Unit – I

ELECTROCHEMISTRY

Unit Syllabus

Electrodes and electrochemical cells.

Electrode potential, standard electrode potential, single electrode potential and its determination.

Types of electrodes – calomel, quinhydrone and glass electrode.

Nernst equation - determination of pH of a solution by using quinhydrone and glass electrode.

Electrochemical series and its applications.

Batteries – Primary (dry battery) and secondary batteries (Lead – acid storage battery and Lithium ion battery) and
next generation batteries

Electrochemical cells and its types. Electrode potential –origin – oxidation and reduction potent

INTRODUCTION

- Electrochemistry is a branch of chemistry.
- It deals with the chemical reactions produced by passing electric current through an electrolyte or production of electric current through a chemical reaction

Conductors

Conductor is a material which allows free flow of electricity.

Example*: All metals, graphite, fused salts, solution of electrolytes*

Non-conductors (Insulators)

Insulators are materials which donot conduct electrical current

Example: *Wood, plastics, most of non metals.*

Types of conductors

(i) Metallic conductors : The solid material, which conduct electric current due to the movement of electron from one end to the other end without producing chemical reaction.

Examples : *All metals & graphite.*

(ii) Electrolytic conductors : They conduct electric current due to the movement of ions from one electrode to another electrode in solution or in fused state. This process is accompanied by a chemical reaction.

Examples : *Metal ions dissolved solvent*

Cell Terminology

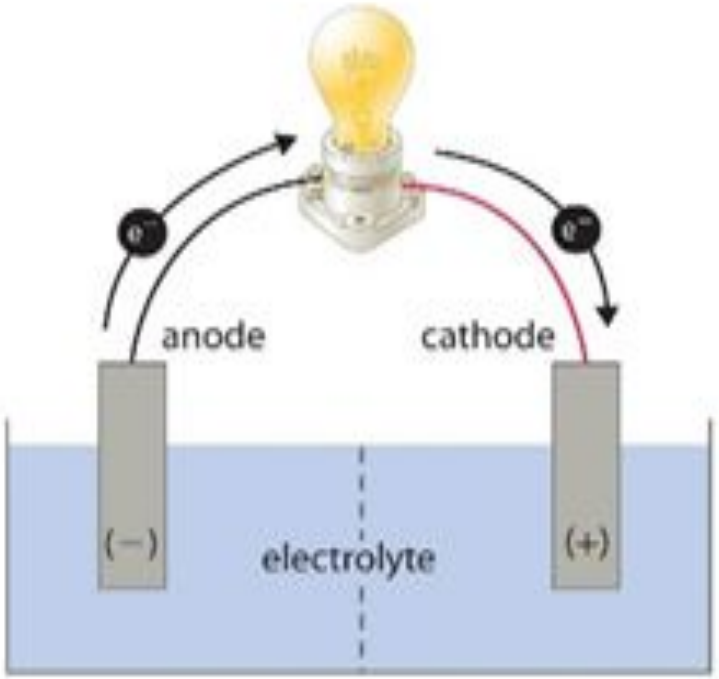
1. **Current:** Flow of electrons through a conductor.
2. **Electrode**: Electrode is a material (rod, bar, strip) which conducts electrons.
3. **Anode:** Electrode at which oxidation occurs.
4. **Cathode:** Electrode at which reduction occurs.
5. **Electrolyte:** Water soluble substance forming ions in solution and conducts electric current

6. **Anode compartment:** Compartment of the cell in which the oxidation half reaction occurs. It contains the anode
7. **Cathode compartment:** Compartment of the cell in which the reduction half reaction occurs. It contains the cathode
8. **Half–cell:** It is the part of a cell, which contains an electrode dipped in an electrolyte. If oxidation occurs in this half-cell, then it is called the oxidation half cell. If reduction occurs at the cell, it is called the reduction half-cell.
9. **Cell:** Device consisting of two half cell. The two half cells are connected through one wire.
10. **Salt bridge:** Contains solutions of a salt (KNO_3 or NH_4NO_3) that literally serve as a bridge to completed the circuit, maintain electro neutrality of electrolyte and minimize. For precise measurement of potential a salt bridge is used.

TYPES OF CELLS

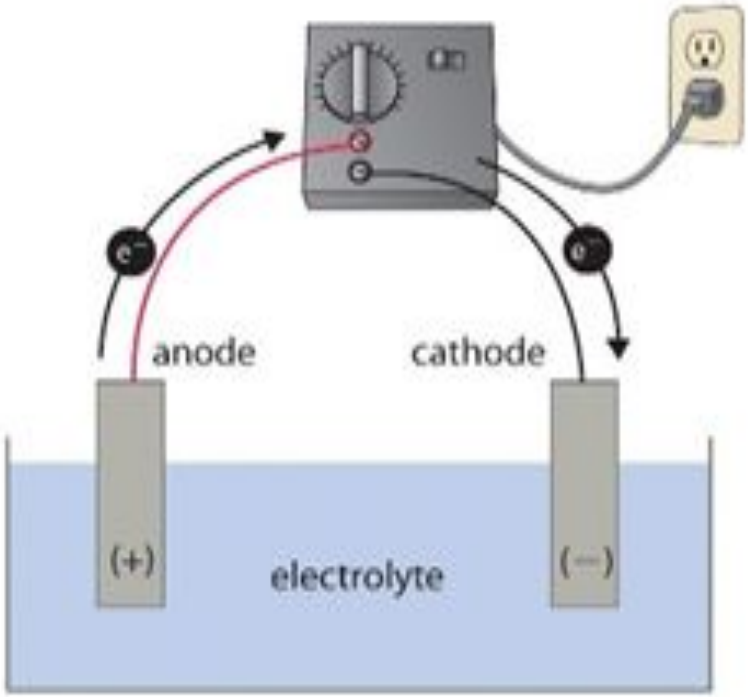
A cell is a device consisting of two half cells. Each half cell consists of an electrode dipped in an electrolyte solution. The two half cells are connected through one wire.

S.No	Electrolytic cell	Electrochemical cell
1	Electrical energy converted to chemical energy. Example: Electrolysis, electroplating.	Chemical energy converted to electrical energy. Example: Daniel Cell
2	Anode carries +ve charge.	Anode carries –ve charge
3	Cathode carries – ve charge.	Cathode carries +ve charge.
4	Electrons are supplied to the cell from an external source.	Electrons are drawn from the cell
5	Amount of electricity is measured by coulometer	Emf produced is measured by potentiometer
6	Extent of chemical change is governed by Faraday's laws.	Emf of the cell depends on the concentration of the electrolyte and the nature of the electrode.



GALVANIC CELL

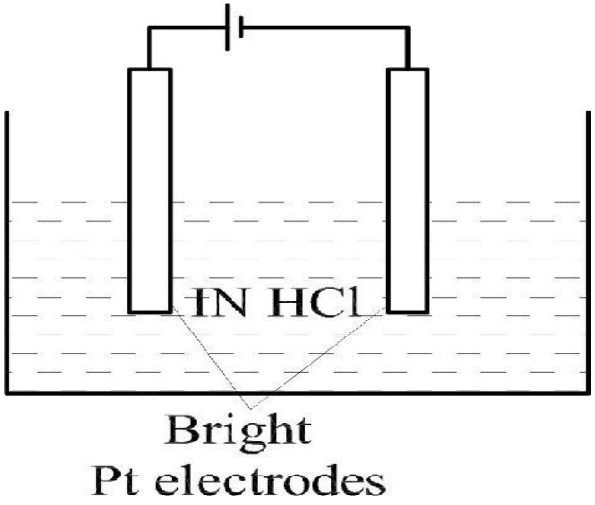
Energy released by spontaneous redox reaction is converted to electrical energy.



ELECTROLYTIC CELL

Electrical energy is used to drive nonspontaneous redox reaction.

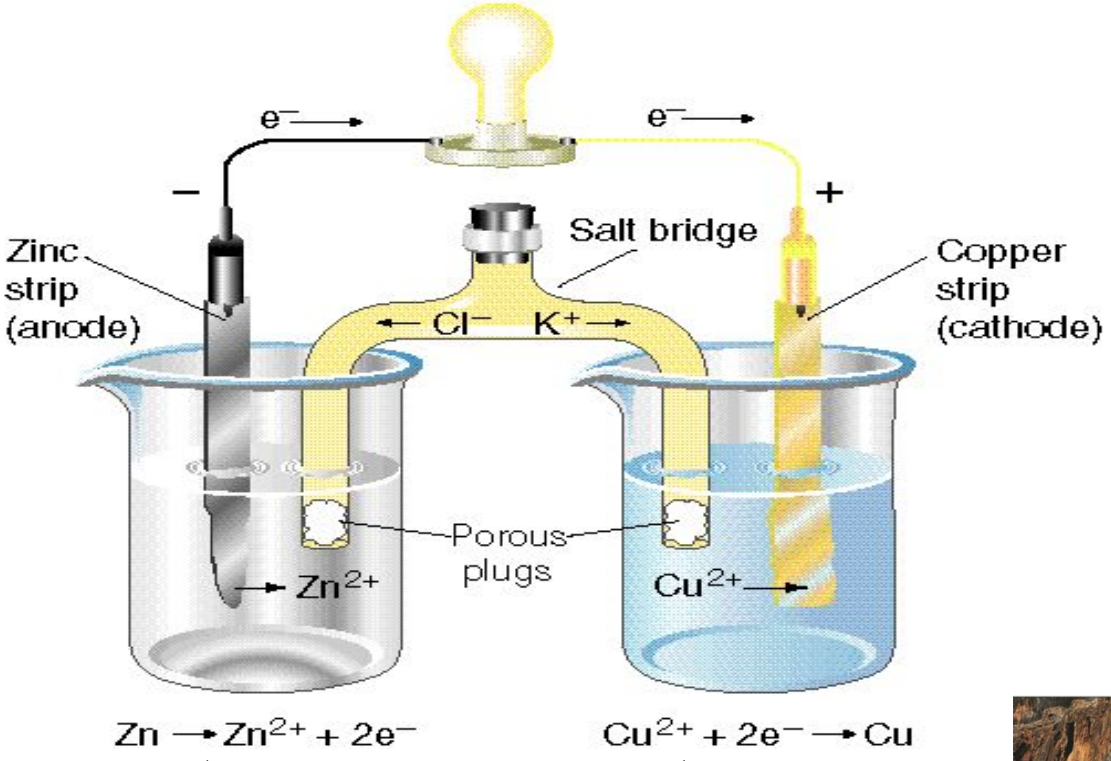
Electrolytic cell - *Example :* *Electrolysis of HCl.*



At anode : $2Cl^- \rightarrow Cl_2 + 2e$ **(oxidation)**

At cathode : $2H^+ + 2e^- \rightarrow H_2$ **(reduction)**

Electrochemical cell - *Example : Daniel cell*

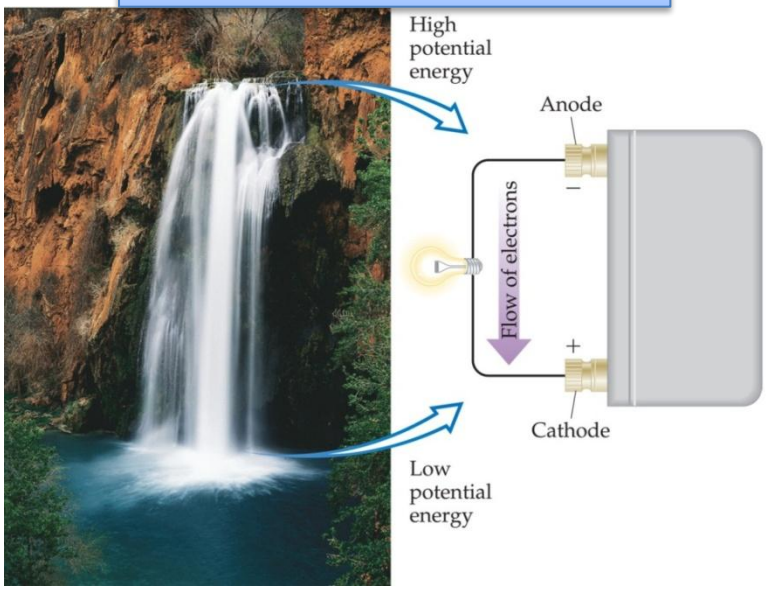


$Zn \rightarrow Zn^{2+} + 2e^-$ (at anode)

$Cu^{2+} + 2e^- \rightarrow Cu$ (at cathode)

$Cu^{2+} + Zn \rightarrow Zn^{2+} + Cu$
(net cell reaction)

Electromotive Force (emf)



Components of a Cell

- **At anode :** Oxidation of Zn to Zn^{2+} place with the liberation of electrons.

- **At cathode :** Reduction of Cu^{2+} to Cu place by the acceptance of electrons. The electrons liberated in oxidation reaction flow through external wire and are consumed by the copper ions at the cathode.

- **Salt bridge :** It consists of a U-tube containing a saturated solution of KCl or $(NH_4)_2NO_3$ agar–agar gel. It connects the two half cells.

Functions

i. It eliminates liquid junction potential.

ii. It provides a path for the flow of electrons between two half cells.

Representation (Cell diagram)

1. Galvanic cell consists of two electrodes, anode and cathode
2. Anode is written on the LHS and cathode on RHS
3. The anode is written with the metal first and then the electrolyte which are separated by a vertical line ***Examples :*** Zn/Zn^{2+} (or) $Zn/ZnSO_4$
4. The cathode is written with the electrolyte first and then the metal.

Examples : Cu^{2+}/Cu (or) $CuSO_4/Cu$

5. The two half cells are separated by a salt bridge, which is indicated by two vertical lines.

Cell is represented as $Zn/ZnSO_4$ (1M) //) $CuSO_4$ (1M) /Cu

ELECTRODE POTENTIAL ORIGIN OF ELECTRODE POTENTIAL

When a metal (M) is placed in a solution of its own salt (M^{n+}) one of the two processes are possible

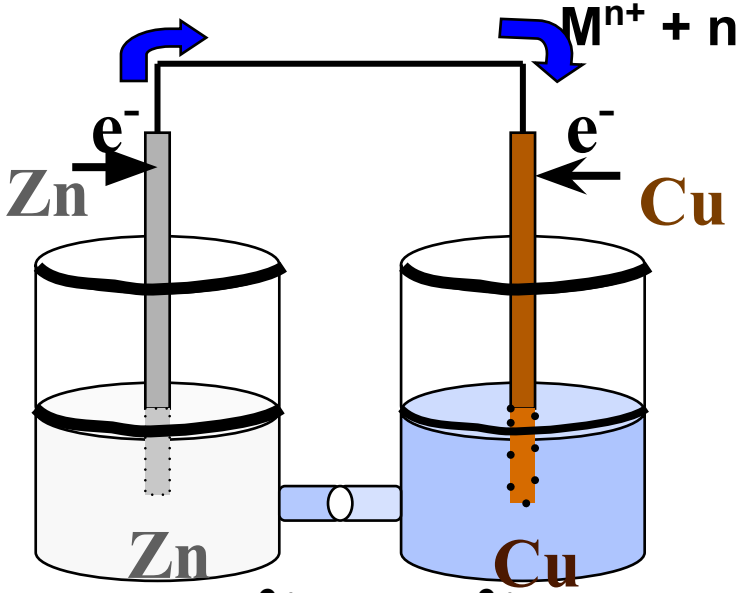
(i) Metal atoms go into solution in the form of ions.

$M \rightarrow M^{n+} + ne^-$ (Oxidation)

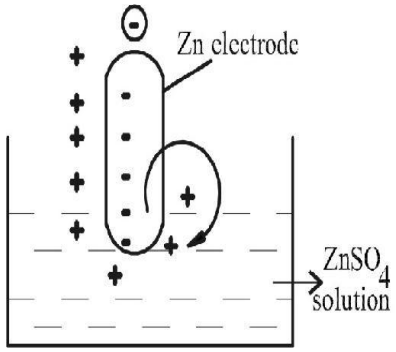
Example :

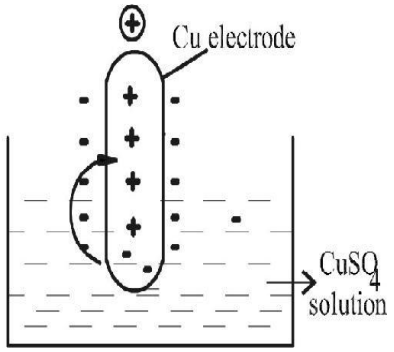
(ii) Metal ions from solution may deposit on the metal

$M^{n+} + ne^- \rightarrow M$ (reduction)



Electrode Potential





At equilibrium, the potential difference becomes a constant value *which is known as the electrode potential of the metal. Thus the tendency of the* electrode to lose electrons is called *Oxidation potential and tendency of an* electrode to gain electrons is called *reduction potential.*

Single electrode potential (E) : It is the tendency of a metallic electrode to lose or gain electrons when it is in contact with a solution of its own salt.

Standard electrode potential (E^o) : It is the tendency of a metallic electrode to lose or gain electrons when it is in contact with a solution of its own salt of 1M concentration at 25^{o}C.

Types of Electrodes

Reference Electrode:

A reference electrode is that electrode whose potential is known and remain constant.

e.g. Saturated calomel electrode (E_{SCE} = 0.242)

Indicator Electrode:

An indicator electrode is that electrode whose potential depends on the activity of ions being titrated or estimated.

e.g. To carry out acid-base potentiometric titration Hydrogen gas. Quinhydrone electrode and glass electrodes are used as indicator electrode.

Measurement Of Single Electrode Potential and its applications.

MEASUREMENT OF SINGLE ELECTRODE POTENTIAL

It is impossible to evaluate the absolute value of a single electrode potential. *Using reference electrode.*

Reference (or) Standard electrode

The potential of unknown electrode can be measured by coupling it with another electrode, called reference electrode whose electrode potential is already known.

Examples : *Standard hydrogen electrode, Standard calomel electrodes.*

Standard hydrogen electrode (SHE)

It is also called as Primary reference electrode because. The potential developed by this electrode is arbitrarily fixed as zero

Construction

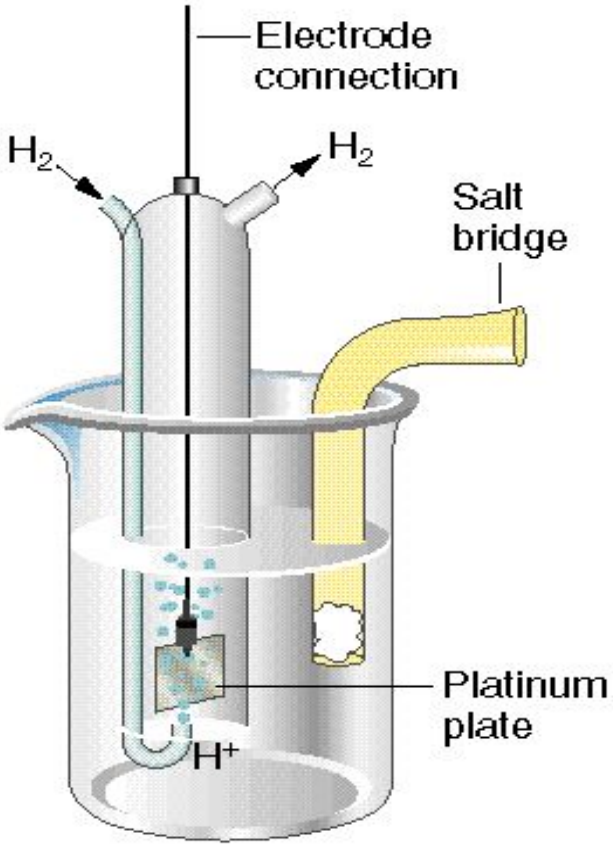
- It consists of a platinum foil that is connected to a platinum wire sealed in a glass tube.

- The Pt foil is dipped in 1M HCl. H_2 gas of 1 atm pressure is passed through the side of glass tube.

$$H_2(g) \rightarrow 2H + 2e$$

- The standard electrode potential of SHE is arbitrarily fix as zero

$Pt , H_2 (1atm) / H^+(1M) ; E^0 = 0V$



Limitations (or) drawbacks of SHE

- It is difficult to get pure hydrogen gas.
- The pressure of hydrogen is to be kept 1 atm all the time.
- It is difficult to set up and transport.
- Hydrogen gas reduces many ions like Ag+ and affects compounds of Hg, Ag etc
- A large volume of test solution is required.
- It cannot be used in solutions of redox systems, the solution may poison platinum surface.

Saturated calomel electrode (SCE) (Secondary reference electrode)

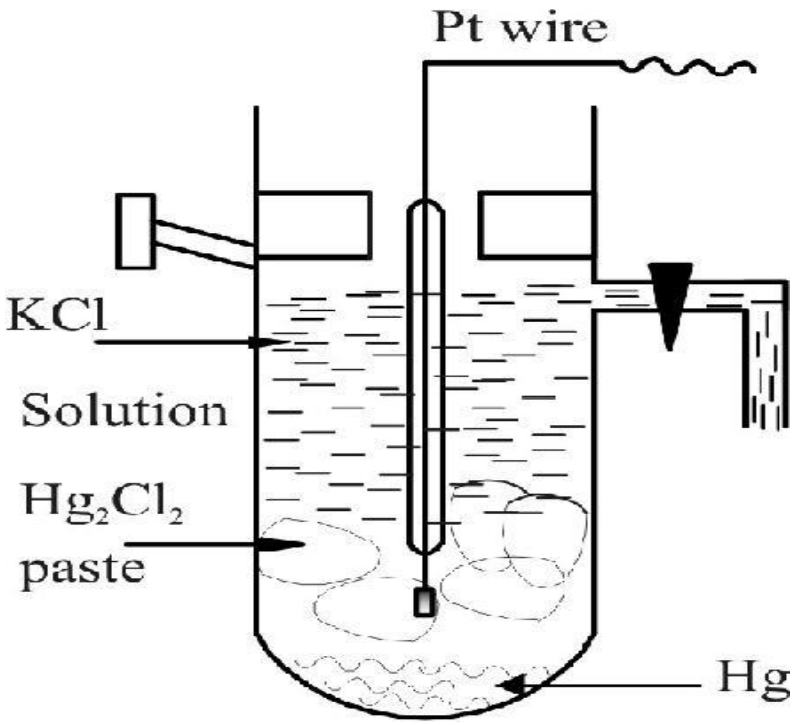
- Glass tube containing pure Hg at the bottom over which mercurous chloride is placed. The remaining portion of the tube is filled with saturated solution of KCl.

- The bottom of the tube is sealed with a platinum wire. The side tube is used for making electrical contact with a salt bridge.

Hg | Hg_2 Cl_2(s) | KCl (Saturated, Solution) E^o = 0.2422V

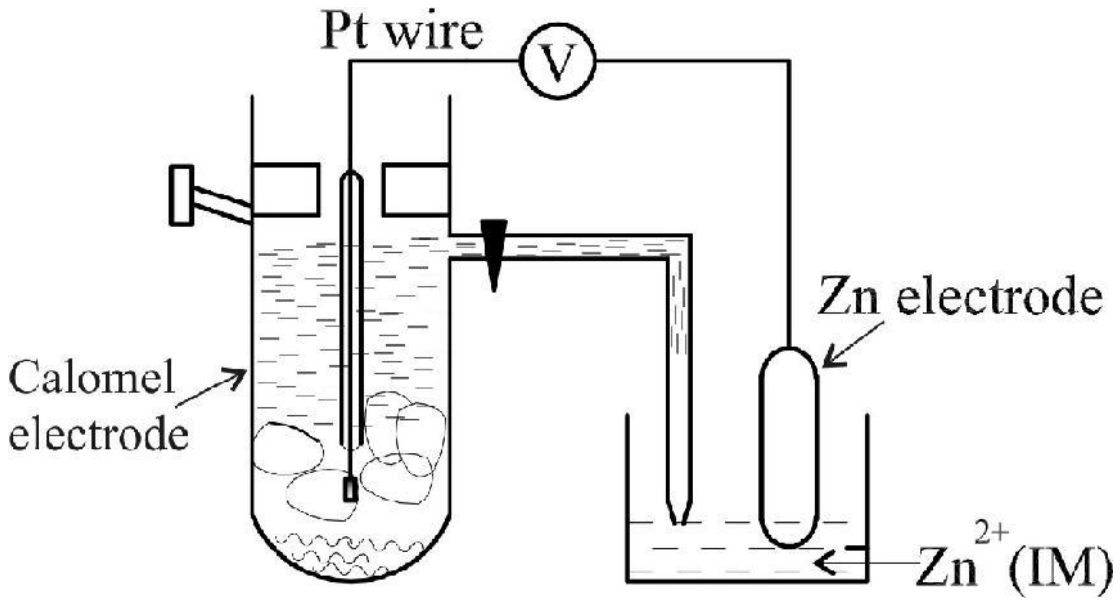
$$2Hg(l) + 2Cl \rightarrow Hg_2Cl_2(s) + 2e$$

$$HgCl_2 + 2e \rightarrow 2Hg + Cl$$



KCl	(v)
0.1N	0.3335 V
1 N	0.281 V
Saturated	0.2422 V

Measurement of single electrode potential using a reference electrode (saturated calomel electrode)



$$Hg_2Cl_2(s) \rightarrow 2Hg_{(\ )} \quad 2Cl$$

The emf of the cell is measured using a potentiometer.

The value of E_{cell} = 1.0025 volt.

$$E = E^{o}_{right\text{-----}} E^{o}_{left}$$

$$E = E^{o}_{cal} \text{ --- } E^{o}_{Zn}$$

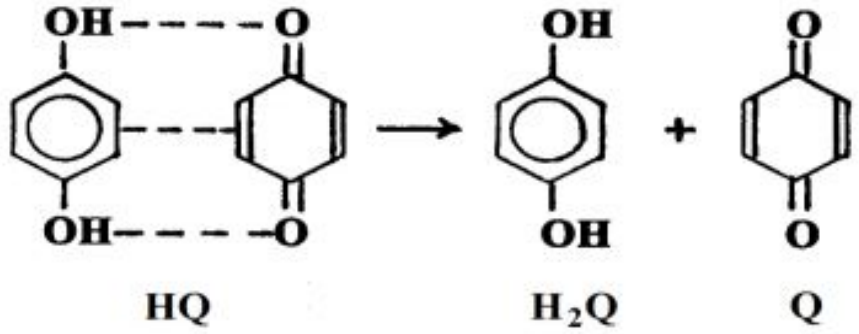
$$E^{o}_{Zn} = E^{o}_{cal} \text{ ---- } E^{o}_{cell}$$

$$= +0.2422 - 1.0025 = -0.7603 \text{ V}$$

Quinhydrone electrode

- The quinhydrone electrode **is a type of redox electrode** which can be used to **measure the hydrogen ion concentration** (pH) of a solution.
- The electrode consists of an **inert metal electrode (usually a platinum wire) in contact with quinhydrone crystals** and a water-based solution.
- Quinhydrone is slightly soluble in water, dissolving to **form a mixture of two substances, quinone and hydroquinone**
- Each one of the two substances **can easily be oxidised or reduced to the other.** The potential at the inert electrode depends on the ratio of the activity of two substances. Quinone + $2H^+ + 2e^-$ ⇋ Hydroquinone

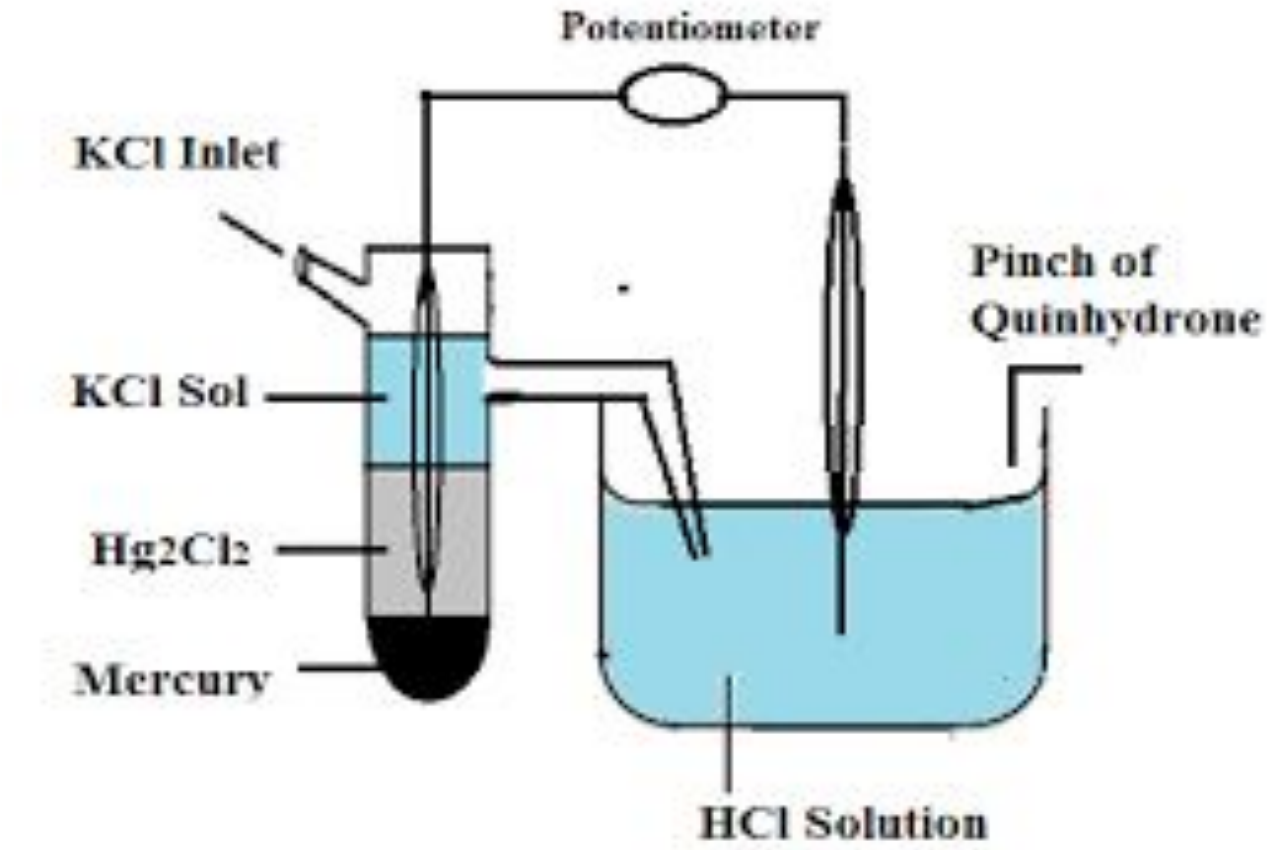
The electrode reaction is:



$C_6H_4O_2 + 2H^+ + 2e^- \Leftrightarrow C_6H_4(OH)_2$

Quinone (Q) Hydroquinone (H_2Q)

Quinhydrone electrode in a cell.



From the Nernst equation: $E = E^o + \frac{2.303RT}{2F} \log \frac{[Q][H^+]^2}{[QH_2]}$ (or)

$$E = E^o - \frac{2.303RT}{2F} \log \frac{[QH_2]}{[Q]\,[H^+]^2}$$

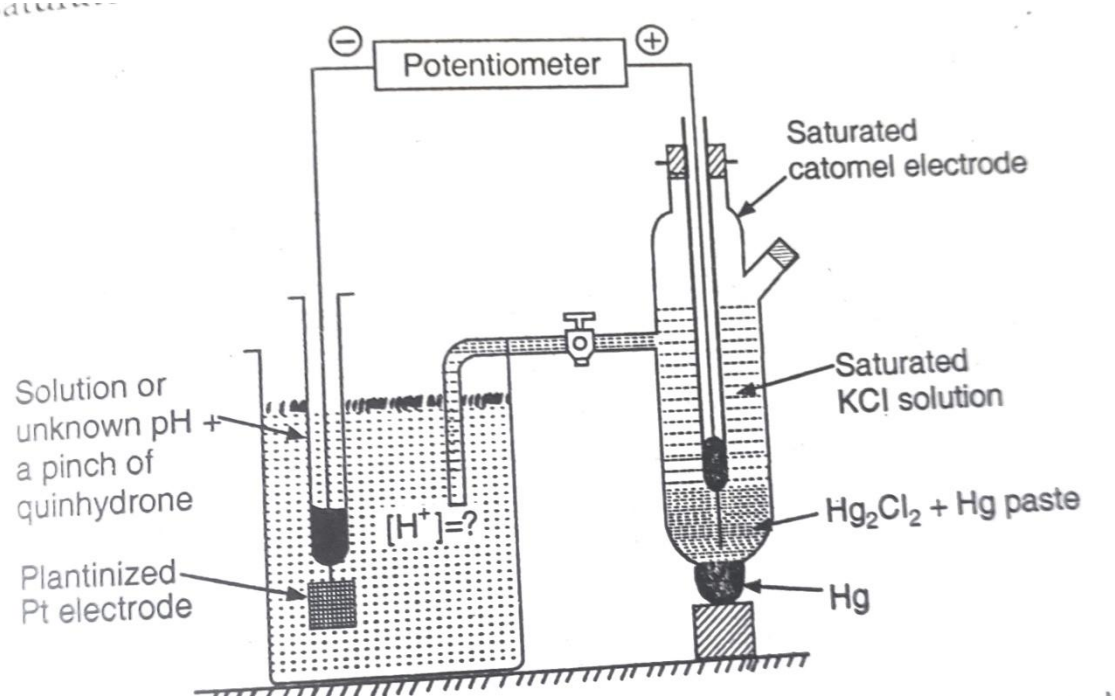
If quinone and hydroquinone are taken in equimolar concentrations, then $[Q] = [QH_2]$ then the above reaction reduces to

$$E = E^o - \frac{2.303RT}{2F} \log \frac{1}{[H^+]^2} = E^o - \frac{2.303RT}{F} \log \frac{1}{[H^+]}$$

$EQ = E^0 - 0.0592v\ pH = 0.6994v - 0.0592v\ pH$

Construction and working

QH electrode can very easily be set up by **adding a pinch of quinhydrone powder to the experimental solution** with stirring until the solution is saturated. Then **indicator electrode usually a bright platinum** is inserted in it. For determining the pH value, **this half cell is combined with saturated calomel electrode** and the emf of the cell is determine potentiometrically.



