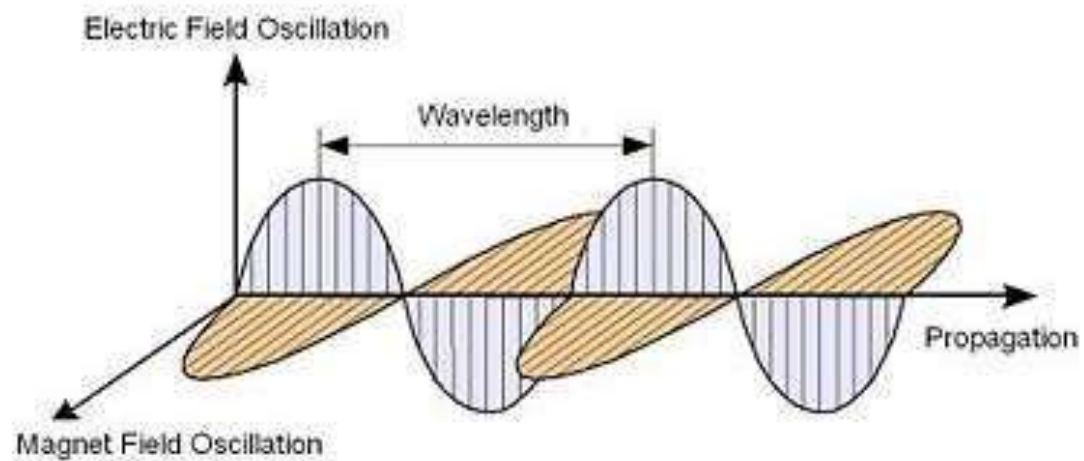


UV-VISIBLE SPECTROSCOPY

ELECTROMAGNETIC RADIATION

- Electromagnetic radiation is a type of energy that is transmitted through space at enormous velocities.
- Radiant energy has wave nature and being associated with electric as well as magnetic field, these radiations are called electromagnetic radiation.
- Electromagnetic radiation has its origin in atomic and molecular processes.
- The field may be represented as electric and magnetic vectors oscillating in mutually perpendicular planes.