The complete cell may be represented as

$^{-}$Pt | H_2Q, Q, H^+(unknown) | | KCl(sat), Hg_2Cl_2(s) | Hg^+

Ecell = E calomel – E QH

Ecell = 0.2422v – 0.6994v - 0.0592v pH

$$\mathbf{pH = \frac{0.6994v - 0.2422v + Ecell}{0.0592v}}$$

Merits and Demerits of the electrode:

Merits:

i. Electrode is easy to set up.
ii. It is also easy to handle.
iii. It can be functioning satisfactorily also in highly acidic solution.
iv. It is used to measure the pH of aqueous and non-aqueous solution.

Demerits:

i. This electrode is functioning only in the pH range of 1 to 8
ii. With the solution of pH greater than 8, the activity ratio is no longer remain equal to 1.
iii. It cannot be functioning in presence of oxidising and reducing agents that can react rapidly with either hydroquinone or quinone.

Glass electrode

When two solutions of **different pH values** are separated by a thin glass membrane, there **develops a difference of potential** between the surfaces of the membrane. The potential value developed is **proportional to the difference in pH** of the test solution.

The **glass membrane functions as an ion exchange resin** and an equilibrium is set up between the **Na^+ ions of the glass and H^+ ions in the solution**.

For a particular type of glass the potential difference varies with H^+ ion concentration, and is given by the expression

- $E_G = E^o_G + 0.0591 \log [H^+]$
- $E_G = E^o_G - 0.0591\ pH$

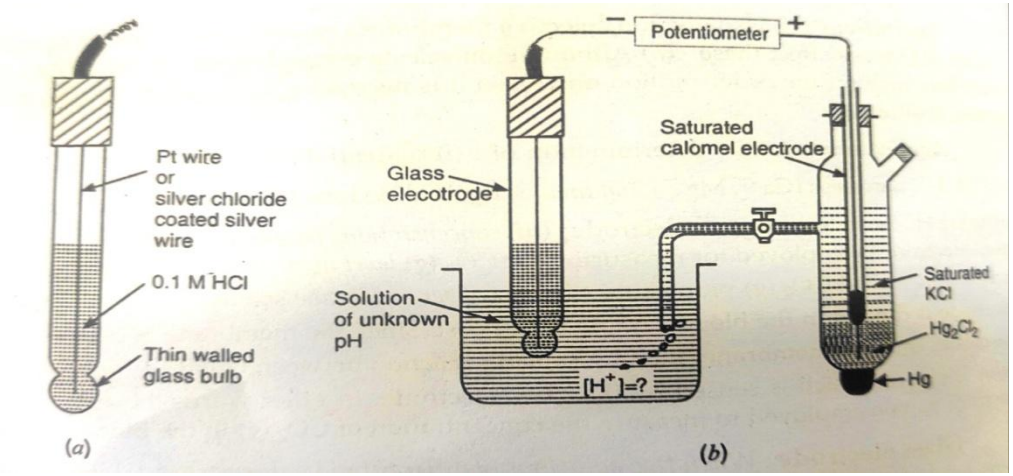
Glass electrode.

- Construction

The glass electrode assembly consists of a **thin glass bulb filled with 0.1 N HCl** and a **silver wire coated with silver chloride** immersed in it.

The Ag/AgCl electrode here acts as the internal reference electrode. The glass electrode is represented as

$^{-}$Ag | AgCl(s) | 0.1 M HCl | glass. Or Pt.0.1MHCl|Glass^{+}



To carry out the **determination of pH** of a solution, **the glass electrode is connected with a saturated calomel electrode**. The emf of the cell is

Glass electrode.

The cell is therefore represented as;

SCE ||Ag, AgCl | HCl (0.1 N) | Glass

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

$$pH = \frac{0.2422v - Ecell - E^{0}G}{0.0592v}$$

The E^{0}_{G} value of a glass electrode can be determined by using a solution of known pH

Advantages of Glass electrode

i) To determine pH of any solution

ii) Small quantity of solution is sufficient for determination

iii) Used even in the presence of metallic ions and poisons

iv) Equilibrium is easily reached

Merits and Demerits of the electrode:

Merits:

i. It provides a measure of pH in the pH range of 1 – 9.

ii. Using a pH meter, pH of the solution can be directly read.

iii. The electrode can be used in all aqueous solutions.

iv. Electrode is not affected by oxidizing and reducing agents or by any organic compound.

v. pH can be determined even for small volume of solution.

Demerits:

i. The electrode cannot function in highly acidic or alkaline medium

ii. It cannot produce proper response with pH > 9 or <0.5.

iii. It cannot function in non-aqueous medium.

iv. It needs standardisation every time before the use.

ELECTROCHEMICAL SERIES (OR) EMF SERIES

Various metals (electrodes) are arranged in the order of their increasing values of standard reduction potential on the hydrogen scale.

Electrode	Electrode reaction	E°, volts	Nature
Li^+/Li	$Li^+ + e \rightleftharpoons Li$	− 3.01	Anodic ↑
Mg^{2+}/Mg	$Mg^{2+} + 2e \rightleftharpoons Mg$	− 2.37	
Pb^{2+}/Pb	$Pb^{2+} + 2e \rightleftharpoons Pb$	−1.12	
Zn^{2+}/Zn	$Zn^{2+} + 2e \rightleftharpoons Zn$	− 0.76	
Fe^{2+}/Fe	$Fe^{2+} + 2e \rightleftharpoons Fe$	-0.44	
Sn^{2+}/Sn	$Sn^{2+} + 2e \rightleftharpoons Sn$	− 0.136	
H^+/H_2	$2H^+ + 2e \rightleftharpoons H_2$	0.00	Pt-reference
Cu^{2+}/Cu	$Cu^{2+} + 2e \rightleftharpoons Cu$	+ 0.34	↓
Ag^+/Ag	$Ag^+ + e \rightleftharpoons Ag$	+ 0.80	
Au^+/Au	$Au^+ + e \rightleftharpoons Au$	+ 1.50	
$½F_2/F^-$	$½ F_2 + e \rightleftharpoons F^-$	+ 2.87	Cathodic

Significance of emf series (or) Application of electrochemical series

- ***Calculation of Standard emf of a Cell :***

We can calculate the standard emf of a cell, if the standard electrode potential values are known ($\mathbf{E_{cell} = E_{RHE} - E_{LHE}}$)

- ***Relative ease of oxidation or reduction***

(a) Fluorine has higher +ve value of standard reduction potential (+2.87V) and shows higher tendency for reduction.

(b) Lithium has highest – ve value (–3.02V) and shows higher tendency towards oxidation.

- ***Displacement of one element by the other***

  Metals with a lower reduction potential will displace metals with a higher reduction potential from their salt solution (Copper will displace silver from its solution).

  Example :

  Zn(-0.76V) will displace copper (+0.34V) from its solution

  $Zn + CuSO_4 \rightarrow ZnSO_4 + Cu$

- ***Determination of equilibrium constant (K) for a reaction***

  Standard electrode potentials are used to determine the equilibrium constants as follows: **$G^o = \ln K \quad 2.303\ RT \log K$**

$$\log K = \frac{G^0}{2.303\ RT} = \frac{nFE^0}{2.303\ RT} [G^0 nFE^0]$$

- ***Hydrogen displacement behavior***

Metals with negative reduction potential (metals placed above H_2) in emf series will displace hydrogen from dilute acids solutions.

Example: Zn (-0.76 V) will displace H_2 from dilute acids whereas, silver (0.8) cannot

- **$Zn + H_2SO_4 \rightarrow ZnSO_4 + H_2$**
- **$Ag + H_2SO_4 \rightarrow$ No reaction**

- ***Predicting the spontaneity of redox reactions***

If E^o of a cell is positive the reaction is spontaneous.

If E^o of a cell is negative the reaction is not feasible.

NERNST EQUATION FOR ELECTRODE POTENTIAL

Consider the following redox reaction

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

For such a redox reversible reaction, the free energy change (ΔG) and its equilibrium constant (K) are inter related as

$$\Delta G = -RT \ln K + RT \ln \frac{[\text{Product}]}{[\text{Reactant}]}$$

$$= \Delta G^\circ + RT \ln \frac{[\text{Product}]}{[\text{Reactant}]} \qquad \ldots\ldots\ldots (1)$$

where,

ΔG° = Standard free energy change

The above equation (1) is known as ***Van't Hoff isotherm.***

The decrease in free energy ($-\Delta G$) in the above reaction will produce electrical energy. In the cell, if the reaction involves transfer of 'n' number of electrons, then '*n*' faraday of electricity will flow. If E is the emf of the cell, then the total electrical energy (nEF) produced in the cell is

$$-\Delta G = nEF$$

(or)

$$-\Delta G^\circ = nE^\circ F \qquad \ldots\ldots\ (2)$$

where,

$-\Delta G$ = decrease in free energy change.

(or) $-\Delta G^\circ$ = decrease in standard free energy change.

Comparing equation 1 and 2, it becomes

$$-nEF = -nE^\circ F + RT \ln \frac{[M]}{[M^{n+}]}. \qquad \text{.....(3)}$$

Dividing the above equation (3) by $-nF$

[∵ the activity of solid metal [M] = 1]

$$E = E^\circ - \frac{RT}{nF} \ln \frac{1}{[M^{n+}]}$$

In general, $E = E^\circ - \frac{RT}{nF} \ln \frac{[\text{Product}]}{[\text{Reactant}]}$

(or)

$$E = E^\circ + \frac{RT}{nF} \ln [M^{n+}]$$

When, R = 8.314 J/K/mole; F = 96500 coulombs ; T = 298 K (25°C), the above equation becomes

$$\mathbf{E = E^{\circ}_{red} + \frac{0.0591}{n} \log [\, M^{n+} \,]} \qquad \text{.....(5)}$$

In general, $E = E^{\circ}_{red} + \frac{0.0591}{n} \log C$

Similarly for oxidation potential

$$\mathbf{E = E^{o}_{oxi} - \frac{0.0591}{n} \log [M^{n+}]} \qquad \text{..... (6)}$$

The above equation 5&6 are known as "Nernst equation for single electrode potential".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BATTERIES


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- Battery is an array of cells connected in series and / or parallel to produce the desired voltage / current output.
- A cell is made up of two electrodes- anode and cathode.
- Each cell / electrode is associated with some charge transfer process called cell / electrode reaction.
- A cell is a device, which converts chemical energy into electrical energy and vice versa.
- Galvanic cell is a device that produces electrical energy from chemical energy
- Electrolytic cells convert electrical energy to chemical energy.

Cells

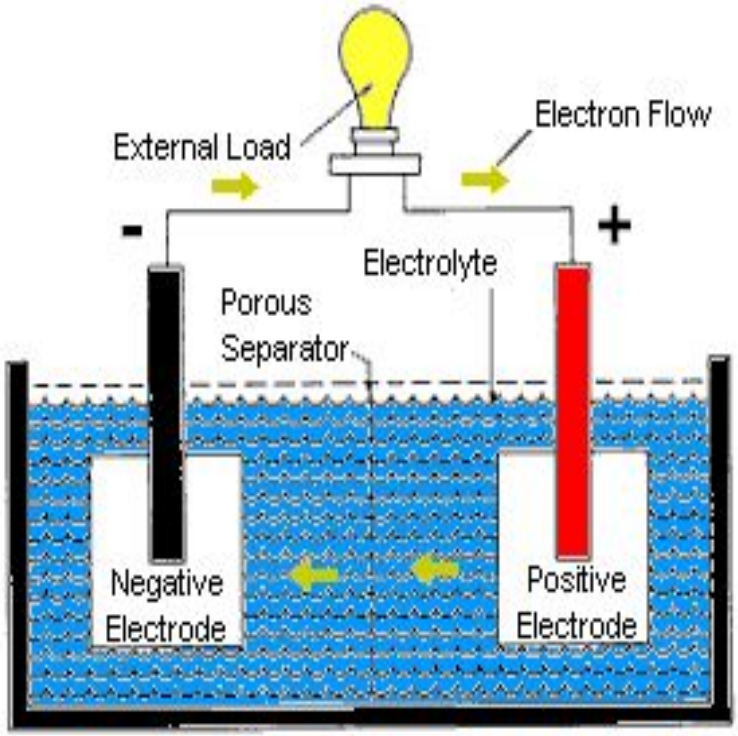
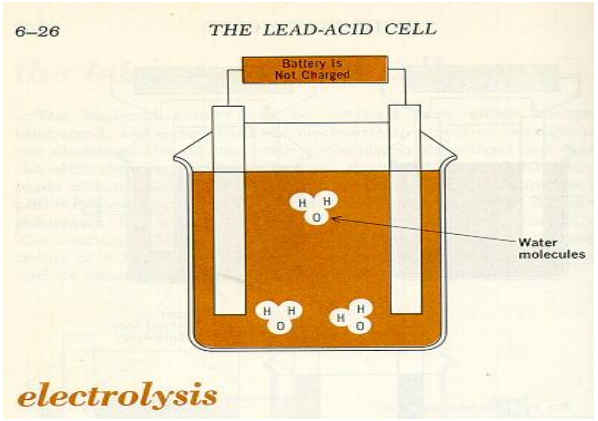
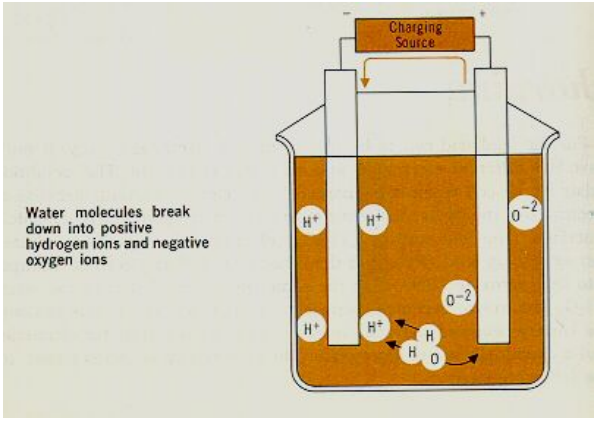


Figure 1 - Components of a Battery Cell (Discharge Circuit)

- Positive electrode
- Negative electrode
- Electrolyte
- Separator

Electrolysis





- The producing of chemical changes by passage of an electric current through an electrolyte.

Types of Batteries

1. Primary or non-rechargeable.
2. Secondary or rechargeable batteries.
3. Flow battery

- The cell reactions for secondary batteries are somewhat **reversible** in nature while that of a primary battery is irreversible.

- Every battery system is characteristic of its anode and cathode active materials.

- Secondary batteries - the cell reaction can be made to proceed in either direction by withdrawing or supplying current to the battery system.

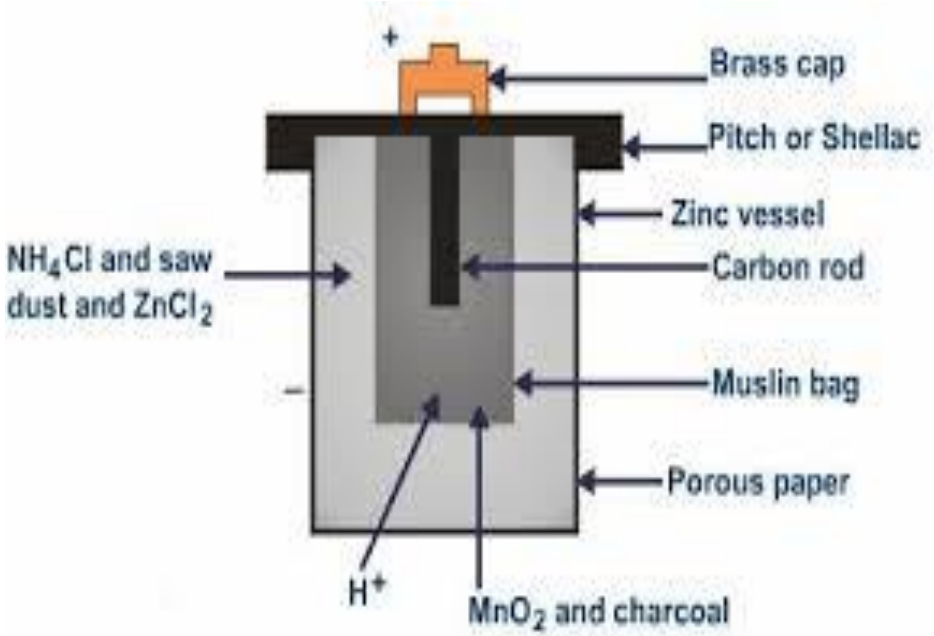
- The current withdrawing process constitutes the discharging process and the current supplying process, as charging process.

DRY CELL

Uses of an electrolytic paste.

- The electrolytic paste reacts with the electrodes to produce a negative charge on one electrode and a positive charge on the other.

- The difference of potential between the two electrodes is the output voltage.



Dry cell

Standard Zinc Carbon Batteries

- Chemistry

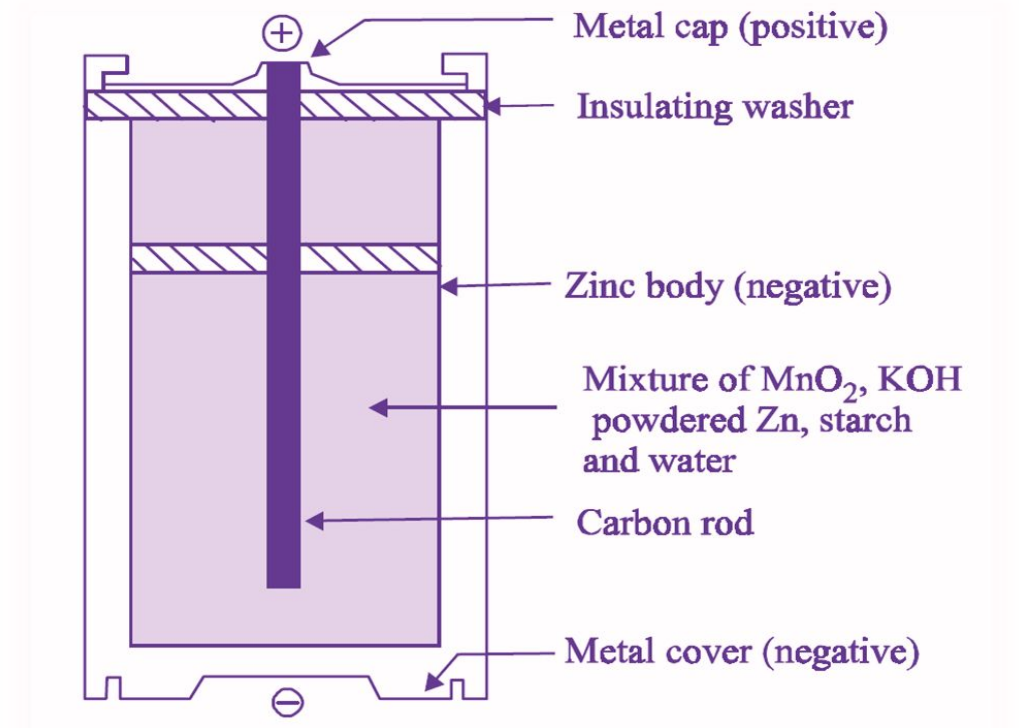
  Zinc (-), manganese dioxide (+)

  Zinc, ammonium chloride aqueous electrolyte

- Features
  - \+ Inexpensive, widely available
  - – Inefficient at high current drain
  - – Poor discharge curve (sloping)
  - – Poor performance at low temperatures

Alkaline batteries

- Improved form of dry cell.
- In this battery, zinc in powdered form is mixed with KOH to get a gel.
- Graphite rod is surrounded by a paste containing MnO_2.
- The outside body is made of zinc.



The cell reactions

- **Anode:**

$$Zn(s) + 2OH^-(aq) \rightarrow Zn(OH)_2(s) + 2e^-$$

- **Cathode:**

$$2\,MnO_2(s) + H_2O(l) + 2e^- \rightarrow Mn_2O_3(s) + 2OH^-(aq)$$

- **Net reaction:**

$$Zn(s) + 2\,MnO_2(s) + H_2O(l) \rightarrow Zn(OH)_2(s) + Mn_2O_3(s)$$

- ---

Advantages of alkaline battery over dry battery

1. Zinc does not dissolve as readily in a basic medium

2. The alkaline battery maintains better its voltage as the current is drawn from it

3. The life a alkaline battery is longer than dry cell, since there is no corrosion of Zn.

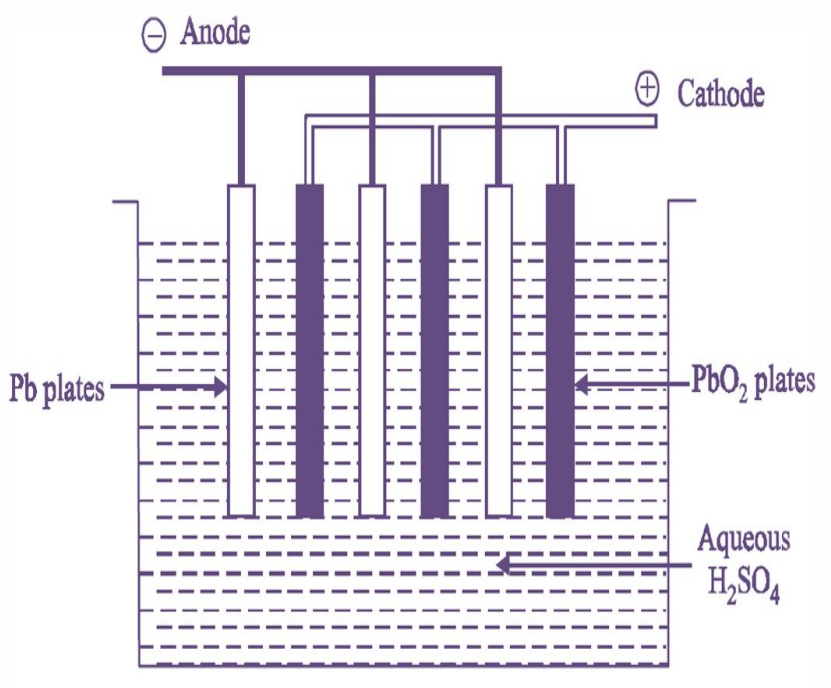
Uses of alkaline battery.

Alkaline batteries find used in camera exposure controls, calculators, watches etc.

Lead-Acid Battery

- Positive terminal or cathode –

  grid of lead-antimony alloy coated with lead dioxide.
- Negative terminal or anode -spongy lead
- Electrolyte- sulphuric acid



Anode : $Pb \rightarrow Pb^{2+} + 2\,e^-$

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

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

Cathode : $PbO_2 + 4\,H^+ + 2e^- \rightarrow Pb^{2+} + 2\,H_2O$

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

$$PbO_2 + 4\,H^+ + SO_4^{2-} + 2e^- \rightarrow PbSO_4 + 2\,H_2O$$

Overall cell reaction:

$$PbO_2 + Pb + 4\,H^+ + SO_4^{2-} + 2e^- \underset{\text{ch}}{\overset{\text{Dch}}{\rightleftharpoons}} 2\,PbSO_4 + 2\,H_2O$$

Uses:

1.SLI (Starting, lighting and ignition purposes) battery

2. Potable power source for remote areas, mountain regions etc.

3. Standby power source / Uninterrupted Power Supply (UPS)

Secondary Alkaline storage batteries:

These batteries use 20-25 % KOH as electrolyte.

- *Examples of this type of batteries are*

1. Nickel-iron (Edison cells),
2. Nickel-cadmium, nickel-hydrogen,
3. Nickel-metal hydride,
4. Silver-zinc etc.

Nickel-Cadmium(NICAD) battery

Example for rechargeable alkaline battery

- *They are more versatile than lead-acid batteries in various aspects.*
- *During charging and discharging, no loss of products and no gas evolution occur at the active electrodes.*
- *They posses low internal resistance , long shelf life without and good cycle life.*

Construction

Anode : ***C****admium as a mixture of metal oxide and /or hydroxide*

Cathode: *Nickel(III) oxide hydroxide (NiO(OH))*

Electrolyte: *KOH*

Anode

$$Cd(s) + 2OH^-(aq) \longrightarrow Cd(OH)_2(s) + 2e^-$$

Cathode

$$2NiO(OH)(s) + 2H_2O(l) + 2e^- \longrightarrow 2Ni(OH)_2(s) + 2OH^-(aq)$$

Cell reaction

$$2\ NiO(OH)\ (s) + Cd\ (s) + 2\ H_2O\ (l) \longrightarrow Cd\ (OH)_2 + 2\ Ni(OH)_2\ (s)$$

Cell representation:

$$Cd\ /\ Cd\ (OH)_2\ //\ KOH\ /\ NiO(OH)\ /\ Ni$$

Cell Voltage : 1.4 V

Advantages and uses of NiCad battery

1. Used in the sealed version for high current applications such as power tools and applications requiring high cycle life, such as computer power supply.

2. Large, sealed Ni - Cd cells are used in space applications, which require excellent system reliability and high cycle life.

3. Sintered Ni - Cd cells are used for standby power and for starting aircrafts.

4. Pocket type Ni - Cd cells are used for starting diesel engines and for emergency lighting.

LITHIUM BATTERIES

- Cells with lithium anodes are called Lithium batteries.
- Lithium primary cells can be broadly classified into

1.Primary cells with solid cathodes: Ex: Li / MnO_2 Cell and

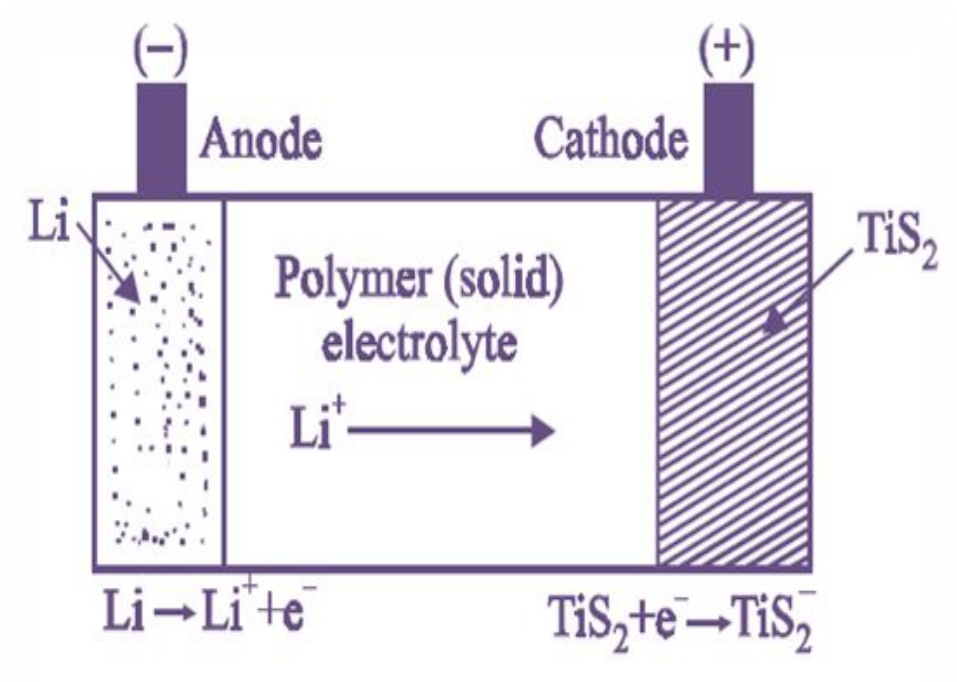
2.Primary cells with liquid cathode: Ex: Li –SO_2 , Lithium-Thionyl chloride Cell

(Secondary) Rechargeable Lithium batteries:

- *Lithium batteries are characterized by high specific energy and high cycle life.*
- *These batteries have either lithium foils as anodes (negatives) or lithiated transition metal oxides as cathodes (positives) with solid polymer electrode.*
- *Electrolyte is immobilized polymer electrolyte with polymer separators.*
- *Examples for lithium batteries : Li- TiS_2,*
- *Li – sulphur ,Li – MnO_2 , Li –V_2O_5 batteries.*

Li- TiS_2 Battery

- *The electrode and cell reactions of this cell are given below:*
- *Anode: Lithium*
- *Cathode: TiS_2*
- *Electrolyte: A solid electrolyte (Polymer packed between the electrodes which permits the passage of ions but not electrons)*
- ***CELL VOLTAGE - 3V***



Cell reactions

At anode: $Li(s) \longrightarrow Li^+ + e^-$

At cathode: $TiS_{2(s)} + e^- \longrightarrow TiS_2^-$

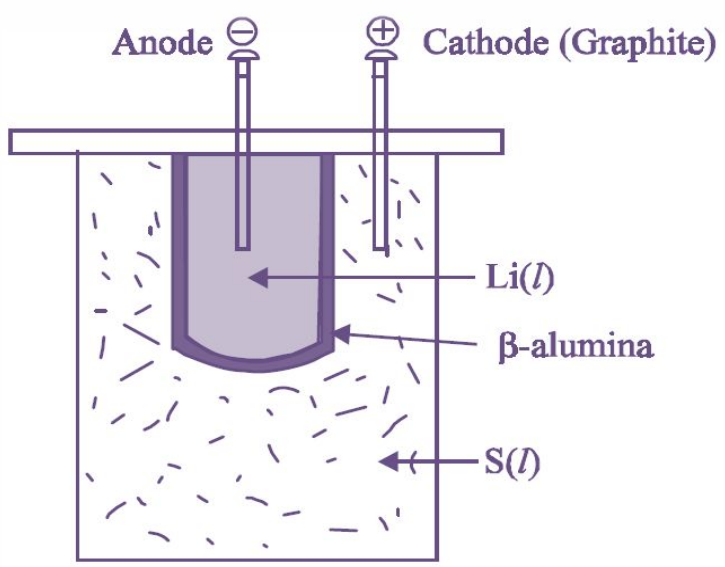
Overall reaction:

$$Li(s) + TiS_{2(s)} \longrightarrow Li^+ + TiS_2^-$$

$$Li^+ + TiS_2^- \longrightarrow LiTiS_2$$

$$LiTiS_2 \longrightarrow Li^+ + TiS_2^-$$

Lithium-Sulphur battery



- *Rechargeable battery.*
- *Anode is made of Li.*
- *Sulphur is the electron acceptor,*
- *The electron from Li is conducted to S by a graphite cathode.*
- *β–Alumina ($NaAl_{11}O_{17}$) is used as the solid electrolyte.*

- *β–Alumina ($NaAl_{11}O_{17}$) allows the Li^+ ions to migrate to equalize the charge, but will not allow the big poly sulphide product ions.*
- *This battery is operated at high temperatures as Li and S should be in their molten states*
- *The direct reaction between lithium and sulphur is prevented by alumina present in the cell.*

Cell Reactions

At Anode: $2\,Li \rightarrow 2Li^+ + e^-$

At Cathode : $S + 2e^- \rightarrow S^{2-}$

Net reaction: $2\,Li + S \rightarrow 2Li^+ + S^{2-}$

Advantages of lithium battery

1. Electrode potential (E^o) of Li / Li^+ is most electronegative, So lithium battery generates a high voltage (3.0) than all other batteries
2. Only 7 g(1mol) of Li metal is needed to produce 1 mol of electrons during discharging
3. Lithium batteries can be made in different shapes and sizes.
4. There is no risk of leakage from the lithium battery, since all its constituents are solid

Applications

1. Lithium batteries are used in potable telephones, computers, and camcorders.
2. Lithium battery research is under progress for use in electric vehicle propulsion and as energy storage devices.
3. Example of such a battery system is FeS2 (positive)– Li Al (negative) cell with molten chloride electrolyte. These batteries are operated at 400°C.
4. Lithium sulphur battery is used in electric cars.

UPS

Medical Device

Power Tool

Robot Vacuum Cleaner

e-Bike

Gardening Tool

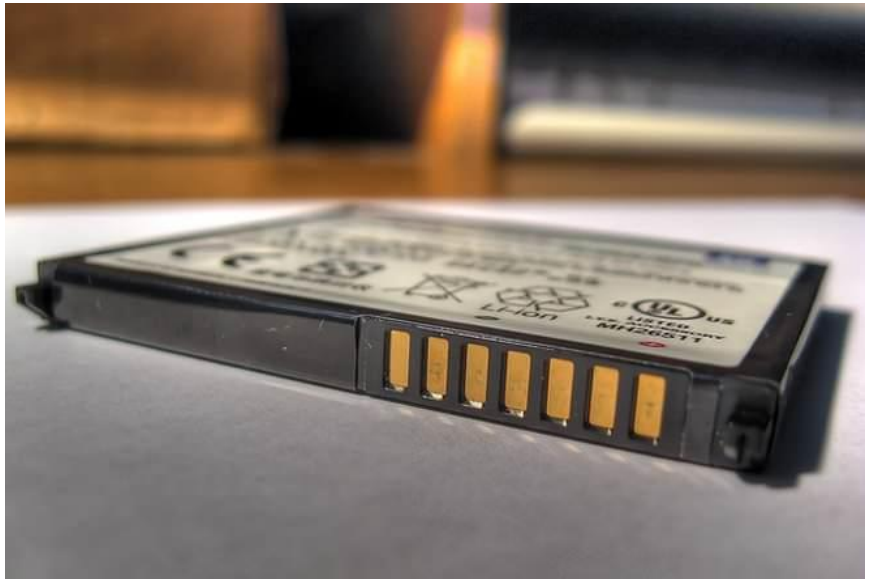
Smart phone

Portable PC

Mobile Phone

Tablet

e-Scooter


LI-ION

NEXT GENERATION BATERRIES.

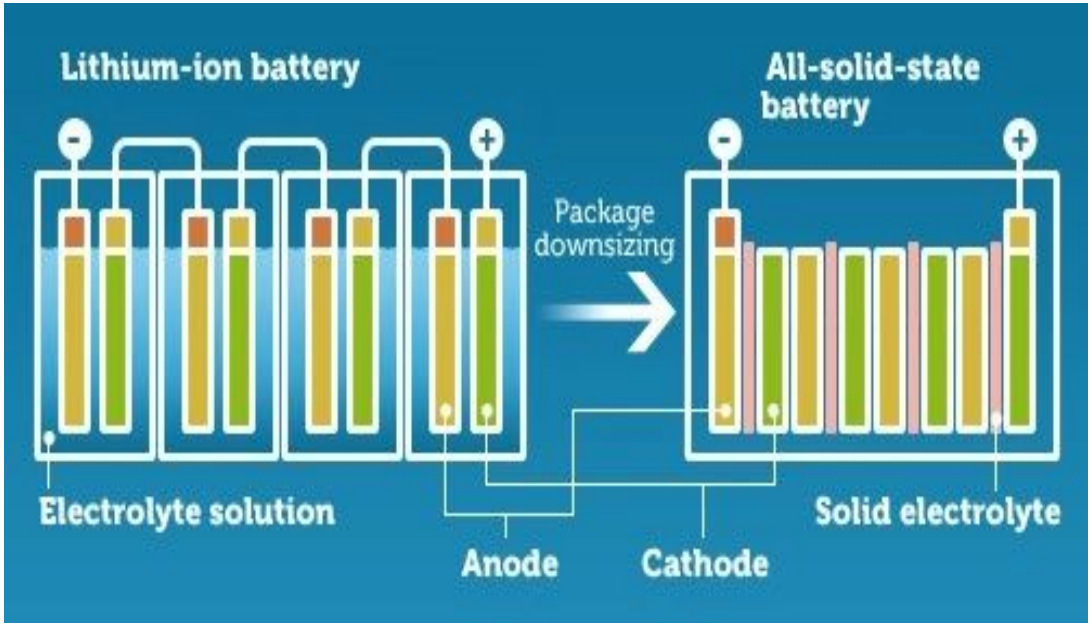
Lithium Solid-state Batteries

These batteries use solid electrodes and a solid electrolyte, instead of the liquid or polymer gel electrolytes found in lithium-ion or lithium polymer batteries.

Anode: Lithium, Graphite

Cathode: Cobalt, Manganese.

Solid electrolyte: Lithium phosphorus oxynitride (LIPON) and the lithium thiophosphates ($Li_2S–P_2S_5$).

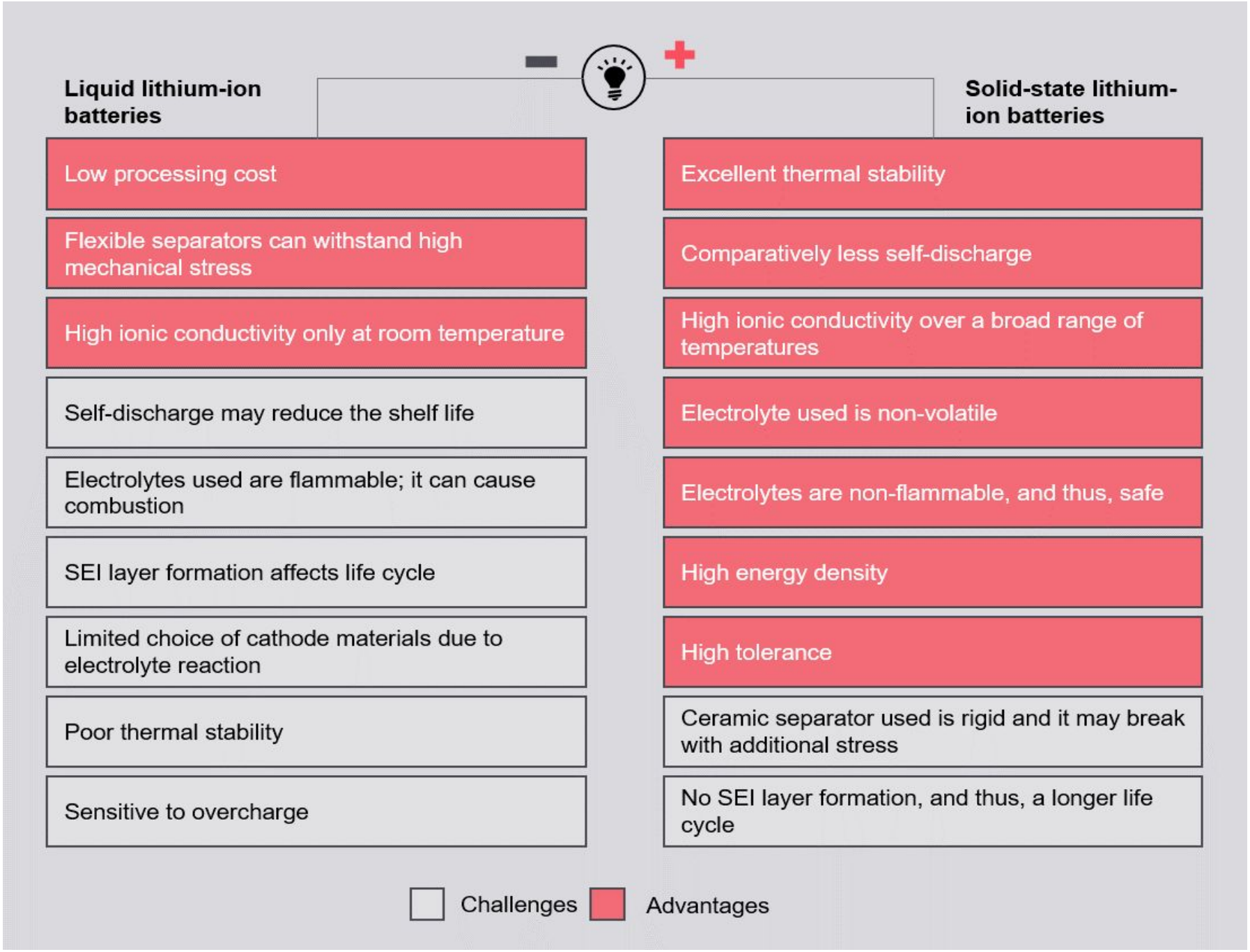


- Solid-state batteries can provide solutions for many problems of liquid Li-ion batteries, such as flammability, limited voltage, unstable solid-electrolyte interphase formation, poor cycling performance and strength.

- In the charging & discharging cycle, ions transfer to and fro between the anode (negative electrode generally made of graphite) and cathode (positive electrode made of lithium).

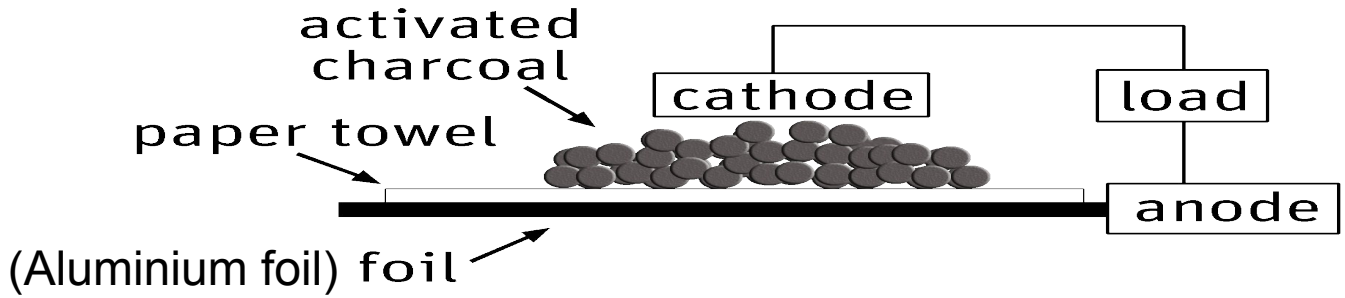
Advantages of the solid-state battery technology

1. Higher cell energy density (by eliminating the carbon anode)
2. Lower charge time (by eliminating the need to have lithium diffuse into the carbon particles in conventional lithium-ion cells)
3. Ability to undertake more charging cycles and longer life.
4. Improved safety and Lower cost.
5. Increase capacity of EV batteries


Liquid lithium-ion batteries
Solid-state lithium-ion batteries
Low processing cost
Flexible separators can withstand high mechanical stress
High ionic conductivity only at room temperature
Self-discharge may reduce the shelf life
Electrolytes used are flammable; it can cause combustion
SEI layer formation affects life cycle
Limited choice of cathode materials due to electrolyte reaction
Poor thermal stability
Sensitive to overcharge
Excellent thermal stability
Comparatively less self-discharge
High ionic conductivity over a broad range of temperatures
Electrolyte used is non-volatile
Electrolytes are non-flammable, and thus, safe
High energy density
High tolerance
Ceramic separator used is rigid and it may break with additional stress
No SEI layer formation, and thus, a longer life cycle
Challenges
Advantages

Aluminium- Air battery

- To generate electrical energy, this battery relies on oxidation of aluminum at the anode, which releases electrons, and a reduction of oxygen at the cathode, which uses electrons. The movement of electrons through an external circuit generates an electric current that can be used to power simple devices. A diagram of the battery and equations for the half and overall reactions are given below:
- **Anode:** Aluminium
- **Cathode:** Oxygen(air)
- **Electrolyte:** KOH or NaOH.



Equations for the half and overall reactions:

- **Anode:** $Al(s) + 3OH^-(aq) \rightarrow Al(OH)3(s) + 3e^-$
  Cathode: $O2(g) + 2H2O(l) + 4e^- \rightarrow 4OH^-(aq)$
  Overall: $4Al(s) + 3O2(g) + 6H2O(l) \rightarrow 4Al(OH)3(s)$

- Aluminum foil provides an affordable supply of aluminum.
- Activated charcoal, which is mostly made of carbon, can conduct electricity and is non-reactive.
- It provides a highly porous surface that is exposed to oxygen in the air. One gram of activated charcoal can have more internal surface area than an entire basketball court!
- This surface provides a large number of sites to which oxygen can bind and participate in the cathode reaction.
- This large reaction area makes it possible for the simple aluminum–air battery to generate 1 volt (1 V) and 100 milliamps (100 mA).
- This is enough power to run a small electrical device and provides a safe and easy way to make a powerful battery at home or industry.

Fuel cell

- Electrochemical cell which converts the chemical energy of fuel into electrical energy by an electrochemical process in which fuel materials are oxidized.

- A fuel cell differs from a conventional battery that it requires continuous replenishment of the fuel electrode, unlike recharging.

- The basic arrangement in a fuel cell can be represented as follows.

- **Fuel/ electrode/electrolyte/electrode/oxidant**

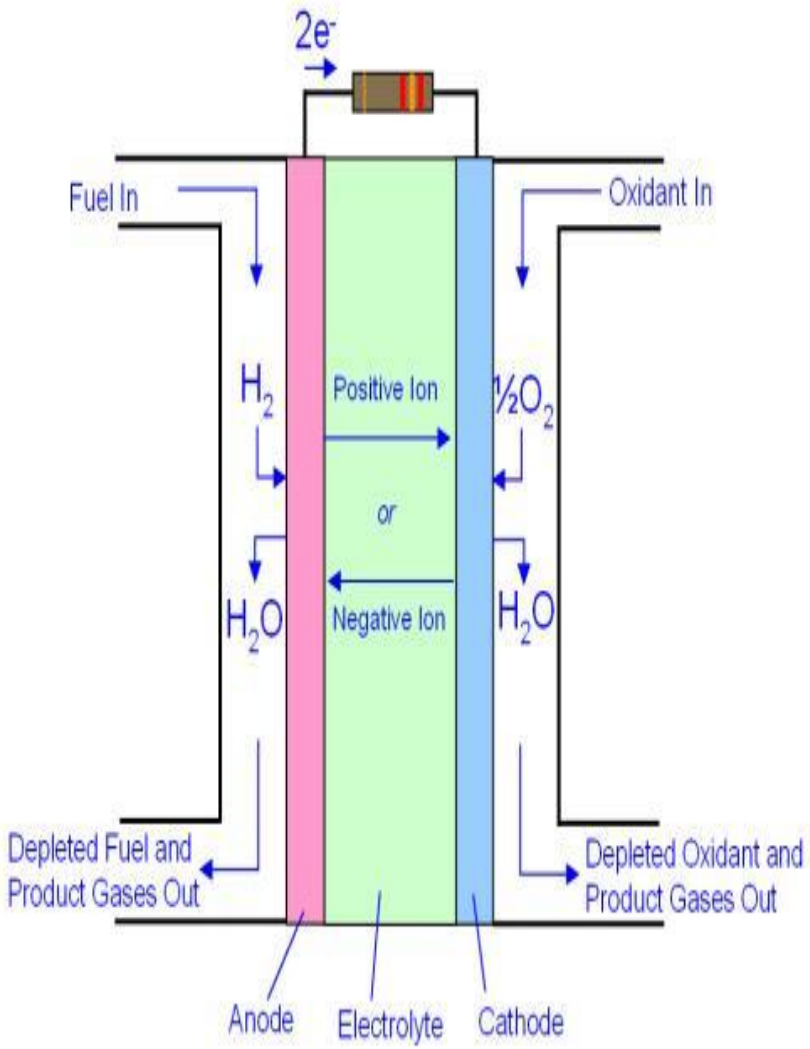
- Fuel undergoes oxidation at the anode liberating electron and the oxidation products of the fuel. The electron so liberated from the oxidation process reduce the oxidant at the cathode.

- Thus movement of electrons constitute electric current.

- Varieties of fuel cells are in use. The important types of fuel cells are hydrogen-oxygen fuel cell, methanol-air fuel cell, phosphoric acid fuel cell etc.

Hydrogen-oxygen fuel cell:

- The electrodes of a fuel cell are referred to as fuel electrode and oxidant electrode. The working of a hydrogen-oxygen fuel cell is based upon the reaction of hydrogen – fuel and oxygen – oxidant to form water.
- ***Construction:*** At the cathode, oxygen is diffused through a porous carbon electrode, impregnated with cobalt oxide, platinum or silver as catalyst. The two electrodes are separated by electrolyte such as KOH solution.

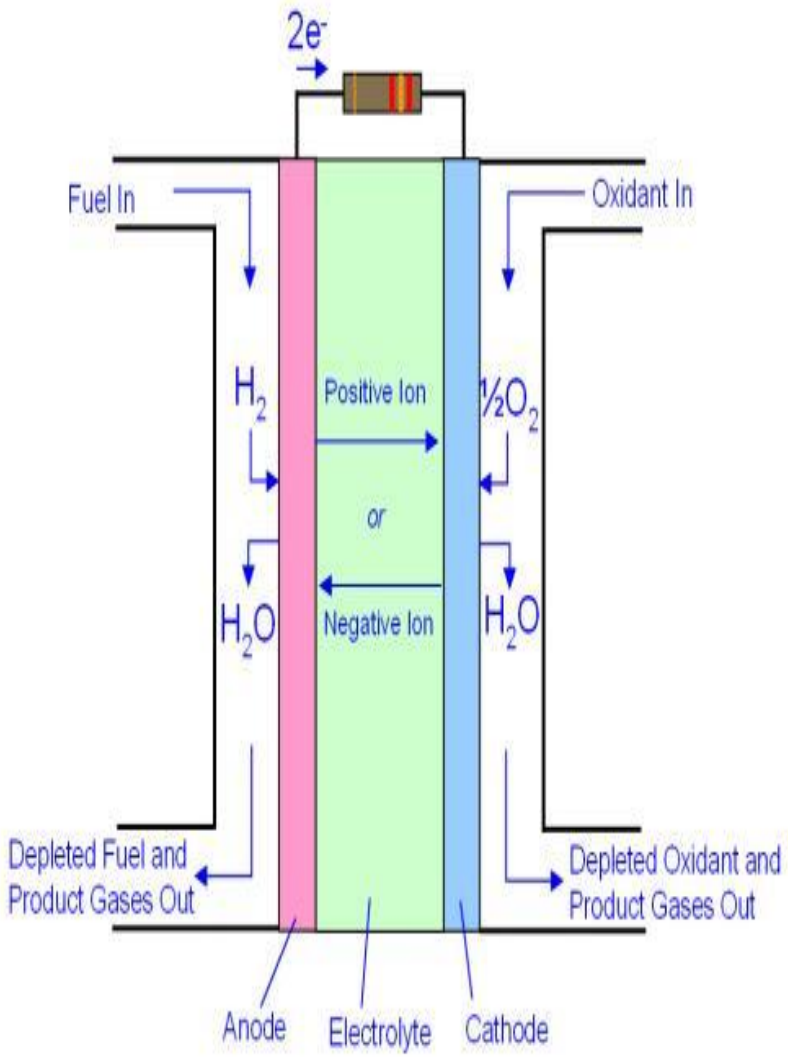


Anode :

- Porous carbon electrode embedded with a catalyst such as finely divided platinum or palladium.
- hydrogen gas is diffused through the electrode

Anodic reaction

$$2\,H_2 + 4\,OH^- \rightarrow 4\,H_2O + 4\,e^-$$



Cathode:

- porous carbon electrode, impregnated with cobalt oxide, platinum or silver as catalyst.
- oxygen is diffused through cathode.
- The two electrodes are separated by electrolyte such as KOH solution.
- Cathodic reaction

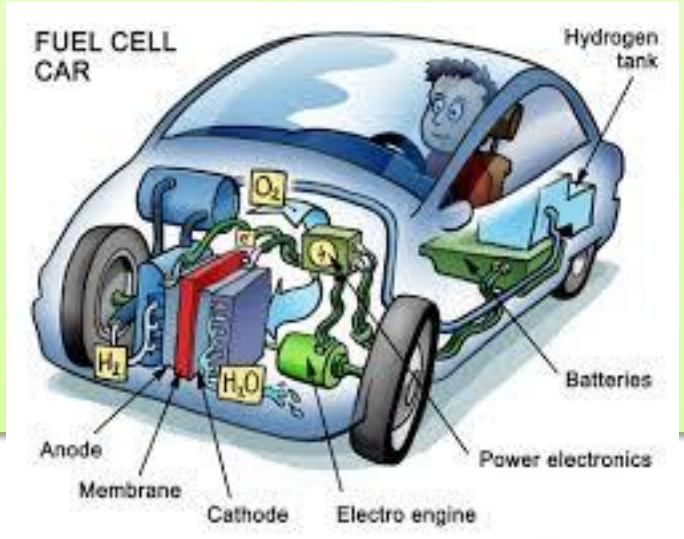
$$O_2 + 2\ H_2O + 4\ e^- \rightarrow 4\ OH^-$$

Overall cell reaction

$$2\ H_2 + O_2 \rightarrow 2\ H_2O$$

Advantages

1. high efficiency
2. ability to operate on a variety of hydrocarbon fuels
3. no objectionable emissions
4. lesser land requirement compared to conventional power plants
5. direct energy conversion
6. without intermediate wastage as heat.



UNIT II: PHOTOCHEMISTRY AND SPECTROSCOPY

Lecture session 10: Introduction to electromagnetic radiation and its properties

INTRODUCTION:

Electromagnetic radiation

Electromagnetic radiation is a form of energy that propagates in free space or through a medium at enormous velocities, which have a dual nature. Light consists of EMRs, which travels in the form of waves. In such a wave, time-varying electric and magnetic fields are mutually linked with each other at right angles and perpendicular to the direction of motion.

General Properties of Electromagnetic Radiation (EMR)

- **EMR** - looked at as sinusoidal waves - composed of a combination of two fields
- **Electric field** - to explain absorption and emission of radiation by analytes
- **Magnetic field at right angle to the electric field** - to explain phenomena - nuclear magnetic resonance in the course of special topics in analytical chemistry.
- **Wavelength (λ) of EMR wave** – inversely related to its energy
- It is defined as a distance between two consecutive maxima or two consecutive minima on the wave. Unit– cm, mm, μm, nm and Angstrom
- **Amplitude (A)** - length of the vector at a maximum or minimum in the wave.

In Fig.1, amplitude - length of any of the vertical arrows perpendicular to the direction of propagation of the wave.

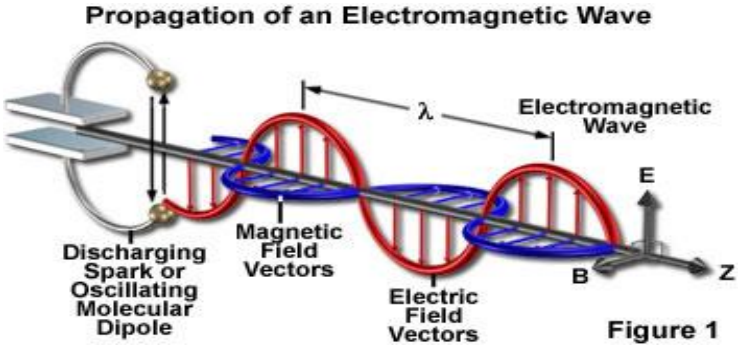


Figure 1

Maxwell (1864) found that the electromagnetic radiation is made up of two mutually perpendicular oscillating electric and magnetic fields in planes at right angles to each other as shown in figure 1.

Frequency of EMR wave - directly proportional to the energy of the wave.

- Defined as the number of wavelengths passing a fixed point in space in one second. unit – s^{-1} or Hz (number of waves per unit time of EMR)

- Period of EMR wave - time in seconds required for one wavelength to pass a fixed point in space
- Frequency of the wave - a constant - a property of the source,
- Decrease in velocity of electromagnetic radiation in media other than vacuum - Attributed to a decrease in the wavelength of radiation upon passage through that medium.

Velocity (c) of EMR wave - The distance travelled by the wave in one second. It is denoted by c, where, $c = \nu\lambda$, (Velocity (c) = 18600 miles per second). Velocity of light in vacuum - greater than its velocity in any other medium. The velocity in light in vacuum is 3×10^8 ms^{-1}.

Wavenumber ($\bar{\nu}$) - The number of waves per unit length (cm). it is equal to the reciprocal of wavelength in cm. Unit - cm^{-1}.
The three main wave properties such as wavelength, frequency and wave number are correlated by the equation,

$$\nu = c/\lambda = c\bar{\nu}$$

According to Planck's Quantum theory, EMR propagates in a space not in continuous manner but in discrete energy packets called quanta.
The energy associated with one packet, i.e one quanta is

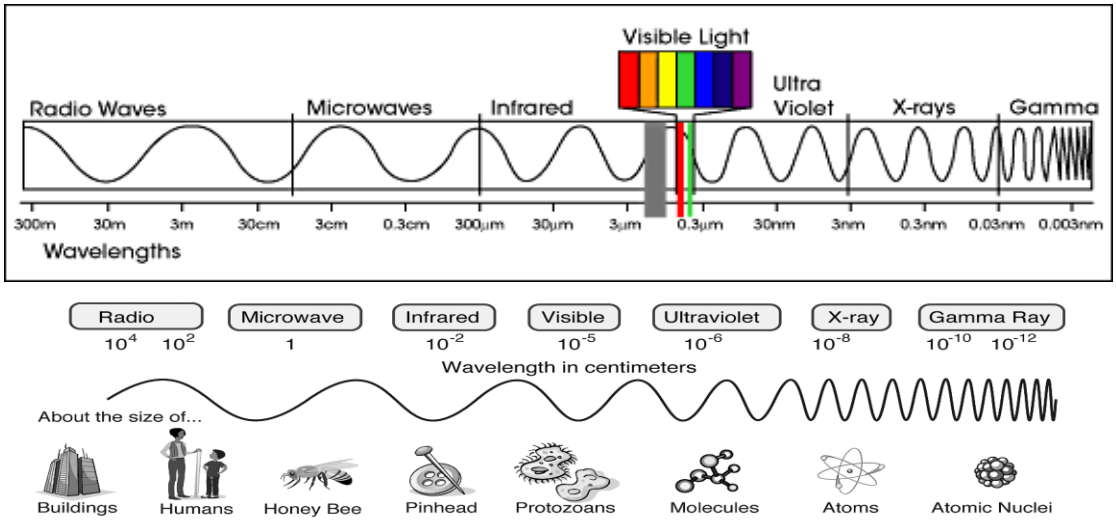
$$E = h\nu = hc/\lambda = h\bar{\nu}$$

Hence, the emission or absorption of energy also takes place in discrete instalments of energy i.e quanta

Electromagnetic Spectrum
The arrangement of all types of EMRs in order of their increasing wavelengths or decreasing frequencies
rays, X-rays, Far UV, UV, Visible, Near IR, IR, Far IR, Microwave, Radio frequency

- EMR - a vast spectrum of frequencies and wavelengths.
- EMR spectrum includes the very energetic gamma-rays radiation with a wavelength range from 0.005 – 1.4 Å to radio waves (RW) in the wavelength range up to meters (exceedingly low energy).
- Region of interest - very limited range from 180-780 nm.
- This limited range covers both ultraviolet and visible radiation.

Diagram below shows the typical EMR spectrum



Lecture session 11: Photochemistry– Photochemical reactions with examples – difference between photochemical and thermal reaction

Photochemistry is the study of chemical reactions resulting from the exposure of light radiations. Light supplies the required energy to take place the photochemical reactions. The visible and UV radiations (2000-8000Å wavelength) are mainly used in photochemical reactions.

Thermochemical reactions (dark reactions) are brought about by molecular collisions. These reactions are spontaneous and are accompanied by a decrease in free energy. But certain photochemical reactions are accompanied by an increase in free energy.
Example: Chemical reactions, which take place by the absorption of heat are called thermal reactions.

$$CaCO_3 \xrightarrow{\Delta} CaO + CO_2$$

Dark Reactions
The chemical reactions, which take place in the absence of light, are called dark reactions.
Example: plant metabolism, Protein activity and cellular metabolism

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. For example, in the combination of hydrogen and chlorine,

the first step is: $Cl_2 + h\nu \rightarrow 2Cl^*$

The activated chlorine atoms (Cl^***)** then undergoes chemical reaction

$$H_2 + Cl^* \rightarrow HCl + H^*$$

It is evident from the above reaction that the second step can occur in absence of light.

Simple reactions involving combination, decomposition, polymerization, oxidation and reduction can be brought about by exposure to such radiations (lower energy).

Examples:

1. Dissociation reaction

$$2HI_{(g)} + h\nu \rightarrow H_{2(g)} + I_{2(g)}$$

2. Double decomposition reaction

$$C_{16}H_{14} + Br_2 + h\nu \rightarrow C_6H_{11}Br + HBr$$

3. Polymerization reaction

$$2(CH_{14}H_{10}) + h\nu \rightarrow C_{28}H_{20}$$

4. Chain reaction

$$H_2 + Cl_2 + h\nu \rightarrow 2HCl$$

***Characteristics of photochemical reaction*:**

1. Photochemical reactions take place by absorption of light.

2. When a light composing number of colours are used, the photochemical reaction may not be initiated by all colours.

3. The free energy change (ΔG) of a photochemical reaction may be either negative or positive.

Differences between photochemical and thermal reactions:

S. No.	Photochemical reactions	Thermochemical reactions
1.	These involve the absorption of light.	These involve either absorption or evolution of heat.
2.	Take place in presence of light.	Take place in dark or in presence of light.
3.	They are independent of temperature.	They are dependent of temperature.
4.	Rate of reactions is dependent on the intensity of the light absorbed.	Rate of reactions is not affected by the intensity of light.
5.	The free energy change is negative or positive.	The free energy change is always negative

Lecture session 12: Laws of Photochemistry - Grotthus – Draper law, Stark–Einstein law and Beer-Lambert Law – Applications and Limitations

LAWS OF PHOTOCHEMISTRY:

Grotthus-Draper Law (or) The Principle of Photochemical Activation:

Grotthus-Draper law states that only the light which is absorbed by a substance can bring about a photochemical change.

However, the absorbed radiation does not necessarily cause a chemical reaction. When the conditions are not favourable for the molecules to react, the light energy may be re-emitted as heat or light or it remains unused.

Stark-Einstein Law of Photochemical Equivalence (or) Principle of Quantum Activation:

It states that in a primary photochemical process (first step) each molecule is activated by the absorption of one quantum of radiation (one photon).

When a molecule absorbs a photon, it is not necessary that only one molecule should react. The absorption of one photon by a molecule is only the first step resulting in the formation of an activated molecule. This further may or may not react or may cause the reaction of many molecules through a chain mechanism.

Some important relations:

Photons	≡	quanta
One molecule absorbs	≡	one photon
One mole of a substance		one mole of quanta (or)
Containing 6.023 x 1023	≡	6.023 x 1023 quanta of
(Avogadro number)		light (or) one Einstein
Molecules absorbs		

One Einstein $= N h\nu$

$= Nhc/\lambda [\because \nu = c/\lambda]$

The energy of photons and Einstein: The energy of a photon (or quantum) E, is given by the equation $E = h\nu = hc/\lambda$, where, h – Planck's constant (6.625×10^{-34} Js; c – velocity of light = 3.0×10^{8} ms^{-1}; λ – wavelength of light.

The energy of an Einstein E, is an Avogadro number (N) of photons. It is given as $E = Nhc/\lambda$ On substituting the values in the above equation it becomes

$E = (6.023 \times 10^{23}) \times (6.625 \times 10^{-34}) \times (3 \times 10^{8})/\lambda$ J $mol^{-1} = 0.1196/\lambda$ J mol^{-1} in SI units

In CGS units: $c = 3 \times 10^{10}$ cm s^{-1}; $h = 6.625 \times 10^{-27}$ erg s^{-1}

$\therefore E = (6.023 \times 10^{23}) \times (6.625 \times 10^{-27}) \times (3 \times 10^{10})/\lambda$ erg $mol^{-1} = 1.196 \times 10^{16}/\lambda$ (in Å) erg mol^{-1}

1 cal = 4.184×10^7 ergs

$\therefore E = 1.196 \times 10^8/4.184 \times 10^7/\lambda$ cal mol^{-1}

$= 2.859/\lambda$ cal mol^{-1}

If l is expressed in Å, then $E = 2.859 \times 10^8/\lambda$ (in Å) cal mol^{-1}

$= 2.859 \times 10^5/\lambda$ (in Å) kcal mol^{-1}

LAMBERT's LAW: When a beam of light is allowed to pass through a transparent medium, the rate of decrease of intensity with the thickness of medium is directly proportional to the intensity of the light.

Mathematically, it may be stated as follows

$$- dI/dl \propto I \text{ (or)} \quad -dI/dl = kI \quad \text{----------} \quad (1)$$

Where I = the intensity if incident light of wavelength λ

l = the thickness of the medium

k = the proportionality factor

on integrating equation 1 and putting $I = I_0$ when l = 0, we get

$$\ln I_0/I = kl \text{ (or) } I = I_0 e^{-kl} \quad \text{----------} \quad (2)$$

BEER's LAW: The intensity of a beam of monochromatic light decreases exponentially with the increase in concentration of the absorbing substance arithmetically.

$$I = I_0 e^{-kc} \quad \text{----------} \quad (3)$$

On combining both laws, we get $\log I_0/I = \varepsilon cl$ ————(4)

The equation 4 is termed as mathematical statement of Beer-Lambert"s law. In the above equation ε = the molar absorption coefficient

$A = \log I_0/I$ is the absorbance (or) optical density (OD)

APPLICATION OF BEER-LAMBERT'S LAW

Determination of unknown concentration

First absorbance As of a standard solution of known concentration C is measured, then according to Beer-Lambert;s law

$$A_s = \varepsilon C_s x$$

$$As/Cs = \varepsilon x \ldots\ldots\ldots\ldots\ldots\ldots\ldots 1$$

Now, absorbance A_u of a solution of unknown concentration C_u is measured. Now we have

$$A_u = \varepsilon C_u x$$

$$A_u/C_u = \varepsilon x \ldots\ldots\ldots\ldots\ldots\ldots\ldots 2$$

From equation 1 and 2, we get

$$A_s/C_s = A_u/C_u$$

$$\therefore C_u = A_u/A_s \times C_s \ldots\ldots\ldots\ldots\ldots 3$$

Since the values of A_u and A_s are experimentally determined and C_s is known. The value C_u (unknown concentration) can be calculated from the equation 3

***<u>Limitations of Beer-Lambert's law</u>*:**

The law is not valid

- ✓ Beer-Lambert's law is not obeyed if the radiation used is not monochromatic.
- ✓ It is applicable only for dilute solutions.
- ✓ The temperature of the system should not be allowed to vary to a large extent.
- ✓ It is not applied to suspensions.
- ✓ Deviation may occur, if the solution contains impurities.
- ✓ Deviation also occurs if the solution undergoes polymerization (or) dissociation.

Lecture session 13: Beer-Lambert Law – problems; determination iron by spectrophotometer

Problems:

1. ***A solution of thickness 2 cm transmits 40% incident light. Calculate the concentration of the solution, given ε = 6000 dm^3 $mol^{-1}cm^{-1}$.***

   Solution:

   Transmittance, $I/I_o = 0.4$ or $I_o/I = 2.5$; $\varepsilon = 6000\ dm^3\ mol^{-1}cm^{-1}$; l or x =2 cm

   $\text{Log } I_o/I = \text{Log } 2.5 = 0.3980 = \varepsilon Cl$

   $C = (0.3980/6000\ dm^3\ mol^{-1}cm^{-1}) \times 2\ cm$

   $= 3.316 \times 10\text{-}5\ mol\ dm^{-3}$.

2. ***Calculate the optical density, if 10 % of incident light is transmitted***

   Solution:

   Optical density, $A = \text{Log } (I_o/I) = \text{Log } (100/10) = \log (10) = 1.0$

3. **Calculate the molar absorptivity of a 1 x 10-4 M solution, which has an absorbance of 0.2, when the path length is 2.5 cm**

Solution:
Here A = 0.20; l = 2.5 cm; C= 1 X 10-4 M/ mol dm-3
Therefore absorptivity,
$\varepsilon = A/Cl = 0.20/(1 \times 10^{-4}\ mol.dm^{-3} \times 2.4\ cm) = 8000\ dm^3mol^{-1}cm^{-1}$

Estimation of Iron by colorimetry

In this analysis the iron present in a sample, form a solution containing Fe^{3+} (ferric) ions. To make the presence of these ions in solution visible, thiocyanate ions (SCN^-) are added. These react with the Fe^{3+} ions to form a blood-red coloured complex:

$$Fe^{3+}_{(aq)} + SCN^-_{(aq)} \rightarrow [FeSCN]^{2+}_{(aq)}$$

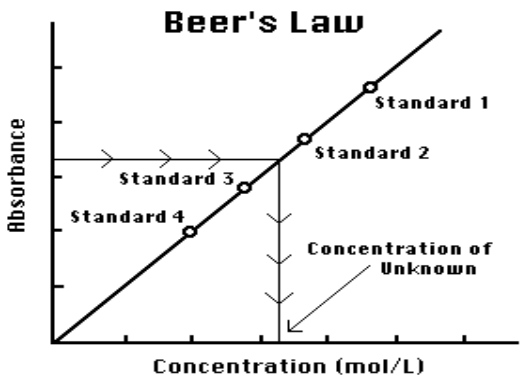
By comparing the intensity of the colour of this solution with the colours of a series of standard solutions, with known Fe^{3+} concentrations, the concentration of iron in solution may be determined. This technique is called colorimetry.