Electromagnetic Radiation



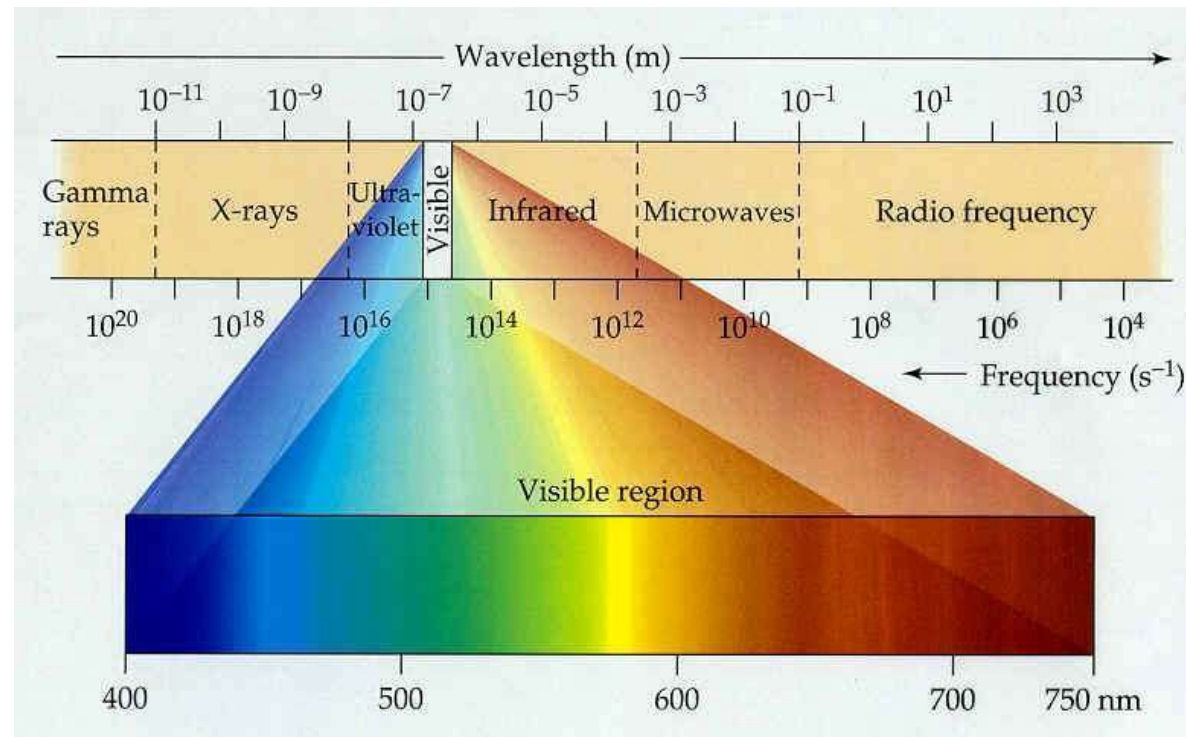


ELECTROMAGNETIC SPECTRUM

The arrangement obtained by arranging various types of electromagnetic waves or radiations in order of their increasing wavelegth or decreasing frequencies is called electromagnetic spectrum.

The electromagnetic spectrum is divided into a number of regions; these are artificial divisions in the sense that they have been defined solely as a result of differences in the instrumentation required for producing and detecting radiation of a given frequency range.

REGIONS OF ELECTROMAGNETIC SPECTRUM





SPECTROSCOPY

Spectroscopy is the measurement and interpretation of electromagnetic radiation absorbed or emitted when the molecules or atoms or ions of a sample moves from one energy state to another energy state