1. Using only the absorbance results obtained for your Fe3+ standard solutions (not your unknown iron sample), prepare a graph with $[Fe^{3+}]$ (in mol L^{-1}) as the horizontal axis and absorbance (at 490 nm) as the vertical axis. Before doing experiment, the colorimeter is set to be zero absorbance for blank solution.
2. Draw a line of best fit for your data points that go through the origin (because absorbance must be zero when Fe^{3+} concentration is zero). This is called as calibration curve, which obeys Beers-Lamberts Law.

3. Now identify the point on your line of best fit which corresponds to the absorbance measured for your unknown iron sample. By drawing a vertical line to the horizontal axis you will be able to determine the concentration of Fe^{3+} in your unknown solution.

4. Use this concentration to calculate the mass of iron (in mg) in your original sample

5. If the absorbance value you measured for your unknown iron sample is greater than the absorbance value for your highest concentration Fe^{3+} standard you will need to modify the above procedure. In the case of an iron tablet, you should repeat the analysis with a more dilute solution of iron samples.



Lecture session 14: Quantum efficiency (Φ) - classification of reactions based on quantum yield – Reason for high and low quantum yield

Quantum Yield (or) Quantum Efficiency (ϕ):

To express the relationship between the number of molecules reacting with the number of photons absorbed, the concept of quantum yield or quantum efficiency (ϕ) is introduced.

Quantum yield is defined as "the number of molecules of the substance undergoing photochemical change per quantum of radiation absorbed. Thus,

$$\phi = \frac{\text{Number of molecules reacting in a given time}}{\text{Number of quanta of light absorbed in the same time}}$$

In certain photochemical reaction, λ = wavelength of light in Å; q = amount of radiation absorbed in certain interval of t s. & n = number of moles of substance reacted in the same time interval (t), then

Number of Einstein's absorbed = $q/(Nhc/\lambda) = q\lambda/Nhc$

∴ Quantum yield, $\phi = n/(q\lambda/Nhc) = nNhc/q\lambda$

In CGS units, $\phi = n/q \times [1.196 \times 10^{16}/\lambda \text{ (in Å)}]$

Classification of photochemical reaction based on quantum yield:
Based on quantum yield, the various photochemical reactions can be divided into three categories.

1. The reaction in which the quantum yield is a small integer like 1, 2.
   Examples: a) Dissociation of HI & HBr; b) Combination of $SO_2 + Cl_2$ and c) Ozonisation of O_2.

2. The reaction in which the quantum yield is less than 1.
   Eaxmples: a) Dissociation of NH_3, CH_3COCH_3& NO_2; b) Transformation of maleic acid into fumaric acid.

3. The reaction in which the quantum yield is extremely high.
   Examples: a) Combination of $CO + Cl_2$; b) Combination of $H_2 + Cl_2$.

High (or) Low Quantum Yield:

The quantum efficiency varies from zero to 10^6. If a reaction obeys the Einstein law, one molecule is decomposed per photon, the quantum yield $\phi = 1$.

High Quantum Yield: When two or more molecules are decomposed per photon, the quantum yield $\phi > 1$ and the reaction has a high quantum yield.

Low Quantum Yield: When the number of molecules decomposed is less than one per photon, the quantum yield $\phi < 1$ and the reaction has a low quantum yield.

Conditions for high and low quantum yield: The reacting molecules should fulfill the following conditions:

1. All the reactant molecules should be initially in the same energy state and hence equally reactive.

2. The reactivity of the molecules should be temperature independent.

3. The molecules in the activated state should be largely unstable and decompose to form the products.

Causes (or) Reasons for high quantum yield:

1. Absorption of radiations in the first step involves production of atoms or free radicals, which initiate a series of chain reactions.

2. Formation of intermediate products will act as a catalyst.

3. If the reactions are exothermic, the heat evolved may activate other molecules without absorbing the additional quanta of radiation.

4. The active molecules, produced after absorption of radiation, may collide with other molecules and activate them which in turn activate other reacting molecules.

Examples:

1. 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:
Primary reaction, one HI molecule absorbs a photon and dissociated to produce one H and one I.

$$HI + h\nu \rightarrow H^* + I^*$$

secondary reaction

$$H^* + HI \rightarrow H_2 + I^*$$

$$I^* + I^* \rightarrow I_2$$

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

The overall reaction shows that the two HI are decomposed for one photon (hν).
Thus, the quantum yield (ϕ) = 2/1=2

2. 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:

Primary reaction: $Cl_2 + h\nu \rightarrow 2\ Cl^*$
Secondary reaction:

$$Cl^* + H_2 \rightarrow HCl + H^*$$

$$H^* + Cl_2 \rightarrow HCl + Cl^* \text{ (step 3)}$$

The Cl atom consumed in step 2 is regenerated in step 3…….. this will propagate the chain reaction. The chain reaction gets terminated when the Cl atoms recombine at the walls of the vessel, where they lose their excess energy.

$$H^* + Cl^* \rightarrow HCl$$

$$Cl^* + Cl^* \rightarrow Cl_2$$

Thus the quantum yield varies from 10^4 to 10^6

***Causes (or) Reasons for low quantum yield*:**

1. Excited molecules may get deactivated before they form products.
2. Excited molecules may lose their energy by collisions with non-excited molecules.
3. Molecules may not receive sufficient energy to anable them to react.
4. The primary photochemical reaction may be reversed.
5. Recombination of dissociated fragments will give low quantum yield.

Example: Dimerization of anthracene to dianthracene

$$2C_{14}H_{10} + h\nu \rightarrow C_{28}H_{20}$$

The quantum yield = 2, but actually it is found to be = 0.5 ; the reason is the above reaction is reversible.

$$2C_{14}H_{10} \leftrightarrow C_{28}H_{20}$$

Processes of photochemical reactions: The overall photochemical reaction consists of

i) *Primary reaction* and ii) *Secondary reaction*.

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

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

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

$$A^* \rightarrow B$$

Photochemical Decomposition of HI: It takes place in the radiation of wave length between 2070 Å - 2820 Å. The quantum yield of the reaction is found to be closer to 2.0.

Lecture session 15: Jablonski Diagram - Internal conversion - Inter-system crossing Fluorescence & Phosphorescence

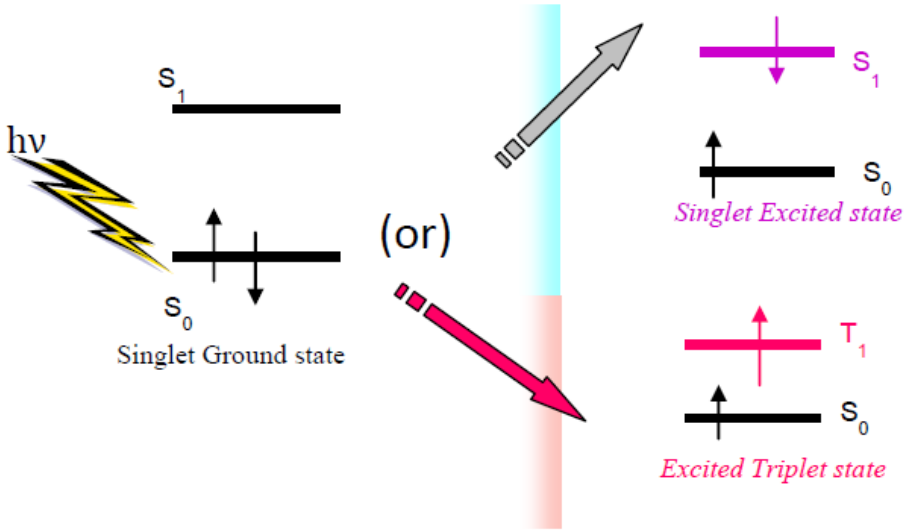
Mechanism of Photophysical Processes (or) Mechanism of Fluorescence and Phosphorescence (or) Jablonski Diagram

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.

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

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

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

b) or anti-parallel (↑↓), then $S = s_1 + s_2 = (1/2) - (1/2) = 0$, $\therefore 2S + 1 = 1$, 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.
$S_1 \rightarrow T_1$; $S_2 \rightarrow T_2$; $S_3 \rightarrow T_3$, etc.

The molecule, whether it is in singlet or triplet excited state, is said to be activated. Thus,

$A_0 + h\nu \rightarrow A^*$ where A_0 – ground state molecule and A* - excited state molecule.

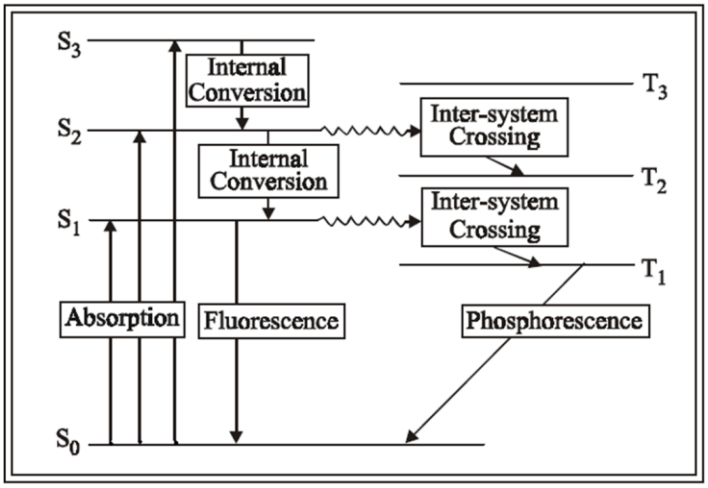


Fig. 3.5 Jablonski diagram of various photophysical processes

Types of transitions: The activated molecules returns to the ground state by emitting its energy through the following general types of transitions.

1. **Non-radiative transitions** do not involve the emission of any radiations, so theses are also known as non-radiative or radiationless transitions. 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.

   $$S_3 \rightarrow S_1;\ S_2 \rightarrow S_1 \text{ (or) } T_3 \rightarrow T_1;\ T_2 \rightarrow T_1$$

   The energy of the activated molecule is given out in the form of heat through molecular collisions. This process is called internal conversion (IC) and occurs in less than about 10^{-11} second.

   b. ***Inter system 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.

2. **Radiative transitions** involve 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. Thus, radiative transitions involve the following two radiations.

a. ***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.

b. ***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.

3. **Quenching of fluorescence**: The fluorescence may be quenched, when the excited molecule collides with a normal molecule before it fluoresces. During quenching, the energy of the excited molecule gets transferred to the molecule with which it collides. Quenching occurs in two ways.

a. ***Internal quenching***: Quenching may also occur, when the molecule changes from the singlet excited state to the triplet excited state. This phenomenon is called internal quenching.

b. ***External quenching***: Quenching may also occur from the addition of an external substance, which absorbs energy from the excited molecule. This phenomenon is called external quenching.

Time scale for different photo physical process is given below

Process	Transition	Timescale (sec)
Light Absorption (Excitation)	$S_0 \rightarrow S_n$	ca. 10^{-15} (instantaneous)
Internal Conversion	$S_n \rightarrow S_1$	10^{-14} to 10^{-11}
Vibrational Relaxation	$S_n^* \rightarrow S_n$	10^{-12} to 10^{-10}
Intersystem Crossing	$S_1 \rightarrow T_1$	10^{-11} to 10^{-6}
Fluorescence	$S_1 \rightarrow S_0$	10^{-9} to 10^{-6}
Phosphorescence	$T_1 \rightarrow S_0$	10^{-3} to 100
Non-Radiative Decay	$S_1 \rightarrow S_0$ $T_1 \rightarrow S_0$	10^{-7} to 10^{-5} 10^{-3} to 100

Lecture session 16: Photosensitization – Mechanism and examples - quenching Difference between Fluorescence and Phosphorescence

ENERGY TRANSFER IN PHOTOCHEMICAL REACTIONS:

Photosensitizations and Quenching: 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.

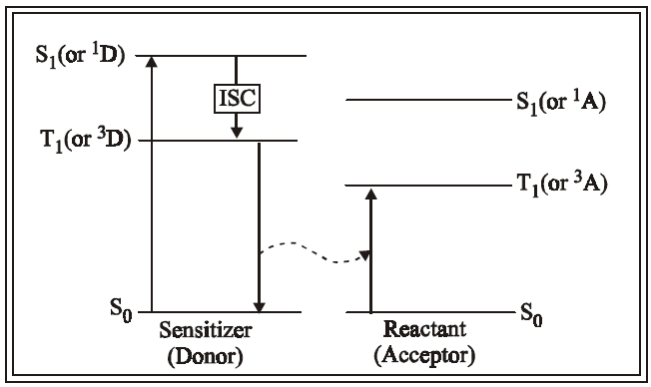
1. ***Photosensitization***: The foreign substance absorbs the radiation and transfers the absorbed energy to the reactants is called a photosensitizer. This process is called photosensitized reaction (or) photosensitization. Examples,

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

2. ***Quenching***: When the excited foreign substance collides with another substance it gets converted into some other product due to the transfer of its energy to the colliding substance. This process is known as quenching.

Mechanism of Photosensitization and Quenching can be explained by considering a general donor (D) and acceptor (A) system. In a donor-acceptor system, the donor D (sensitizer)

absorbs the incident photon and gets excited from ground state (S_0) to singlet state (S_1). Then the donor attains the triplet excited state (T_1 or ^3D). The triplet state of the donor is higher than the triplet state of the acceptor (A). This triplet excited state of the donor collides with the acceptor produces the triplet excited state of the acceptor (^3A) and returns to the ground state (S_0). If the triplet excited state of the acceptor (^3A) gives the desired products, the mechanism is called photosensitization. If the products are resulted directly from the excited state of the donor (^3D), then A is called quencher and the process is called quenching.



Mechanism of photosensitization:

The sequence of photosensitization and quenching may be represented as follows:

$D + h\nu \rightarrow {}^1D$

${}^1D \rightarrow {}^3D$

${}^3D + A \rightarrow D + {}^3A$

${}^3A \rightarrow$ Products (photosensitization)

${}^3D \rightarrow$ Products (quenching)

It is necessary that the energy of the triplet excited state of the donor (sensitizer) must be higher than the triplet excited state of the acceptor (reactant). Thus the energy available is enough to excite the reactant molecule to its excited state. The dotted line indicates the transfer of energy from the sensitizer to reactant.

Examples for photosensitized reactions:

1. ***Dissociation of hydrogen molecule***: 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.

$$Hg + h\nu \rightarrow Hg^*$$
$$Hr^* + H_2 \rightarrow H_2^* + Hg$$
$$H_2^* \rightarrow 2H$$

2. ***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.

$$\text{Photosynthesis:} \quad \text{Chll} + h\nu \rightarrow {}^*\text{Chll} \ \text{(excited)}$$

$$6\ H_2O + 6\ CO_2 + {}^*\text{Chll} \rightarrow C_6H_{12}O_6 + 6\ O_2 + \text{Chll} \ , \qquad \Delta G = -\text{Ve}$$

In the presence of light and chlorophyll ΔG^o becomes negative; thereby the reaction proceeds and produces glucose. But in the absence of chlorophyll, the ΔG^o for this reaction is +2875 kJ. Since ΔG^o is positive, the above reaction is not possible.

PHOTOPHYSICAL PROCESS: 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 photo physical process.

Types of photophysical process:
Photophysical process is of two types,

i) Fluorescence and
ii) Phosphorescence.

i) **Fluorescence**:
When a molecule or atom absorbs radiation of higher frequency (shorter wavelength), it gets excited. Then the excited atom or molecule re-emits the radiation of the same frequency or lower frequency within short time (about 10^{-8} sec.). This process is called fluorescence, stops as soon as the incident radiation is cut off. The substance which exhibits fluorescence is called fluorescent substance.

***Examples*:** CaF_2, uranium, petroleum, organic dyes like eosin, fluorescein), chlorophyll, quinine sulphate solution, vapours of sodium, iodine, mercury, etc.

Types of fluorescence:
a) ***Resonance fluorescence***: If the excited atom emits the radiation of the same frequency, the process is known as resonance fluorescence.
Example, when mercury vapour at low pressure is exposed to radiation of wavelength 253.7 nm, it gets excited. Subsequently, when it returns to its ground state, it emits radiation of the same frequency, which it absorbed.

b) ***Sensitized fluorescence***: If the molecule is excited, due to the transfer of part of excitation energy from the foreign substance, it emits the radiation of lower frequency, the process is known as sensitized fluorescence.

Example, if the mercury vapour is mixed with the vapours of silver, thalium, lead or zinc, which do not absorb radiation at 253.7 nm and then exposed to the radiation, a part of the excitation energy from mercury is transferred and gets excited to higher energy state. When it returns to its ground state, it emits radiation of lower frequency.

ii) **Phosphorescence**: When a substance absorbs radiation of higher frequency, the emission of radiation is continuous for some time even after the incident light is cut off. This process is called phosphorescence (or) delayed fluorescence. The substance which shows phosphorescence is called phosphorescent substance.

Differences between fluorescence and phosphorescence

Fluorescence	Phosphorescence
1. Its decay period is much longer, 10^{-4} – 100 s.	Its decay period is very short, 10^{-9} – 10^{-4} sec.
2. 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.
3. It is not observed in solution at room temperature.	It can be observed in solution at room temperature.
4. Its spectrum is mirror image of the absorption spectrum.	Its spectrum is not mirror image of the absorption spectrum.
5. It is exhibited by some elements in vapour state.	It is rarely observed in gaseous or vapours.
6. Examples: uranium, petroleum, organic dyes, chlorophyll, CaF_2, etc.	Examples: ZnS, sulphides of alkaline earth metals.

Lecture session 17: Photochemical reaction kinetics with example

Photochemical equilibrium

In some photochemical reactions, equilibrium is maintained in the reactants and the product of the decomposition. The forward reaction in most cases is indicated by light, while the backward reaction by dark

$$\text{Reactants} \underset{\text{Dark}}{\overset{\text{light}}{\rightleftharpoons}} \text{Products}$$

The quantum yields of the two processes in some case are different. This is known as photochemical equilibrium or photostatonary state.

Photochemical equilibrium is different from the normal thermal equilibrium, since the energy in case of photochemical equilibrium is provided through the absorbed radiation

Equilibrium constant

Consider the reaction which is light in forward direction and dark/thermal sensitive in reverse direction

$$A \underset{k_{-1},\ \text{Dark}}{\overset{k_1,\ \text{light}}{\rightleftharpoons}} B$$

Rate of the forward reaction $= k_1 I_{abs}$
Rate of the reverse reaction $= k_{-1} C_B$

At equilibrium: $k_1 I_{abs} = k_{-1} C_B$

$$K = \frac{k_{-1}}{k_1} = \frac{I_{abs}}{C_B}$$

Hence, photochemical equilibrium constant K, is directly proportional to the intensity of the light absorbed.

Example
Kinetics of photochemical synthesis of HCl

This reaction is accompanied by exceptionally high quatum yield ranging from 10^4 -10^6 in the light of wavelength 4800Å. Nernst gave a chain mechanism, which is universally accepted now-a-days

When exposed to the light of wavelength 4785Å, the primary step I photochemical dissociation of Cl molecule

$$Cl_2 + hv \overset{k_1}{\leftrightarrow} 2Cl \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 1$$

The other stages are

$$Cl + H_2 \overset{k_2}{\leftrightarrow} HCl + H\ (exothermic) \ldots\ldots\ldots\ldots\ldots\ldots\ldots 2$$

$$H + Cl_2 \overset{k_3}{\leftrightarrow} HCl + Cl \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 3$$

The Cl atom is generated in Eq. 3 again reacts with hydrogen molecule to follow the reaction as in eq. 2 and 3 to occur again and the chain is propagated in this way. Therefore, the quantum yield of the reaction is high as compared to hydrogen-bromine reaction, which is characterized by an endothermic process.

It was found that in absence of oxygen, the rate of the reaction is proportional to the intensity of the light absorbed. The chain is terminated by the reaction vessel, i.e.,

$$Cl + walls \overset{k_4}{\leftrightarrow} \frac{1}{2} Cl_2 \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 4$$

The rate of formation of HCl may be calculated by the fact that is formed in eq. 2 and 3. Thus k_1, k_2, k_3 and k_4 be the rate constants, then:

$$\frac{d[HCl]}{dt} = k_2\,[Cl]\,[H_2] + k_3\,[H]\,[Cl_2] \ldots\ldots\ldots\ldots\ldots\ldots 5$$

For Cl atom: Considering the stationary state, the Cl atom is formed in eq. 1 and 3 and removed in eq 2 and 4, so it follows

$$k_1 I_{abs} + k_3[H][Cl_2] = k_2\,[Cl][H_2] + k_4\,[Cl] \ldots\ldots\ldots\ldots\ldots\ldots 6$$

For Hydrogen atom: Similarly, hydrogen atoms are formed in eq.2 and removed by eq.3. For the stationary stae, we have:

$$k_2\,[Cl]\,[H_2] = k_3\,[H]\,[Cl_2] \ldots\ldots\ldots 7$$

Eq.6 + eq.7 gives:

$$k_1 I_{abs} = k_4\,[Cl]$$

$$[Cl] = \frac{k_1 I_{abs}}{k_4} \ldots\ldots\ldots\ldots\ldots 8 \quad \text{or}$$

Substituting the value of [Cl] in eq. 7, we get

$$k_2[H_2]\,\frac{k_1 I_{abs}}{k_4} = k_3\,[H]\,[Cl_2]$$

$$[H] = \frac{k_2\,[H_2]}{k_3\,[Cl_2]} \cdot \frac{k_1 I_{abs}}{k_4} \ldots\ldots\ldots\ldots\ldots\ldots\ldots 9 \quad \text{or}$$

Now Substituting the values of [Cl] and [H_2] from eq. 8 and 9 in eq. 5, we get

$$\frac{d[HCl]}{dt} = k_2\,[H_2]\frac{k_1 I_{abs}}{k_4} + k_3\,[Cl_2].\frac{k_2}{k_3}.\frac{k_1}{k_4}\frac{[H_2].I_{abs}}{[Cl_2]}$$

$$= k_1\,k_2\frac{[H_2].I_{abs}}{k_4} + k_1\,k_2\,\frac{[H_2].I_{abs}}{k_4}$$

Or

$$\frac{d[HCl]}{dt} = 2.k_1\,k_2\frac{[H_2].I_{abs}}{k_4} \ldots\ldots\ldots\ldots\ldots 10$$

Or

$$\frac{d[HCl]}{dt} = k\,[H_2].I_{abs}$$

Where, $k = \frac{k_1 k_2}{k_4}$

i.e., the rate of the formation of HCl is directly proportional to the intensity of light absorbed

Lecture session 17: Stern-Volmer relationship and Applications of photochemistry

Stern-Volmer relationship

Fluorescence may be quenched (i.e., stopped) when the excited state species undergoes collision with a normal molecule before it has the chance to fluoresce. The quenching of fluorescence occurs became of the energy transfer from the excited state species to the molecule with which it collides.

Quenching may also occur when the molecule changes from the singlet excited state to the triplet excited state. This phenomenon is called internal quenching. Quenching may also result from the presence of an externally added species which takes up energy from the

excited state molecule. This phenomenon is called external quenching. If Q is the quencher, we may then write :

$$A + hv \rightarrow A^* \quad (activation)$$
$$A^* \xrightarrow{k1} A + hv \quad (fluorescence)$$
$$A^* \xrightarrow{k2} A \quad (internal\ quenching)$$
$$A^* + Q \xrightarrow{k3} A + Q' \quad (external\ quenching)$$

By applying s.s.a to A*, we have

$I_a = k_1[A^*] + k_2[A^*] + k_3[A^*][Q]$

Where I_a is the intensity of light absorbed
If I_f represents the intensity of fluorescence, the quantum yield for the fluorescence is given by

Φ_f or $\phi_q = I_f/Ia = k_1[A^*] / (k_1[A^*] + k_2[A^*] + k_3[A^*][Q])$

$=k_1 / (k_1 + k_2 + k_3 [Q])$

In the absence of the quencher, i.e., when [Q]=0, the quantum yield

$\phi_0 = k_1/(k_1+k_2)$

Hence, the ratio of the two quantum yields

$\phi_0/\phi_q = (k_1+k_2+k_3[Q]) / (k_1+k_2) = 1 + (k_3 [Q] / k_1+k_2)$

Put $1/k_2+k_2 = \tau$

$\varphi_0/\varphi_Q=1+k_3 \tau[Q]$

or

$\varphi_0/\varphi_Q=1+k_{sv}[Q]$

where, $K_{sv} = k_3\tau$ and $\tau = 1/(k_1+k_2)$

This is known as a Stern-Volmer equation in which K_{sv} is called the Stern- Volmer constant, τ is lifetime of A* in the absence of external quenching.

From stern-Volmer equation we see that φ_0/φ_Q depends linearly on [Q]. The slop of the line gives $k_3\tau$ from which τ can be determined.

Applications of photochemistry

Photochemistry has many practical applications. One of the main branches in photochemistry is concerned with investigating different types of chemical reactions that occur when molecules are exposed to light.

In particular, photochemical studies have been used extensively for research on new drug development as well as solar energy conversion technology. Applications of photochemistry in everyday life include decontamination of drinking water, production of hydrogen fuel, and food processing, etc.

Decontamination of drinking water

When it comes to the treatment of drinking water, photochemistry is a very important part. It can be used in many different ways including purification and decontamination.

The first example of using the process for decontamination would be UV light being used on bacteria or viruses present in water tanks where no chemicals are able to dissolve properly yet. After this step has been completed, other steps involving filters that remove chemical particles could then take place.

Production of hydrogen fuel

Hydrogen is used in all types of gas turbines. Gas turbine technology is also being developed for vehicles, and these engines are the most efficient type so far available.

Splitting of water through photo catalyst is available now –a-days for the production of Hydrogen and Oxygen. The hydrogen fuel cells that power electric cars are another example of photochemistry.

The water molecules needed during this process can be provided by splitting them into their components with additional electricity from solar panels on the vehicle roof or other renewable sources plugged in when parked at home overnight.

Food processing

Photochemistry, the use of light for chemical reactions, is common in food processing. This can be used to either reduce or increase production time or potentially improve quality. The uses of photochemistry include:

- Draining liquid from brined foods; helps remove any excess salt after curing.
- Sterilization – exposure to ultraviolet radiation kills pathogens present on surfaces such as equipment that comes into contact with ready-to-eat food like salads. It does not interfere with the taste, smell, or texture of the product which makes it an efficient way to keep products safe once they are packed
- Slow down ripening processes by blocking certain wavelengths of light. This is a popular technique for extending the shelf life and improving the quality of foodstuffs such as tomatoes

- Increase shelf life by reducing the amount of oxygen in packaging which prevents oxidative rancidity.

Medicine

One of the most important uses for photochemistry in medicine is to create a photosensitizer. Photosensitizers are drugs that respond to light by becoming activated and killing cells, sometimes only cancerous cells. This can be used to kill bacteria or viruses, destroy diseased tissues such as tumors, treat skin conditions like psoriasis and eczema, or even combat arthritis.

Another medical application where photochemistry plays an important role is laser eye surgery. Lasers use light energy at high intensities so that it focuses on very specific parts of your cornea without damaging surrounding tissue. The lasers cut away sections of the cornea using heat generated from photo-acoustic waves caused when photons interact with water molecules.

Environment protection

There are several ways photochemistry is used to protect the environment. One way is used to detect and identify pollutants in water. Water molecules that contain impurities absorb ultraviolet (UV) radiation, which results in a change of wavelength for the emitted fluorescent photons. This can be measured by instruments called fluorometers, which output an electronic signal indicating the presence of certain materials such as sewage or oil spills. The more intense this fluorescence, the higher level of contamination present.

Photography

Silver halide photographic film uses a chemical reaction involving light to create an image on the film. In modern photography, there are three types of films: black and white negative (neg), color reversal camera negative (reversal) and color print paper positive (print). Photography is also found in printing processes such as digital photo printers which use lasers to expose photosensitive materials before developing them into prints that can be viewed under visible light or projected onto screens with slide projectors.

Because photochemistry has been around for so long it has become a fundamental process involved in most aspects of everyday life from how we produce food through refrigeration all the way up to advanced scientific research.

NANOCHEMISTRY

INTRODUCTION

Nanochemistry is the study of chemistry at the nanoscale. One nanometer (nm) is one billionth of a meter, so nanochemistry deals with materials and structures that are between 1 and 100 nanometers in size. This is the size range where materials exhibit unique properties that are different from their bulk counterparts.

For example, gold nanoparticles are much more catalytically active than bulk gold. This is because the small size of the nanoparticles gives them a high surface area to volume ratio, which means that there are more atoms on the surface of the nanoparticles that can react with other molecules.

Nanochemistry is a rapidly growing field with applications in a wide range of areas, including electronics, energy, medicine, and environmental science. For example, nanomaterials are being used to develop new types of solar cells, batteries, and drug delivery systems.

Here is a summary of the introduction to nanochemistry that you provided:

- **The prefix "nano" means one billionth.**
- **Atoms are very small, with diameters ranging from 0.1 to 0.5 nanometers.**
- **Nanochemistry deals with structures of matter that are between 1 and 100 nanometers in size.**
- **Materials at the nanoscale exhibit unique properties that are different from their bulk counterparts.**
- **Nanochemistry is a rapidly growing field with applications in a wide range of areas.**

Nanoparticles

Nanoparticles are particles with a size of 1-100 nanometers (nm). They are often obtained as colloids, which are suspensions of particles in a liquid. Colloidal nanoparticles have a tendency to remain single crystals, and hence are called nanocrystals. A large percentage of atoms in nanocrystals are present on the surface, which gives them unique electronic, magnetic, and optical properties. Nanoparticles can also be called quantum dots, because they exhibit electronic behavior governed by quantum physics.

Nanomaterials

Nanomaterials are materials having components with a size less than 100 nm in at least one dimension. They can be categorized into one-dimensional (layers), two-dimensional (tubes), and three-dimensional (particles) nanomaterials. Some examples of nanomaterials include:

- **Inorganic nanomaterials:** metal nanomaterials (Ag, Au, Al, Cd, Cu, Fe, Zn, Pb), metal oxide nanomaterials (ZnO, CuO, $MgAl_2O_4$, TiO_2, CeO_2, Fe_2O_3, SiO_2, Fe_3O_4)
- **Carbon-based nanomaterials:** graphene, fullerene, single-walled carbon nanotube, multiwalled carbon nanotube, carbon fiber, activated carbon, carbon black
- **Organic nanomaterials:** dendrimers, cyclodextrin, liposome, micelle
- **Composite nanomaterials:** any combination of metal, metal oxide, carbon, and/or organic nanomaterials

Nanochemistry

Nanochemistry is the study of chemistry at the nanoscale. It is a highly interdisciplinary field, drawing on concepts from chemistry, physics, materials science, and biology. Nanochemistry is concerned with the synthesis, characterization, and properties of nanomaterials. It also investigates the unique chemical and physical interactions that occur at the nanoscale.

Nanotechnology

Nanotechnology is the application of nanochemistry to the design and construction of devices, materials, and systems at the nanoscale. It is a rapidly developing field with a wide range of potential applications in areas such as electronics, medicine, energy, and environmental science.

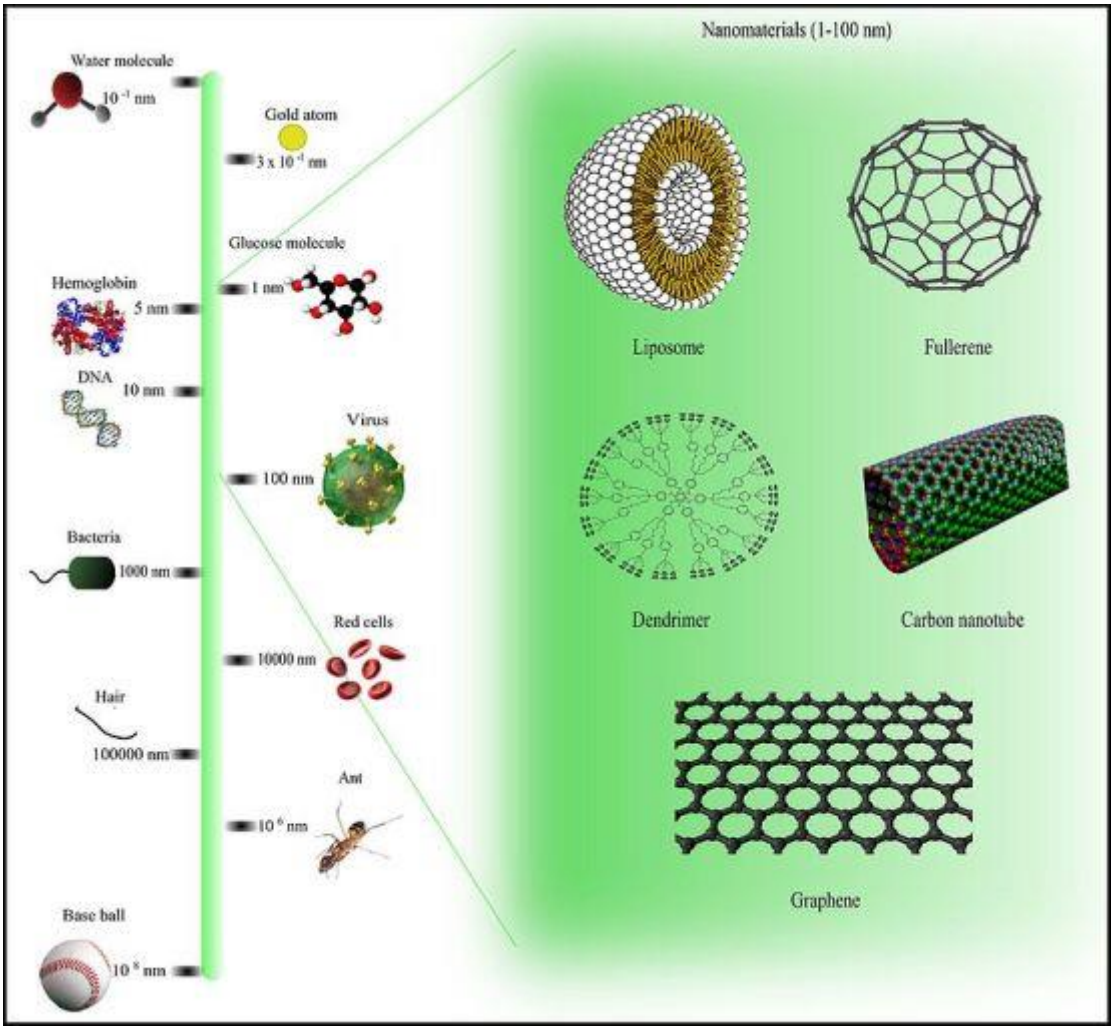


Figure 01: Comparison between Nanomaterials and Bulk Materials

There are many applications of these materials in various manufacturing processes, healthcare applications, various products including paints, filters, lubricant additives, etc. For example, nanozymes are substances that are nanoparticles, and they have enzyme-like characteristics.

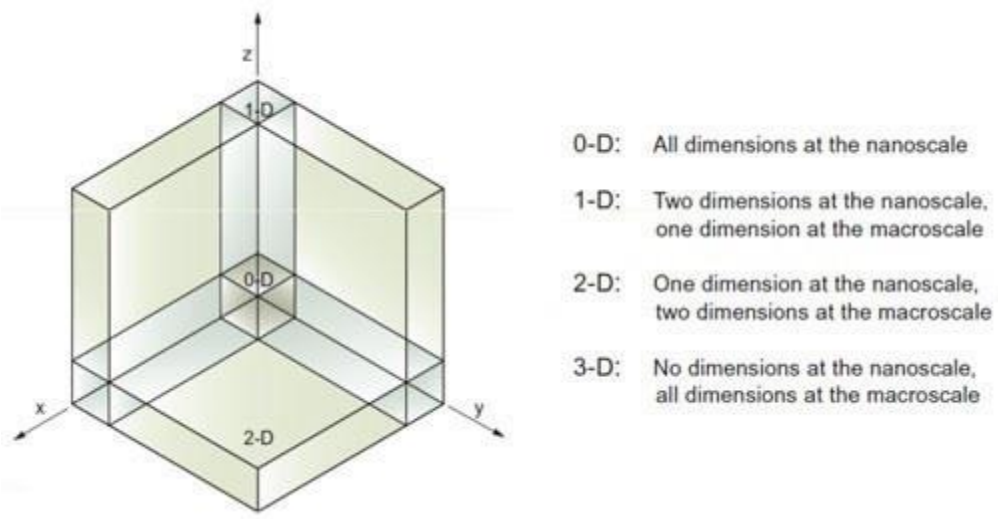
What are Bulk Materials?
Bulk materials are particles that have their size above 100 nm in all dimensions. Most of the times, we use this term in order to name a substance that is granular or lumpy and exists in free-flowing form. we use the grain size and grain distribution in characterizing these materials. Moreover, we can explain their properties using the bulk density, moisture content, temperature, etc. There are two forms of these materials as follows:

1. Cohesionless, free-flowing bulk materials
2. Cohesive bulk materials

Bulk materials include the material we use in the construction field; plaster, sand, gravel, cement, etc. Moreover, it includes raw materials that we use for various industries such as ore, slag, salts, etc. In addition to that, this includes powdery materials such as pigments, fillers, granules, pellets, etc.

What is the Difference Between Nanomaterials and Bulk Materials?

Nanomaterials are materials with at least one dimension that is less than 100 nanometers (nm). **Bulk materials** are materials with all dimensions greater than 100 nm.



Nanomaterials have different properties than bulk materials due to their small size and high surface area to volume ratio. The following are some of the key differences in properties between nanomaterials and bulk materials:

- **Optical properties:** Nanomaterials can have different optical properties than bulk materials, such as different colors, absorption spectra, and scattering properties. This is because the size and shape of nanoparticles can affect the way they interact with light.
- **Electrical properties:** Nanomaterials can also have different electrical properties than bulk materials. For example, nanoparticles can be more conductive or semiconducting than bulk materials. This is because the surface of nanoparticles can have different electronic properties than the interior.

- **Mechanical properties:** Nanomaterials can also have different mechanical properties than bulk materials, such as increased strength and hardness. This is because the small size of nanoparticles allows them to resist deformation and fracture.
- **Chemical properties:** Nanomaterials can also have different chemical properties than bulk materials. For example, nanoparticles can be more reactive than bulk materials. This is because the high surface area to volume ratio of nanoparticles gives them more atoms that are exposed to the environment.

The following table summarizes some of the key differences in properties between nanomaterials and bulk materials:

Property	Nanomaterials	Bulk materials
Size	At least one dimension less than 100 nm	All dimensions greater than 100 nm
Surface area to volume ratio	High	Low
Optical properties	Can be different from bulk materials	Similar to bulk materials
Electrical properties	Can be different from bulk materials	Similar to bulk materials
Mechanical properties	Can be different from bulk materials, such as increased strength and hardness	Similar to bulk materials
Chemical properties	Can be different from bulk materials, such as increased reactivity	Similar to bulk materials

Due to their different properties, nanomaterials have a wide range of applications in areas such as medicine, energy, electronics, and environmental engineering. For example, nanoparticles are used in drug delivery systems, solar cells, and water purification filters.

Here are some specific examples of how the properties of nanomaterials are different from those of bulk materials:

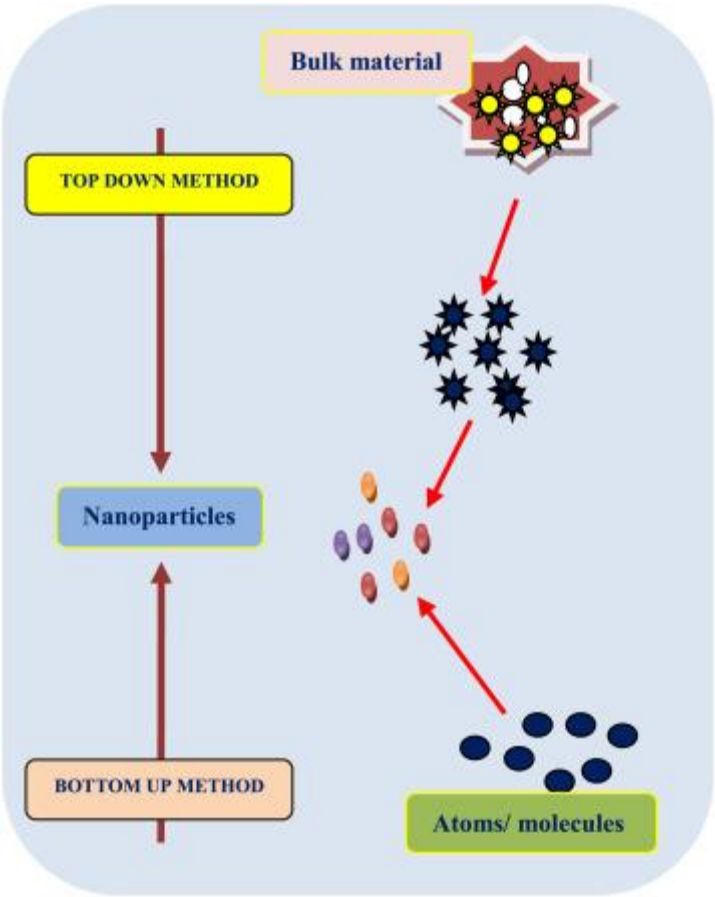
- Gold nanoparticles are red in color, while bulk gold is yellow.
- Carbon nanotubes are stronger than steel, but they are also much lighter.
- Silver nanoparticles are more antimicrobial than bulk silver.
- Zinc oxide nanoparticles are more effective at absorbing UV light than bulk zinc oxide.

Researchers are still actively studying the properties of nanomaterials and developing new applications for them.

SYNTHESIS OF NANO –MATERIALS

For the preparation of metallic nanoparticles, various methods are used, which are classified into two types: bottom-up methods and top-down methods, and are listed in Table. The preparation of nanoparticles' starting material is where both processes diverge most. While atoms or molecules are the starting materials in bottom-up approaches, top-down methods start with bulk material and use various physical, chemical, and mechanical processes to reduce particle size to nanoparticles. (Fig.)

Sr. No.	Top down methods		Bottom up methods	
	Methods	**Examples**	**Methods**	**Examples**
1	Mechanical milling	Ball milling Mechanochemical method	Solid state methods	Physical vapor deposition Chemical vapor deposition
2	Laser ablation		Liquid state synthesis methods	Sol gel methods Chemical reduction Hydrothermal method Solvothermal method
3	Sputtering		Gas phase methods	Spray pyrolysis Laser ablation Flame pyrolysis
4			Biological methods	Bacteria Fungus Yeast Algae Plant extract
5			Other methods	Electrodeposition process Microwave technique Supercritical fluid precipitation process Ultra sound technique



Top down methods

1. ***Mechanical milling***

Ball milling

The working principal of mechanical milling is reduction in the particle size with high energy ball milling. In 1970, John Benjamin has developed this method of particle size reduction. This intern is responsible for modification of surface properties. The success of mechanical milling is affected by process variable and properties of milling powder. It is categorized into low energy and high energy milling that depend on induced mechanical energy to powder mixture. Nanosized particles are generally produced using high energy ball milling process. This method is widely preferred for intermetallic nanoparticles synthesis.

Step 1: Add the material to be milled and grinding balls to a cylindrical container.

Step 2: Rotate the container around its axis at high speed.

Step 3: The grinding balls collide with each other and with the material, reducing its particle size.

Step 4: Continue milling until the desired particle size is achieved.

Advantages

- Uses for large scale production of high purity nanoparticles with superior physical properties such as enhanced solubility of the drug components which

are poorly water soluble in a cost-effective manner.

- *It gives rise to some new and improved properties for the components based on their grain size and material composition.*

Disadvantages

- High energy required.
- Extensive long period of milling time.
- Contamination of powder due to steel balls.
- Very sensitive microstructure can be grinded.

Applications

- This method is preferred to blend aluminium with magnesium and carbon in order to alter its chemical properties and combustion behavior.
- Preparation of elemental powder of aluminium (Al) and beta-silicon carbide (β-SiC).
- Recently the ceramic nanoparticles WC-14% magnesium oxide (MgO) has been prepared.
- It is widely used method for mechanical alloying to produce amorphous alloys such as metal-metal, transition metal-metalloid, and metal-carbon systems for various purposes.

2. Mechanochemical synthesis

Procedure for mechanochemical synthesis of nanoparticles:

1. Mix the starting materials (reactants) stoichiometrically.
2. Mill the reactants using a ball mill at low temperatures without any external heating.
3. During milling, the reactants will undergo deformation, fracture, and welding.
4. Chemical reactions will occur at the surface interface between the reactants.
5. The nanoparticles produced will be surrounded by the byproduct material, which is dispersed in a soluble salt matrix.
6. Remove the byproduct by washing with a suitable solvent.
7. Dry the nanoparticles at 105°C for 12 hours.

Example:

To synthesize Fe_3O_2 nanoparticles using the mechanochemical method, mix sodium carbonate (Na2CO3) and chloride hexahydrate ($FeCl_3 \cdot 6H_2O$) stoichiometrically and mill them using a ball mill at low temperatures without any external heating. During milling, the reactants will undergo deformation, fracture, and welding. Chemical reactions will occur at the surface interface between the reactants, resulting in the formation of Fe_3O_2 nanoparticles. The nanoparticles produced will be surrounded by the byproduct material, which is sodium chloride (NaCl). Remove the NaCl by washing with water. Dry the Fe_3O_2 nanoparticles at 105°C for 12 hours.

Disadvantages

The microstructures (nanostructures/nanoparticles) formed are highly sensitive to grinding condition and may get affected from unwanted contamination from milling media and atmosphere.

For the preparation of smaller particles (smaller than 20 nm) long term milling is required.

Applications

- Simple and efficient method of nanoparticle preparation.
- Can be performed at low temperatures without the use of external heating.
- Can be used to synthesize a wide range of nanoparticles.
- Environmentally friendly, as it does not require the use of organic solvents.

8. Laser ablation

Procedure of laser ablation method

1. Place solid target material under a thin layer of liquid.
2. Expose the target to pulsed laser irradiation.
3. Laser irradiation fragments the target material into nanoparticles.
4. Nanoparticles remain in liquid, forming a colloidal solution.

Key parameters:

- Laser type (e.g., Nd:YAG, Ti:Sapphire, copper vapor)
- Laser pulse duration and energy
- Liquid type and volume
- Presence or absence of surfactant

Example:

To produce gold nanoparticles, a gold target would be placed under a thin layer of water. The target would then be exposed to pulsed Nd:YAG laser irradiation. Laser irradiation would fragment the gold target into nanoparticles. Nanoparticles would remain in water, forming a colloidal solution. The size and distribution of the gold nanoparticles could be controlled by adjusting the laser parameters.

Advantages

- Can produce nanoparticles of a wide variety of materials
- Precise control over particle size and distribution
- High-purity nanoparticles
- Scalable process

Disadvantage

Prolong time laser ablation leads to formation of high amount of nanoparticles in the colloidal solution which block the laser path and also laser energy is get absorbed by already formed nanoparticles instead of target surface. This overall leads to reduction in ablation rate.

Application

- Preparation of Al_2O_3 nanoparticles coating.
- Preparation of silicon nanoparticles.

9. Ion sputtering

Ion sputtering method includes vaporization of a solid through sputtering with a beam of inert gas ions. Recently this method was used for the preparation of nanaoparticles from several metals using magnetron sputtering of metal targets. In this method collimated beams of the nanoparticles is formed and the mass nanostructured films are deposited on the silicon substrates. The entire process is performed at relatively low pressures (1 mTorr).

Sputter deposition is done in evacuated vacuum chamber where sputtering gas is admitted and working pressure (eg. 0.05 and 0.1 mbar) is maintained. A very high voltage is introduced in to the target (cathode) and free electrons are moved in spiral path using magnetic system where they collide with sputtering gas (argon) atoms and leads to ionization of gas. This continuous process produces a glow discharge (plasma) to ignite. The positively charged gas ions attracted towards target where they continuously impinge. This event repeated occurs and approaches the surface of target with energy above the surface binding energy, an atom can be expelled. The collisions occur between metal atoms and gas molecules continuously in vacuum chamber that leads to scattering of atoms forming a diffuse cloud.

Advantages

- The composition of sputtered material is not altered and remains same as that of the target material.
- Method of choice for refractory metals and intermetallic compounds than other methods like evaporation and laser ablation.
- Economical method as the sputtering equipment is less expensive than electron-beam lithography systems.
- Less impurities are generated than those created by chemical methods.
- Alloy nanoparticles can be produced with easier control on composition than other chemical reduction methods.
- This method is a versatile technique to synthesize ionic nanoparticles with spacious sizes and compositions that are not obtainable in solution.
- Slow deposition of heavier ions or mass-selected ions gives unparalleled control of different parameters such as size, composition and charges of ions deposited onto surfaces.

Disadvantages

The nature sputtering gas (He, Ne, Ar, Kr, and Xe) can produce effect on surface morphology, composition, texture, and the optical properties of the nanocrystalline metal oxide films.

Application

- Synthesis of variety of nanomaterials on surface that employed for catalysis process, photovoltaics, magnetism, memory, cluster-surface interactions, hydrophobic coatings, and “nanoportals” for hydrogen storage.
- For preparation of core-satellite Si–Ag and stable Pd-core MgO-shell nanoparticles for the catalytic methanol oxidation reaction.
- Heavy and complex ions such as peptides, proteins, protein assemblies, organometallic complexes, metal clusters, and nanoparticles can be easily placed on the substrates without altering their basic properties.

- This method allows deposition of large molecules like large non-volatile species that are not easy to deposit by traditional atomic and molecular layer deposition techniques.

Bottom up methods

Nanoparticle synthesis using bottom up approach is based on formation nanoparticles from smaller molecules like joining of atoms, molecules or small particles. In this method, nanostructured building blocks of the nanoparticles first formed and then assembled to produce final nanoparticle.

Solid state methods

1. Physical vapor deposition method

Procedure for physical vapor deposition (PVD)

1. Place the substrate in a vacuum chamber.
2. Vaporize the material to be deposited using a thermal or sputtering process.
3. Condense the vaporized material on the substrate to form a thin film or nanoparticles.

Pulsed laser deposition (PLD) is a type of PVD that uses a laser to vaporize the material to be deposited. This method is often used to deposit thin films of lanthanum strontium cobalt and metal nanoparticles on carbon nanotubes.

PLD procedure:

1. Place the substrate in a vacuum chamber.
2. Focus a laser on a solid target of the material to be deposited.
3. The laser ablates (vaporizes) the target, forming a plasma of ablated species.
4. The ablated species are deposited on the substrate to form a film.

Example:

To deposit a thin film of lanthanum strontium cobalt on a carbon nanotube substrate using PLD, you would:

1. Place the carbon nanotube substrate in a vacuum chamber.
2. Focus a laser on a solid target of lanthanum strontium cobalt.
3. The laser ablates the target, forming a plasma of ablated lanthanum strontium cobalt species.
4. The ablated species are deposited on the carbon nanotube substrate to form a thin film of lanthanum strontium cobalt.

Advantages of PVD:

- PVD can be used to deposit a wide variety of materials, including metals, ceramics, and polymers.
- PVD films can be very thin and uniform.
- PVD films can be deposited on a variety of substrates.

Disadvantages of PVD:

- PVD can be a complex and expensive process.
- PVD films can be susceptible to defects.

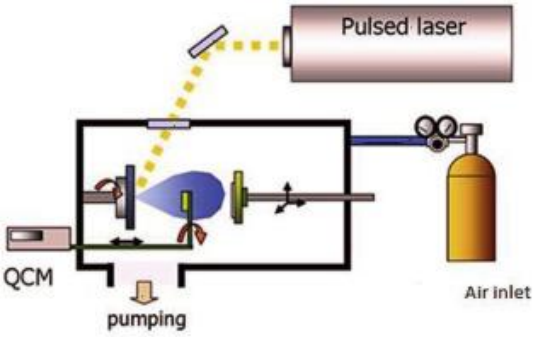


Fig. Pulsed laser deposition of ablated species.

Application

- Preparation of thin film of tungsten selenides.
- Preparation of platinum-ruthenium (Pt–Ru) nanoparticles.
- Formation of Yttria-stabilized zirconia.
- This method is used for the formation of most efficient thin-film solar cells, Cu (In,Ga) Se2 thin film using pulsed laser deposition (PLD). The femtosecond (fs)-pulsed laser deposition (Fs-PLD) derived copper indium gallium selenide (CIGS) thin films shows prominent antireflection and excellent crystalline structure.

2. Chemical vapor deposition method

CVD is a process of depositing a thin film of a material on a substrate surface through a chemical reaction of gaseous molecules containing the desired material.

Steps involved:

1. Place the substrate in a vacuum chamber.
2. Introduce a precursor gas into the chamber.
3. Heat the chamber to a high temperature.
4. The precursor gas reacts on the substrate surface to form a thin film of the desired material.
5. Remove the substrate from the chamber.

Types of CVD:

- **Thermally activated CVD (TACVD)**: The precursor gas is decomposed by heat.
- **Plasma enhanced CVD (PECVD)**: The precursor gas is decomposed by plasma.
- **Photo-initiated CVD (PICVD)**: The precursor gas is decomposed by light.

Advantages of CVD:

- Can be used to deposit a wide variety of materials.
- Can be used to produce thin films with precise thickness and composition.

- Can be used to deposit films on a variety of substrates.

Disadvantages of CVD:

- Requires expensive equipment.
- Can be a complex process to control.
- Can produce hazardous byproducts.

Applications of CVD:

- Manufacturing semiconductors and other electronic devices.
- Coating optical components.
- Depositing protective coatings on metals and other materials.

Example:

To deposit a thin film of silicon dioxide (SiO2) on a silicon substrate using CVD, the following steps would be taken:

1. Place the silicon substrate in a vacuum chamber.
2. Introduce a precursor gas, such as silane (SiH4), into the chamber.
3. Heat the chamber to a temperature of about 400 degrees Celsius.
4. The silane gas reacts on the silicon substrate surface to form a thin film of silicon dioxide.
5. Remove the silicon substrate from the chamber.

The thickness and composition of the silicon dioxide film can be controlled by varying the process parameters, such as the temperature, pressure, and flow rate of the precursor gas.

Liquid state synthesis methods

1. Sol gel method

Procedure of sol-gel method for nanoparticles synthesis:

1. Mix a metal alkoxide (precursor) with a solvent (usually alcohol).
2. Add a catalyst to initiate the reaction.
3. The reaction undergoes hydrolysis and condensation, forming a sol (colloidal suspension of nanoparticles).
4. The sol is then dried to form a gel.
5. The gel can be heated to form a ceramic or thin film.

Advantages:

- Simple and versatile method for synthesizing a wide range of nanoparticles.
- Good control over particle size and morphology.

Applications:

- Synthesis of a variety of metal oxide nanoparticles, such as ZnO2, NiO2, and TiO2.
- Preparation of thin metal films.
- Production of catalysts, sensors, and other nanomaterials.

Simplified example:

To synthesize ZnO2 nanoparticles using the sol-gel method:

1. Mix zinc acetate (precursor) with ethanol (solvent).
2. Add a few drops of nitric acid (catalyst).
3. Stir the mixture until a clear sol is formed.
4. Pour the sol into a Petri dish and allow it to dry.
5. Heat the dried gel at 500°C to form ZnO2 nanoparticles.

The ZnO2 nanoparticles can then be used for a variety of applications, such as catalysis, gas sensing, and UV light detection.

2. Chemical reduction method

Procedure for chemical reduction method of metal nanoparticle synthesis:

1. Dissolve the ionic salt in an appropriate medium.
2. Add a surfactant to the solution.
3. Add a reducing agent to the solution.
4. Reduce the ionic salt to metal nanoparticles.
5. Cap the metal nanoparticles with a stabilizer.

Advantages:

- Simple
- Versatile

Disadvantages:

- Reducing agents may be toxic, expensive, or have poor reducing ability.

Applications:

- Preparation of a variety of metal nanoparticles, including copper, silver, and gold nanoparticles.

Example:

To prepare copper nanoparticles using potassium borohydride as a reducing agent:

1. Dissolve copper sulfate pentahydrate in water.
2. Add sodium dodecyl sulfate (SDS) to the solution.
3. Add potassium borohydride to the solution.
4. The copper sulfate will be reduced to copper nanoparticles.
5. The copper nanoparticles will be capped by the SDS molecules.

The resulting copper nanoparticle dispersion can be used for a variety of applications, such as catalysis and sensing.

3. Hydrothermal method

Hydrothermal Synthesis Procedure:

1. Mix aqueous solutions of metal salts in a sealed vessel.
2. Heat the vessel to high pressure and temperature.
3. Nanoparticles of metal oxides will form inside the vessel.
4. Cool the vessel and recover the nanoparticles.

Advantages:

- Can produce nanoparticles of desired size and shape
- Can produce well-crystallized nanoparticles
- Can produce nanoparticles with high crystallinity

Disadvantages:

- Processes are difficult to control
- Limited reliability and reproducibility

Applications:

- Suitable for preparation of powders in the form of nanoparticles or even single crystals

Example:

To synthesize titanium dioxide (TiO2) nanoparticles using the hydrothermal method, you would mix aqueous solutions of titanium chloride (TiCl4) and sodium hydroxide (NaOH) in a sealed vessel. You would then heat the vessel to a temperature of 180 degrees Celsius and a pressure of 20 MPa for 12 hours. After cooling the vessel, you would recover the TiO2 nanoparticles using filtration.

Note: The hydrothermal method is a versatile technique that can be used to synthesize a wide variety of nanoparticles, including metal oxides, semiconductors, and ceramics.

4. Solvothermal method

Procedure for solvothermal method:

1. **Prepare a solution of precursor chemicals in a solvent.** The solvent can be water, methanol, ethanol, or polyol.
2. **Place the solution in a pressure vessel and seal it.**
3. **Heat the vessel to a temperature above the boiling point of the solvent.** This will create high pressure and temperature inside the vessel.
4. **Maintain the high pressure and temperature for a period of time.** This will allow the precursors to react and form nanocrystals.
5. **Cool the vessel and remove the nanocrystals.**

Advantages of solvothermal method:

- Produces high quality crystallized monodispersed nanocrystals.
- Preferred over conventional oil bath heating for preparing nanocrystallites with narrow size distribution and high degree of crystallization.

Applications of solvothermal method:

- Synthesis of silver nanoparticles.
- Rapid synthesis of nanostructures of Pt, Pd, Ag, and Au using polyethylene glycol or methanol as reducing agent under microwave assisted condition.
- Preparation of high quality crystallized monodispersed nanocrystals of nitrites, metal oxides, and new semiconductor materials.

Gas phase methods

Pyrolysis procedure for nanoparticle preparation:

1. **Prepare a precursor solution.** This can be done by dissolving a suitable metal salt (e.g., acetate, nitrate, chloride) in a solvent (e.g., water, ethanol).
2. **Atomize the precursor solution.** This can be done using a nebulizer, ultrasonic atomizer, or other atomization technique.

3. **Introduce the atomized precursor solution into a hot reactor.** The reactor temperature should be high enough to decompose the precursor and vaporize the solvent.
4. **Collect the nanoparticles.** This can be done using a filter, electrostatic precipitator, or other collection technique.

Advantages of spray pyrolysis:

- Relatively simple and low-cost method.
- The particle size can be controlled and reproducible.

Applications of spray pyrolysis:

- Synthesis of nano-metal oxides and mixed metal oxides.
- Preparation of nanoparticles for various applications, such as catalysis, sensors, and solar cells.

Simplified example:

To synthesize zinc oxide nanoparticles by spray pyrolysis:

1. Prepare a precursor solution by dissolving zinc acetate in water.
2. Atomize the precursor solution using a nebulizer.
3. Introduce the atomized precursor solution into a hot reactor at a temperature of around 500 degrees Celsius.
4. Collect the zinc oxide nanoparticles using a filter.

The resulting zinc oxide nanoparticles can be used for a variety of applications, such as catalysis, sensors, and solar cells.

Biological method/biomimetic method/green synthesis method

Procedure

1. **Choose a biological source:** This could be bacteria, fungi, plants, or plant extracts.
2. **Prepare the biological source:** This may involve growing the microorganisms, extracting the plant compounds, or purifying the enzymes.
3. **Mix the biological source with a solution of metal ions:** This is the solution that you want to synthesize nanoparticles from.
4. **Incubate the mixture:** This will allow the biological source to reduce the metal ions and form nanoparticles.
5. **Purify the nanoparticles:** This may involve washing the nanoparticles with water or another solvent, or using centrifugation to separate the nanoparticles from the rest of the mixture.

Advantages of biological nanoparticle synthesis

- Cost-effective
- Eco-friendly

- Easy to scale up for large-scale production
- Does not involve the use of high pressure, energy, temperature, or toxic chemicals

Examples of biological nanoparticle synthesis

- **Bacteria:** Silver nanoparticles can be synthesized using bacteria such as Lactobacillus species and Klebsiella pneumoniae.
- **Fungi:** Gold nanoparticles can be synthesized using fungi such as Fusarium oxysporum and Aspergillus fumigatus.
- **Plants:** Copper nanoparticles can be synthesized using plants such as Brassica juncea and Ilex crenata.

Applications of biological nanoparticles

- Medicine: Nanoparticles can be used to deliver drugs to specific cells in the body, or to kill cancer cells.
- Agriculture: Nanoparticles can be used to improve the growth of plants or to protect them from pests and diseases.
- Environment: Nanoparticles can be used to clean up pollution or to generate renewable energy.

Overall, biological nanoparticle synthesis is a simple, cost-effective, and eco-friendly way to produce nanoparticles with a wide range of applications.

Other methods of nanoparticle synthesis

1. Electrochemical deposition

Procedure:

1. Prepare an electrolytic bath containing metal salts. The baths are either acidic or basic and use a three terminal potentiostat.
2. Attach the cathode electrode to the substrate where the metal nanoparticles are to be deposited.
3. Apply a slight voltage for a suitable time.
4. Rinse the substrate and dry it.

Example:

Synthesis of gold nanoparticles (AuNPs) using ED:

1. Prepare an electrolytic bath containing gold chloride (HAuCl4).
2. Attach the cathode electrode to a glassy carbon electrode.
3. Apply a voltage of -0.3 V for 10 minutes.
4. Rinse the glassy carbon electrode with water and dry it.

This will produce a thin film of AuNPs on the surface of the glassy carbon electrode.

- .

Applications

- Synthesis of nanoparticles, nanowire, and nanorods.
- Nanomaterial production such as nanowires of Au, Co, Ni, and Pt.

2. Microwave assisted nanoparticles preparation

Nowadays microwave techniques are more proffered over thermal heating for the preparation nanoparticles. Microwave frequency of range 300 MHz to 300 GHz is applied that leads to orientation of polar molecule such as H_2O with the electric field. The re-orientation of dipolar molecules with an alternating electric field causes molecular friction and loss of energy in the form of heat. Recently this technique was successfully implemented for the preparation of silver nanoparticles where silver nitrate solution is irradiated with carboxymethyl chitosan, which acts as reducing agent and a stabilizer.

Advantages

- Highly effective technology for nanoparticle preparation.
- Simple, rapid volumetric heating and the consequent dramatic increase in reaction rate.
- Homogenous heating throughout the process can speed up the reaction rate by the orders of magnitude compared with conventional heating.

Disadvantages

Shorter crystallization time and homogeneous nucleation because of uniform heat of microwave oven.

Applications

- Useful technique in various fields of chemistry and materials science.
- Widely used for several plant-based extracts to prepare various metal nanoparticles.

Ultra sound technique

The following is a simplified procedure for the sonochemistry method of ultrasound-assisted material synthesis:

1. Prepare a solution containing the precursor materials for the desired nanostructure.
2. Place the solution in a sonochemical reactor, such as an ultrasonic cleaning bath, direct-immersion ultrasonic horn, or flow reactor.
3. Apply high-intensity ultrasound to the solution.
4. The ultrasound will induce acoustic cavitation, which will generate high temperatures and pressures in the vicinity of the collapsing bubbles.
5. These extreme conditions will promote the chemical reactions necessary to produce the desired nanostructure.
6. Once the synthesis is complete, the nanostructures can be collected from the solution.

Advantages of the sonochemistry method:

- Eco-friendly and green
- Fast and easy
- Can be used to synthesize a wide variety of nanostructures from different materials
- Does not require reducing agents for the synthesis of noble metal nanostructures

Disadvantages of the sonochemistry method:

- The rate of the reaction depends on the ultrasonic frequency

Applications of the sonochemistry method:

- Synthesis of unusual nanostructured inorganic materials
- Synthesis of nanostructured materials from volatile organometallic compounds

Examples of sonochemical synthesis:

- Synthesis of gold nanoparticles from gold chloride solution

- Synthesis of silver nanoparticles from silver nitrate solution
- Synthesis of zinc oxide nanoparticles from zinc acetate solution
- Synthesis of titanium dioxide nanoparticles from titanium isopropoxide solution
- Synthesis of carbon nanotubes from methane gas

The sonochemistry method is a powerful tool for the synthesis of nanostructured materials with a variety of potential applications in catalysis, electronics, energy storage, and environmental remediation.

Nanolithography

Nanolithography is a process used to create structures on the nanometer scale. It is used in a variety of industries, including semiconductor manufacturing, MEMS/NEMS devices, and drug delivery.

Simplified procedure:

1. A photoresist is applied to a substrate.
2. A mask is placed over the photoresist and exposed to light or electrons.
3. The photoresist is developed, removing the exposed areas.
4. The substrate is etched, transferring the pattern from the photoresist to the substrate.
5. The remaining photoresist is removed.

Optical beam lithography:

Optical beam lithography uses light to expose the photoresist. The wavelength of the light determines the minimum feature size that can be created.

Electron beam lithography:

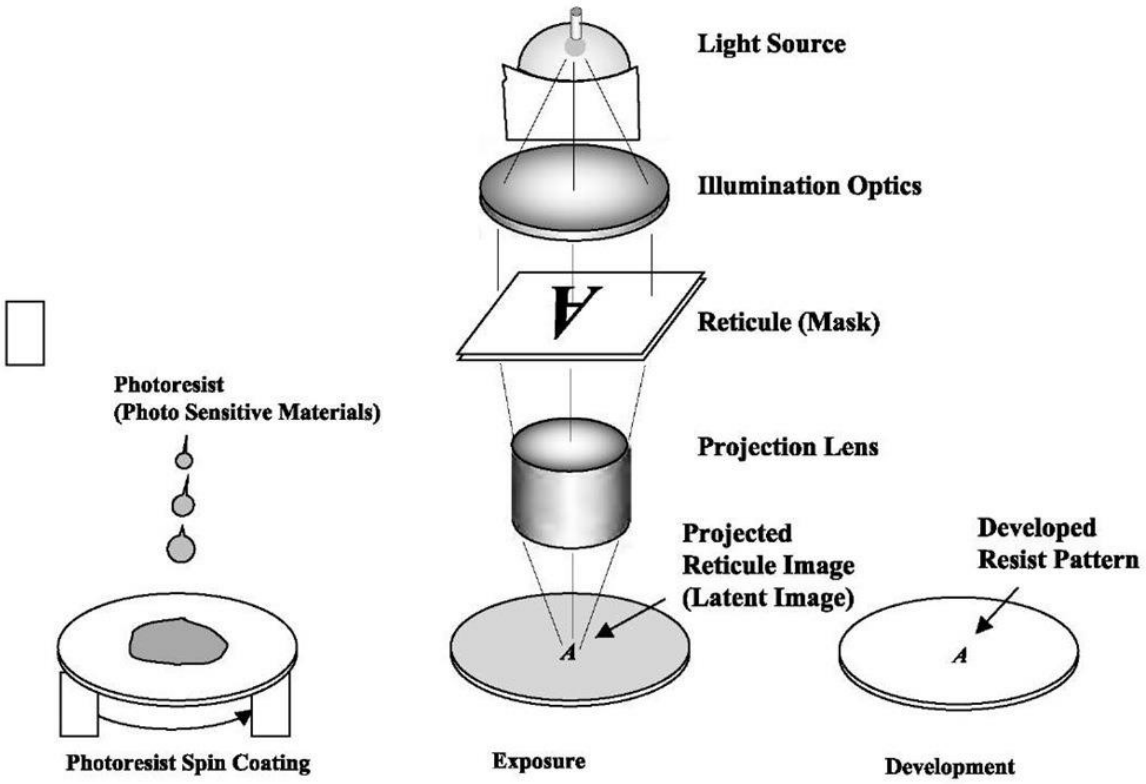
Electron beam lithography uses a focused beam of electrons to expose the photoresist. This technique can create smaller features than optical beam lithography, but it is slower and more expensive.