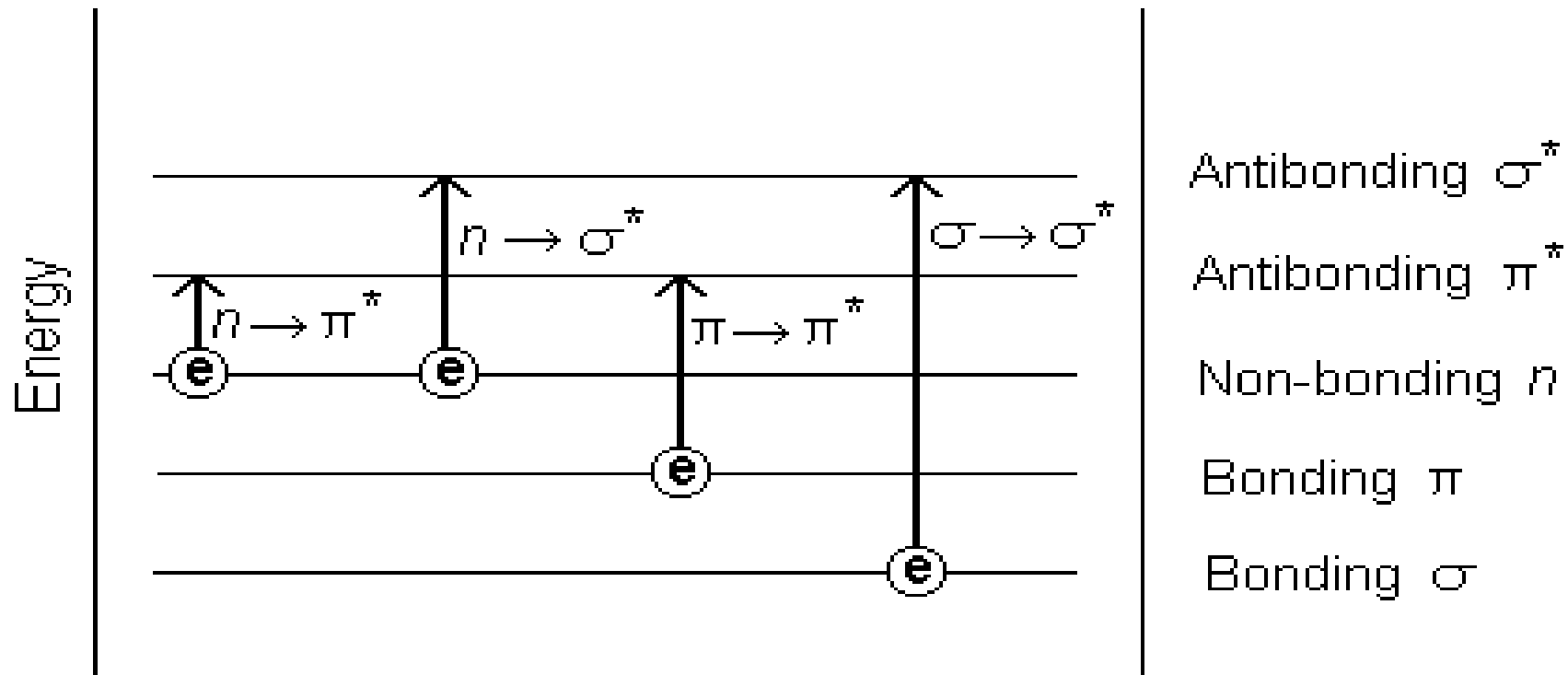


UV SPECTROSCOPY

- UV spectroscopy is concerned with the study of absorption of uv radiation which ranges from 200-400nm.
- Valence electrons absorb the energy thereby molecules undergoes transition from ground state to excited state.
- This absorption is characteristic and depends on the nature of electrons present.
- Types of electrons

σ	in saturated compounds
electrons:	in unsaturated compounds
π	in non bonded electrons
electrons:	
n	
electrons:	

ELECTRONIC TRANSITIONS





➤ **BEER'S LAW**

According to this law, when a beam of monochromatic radiation is passed through a solution of absorbing species, the intensity of beam of monochromatic light decreases exponentially with increase in concentration of absorbing species

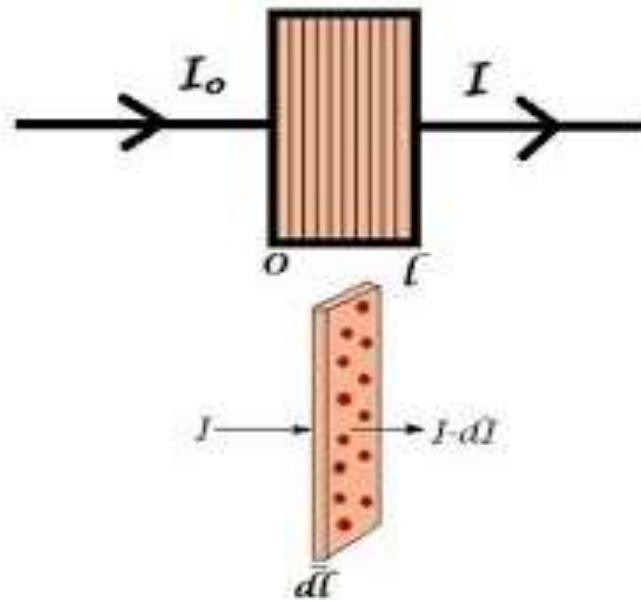
$$-dI/dc \propto l$$

➤ **LAMBERT'S LAW**

Lambert's law states that the rate of decrease of intensity of monochromatic light with the thickness of the medium is directly proportional to the intensity of incident light.

$$-dI/dt \propto C$$

BEER-LAMBERT'S LAW



$$-\frac{dI}{dl} \propto cI$$

$$-\frac{dI}{I} = kcdl$$

$$A = \epsilon cl$$

PH METER

- pH meter has two basic components: **the digital meter** (with a numeric display), and either **one or two probes** that we insert into the test solution.
- The electrode that does the most important job, is the **glass electrode**, having a silver based electrical wire suspended in a solution of hydrogen chloride, contained inside a thin bulb made from a special glass containing metal salts (typically compounds of sodium and calcium).
- The other electrode is called the **reference electrode** and has a silver chloride wire suspended in a solution of potassium chloride.

PH ELECTRODE