Example:

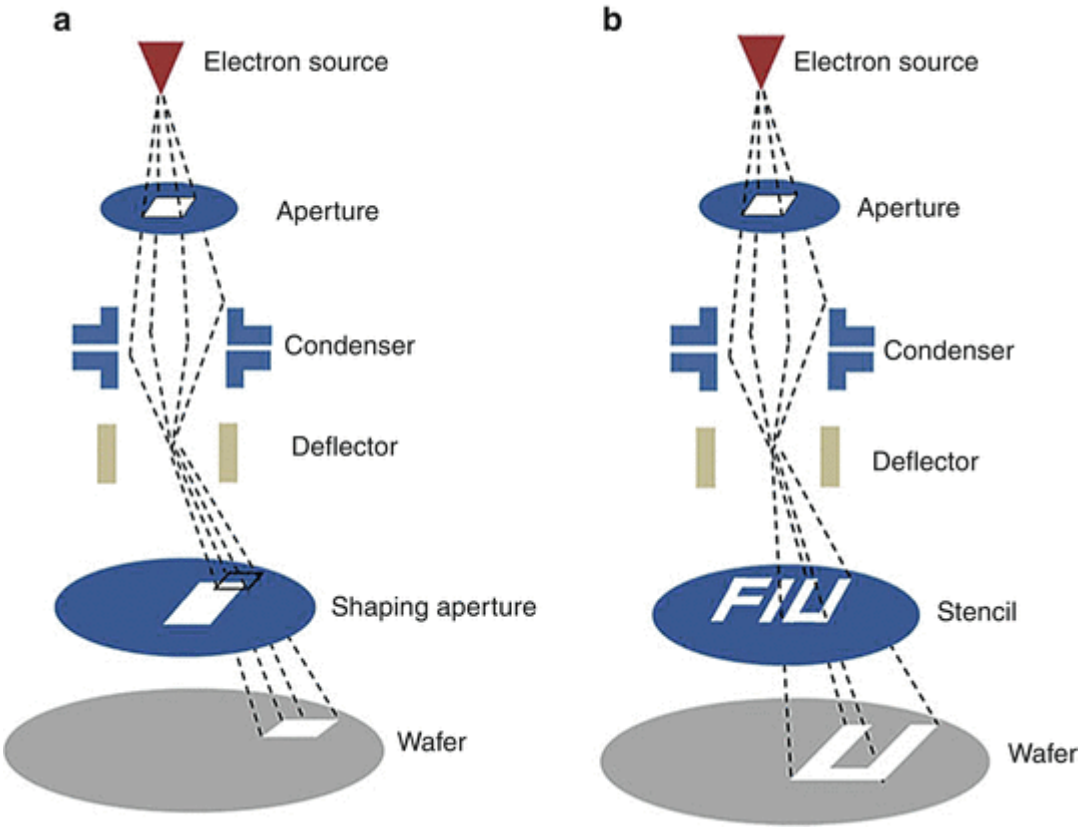
To create a transistor, the following steps would be taken:

1. A photoresist is applied to a silicon wafer.
2. A mask with the pattern of the transistor is placed over the photoresist and exposed to UV light.
3. The photoresist is developed, removing the exposed areas.
4. The silicon wafer is etched, transferring the pattern of the transistor to the silicon.
5. The remaining photoresist is removed.

Nanolithography is a powerful tool that can be used to create a wide variety of nanostructures. It is essential for the manufacturing of many modern devices, including smartphones, computers, and medical devices.



Optical beam lithography



Electron Beam Lithography

Nanophotonics-Fundamentals, Challenges, Future Prospects and Applied Applications.

Nanophotonics is a rapidly growing field of science and technology that deals with the interaction of light with matter at the nanoscale. The nanoscale is typically defined as the range of dimensions from 1 to 100 nanometers, which is equivalent to one-billionth of a meter. At this scale, light and matter interact in ways that are different from what is observed at larger scales.

Fundamentals of nanophotonics

One of the key fundamentals of nanophotonics is the concept of **nanoconfinement**. Nanoconfinement occurs when light is confined to a region that is smaller than its wavelength. This can be achieved using a variety of nanostructures, such as waveguides, resonators, and antennas. Nanoconfinement can lead to a number of interesting effects, such as enhanced light-matter interactions, slow light, and subwavelength imaging.

Another key fundamental of nanophotonics is the concept of **quantum confinement**. Quantum confinement occurs when the dimensions of a material are comparable to the de Broglie wavelength of its charge carriers. This can lead to a number of interesting optical effects, such as bandgap engineering and quantum well lasers.

Challenges in nanophotonics

One of the main challenges in nanophotonics is the fabrication of nanostructures with the desired optical properties. This can be difficult because the tolerances for nanoscale structures are extremely small. Another challenge is the integration of nanophotonic devices into existing optical systems. This can be difficult because nanophotonic devices often operate at a different wavelength range than traditional optical components.

Future prospects of nanophotonics

The future prospects of nanophotonics are very bright. Nanophotonic devices have the potential to revolutionize a wide range of industries, including telecommunications, computing, and healthcare. For example, nanophotonic devices could be used to develop new types of optical communication systems that are faster and more efficient than current systems. Nanophotonic devices could also be used to develop new types of optical computing devices that are smaller and more powerful than current devices. Finally, nanophotonic devices could be used to develop new types of medical devices for imaging, diagnostics, and therapy.

Applied applications of nanophotonics

Nanophotonics is already being used in a number of applications, including:

- **Optical communications:** Nanophotonic devices are being used to develop new types of optical communication systems that are faster and more efficient

than current systems. For example, nanophotonic devices are being used to develop new types of optical amplifiers and optical switches.

- **Optical computing:** Nanophotonic devices are being used to develop new types of optical computing devices that are smaller and more powerful than current devices. For example, nanophotonic devices are being used to develop new types of optical interconnects and optical processors.
- **Healthcare:** Nanophotonic devices are being used to develop new types of medical devices for imaging, diagnostics, and therapy. For example, nanophotonic devices are being used to develop new types of optical microscopes, optical biosensors, and optical imaging agents.
- **Energy:** Nanophotonic devices are being used to develop new ways to generate, store, and transmit energy. For example, nanophotonic devices are being used to develop new types of solar cells, batteries, and fuel cells.

Quantum confined materials-Size effect, (surface plasmon resonance (SPR)-principle, application).

Quantum confined materials are materials whose electronic properties are altered due to their small size. This size effect is caused by the confinement of electrons to a small region of space, which changes their energy levels and wavefunctions. Quantum confined materials can have a variety of unique properties, such as tunable bandgaps, enhanced optical absorption, and increased electrical conductivity.

One important property of quantum confined materials is **surface plasmon resonance (SPR)**. SPR is a phenomenon that occurs when light interacts with the collective oscillations of free electrons on the surface of a metal. SPR is highly sensitive to the size, shape, and composition of the metal nanoparticles, and it can be used to detect and monitor a wide range of molecules and biological systems.

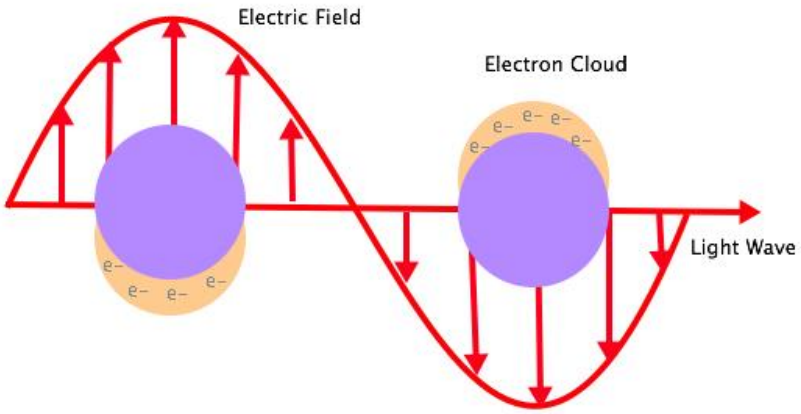


Figure - Shows how as a light wave passes through a material, the induced electric field creates a charge separation in the atoms, creating an electron cloud that then allows for electrons to move freely.

Size effect

The size effect in quantum confined materials is caused by the confinement of electrons to a small region of space. This confinement changes the energy levels and wavefunctions of the electrons, which in turn can have a significant impact on the optical and electrical properties of the material.

For example, the bandgap of a quantum confined semiconductor can be tuned by changing the size of the semiconductor nanocrystals. This is because the energy

levels of the electrons and holes in the semiconductor are quantized, meaning that they can only take on certain values. By changing the size of the nanocrystals, it is possible to change the energy of the bandgap, which can be useful for applications such as solar cells and light-emitting diodes.

Surface plasmon resonance (SPR)

Surface plasmon resonance (SPR) is a phenomenon that occurs when light interacts with the collective oscillations of free electrons on the surface of a metal. SPR is highly sensitive to the size, shape, and composition of the metal nanoparticles, and it can be used to detect and monitor a wide range of molecules and biological systems.

When light interacts with a metal nanoparticle, it can excite the free electrons in the nanoparticle to oscillate. These oscillating electrons create a surface plasmon wave, which is a wave of electromagnetic radiation that propagates along the surface of the nanoparticle. The frequency of the surface plasmon wave is determined by the size, shape, and composition of the metal nanoparticle, as well as the refractive index of the surrounding medium.

Applications

Quantum confined materials and SPR have a wide range of potential applications in a variety of fields, including:

- **Electronics:** Quantum confined materials can be used to create new types of electronic devices, such as transistors, solar cells, and light-emitting diodes.
- **Photonics:** Quantum confined materials can be used to develop new types of optical devices, such as lasers and waveguides.
- **Biomedicine:** SPR can be used to develop new types of biosensors to detect and monitor diseases.
- **Food safety:** SPR can be used to develop new methods to detect and monitor foodborne pathogens.
- **Environmental monitoring:** SPR can be used to develop new methods to detect and monitor environmental pollutants.

UNIT IV	CHEMICAL SENSOR	9
Sensors, sensor science and technology, types of sensors. Chemical Sensors - characteristics of a chemical sensor, elements of chemical sensors. Electro chemical sensors – voltammetry, potentiometric sensors, amperometric sensors, polarization techniques.		

1. Sensors, sensor science and technology

2. Sensor Characteristics & Types of Sensors

3. Chemical sensors

4. Breathalyzer: Chemistry of breathalyzer Breathalyzer sensors Characteristics of a Chemical Sensor

5. Electrochemical sensors, Principles, Characteristics of electrochemical sensors & Application of electrochemical sensors

6. Voltammetry, Current In Voltammetry, Sign Conventions The types of voltammetry

7. Cyclic voltammetry, The Three Electrode System & Instrumentation

8. Differential pulse voltammetry – Polarography & Definition of Electric Polarization

9. Potentiometric sensor, Classification & Application. Amperometry and its Application.

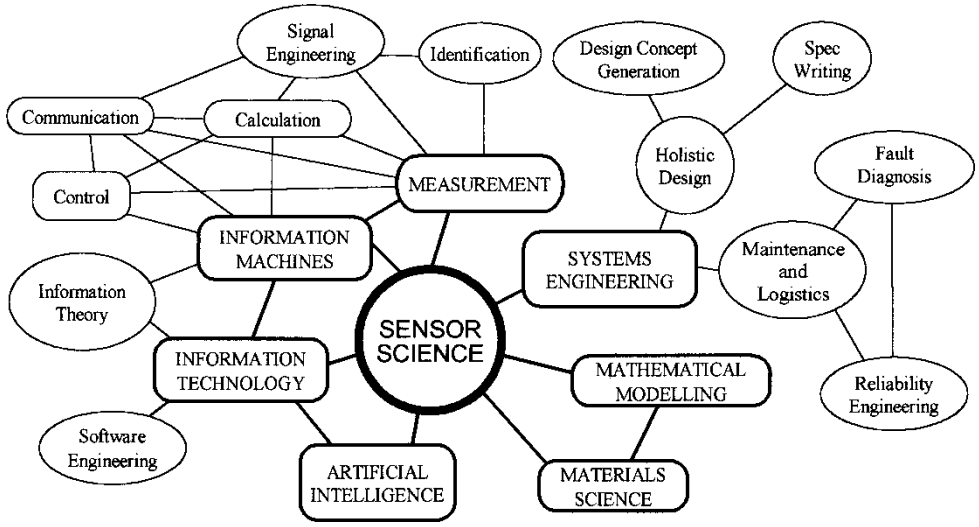
A sensor is a device that produces an output signal for the purpose of sensing a physical phenomenon.

Sensor Science

Sensor science is the study of the underlying principles of sensor operation. This includes the study of the physical and chemical properties of sensor materials, the mechanisms of signal transduction, and the development of new sensor technologies.

Sensor Technology

Sensor technology is the development of practical sensors that can be used in real-world applications. This includes the design and fabrication of sensor devices, the development of signal processing and data analysis algorithms, and the integration of sensors into larger systems.

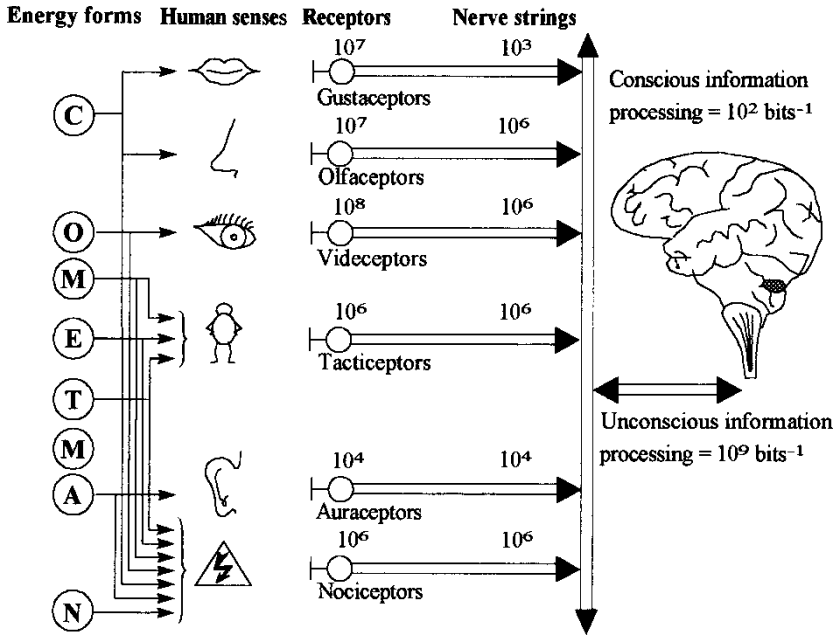


A bubble and block diagram illustrating the contributing fields of sensor science

The human senses are a remarkable gift that allow us to experience and interact with the world around us. They provide us with information about our environment, help us to avoid danger, and enable us to connect with others. The five basic senses are sight, hearing, touch, taste, and smell. Each of these senses has a specialized organ that detects and transmits information to the brain.

- **Sight** is the ability to perceive light and images. The eyes are the organs of sight, and they contain specialized cells called photoreceptors that convert light into electrical signals. These signals are then sent to the brain, where they are interpreted as visual information.
- **Hearing** is the ability to perceive sound waves. The ears are the organs of hearing, and they contain specialized cells called hair cells that convert sound waves into electrical signals. These signals are then sent to the brain, where they are interpreted as auditory information.

- **Touch** is the ability to perceive pressure, temperature, and pain. The skin is the organ of touch, and it contains specialized cells called mechanoreceptors that detect these stimuli. These signals are then sent to the brain, where they are interpreted as tactile information.
- **Taste** is the ability to perceive the five basic tastes: sweet, sour, salty, bitter, and umami. The tongue is the organ of taste, and it contains specialized cells called taste buds that detect these stimuli. These signals are then sent to the brain, where they are interpreted as gustatory information.
- **Smell** is the ability to perceive odor molecules. The nose is the organ of smell, and it contains specialized cells called olfactory receptors that detect these stimuli. These signals are then sent to the brain, where they are interpreted as olfactory information.



The human senses in their COMETMAN environment

Sensor Characteristics:

Sensors are devices that convert one type of physical quantity into another. They are used in a wide variety of applications, including measuring temperature, pressure, light, and sound. The characteristics of a sensor can be divided into two main categories: static and dynamic.

Static characteristics are those that describe the sensor's performance under steady-state conditions. These characteristics include:

- **Sensitivity:** This is a measure of how much the sensor's output changes in response to a change in the input.
- **Resolution:** This is the smallest change in the input that the sensor can detect.
- **Linearity:** This is a measure of how closely the sensor's output is proportional to the input.
- **Zero drift:** This is the tendency of the sensor's output to change over time, even when the input is constant.
- **Full-scale drift:** This is the change in the sensor's output over its entire range.
- **Range:** This is the range of inputs that the sensor can measure.
- **Repeatability:** This is the ability of the sensor to produce the same output for the same input, under the same conditions.
- **Reproducibility:** This is the ability of the sensor to produce the same output for the same input, under different conditions.

Dynamic characteristics are those that describe the sensor's performance under transient conditions. These characteristics include:

- **Rise time:** This is the time it takes for the sensor's output to reach 90% of its final value, after a step change in the input.
- **Fall time:** This is the time it takes for the sensor's output to fall to 10% of its initial value, after a step change in the input.
- **Time constant:** This is the time it takes for the sensor's output to reach 63.2% of its final value, after a step change in the input.
- **Bandwidth:** This is the range of frequencies that the sensor can respond to.
- **Damping factor:** This is a measure of how quickly the sensor's output decays after a transient input.

The specific characteristics that are important for a particular sensor will depend on the application. For example, a sensor that is used to measure temperature in a furnace may need to have a high sensitivity and a wide range, while a sensor that is used to measure pressure in a tire may need to have a high accuracy and a low drift rate.

In addition to the static and dynamic characteristics listed above, there are a number of other factors that can affect the performance of a sensor. These factors include:

- **Noise:** This is unwanted electrical or optical interference that can affect the sensor's output.
- **Temperature:** The output of many sensors is affected by temperature.
- **Humidity:** The output of some sensors is affected by humidity.
- **Vibration:** The output of some sensors is affected by vibration.

- **Chemical exposure:** Some sensors are sensitive to certain chemicals.

The choice of sensor for a particular application will depend on a number of factors, including the required performance, the operating environment, and the cost.

Future of sensor technology

Sensors can improve the world through diagnostics in medical applications; improved performance of energy sources like fuel cells and batteries and solar power; improved health and safety and security for people; sensors for exploring space and the known university; and improved environmental monitoring.

Types of Sensors

There are many different types of sensors, but some of the most common include:

- **Position sensors** measure the position of an object. Examples include linear potentiometers, rotary encoders, and optical encoders.

Position sensors

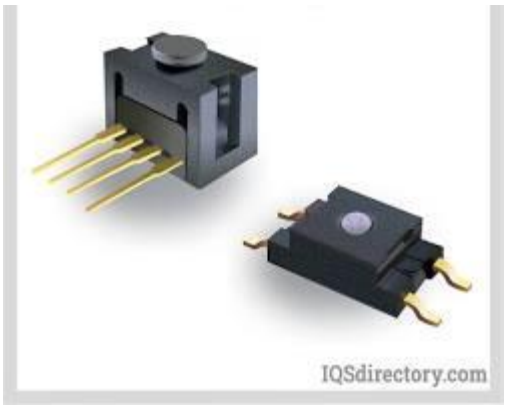
- **Pressure sensors** measure the pressure of a fluid or gas. Examples include strain gauges, diaphragms, and piezoelectric sensors.

Pressure sensors

- **Temperature sensors** measure the temperature of an object or environment. Examples include thermocouples, thermistors, and RTDs.

Temperature sensors

- **Force sensors** measure the force applied to an object. Examples include load cells, strain gauges, and piezoelectric sensors.

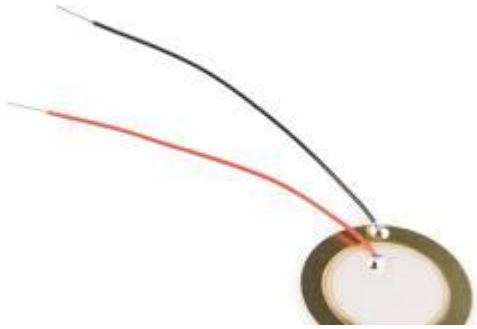


Force sensors

- **Vibration sensors** measure the vibration of an object or surface. Examples include accelerometers, geophones, and piezoelectric sensors.

Vibration sensors

- **Piezo sensors** generate an electrical signal when subjected to mechanical stress. Examples include piezoelectric accelerometers, piezoelectric pressure sensors, and piezoelectric microphones.



Piezo sensors

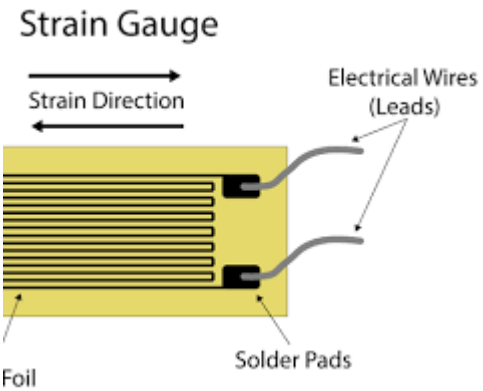
- **Fluid property sensors** measure the properties of a fluid, such as its viscosity, density, and flow rate. Examples include flowmeters, level sensors, and viscosity meters.

Fluid property sensors

- **Humidity sensors** measure the humidity of an environment. Examples include capacitive humidity sensors, resistive humidity sensors, and gravimetric humidity sensors.

Humidity sensors

- **Strain gauges** measure the strain in a material. Examples include foil strain gauges, wire strain gauges, and semiconductor strain gauges.



Strain gauges

- **Photo optic sensors** detect the presence or absence of light. Examples include photodiodes, phototransistors, and photoresistors.

Photo optic sensors

- **Flow and level switches** detect the flow of a fluid or the level of a liquid or solid. Examples include flow switches, level switches, and pressure switches.

Flow and level switches

Applications of Sensors

Sensors are used in a wide variety of applications, including:

- **Medical diagnostics:** Sensors are used in a variety of medical devices, such as blood pressure monitors, heart rate monitors, and glucose monitors.
- **Environmental monitoring:** Sensors are used to monitor air quality, water quality, and soil quality. They are also used to monitor for hazardous substances, such as pollutants and toxins.
- **Industrial automation:** Sensors are used in a variety of industrial applications, such as robotics, manufacturing, and process control.

- **Consumer electronics:** Sensors are used in a variety of consumer electronics devices, such as smartphones, tablets, and wearable devices.

The Future of Sensor Technology

The future of sensor technology is bright. Sensors are becoming increasingly sophisticated, smaller, and cheaper. This is leading to a wide range of new applications for sensors. Some of the key trends in sensor technology include:

- **Miniaturization:** Sensors are becoming increasingly smaller, which is making them more versatile and easier to integrate into new applications.
- **Wireless technology:** Sensors are increasingly being equipped with wireless capabilities, which is making them easier to deploy and use in a wider range of applications.
- **Artificial intelligence:** Sensors are increasingly being integrated with artificial intelligence (AI), which is making them more intelligent and capable of making more informed decisions.

Sensors are playing an increasingly important role in our lives. They are making our lives safer, healthier, and more efficient. The future of sensor technology is bright, and we can expect to see even more innovative and sophisticated sensors in the years to come.

Chemical sensors

What is a chemical sensor?

Chemical sensors are devices that detect and convert chemical information into a measurable signal. They are used in a wide variety of applications, including environmental monitoring, industrial process control, and medical diagnostics.

Essential components of a chemical sensor:

- **Recognition element:** This is the part of the sensor that interacts with the target analyte and generates a signal.
- **Transducer:** This is the part of the sensor that converts the signal from the recognition element into a measurable output.

Types of chemical sensors:

- **Electrochemical sensors:** These sensors measure changes in electrical properties, such as conductivity or potential, in response to the presence of an analyte.
- **Optical sensors:** These sensors measure changes in optical properties, such as absorption or emission of light, in response to the presence of an analyte.
- **Mass sensors:** These sensors measure changes in mass in response to the presence of an analyte.

Applications of chemical sensors:

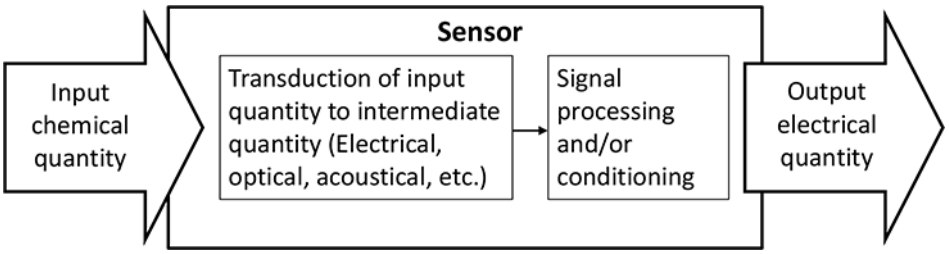
- **Environmental monitoring:** Chemical sensors are used to monitor air and water quality for pollutants such as carbon monoxide, nitrogen dioxide, and sulfur dioxide.
- **Industrial process control:** Chemical sensors are used to monitor and control industrial processes, such as chemical production and refining.
- **Medical diagnostics:** Chemical sensors are used to diagnose diseases, such as diabetes and kidney disease.

Examples of chemical sensors:

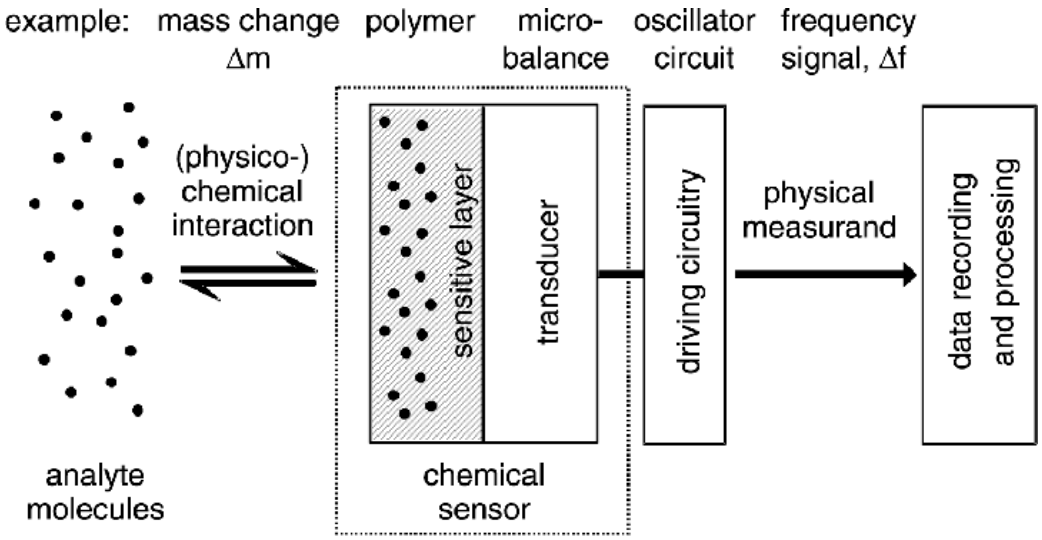
- **Carbon monoxide detectors:** These sensors are used to detect the presence of carbon monoxide, a colorless, odorless gas that can be fatal in high concentrations.
- **Breathalyzers:** These sensors are used to measure blood alcohol content (BAC) by detecting the presence of alcohol in breath.

- **pH meters:** These sensors are used to measure the pH of a solution, which is a measure of its acidity or alkalinity.

Chemical sensors are a versatile and powerful tool that is used in a wide variety of applications. As technology advances, chemical sensors are becoming increasingly sensitive, selective, and affordable. This is making them even more valuable in the effort to monitor and control our environment, improve industrial processes, and diagnose and treat diseases.



Schematic diagram of a sensor that produces an electrical output in response to the presence of an input quantity.



Chemical Sensor Diagram

Breathalyzer:

A breathalyzer is a device that measures blood alcohol content (BAC) by detecting the presence of ethanol in a person's breath. It works by using a chemical reaction to change the color of a solution, and the amount of color change is proportional to the amount of ethanol present. The most common type of breathalyzer uses a solution of potassium dichromate, which turns green when it reacts with ethanol. The amount of green color is measured by a photocell, and this information is used to calculate the BAC.

Breathalyzers are used by law enforcement to determine whether or not a person is safe to drive, and they are also used in some workplaces to test employees for alcohol consumption.

Overview of the breathalyzer process:

1. The person blows into the breathalyzer.
2. The ethanol in the person's breath reacts with the potassium dichromate solution, turning it green.
3. The amount of green color is measured by a photocell.
4. This information is used to calculate the BAC.

The BAC is a measure of the amount of alcohol in a person's blood. The legal limit for BAC in most countries is 0.08%. A person with a BAC of 0.08% is considered to be legally intoxicated.

When the user exhales into a breath analyzer, any ethanol present in their breath is oxidized to acetic acid at the anode:

$C_2H_5OH(g) + H_2O(l) \rightarrow CH_3COOH(l) + 4H+(aq) + 4e^-$

At the cathode, atmospheric oxygen is reduced:

$O_2(g) + 4H^+(aq) + 4e- \rightarrow 2H_2O(l)$

The overall reaction is the oxidation of ethanol to acetic acid and water.

$C_2H_5OH(l) + O_2(g) \rightarrow CH_3COOH(aq) + H_2O(l)$

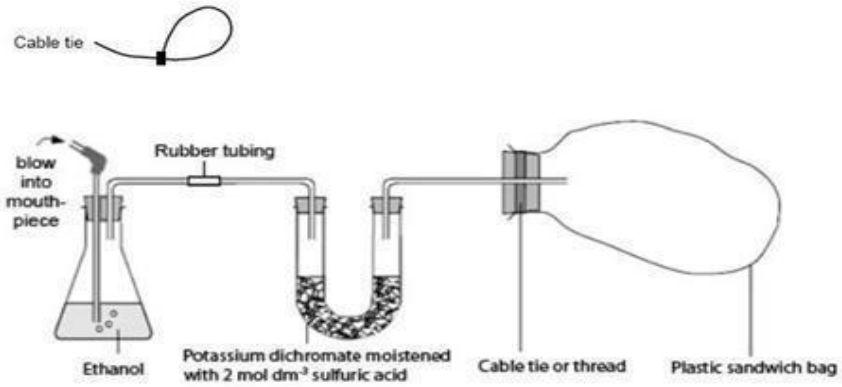
The provided text describes the preparation and procedure for a breathalyzer test using acidified potassium dichromate. It also explains the chemical reactions involved in the test and the safety precautions to be taken. Here's a summary of the key points:

Preparation

1. Wear protective gloves and eye protection.
2. Weigh out potassium dichromate crystals and dilute sulfuric acid in a beaker.
3. Mix the crystals and acid to produce moistened crystals of potassium dichromate.
4. Half-fill a U-tube with the crystals.
5. Fill a conical flask with ethanol.
6. Attach a sterile mouthpiece to the longer glass tube of the flask.
7. Insert the shorter glass tube into the ethanol and attach a plastic bag to the rubber bung.

Procedure

1. Deflate the plastic bag.
2. Blow air through the ethanol to saturate it with ethanol vapor.
3. Connect the flask, U-tube, and plastic bag.
4. Gently blow into the flask to pass ethanol vapor over the acidified potassium dichromate.
5. Observe the color change of the crystals from orange to brown and eventually to green.
6. For a complete color change, connect a filter pump to draw ethanol vapor over the crystals for several minutes.
7. Disconnect the U-tube and remove the stoppers.
8. Smell the products of the reaction and compare them to ethanal and ethanoic acid.



Model an early ‘breathalyser’ test using acidified potassium dichromate in this demonstration featuring the same reaction with ethanol

Electrochemical sensors

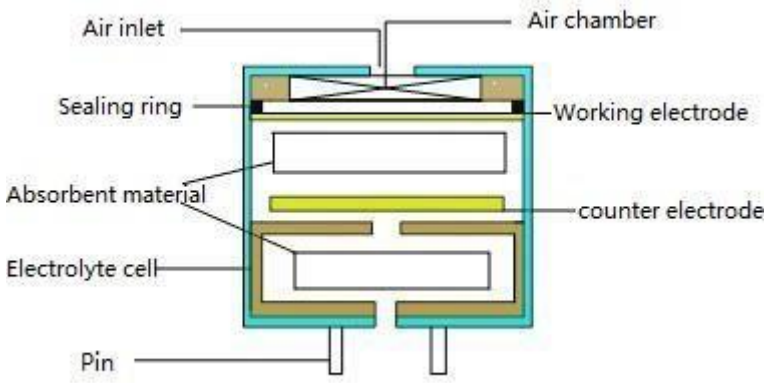
Electrochemical sensors are a versatile and widely used analytical tool that relies on the principles of electrochemistry to measure the concentration of various substances. They are based on the interaction between an analyte, or target substance, and an electrode, which generates an electrical signal that is proportional to the analyte concentration. This signal can then be converted into a measurable value, such as a voltage or current, which can be used to determine the concentration of the analyte.

Electrochemical sensors can be classified into several different types based on the type of electrochemical measurement they perform. These include:

1. **Potentiometric sensors:** These sensors measure the potential difference between two electrodes, one of which is sensitive to the analyte. The potential difference is directly proportional to the analyte concentration.
2. **Conductivity sensors:** These sensors measure the conductivity of a solution, which is a measure of its ability to conduct electricity. The conductivity of a solution is affected by the presence of ions, and therefore can be used to measure the concentration of dissolved ions.
3. **Amperometric sensors:** These sensors measure the current flowing through a solution between two electrodes. The current is proportional to the rate of electrochemical reaction occurring at the electrodes, which is in turn proportional to the analyte concentration.
4. **Voltammetric sensors:** These sensors measure the current flowing through a solution as the potential between two electrodes is varied. The resulting current-voltage curve, or voltammogram, can be used to identify and quantify the analyte.
5. **Impedimetric sensors:** These sensors measure the impedance of a solution, which is a measure of its resistance to the flow of alternating current. The impedance of a solution is affected by the presence of ions, and therefore can be used to measure the concentration of dissolved ions.

Principles of Electrochemical Sensors

Electrochemical sensors are a type of sensor that detects and measures the concentration of a target gas or substance by converting the chemical reaction between the target gas and the sensor's electrodes into an electrical signal. The electrical signal is typically a current or voltage that is proportional to the concentration of the target gas.



Electrochemical sensor structure diagram

Components of an Electrochemical Sensor

An electrochemical sensor typically consists of three main components:

1. **Working electrode:** The working electrode is the electrode where the chemical reaction between the target gas and the sensor occurs. The material of the working electrode is chosen based on its ability to catalyze the desired reaction.
2. **Reference electrode:** The reference electrode provides a stable potential that is used to measure the potential of the working electrode. The reference electrode is typically made of a material that has a stable and well-known potential, such as silver/silver chloride (Ag/AgCl).
3. **Counter electrode:** The counter electrode is used to complete the electrical circuit and allow current to flow between the working electrode and the reference electrode. The counter electrode is typically made of a conductive material, such as platinum or gold.

Operation of an Electrochemical Sensor

When the target gas enters the sensor, it reacts with the working electrode, causing a change in the potential of the working electrode. This change in potential is measured by comparing it to the potential of the reference electrode. The resulting electrical signal is proportional to the concentration of the target gas.

Advantages of Electrochemical Sensors

Electrochemical sensors have several advantages over other types of sensors, including:

- High sensitivity
- Fast response time
- Low cost
- Portability
- Versatility

Disadvantages of Electrochemical Sensors

Electrochemical sensors also have some disadvantages, including:

- Limited selectivity
- Short lifespan
- Susceptibility to interference from other gases

Applications of Electrochemical Sensors

Electrochemical sensors are used in a wide variety of applications, including:

- Environmental monitoring
- Industrial safety
- Medical diagnostics
- Automotive sensors
- Food safety

Voltammetry

Voltammetry is an electroanalytical technique that measures the current as a function of applied potential. It is a powerful tool for studying the electrochemical properties of materials, including their reduction and oxidation potentials, electron transfer rates, and surface reactivity.

Current in Voltammetry

The current in voltammetry is a result of the transfer of electrons between the working electrode and the analyte. When the potential of the working electrode is changed, the energy of the electrons in the electrode is also changed. If the energy of the electrons in the electrode is high enough, they can be transferred to the analyte, resulting in a reduction reaction. Conversely, if the energy of the electrons in the electrode is low enough, they can be taken from the analyte, resulting in an oxidation reaction.

The current in voltammetry is proportional to the rate of electron transfer. The rate of electron transfer is a function of the potential of the working electrode, the concentration of the analyte, the temperature, and other factors.

Sign Conventions

In voltammetry, the sign of the current is used to indicate whether a reduction or oxidation reaction is occurring. A positive current indicates that a reduction reaction is occurring, while a negative current indicates that an oxidation reaction is occurring.

Types of Voltammetry

There are many different types of voltammetry, each with its own strengths and weaknesses. Some of the most common types of voltammetry include:

- **Linear sweep voltammetry (LSV)**: In LSV, the potential of the working electrode is scanned linearly from a starting potential to a final potential. The current is measured as a function of potential.
- **Cyclic voltammetry (CV)**: In CV, the potential of the working electrode is scanned from a starting potential to a final potential, and then back to the starting potential.
- **Pulsed voltammetry**: In pulsed voltammetry, the potential of the working electrode is applied in a series of pulses. The current is measured during each pulse.
- **Square wave voltammetry (SWV)**: In SWV, the potential of the working electrode is applied in a series of square waves. The current is measured at the end of each positive and negative pulse.

- **Differential pulse voltammetry (DPV)**: In DPV, the potential of the working electrode is applied in a series of square waves, superimposed with a small sinusoidal wave. The current is measured at the end of each positive and negative pulse.

Applications of Voltammetry

Voltammetry has a wide range of applications in analytical chemistry, environmental science, materials science, and bioelectrochemistry. Some of the specific applications of voltammetry include:

- **Determination of the concentration of analytes**: Voltammetry can be used to determine the concentration of analytes in solution by measuring the current as a function of potential.
- **Study of redox reactions**: Voltammetry can be used to study the redox reactions of analytes by measuring the potential at which the current is zero.
- **Characterization of materials**: Voltammetry can be used to characterize the surface properties of materials by measuring the current as a function of potential.
- **Development of sensors**: Voltammetry can be used to develop sensors for the detection of analytes in solution.

Voltammetry is a versatile and powerful technique that has a wide range of applications. It is a valuable tool for scientists and engineers in many different fields.

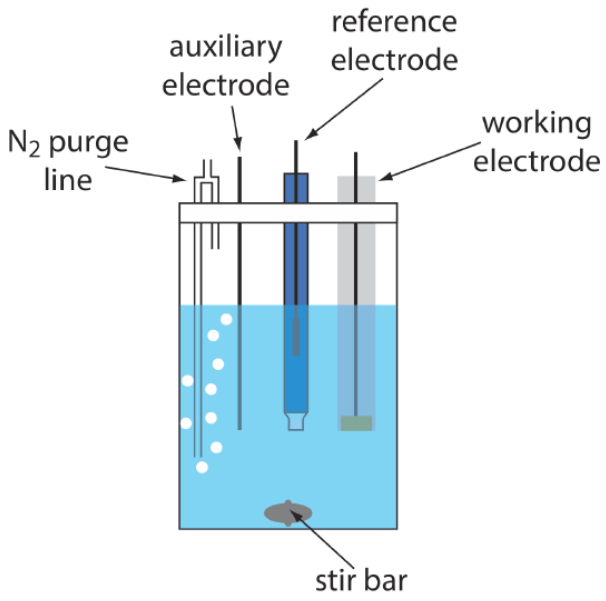
Cyclic voltammetry

Cyclic voltammetry (CV) is a powerful electrochemical technique used to investigate the redox properties of molecules in solution. It involves applying a linearly varying potential to a working electrode while measuring the resulting current. The resulting cyclic voltammogram provides information about the oxidation and reduction potentials, reversibility of the redox process, and the kinetics of the electron transfer reaction.

The Three Electrode System

The three electrode system is essential for accurate cyclic voltammetry measurements. It consists of three electrodes:

1. **Working electrode (WE)**: The electrode at which the redox reaction of interest occurs. The WE is typically a small, inert electrode made of a material such as gold, platinum, or glassy carbon.
2. **Counter electrode (CE)**: The electrode that provides the current necessary to balance the current flowing at the WE. The CE is typically a larger electrode made of a conductive material such as platinum or graphite.
3. **Reference electrode (RE)**: The electrode that provides a stable and well-defined potential. The RE is typically a non-polarizable electrode that maintains a constant potential against a known redox couple. Common REs include the standard hydrogen electrode (SHE) and the silver/silver chloride electrode (Ag/AgCl).



Three-electrode setup: (1) working electrode; (2) auxiliary electrode; (3) reference electrode

Instrumentation

Cyclic voltammetry is typically performed using a potentiostat, an instrument that can control the potential of the working electrode and measure the resulting current. The potentiostat is connected to the three electrodes in the electrochemical cell. The potential of the WE is swept linearly from an initial potential (Ei) to a vertex potential (E1), then reversed back to Ei, and finally swept to a second vertex potential (E2). The current flowing at the WE is measured as a function of the applied potential, and the resulting cyclic voltammogram is plotted.

Applications of Cyclic Voltammetry

Cyclic voltammetry has a wide range of applications in chemistry, including:

- **Determining redox potentials of molecules**
- **Investigating the reversibility of redox processes**
- **Studying the kinetics of electron transfer reactions**
- **Characterizing catalysts**
- **Analyzing the stability of organic and inorganic compounds**
- **Monitoring the progress of chemical reactions**

Cyclic voltammetry is a versatile and powerful technique that is widely used in electrochemical research. It provides valuable information about the redox properties of molecules and is an essential tool for understanding the mechanisms of electron transfer reactions.

Differential pulse voltammetry

Differential pulse voltammetry (DPV) is a highly sensitive electrochemical technique used to measure the current responses of electroactive species in solution. It is a derivative of linear sweep voltammetry (LSV) and staircase voltammetry (SV), with the key difference being that a series of small, regular voltage pulses are superimposed on the linear or staircase potential sweep. This modification provides several advantages over LSV and SV, including:

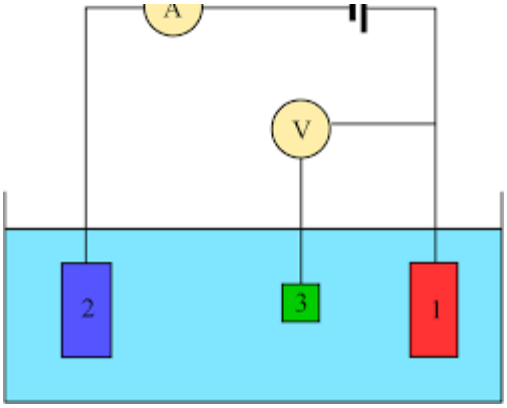
- **Improved sensitivity:** DPV is significantly more sensitive than LSV and SV due to the cancellation of non-faradaic currents, such as the charging current. This allows for the detection of analytes at lower concentrations.
- **Enhanced selectivity:** The differential nature of the DPV signal makes it more selective than LSV and SV, as it is less susceptible to interference from background currents. This is particularly important in complex samples containing multiple electroactive species.
- **Better resolution:** DPV produces sharper peaks than LSV and SV, which makes it easier to distinguish between closely spaced redox events.

Instrumentation

A typical DPV setup consists of the following components:

- **Potentiostat:** A potentiostat is an electronic device that is used to control the potential of the working electrode.
- **Working electrode:** The working electrode is the electrode at which the electrochemical reaction occurs. It is typically made of a noble metal, such as gold or platinum.
- **Reference electrode:** The reference electrode is a stable electrode that provides a fixed potential against which the working electrode potential is measured. A common reference electrode is the silver/silver chloride (Ag/AgCl) electrode.
- **Counter electrode:** The counter electrode is an electrode that provides a path for the current to flow. It is typically made of a large, inert material, such as graphite or stainless steel.
- **Solution:** The solution is the sample that contains the analyte to be measured. It is typically an aqueous solution containing a supporting electrolyte.
- **Data acquisition system:** A data acquisition system is used to record the current as a function of potential.

The following is a simplified diagram of a DPV setup:



differential pulse voltammetry setup

Procedure

In a DPV experiment, the potential of the working electrode is scanned linearly from an initial potential to a final potential. A series of small, regular voltage pulses are superimposed on the linear potential sweep. The current is measured immediately before each potential change, and the current difference is plotted as a function of potential. The resulting plot is called a differential pulse voltammogram (DPV).

Applications

DPV is a versatile technique that can be used to study a wide variety of electrochemical reactions. Some common applications of DPV include:

- **Determination of trace metals:** DPV is a highly sensitive technique for the determination of trace metals in solution.
- **Study of redox reactions:** DPV can be used to study the kinetics and thermodynamics of redox reactions.
- **Analysis of pharmaceuticals:** DPV can be used to analyze pharmaceuticals and their metabolites in biological fluids.
- **Characterization of nanomaterials:** DPV can be used to characterize the electrochemical properties of nanomaterials.

DPV is a powerful tool for the study of electrochemistry. It is a sensitive, selective, and versatile technique that can be used to study a wide variety of electrochemical systems.

Polarography

Polarography is an electroanalytical technique that measures the current flowing between two electrodes in a solution as a function of applied voltage. It is used to identify and quantify oxidizable or reducible substances in a solution. The main component of a polarograph is the dropping mercury electrode (DME), which is a continuously forming mercury droplet that serves as the working electrode. The other electrode, the reference electrode, is a non-polarizable electrode that provides a stable potential.

Instrumentation of Polarography

A typical polarograph consists of the following components:

1. **Dropping Mercury Electrode (DME)**: The DME is the heart of the polarograph. It is a capillary tube that continuously forms mercury droplets at its tip. The fresh surface of the mercury droplet provides a consistently reproducible electrode surface.
2. **Reference Electrode**: The reference electrode provides a stable potential against which the DME potential is measured. Common reference electrodes include the saturated calomel electrode (SCE) and the silver/silver chloride electrode (Ag/AgCl).
3. **Polarographic Cell**: The polarographic cell is the container that holds the solution to be analyzed. It has two or three compartments, one for the solution, one for the reference electrode, and sometimes one for an inert gas that is bubbled through the solution to remove oxygen.
4. **Power Supply**: The power supply provides a voltage that is applied across the electrodes. The voltage is gradually increased, and the current flowing between the electrodes is measured.
5. **Recorder**: The recorder plots the current flowing between the electrodes as a function of applied voltage. This plot, called a polarogram, is used to identify and quantify the substances in the solution.

Types of Polarography

There are two main types of polarography:

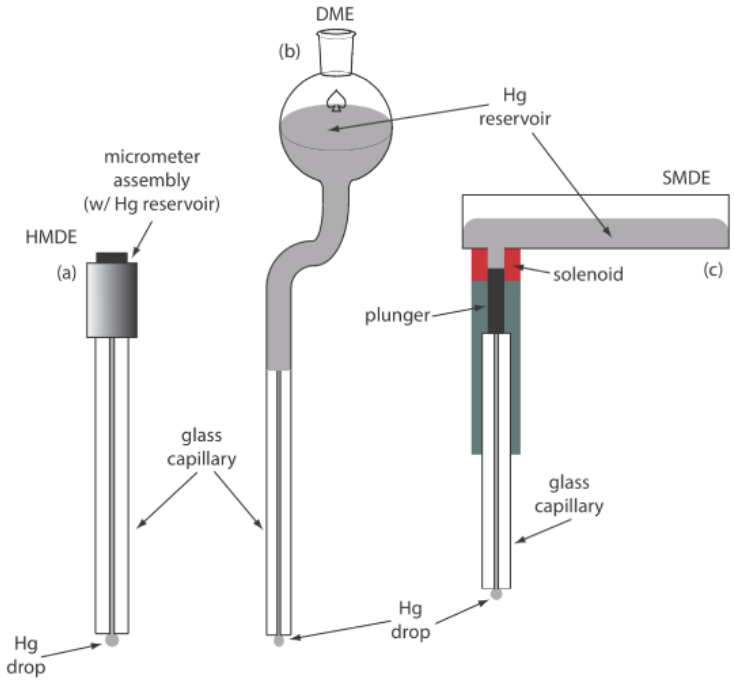
1. **DC Polarography**: This is the original form of polarography, in which a direct current (DC) voltage is applied to the electrodes.
2. **Pulse Polarography**: This is a more modern technique, in which a pulsed voltage is applied to the electrodes. Pulse polarography is more sensitive than DC polarography and is less susceptible to interference from dissolved oxygen.

Applications of Polarography

Polarography has a wide range of applications in analytical chemistry, including:

1. **Qualitative Analysis**: Polarograms can be used to identify the presence of certain substances in a solution.
2. **Quantitative Analysis**: Polarograms can be used to quantify the concentration of certain substances in a solution.
3. **Study of Electrode Processes**: Polarography can be used to study the kinetics and thermodynamics of electrode reactions.

Polarography is a versatile and powerful technique that has been used for many decades in analytical chemistry. It is a relatively simple and inexpensive technique that can be used to analyze a wide range of substances.



Potentiometric Sensor: Definition, Classification & Applications

Definition

A potentiometric sensor is a type of electrochemical sensor that measures the electrical potential of an electrode when no current is flowing through it. This potential, known as the electrode potential, is related to the concentration of the analyte in the solution or gas being measured. Potentiometric sensors are widely used in a variety of applications, including environmental monitoring, industrial process control, and clinical diagnostics.

Classification

Potentiometric sensors can be classified into two main types:

- **Membrane sensors:** These sensors have an ion-selective membrane that allows only specific ions to pass through it. The potential difference between the reference electrode and the working electrode is related to the concentration of the target ion in the solution.
- **Solid-state sensors:** These sensors have a solid electrolyte that allows the transport of ions. The potential difference between the reference electrode and the working electrode is related to the concentration of the target ion in the gas or solid being measured.

Applications

Potentiometric sensors are used in a wide variety of applications, including:

- **Environmental monitoring:** Potentiometric sensors are used to monitor the concentration of pollutants in air, water, and soil.
- **Industrial process control:** Potentiometric sensors are used to monitor the concentration of chemicals in industrial processes.
- **Clinical diagnostics:** Potentiometric sensors are used to measure the concentration of ions in blood and other bodily fluids.

Examples of Potentiometric Sensors

- **pH electrode:** This sensor measures the concentration of hydrogen ions (H+) in a solution.
- **Ion-selective electrode:** This sensor measures the concentration of a specific ion in a solution.
- **Oxygen sensor:** This sensor measures the concentration of oxygen in a gas or liquid.

Advantages of Potentiometric Sensors

Potentiometric sensors have several advantages over other types of sensors, including:

- **Selectivity:** Potentiometric sensors can be very selective for specific ions or gases.
- **Sensitivity:** Potentiometric sensors can be very sensitive to changes in analyte concentration.
- **Stability:** Potentiometric sensors are relatively stable over long periods of time.
- **Simplicity:** Potentiometric sensors are relatively simple to operate and maintain.

Disadvantages of Potentiometric Sensors

Potentiometric sensors also have some disadvantages, including:

- **Limited range:** Potentiometric sensors have a limited range of measurement.
- **Interferences:** Potentiometric sensors can be affected by interferences from other ions or gases.
- **Response time:** Potentiometric sensors can have a relatively slow response time.

Overall, potentiometric sensors are a versatile and valuable tool for measuring the concentration of ions and gases in a variety of applications.

Amperometry

Amperometry is an electroanalytical technique that measures the current produced by a chemical reaction occurring at an electrode. The current is directly proportional to the concentration of the analyte, making amperometry a sensitive and quantitative method for analysis.

Principles of Amperometry

Amperometry is based on the principle that when an electrochemical reaction occurs at an electrode, a flow of electrons is generated. This flow of electrons is measured as an electric current. The magnitude of the current is proportional to the rate of the electrochemical reaction, which in turn is proportional to the concentration of the analyte.

Instrumentation for Amperometry

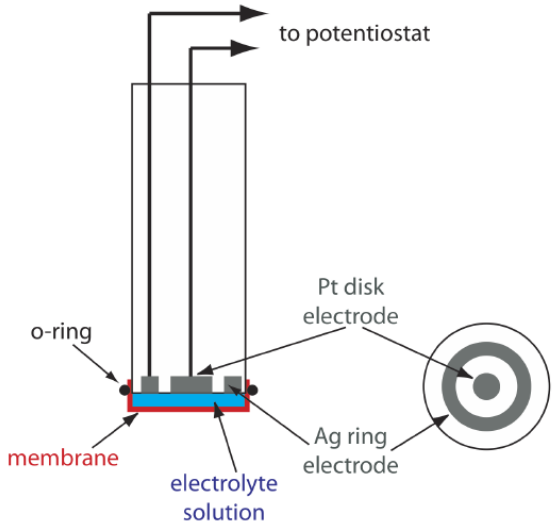
The basic instrumentation for amperometry consists of a working electrode, a reference electrode, and a potentiometer or amperometer. The working electrode is the electrode at which the electrochemical reaction occurs. The reference electrode is used to establish a stable potential between the working electrode and the solution. The potentiometer or amperometer is used to measure the current produced by the electrochemical reaction.

Applications of Amperometry

Amperometry is a versatile technique that has a wide range of applications in analytical chemistry. Some of the most common applications of amperometry include:

- **Determination of inorganic and organic compounds:** Amperometry can be used to determine a wide variety of inorganic and organic compounds, including metals, anions, cations, and organic molecules.
- **Titrations:** Amperometry can be used to determine the endpoint of titrations. In an amperometric titration, the current is monitored as a titrant is added to the solution. The endpoint of the titration is reached when the current reaches a maximum or minimum value.
- **Flow analysis:** Amperometry is a common detection method in flow analysis. In flow analysis, the sample is injected into a flowing stream of carrier solution. The sample is then passed through a detector, such as an amperometric detector, which measures the concentration of the analyte.

Amperometry is a powerful and versatile technique that has a wide range of applications in analytical chemistry. It is a sensitive, quantitative, and relatively simple technique that can be used to determine a wide variety of compounds.



The terms "current" and "potential" are often used interchangeably, but they have distinct meanings in physics and other contexts. Here's a comparison and contrast between current and potential:

Current

In physics, electric current is the flow of electric charge through a conductor. It is measured in amperes (A) and represents the rate at which charge passes through a specific point or cross-section of a conductor. Electric current is analogous to the flow of water in a pipe. The higher the current, the faster the charge is moving through the conductor.

Potential

Electric potential, also known as voltage, is the electrical energy stored per unit charge. It is measured in volts (V) and represents the difference in energy between two points in an electric field. Electric potential is analogous to the elevation of water in a reservoir. The higher the potential, the greater the potential energy stored per unit charge.

Comparison

Both current and potential are fundamental concepts in electricity. Current is the movement of charge, while potential is the energy associated with that movement. They are related by Ohm's law, which states that the current through a conductor is directly proportional to the potential difference across it and inversely proportional to its resistance.

Contrast

The key difference between current and potential is that current is a flow of charge, while potential is a measure of energy. Current exists when charges are moving, while potential can exist even when there is no current flow. Additionally, current is measured in amperes (A), while potential is measured in volts (V).

Feature	Current	Potential
Definition	Flow of electric charge	Electrical energy per unit charge
Units	Amperes (A)	Volts (V)
Analogy	Flow of water in a pipe	Elevation of water in a reservoir
Relationship	Current is directly proportional to potential difference and inversely proportional to resistance (Ohm's law)	

Comparative explanation of each technique:

Feature	Voltammetry	Potentiometric sensors	Amperometric sensors	Polarization techniques
Measurement principle	Measures the current flowing between two electrodes as the potential is varied	Measures the potential difference between two electrodes	Measures the current flowing through a working electrode as the potential is varied	Applies a potential to an electrode and measures the resulting current or potential

Applications	Analyzes the concentration of a dissolved species in a solution	Measures the concentration of a dissolved species in a solution	Measures the concentration of a dissolved species in a solution	Studies the kinetics of electrochemical reactions
Advantages	High sensitivity	Simple to use	High sensitivity	Can be used to study a wide range of electrochemical reactions
Disadvantages	Requires a relatively large sample size	Can be susceptible to interference from other dissolved species	Requires a relatively large sample size	Can be time-consuming

Voltammetry is an electrochemical technique that measures the current flowing between two electrodes as the potential is varied. The current is a function of the concentration of the dissolved species, so voltammetry can be used to analyze the concentration of a dissolved species in a solution.

Potentiometric sensors are electrochemical sensors that measure the potential difference between two electrodes. The potential difference is a function of the concentration of the dissolved species, so potentiometric sensors can be used to measure the concentration of a dissolved species in a solution.

Amperometric sensors are electrochemical sensors that measure the current flowing through a working electrode as the potential is varied. The current is a function of the concentration of the dissolved species, so amperometric sensors can be used to measure the concentration of a dissolved species in a solution.

Polarization techniques are a group of techniques that apply a potential to an electrode and measure the resulting current or potential. Polarization techniques can be used to study the kinetics of electrochemical reactions.

UNIT-IV INSTRUMENTATION TECHNIQUES

Lecture session 28: Topics: Treatment of analytical data, Mean,The Median, Precision, Accuracy-including error analysis-types-Determinate and indeterminate errors.

Treatment of analytical data

Statistical treatment of Analytical data is written for professional analytical chemists in industry,government and research institutions who requires a practical understanding of the application of statistical in day to day activities in the analytical laboratory.

Statistical treatment of data greatly depends on the kind of experiments and the desired results from the experiments. For example, in a survey regarding the election of meyor, parameters like age, gender, occupation, etc.would be important in influencing the person's decision to vote for a particular candidate.

Error analysis

Error analysis is a method used to document the errors that appear in learner language, determine whether those errors are systematic, and (if possible) explain what cause them.

Examples in the category are spills, misreading a device as a burette, misintrepretation of the procedure, incorrect handling of a micro-pipette, and forgetting to rinse out a beaker when doing a quantitative transfer.

Chemical Analysis in Error

- Measurements invariably involve errors and uncertainties.
- It is impossible to perform a chemical analysis that is totally free of errors or uncertainties
- We can only hope to minimize errors and estimate their size with acceptable accuracy
- Errors are caused by faulty calibrations or standardizations or by random variations and uncertainties in results.
- Frequent calibrations, standardizations, and analyses of known samples can sometimes be used to lessen all but the random errors and uncertainties.

The term error has two slightly different meanings.

1) error refers to the difference between a measured value and the "true" or "known" value.

2) error often denotes the estimated uncertainty in a measurement or experiment.

" We can only hope to minimize errors and estimate their size with acceptable accuracy.

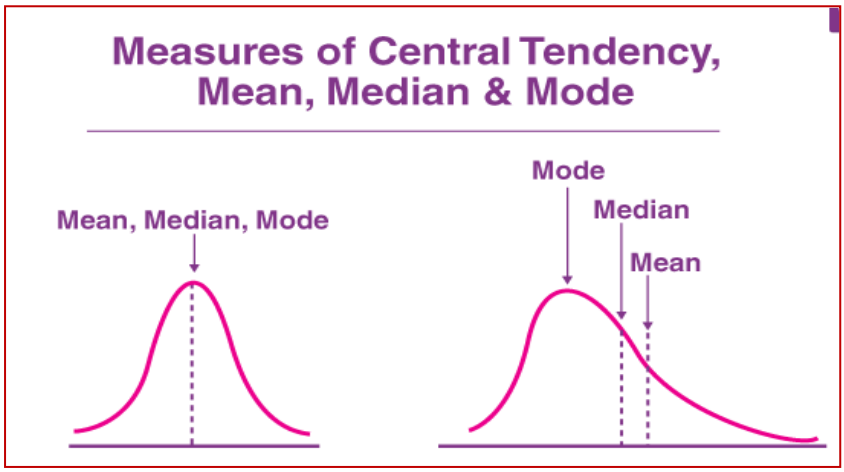
Every measurement is influenced by many uncertainties, which combine to produce a scatter of results

The Mean and the Median

The mean, also called the arithmetic mean or the average, is obtained by dividing the sum of replicate measurements by the number of measurements in the set: The symbol xi means to add all of the values xi for the replicates; xi represents the individual values of x making up the set of N replicate measurements.

$$\bar{x} = \frac{1}{n} \sum_{i=1}^{n} x_i$$

The median is the middle value in a set of data that has been arranged in numerical order. The median is used advantageously when a set of data contain an outlier. An outlier is a result that differs significantly from others in the set. An outlier can have a significant effect on the mean of the set but has no effect on the median.



EXAMPLE 5-1

Calculate the mean and median for the data shown in Figure 5-1.

Solution

$$\text{mean} = \bar{x} = \frac{19.4 + 19.5 + 19.6 + 19.8 + 20.1 + 20.3}{6} = 19.78 \approx 19.8 \text{ ppm Fe}$$

Because the set contains an even number of measurements, the median is the average of the central pair:

$$\text{median} = \frac{19.6 + 19.8}{2} = 19.7 \text{ ppm Fe}$$

Precision

Precision describes the agreement among several results obtained in the same way. Describes the reproducibility of measurements. Precision is readily determined by simply repeating the measurement on replicate samples. Precision of a set of replicate data may be expressed as standard deviation, variance, and coefficient of variation. * di, deviation from mean, is how much xi, the individual result, deviates from the mean.

di = (xi - x)

Accuracy

Accuracy indicates the closeness of the measurement to the true or accepted value and is expressed by the error. Accuracy measures agreement between a result and the accepted value. Accuracy is often more difficult to determine because the true value is usually unknown. An accepted value must be used instead. Accuracy is expressed in terms of either absolute or relative error.

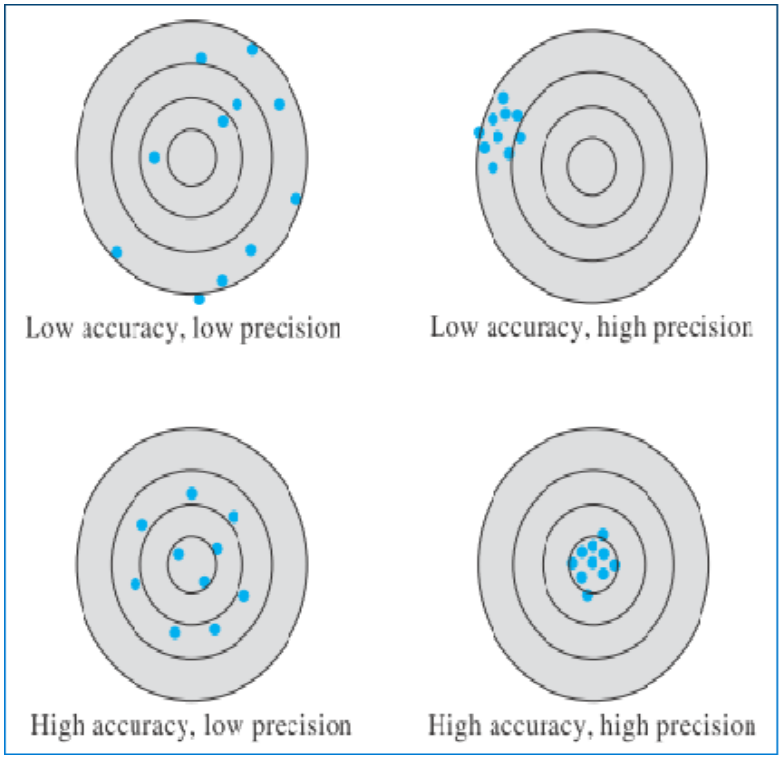


Figure 5-2 Note that we can have very precise results (upper right) with a mean that is not accurate and an accurate mean (lower left) with data points that are imprecise.

Absolute Error

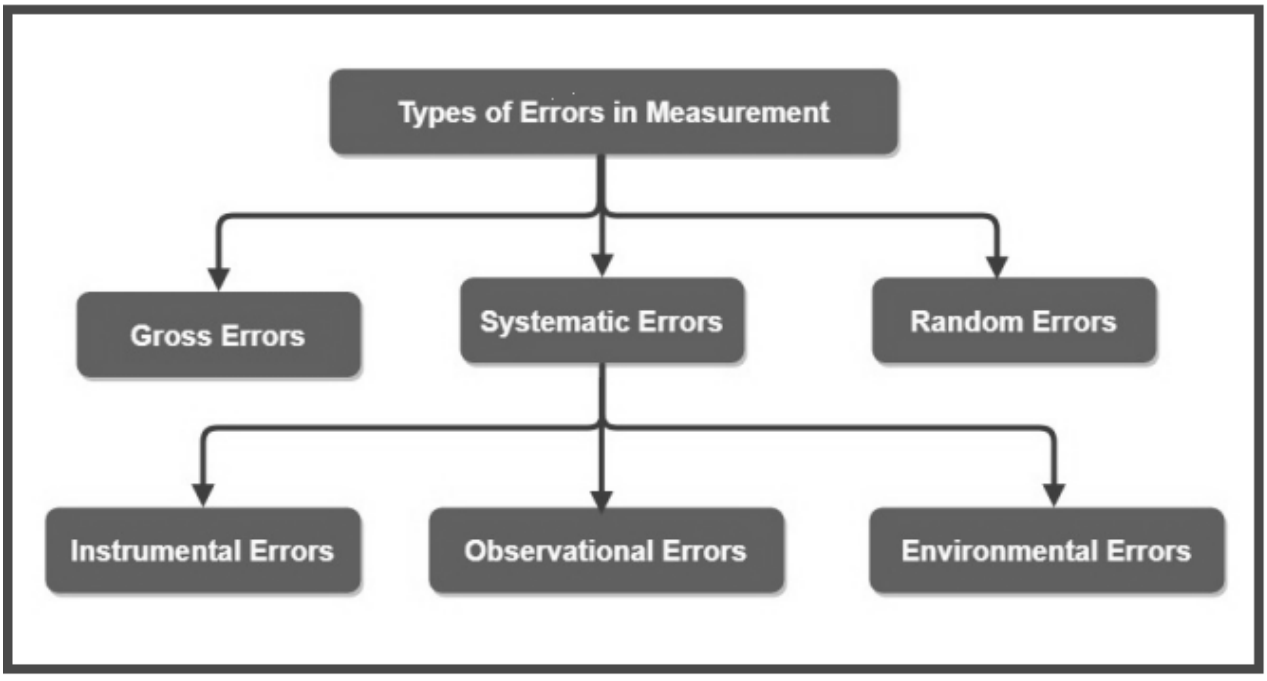
The absolute error of a measurement is the difference between the measured value and the true value. If the measurement result is low, the sign is negative; if the measurement result is high, the sign is positive.

$$E = xi - xt$$

Relative Error

The relative error of a measurement is the absolute error divided by the true value. Relative error may be expressed in percent, parts per thousand, or parts per million, depending on the magnitude of the result.

$$Er = \frac{xi-xt}{xt} \times 100\%$$

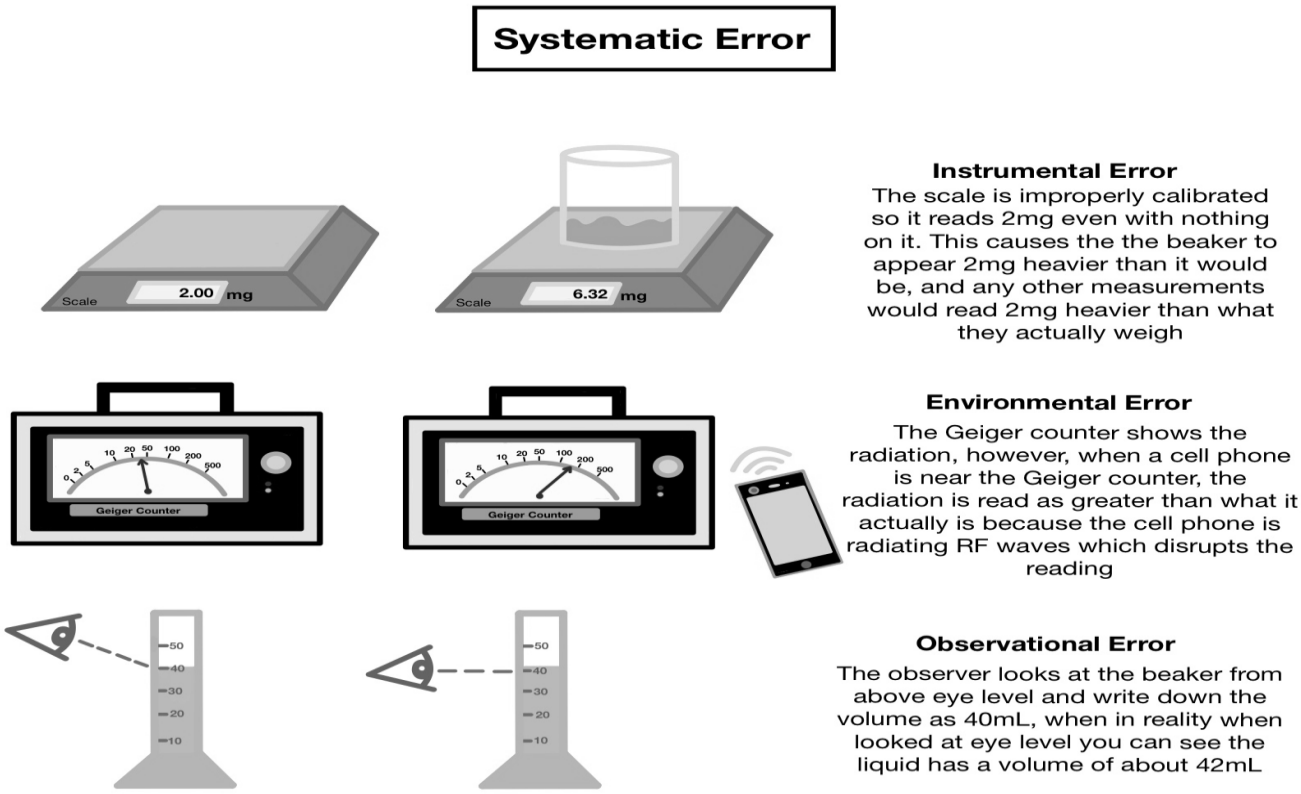


1. Determinate errors

Determinate or systematic errors are those errors that have definite values and have some assignable cause. For every repeated measurement carried out in the same manner, these errors are consistently the same. Systematic errors usually introduce bias into the outcome of the measurement. The accuracy of the results is influenced by significant mistakes. These mistakes can also be identified and corrected because they are reproducible. Bias measures the systematic error associated with analysis. It has a -ve sign if it causes results to be low and has positive sign if the results are high.

Personal error: During the measurement of the analytical experiments, there is often a need for personal judgment. For example: estimating the portion of the pointer between two scale divisions, the color of the solution at the endpoint, the level of the liquid of the mark in pipette or burette, etc. The main source of personal error is prejudice or bias. Human has a tendency to estimate scale reading to the precision in a set of results.
We sometimes knowingly cause the result to fall closer to the true value. Nu0mber bias is also another important source of personal error. Colour blindness person can cause a personal error in volumetric analysis.

Instrumental or reagent error: The measuring tools also have a certain amount of determinate error. Burette, pipette, and volumetric flask, for instance, always deliver slightly differently from what the scale indicates. These inconsistencies primarily result from using the glassware at a temperature that is different than the calibration since doing so damages the container wall when it is heated to dry because of contamination on the interior surface. Due to excessive use and the battery's low voltage, electronic devices may also experience errors. The failure to accurately and often calibrate the instruments could possibly be the cause of the errors. Similar to how changing temperatures can affect numerous electronic components, errors can result from these fluctuations.



Methodic error: The non-ideal type of chemical and physical behavior of reagents and reactions on which an analysis is based can introduce methodic errors. The slowness of reaction, in the completeness of reaction, un-stability of chemical species, and possible occurrence of side reaction can cause methodic errors which may interfere with the measurement process.

For example, in volumetric analysis, a small amount of excess reagent is necessary to change the color of an indicator to signify the completion of the reaction. The errors that are associated with the methods are often very difficult to detect and the most serious type of error out of all types of systematic error.

Constant or proportional error: Constant type of determinate errors are independent of the size of the sample analyzed. When there are constant mistakes, the relative error changes as the sample size is altered, but the absolute error remains constant. As the size of the quantity being measured shrinks, the effect of constant error becomes more pronounced. Meanwhile, Proportional errors decrease or increase in proportion to the size of the sample. The presence of interfering impurities in the sample is the main cause of the proportional error.

Data are distributed more or less symmetrically around the mean value as a result of the indeterminate error. The precision of measurement reflects the random error. Hence, measurement precision is impacted by random or indeterminate errors.Variable fluctuations that are unavoidable or unknown that may have an impact on the findings of experiments are what create indeterminate (or random) errors. Uncertainties in measurements can lead to random or indeterminate errors.

Errors of this kind, which are random or indeterminate, always exist in measurements. Such an error can never be completely ruled out. They are a significant factor in the determination of the analyte's uncertainty. Most of the causes of random errors are impossible to pinpoint. Due to the low value of individual causes of such errors, they cannot be quantified even if their sources are known. However, the combined impact of all errors leads to large variability in the measurement at random.

3. Gross errors

Either too high or too low findings are the outcome of this kind of error. They are the outcome of human mistakes. Outliers, or results that appear to differ significantly from all other measured data in a set of repeated measurements, are frequently the result of gross error.

Difference between Systematic and Random Error

Errors can be divided into two primary kinds, systematic and random errors. Systematic error, as the name implies, is a consistent, repeatable error that deviates from the true value of measurement by a fixed amount. Systematic error is the one that occurs in the same direction each time due to the fault of the measuring device. On the contrary, any type of error that is inconsistent and does not repeat in the same magnitude or direction except by chance is considered to be a random error. Random errors are sometimes called statistical errors.

Lecture session 29: Topics: Classification of analytical methods-Chemical and Instrumental.

The instrumental methods of chemical analysis are divided into categories according to the property of the analyte that is to be measured. Many of the methods can be used for both qualitative and quantitative analysis. The major categories of instrumental methods are the spectral, electroanalytical, and separatory.

What are the classification of analytical method?

There are four major areas of analytical chemistry that are of importance in their application to diverse scientific disciplines. These areas are spectroscopy, acid-base methods, potentiometry, and chromatography.

What is the difference between classical and instrumental methods of analytical chemistry?
The majority of the classical analytical methods rely on chemical reactions to perform an analysis. In contrast, instrumental methods typically depend on the measurement of a physical property of the analyte.

Electrochemical analysis

In this chapter we introduced three electrochemical methods of analysis: potentiometry, coulometry, and voltammetry. In potentiometry we measure the potential of an indicator electrode without allowing any significant current to pass through the electrochemical cell. In principle we can use the Nernst equation to calculate the analyte's activity-junction potentials, however, require that we standardize the electrode.

There are two broad classes of potentiometric electrodes: metallic electrodes and membrane electrodes. The potential of a metallic electrode is the result of a redox reaction at the electrode's surface.

An electrode of the first kind responds to the concentration of its cation in solution; thus, the potential of a Ag wire is determined by the activity of Ag^+ in solution. If another species is in equilibrium with the metal ion, the electrode's potential also responds to the concentration of that species. For example, the potential of a Ag wire in a solution of Cl^- responds to the concentration of Cl^- because the relative concentrations of Ag^+ and C^{l-} are fixed by the solubility product for AgCl. We call this an electrode of the second kind.

The potential of a membrane electrode is determined by a difference in the composition of the solution on each side of the membrane. Electrodes using a glass membrane respond to ions that bind to negatively charged sites on the membrane's surface. A pH electrode is one example of a glass membrane electrode.

Other kinds of membrane electrodes include those using insoluble crystalline solids or liquid ion-exchangers incorporated into a hydrophobic membrane. The F^- ion-selective electrode, which uses a single crystal of LaF_3 as the ion-selective membrane, is an example of a solid-state electrode. The Ca^{2+} ion-selective electrode, in which the chelating di-(n-decyl) phosphate is immobilized in a PVC membrane, is an example of a liquid-based ion-selective electrode.

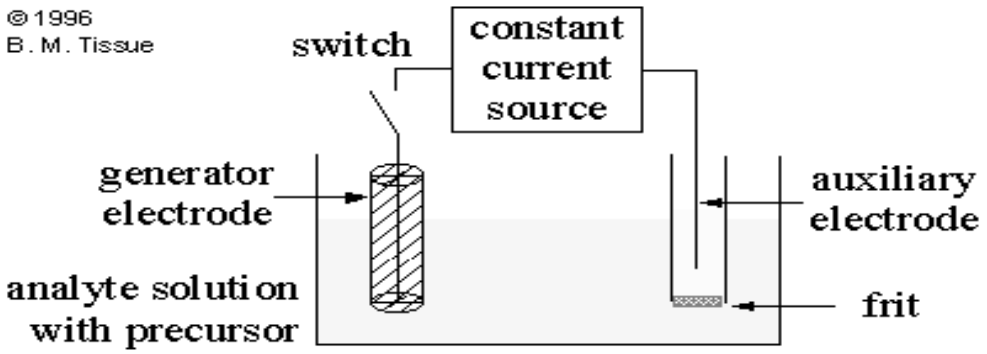
Coulometry

What is coulometry and its principle?

Coulometry is an electrochemical method in which the total charge (the number of coulombs) consumed in the redox conversion of an analyte at an electrode is measured. It is not to be confused with colorimetry, the spectroscopic method.

Coulometric methods are based on Faraday's law that the total charge or current passed during an electrolysis is proportional to the amount of reactants and products in the redox reaction.
If the electrolysis is 100% efficient-meaning that only the analyte is oxidized or reduced-then we can use the total charge or current to determine the amount of analyte in a sample.
In controlled-potential coulometry we apply a constant potential and measure the resulting current as a function of time. In controlled-current coulometry the current is held constant and we measure the time required to completely oxidize or reduce the analyte.

Potentiometric electrodes can be designed to respond to molecules by using a chemical reaction that produces an ion whose concentration can be determined using a traditional ion-selective electrode. A gas-sensing electrode, for example, include a gas permeable membrane that isolates the ion-selective electrode from the gas. When the gas diffuses across the membrane it alters the composition of the inner solution, which is monitored with an ion-selective electrode. An enzyme electrodes operate in the same way.



Coulometry determines the amount of matter transformed during an electrolysis reaction by measuring the amount of electricity (in coulombs) consumed or produced. It can be used for precision measurements of charge, and the amperes even used to have a coulometric definition.

What is coulometer used for?

The silver coulometer is a standard instrument used to determine the mass of silver deposited at a platinum cathode by the passage of an electric current through an aqueous silver nitrate solution.

Voltammetry

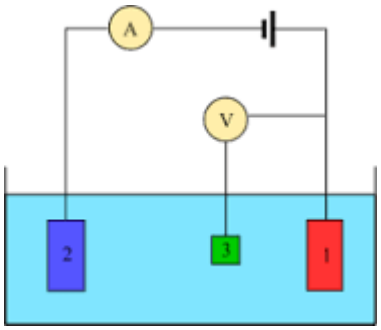
In voltammetry we measure the current in an electrochemical cell as a function of the applied potential. There are several different voltammetric methods that differ in terms of the type of working electrode, how we apply the potential, and whether we include convection (stirring) as a means for transporting of material to the working electrode.

Polarography is a voltammetric technique that uses a mercury electrode and an unstirred solution. Normal polarography uses a dropping mercury electrode, or a static mercury drop electrode, and a linear potential scan. Other forms of polarography include normal pulse polarography, differential pulse polarography, staircase polarography, and square-wave polarography, all of which use a series of potential pulses.

What is voltammetry used for?

Voltammetry is a technique used **to detect neurochemicals capable of undergoing oxidation reactions**. These neurochemicals include neurotransmitters such as serotonin and the catecholamines (e.g., epinephrine, norepinephrine, and dopamine).

What is the principle of voltammetry?



Voltammetry is **the study of current as a function of applied potential**. These curves I = f(E) are called voltammograms. The potential is varied arbitrarily, either step by step or continuously, and the resulting current value is measured as the dependent variable.

In hydrodynamic voltammetry the solution is stirred using either a magnetic stir bar or by rotating the electrode. Because the solution is stirred a dropping mercury electrode can not be used; instead we use a solid electrode. Both linear potential scans and potential pulses can be applied.

In stripping voltammetry the analyte is first deposited on the electrode, usually as the result of an oxidation or reduction reaction. The potential is then scanned, either linearly or by using potential pulses, in a direction that removes the analyte by a reduction or oxidation reaction.
Amperometry is a voltammetric method in which we apply a constant potential to the electrode and measure the resulting current. Amperometry is most often used in the construction of chemical sensors for the quantitative analysis of single analytes. One important example is the Clark O2 electrode, which responds to the concentration of dissolved O2 in solutions such as blood and water.

Classical methods

Qualitative – identification by color, indicators, boiling or melting points, odors

Quantitative – mass or volume (e.g. gravimetric, volumetric)

(1) A type of chemical analysis by which the analyte or analytes in a sample are identified
(2) A type of chemical analysis by which the amount of each analyte or analytes in a sample is determined.

Qualitative – chromatography, electrophoresis and identification by measuring physical property (e.g. spectroscopy, electrode potential)

Quantitative – measuring property and determining relationship to concentration (e.g. spectrophotometry, mass spectrometry)
Often, same instrumental method used for qualitative and quantitative analysis.

Lecture session 30: Topics: Types of instrumental method -Spectral, electroanalytical, and separatory.

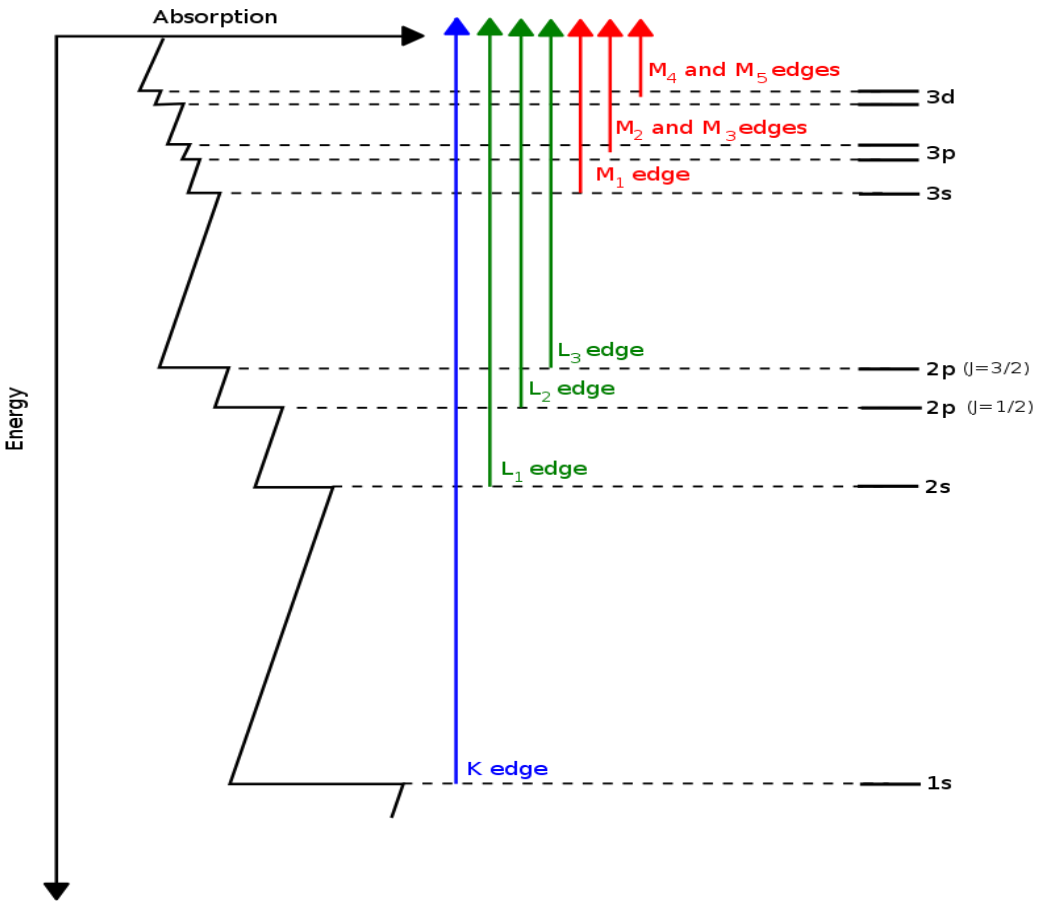
Types of Instrumental Method

Signal	Example method
Radiation emission	Emission spectroscopy (X-ray, UV, visible), fluorescence, phosphorescence, luminescence
Radiation absorption	Absorption spectrosc spectrophotometry, photometry, NMR electron spin resonance
Radiation Scattering	Raman spectroscopy
Radiation refraction	Refractometry

Radiation diffraction	X-ray and Electron diffraction method
Radiation rotation	Polarimetry
Electrical potential	Potentiometry
Electrical charge	Coulometry
Electrical current-	Voltammetry-amperometry- polarography
Electrical resistance-	Conductometry
Mass	Gravimetry
Mass-to-charge ratio	Mass spectrometry
Rate of reaction	Flow injection analysis

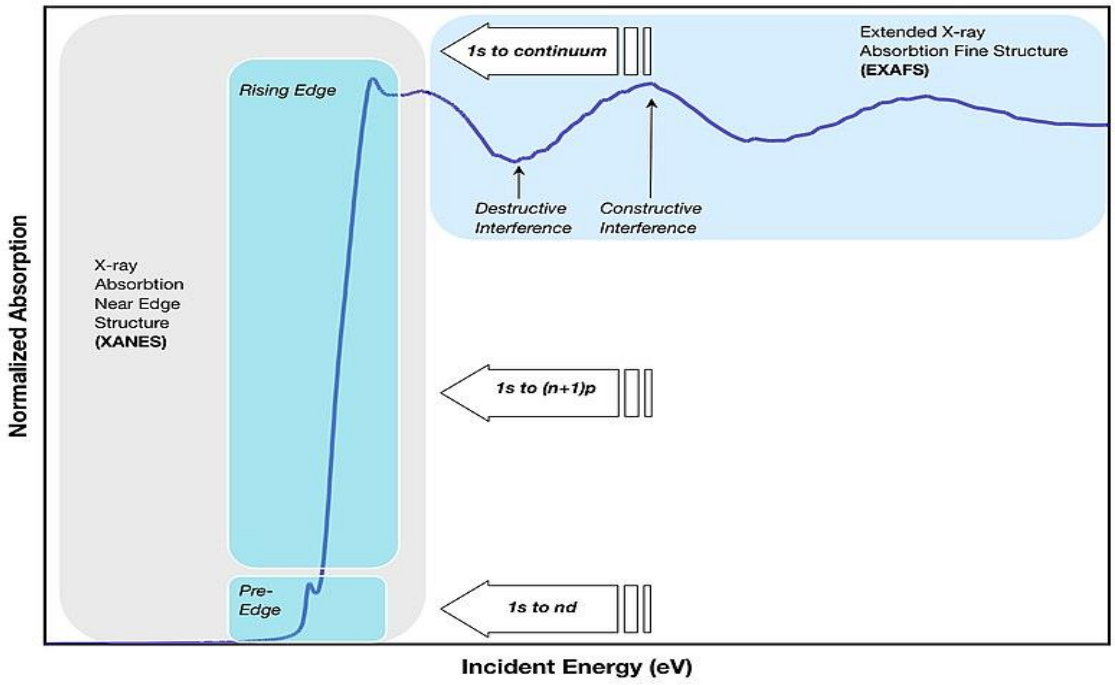
X-ray absorption spectroscopy (XAS)

X-ray absorption spectroscopy (XAS) is a widely used technique for determining the local geometric and/or electronic structure of matter. The experiment is usually performed at synchrotron radiation facilities, which provide intense and tunable X-ray beams. Samples can be in the gas phase, solutions, or solids.



XAS data is obtained by tuning the photon energy,[3] using a crystalline monochromator, to a range where core electrons can be excited (0.1-100 keV). The edges are, in part, named by which core electron is excited: the principal quantum numbers n = 1, 2, and 3, correspond to the K-, L-, and M-edges, respectively.[4] For instance, excitation of a 1s electron occurs at the K-edge, while excitation of a 2s or 2p electron occurs at an L-edge (Figure 1).

There are three main regions found on a spectrum generated by XAS data which are then thought of as separate spectroscopic techniques (Figure 2):



The absorption threshold determined by the transition to the lowest unoccupied states:
the states at the Fermi level in metals giving a "rising edge" with an arc tangent shape; the bound core excitons in insulators with a Lorentzian line-shape (they occur in a pre-edge region at energies lower than the transitions to the lowest unoccupied level);

The X-ray absorption near-edge structure (XANES), introduced in 1980 and later in 1983 and also called NEXAFS (near-edge X-ray absorption fine structure), which are dominated by core transitions to quasi bound states (multiple scattering resonances) for photoelectrons with kinetic energy in the range from 10 to 150 eV above the chemical potential, called "shape resonances" in molecular spectra since they are due to final states of short life-time degenerate with the continuum with the Fano line-shape. In this range multi-electron excitations and many-body final states in strongly correlated systems are relevant;

In the high kinetic energy range of the photoelectron, the scattering cross-section with neighbor atoms is weak, and the absorption spectra are dominated by EXAFS (extended X-ray absorption fine structure), where the scattering of the ejected photoelectron of neighboring atoms can be approximated by single scattering events. In 1985, it was shown that multiple scattering theory can be used to interpret both XANES and EXAFS; therefore, the experimental analysis focusing on both regions is now called XAFS.

Application

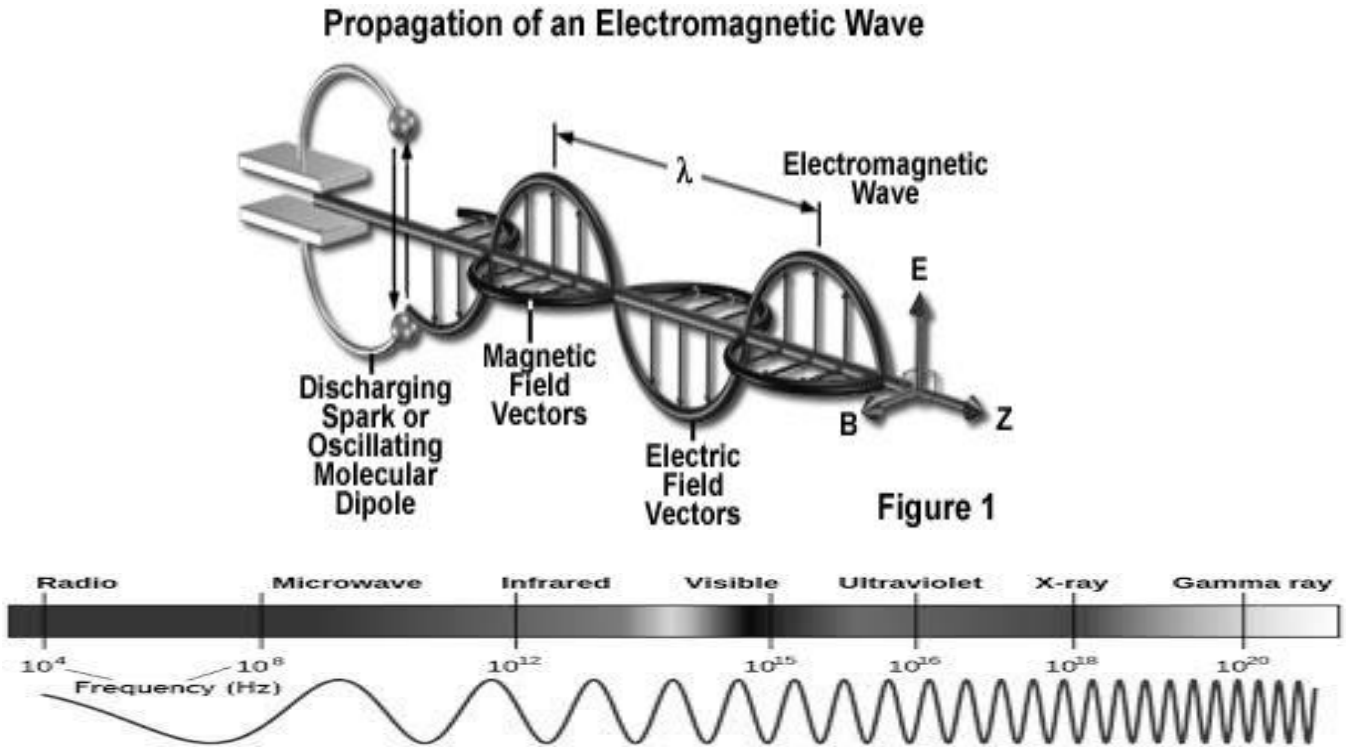
XAS is a technique used in different scientific fields including molecular and condensed matter physics, materials science and engineering, chemistry, earth science, and biology. In particular, its unique sensitivity to the local structure, as compared to x-ray diffraction, have been exploited for studying:

- Amorphous solids and liquid systems
- Solid solutions
- Doping and ion implantation materials for electronics
- Local distortions of crystal lattices
- Organometallic compounds
- Metalloproteins
- Metal clusters
- Catalysis
- Vibrational dynamics[citation needed]
- Ions in solutions
- Speciation of elements
- Liquid water and aqueous solutions
- Used to detect bone fracture
- *Used to determine the concentration of any liquid in any tank*

Lecture session 31: Topics: Electromagnetic radiation- Defintion, properties and its types- gamma rays, X-rays, ultraviolet radiation, visible light, infrared radiation, and radio waves.

Electromagnetic radiation

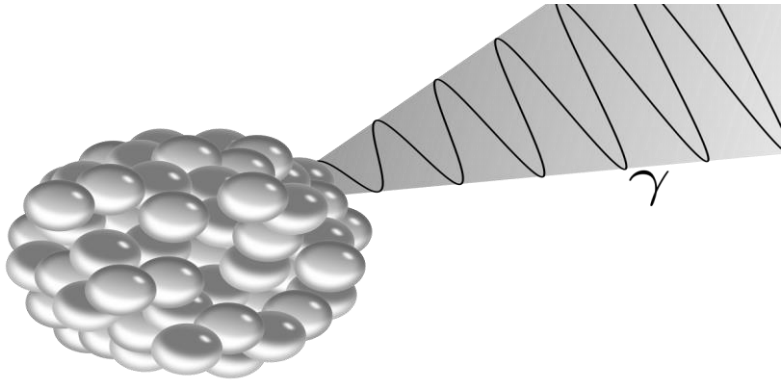
Electromagnetic radiation is a form of energy that propagates in free space or through a medium at enormous velocities, which have a dual nature. Light consists of EMRs, which travels in the form of waves. In such a wave, time-varying electric and magnetic fields are mutually linked with each other at right angles and perpendicular to the direction of motion.



Gamma ray:

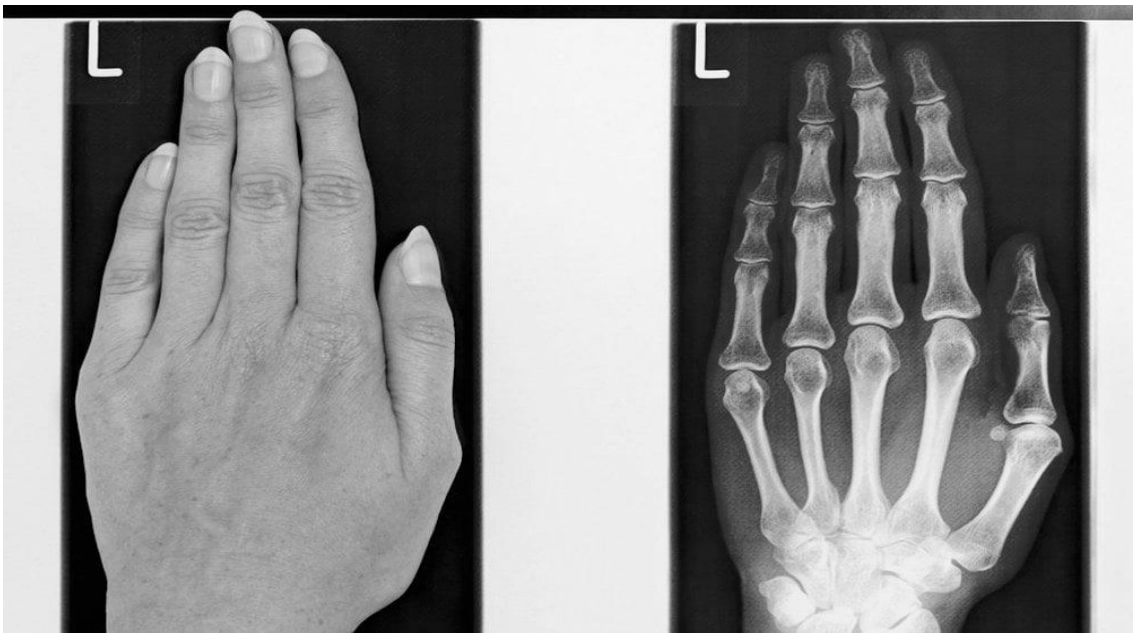
A gamma ray, also known as gamma radiation, is a penetrating form of electromagnetic radiation arising from the radioactive decay of atomic nuclei. It consists of the shortest wavelength electromagnetic waves, typically shorter than those of X-rays.

Gamma waves examples include radiotherapy, food irradiation, and quality control.



X-rays:

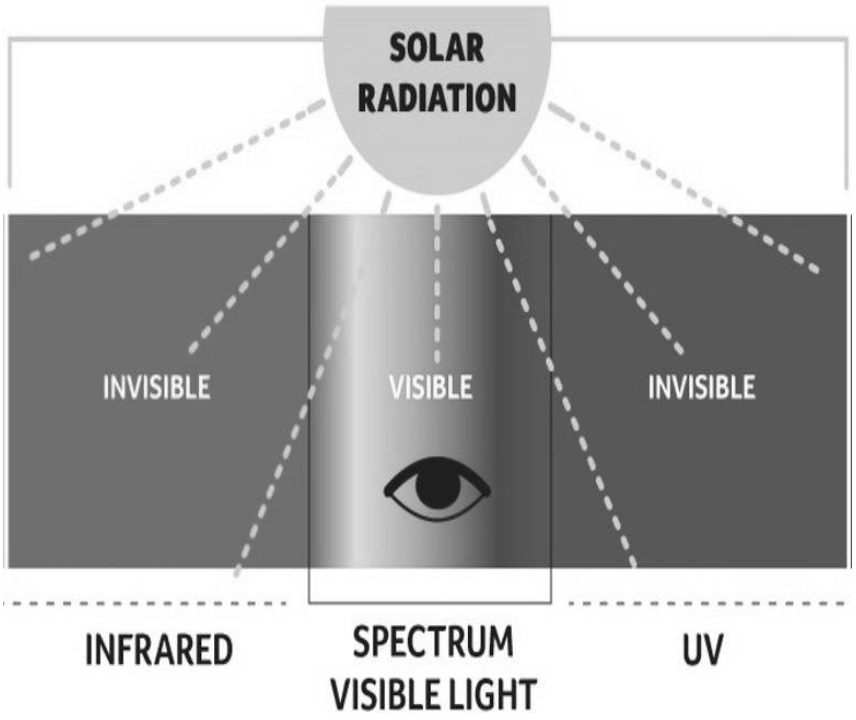
X-rays are a type of radiation called electromagnetic waves. X-ray imaging creates pictures of the inside of your body. The images show the parts of your body in different shades of black and white. This is because different tissues absorb different amounts of radiation.



Is X-ray related to chemistry?

The incident X-ray beam is scattered by these electron densities and generates a diffraction pattern that can be used to determine the crystal structure of a given chemical.
Impurities of water.

Ultraviolet is a form of electromagnetic radiation with wavelength from 10 nm to 400 nm, shorter than that of visible light, but longer than X-rays. UV radiation is present in sunlight, and constitutes about 10% of the total electromagnetic radiation output from the Sun.

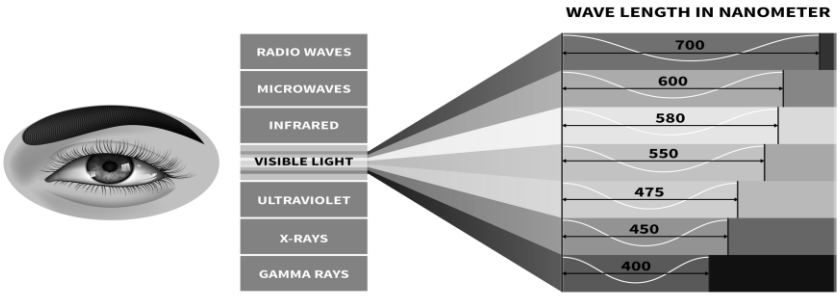


Visible Radiation

Light or "visible light" refers to the visible region of the electromagnetic spectrum – that is, the range of wavelengths that trigger brightness and colour perception in humans. It lies between UV and infrared radiation.

What is visible light and how does it travel?

Visible light — which, like all electromagnetic radiation, travels in waves — includes wavelengths between about 380 nanometers (violet) and about 740 nanometers (red). Radiation with wavelengths shorter than visible light includes gamma rays, X-rays and ultraviolet light.



Radio wave radiation

What is radiofrequency (RF) radiation? Radiofrequency (RF) radiation, which includes radio waves and microwaves, is at the low-energy end of the electromagnetic spectrum. It is a type of non-ionizing radiation. Non-ionizing radiation does not have enough energy to remove electrons from an atom.

Radio waves uses

Radio waves are electromagnetic waves with the longest wavelengths. They are used to transmit data from radios, satellites, and radar. These waves are a type of electromagnetic radiation with frequencies ranging from high 300 GHz to low as 3 kHz, though it is commonly defined as microwaves above 3 GHz

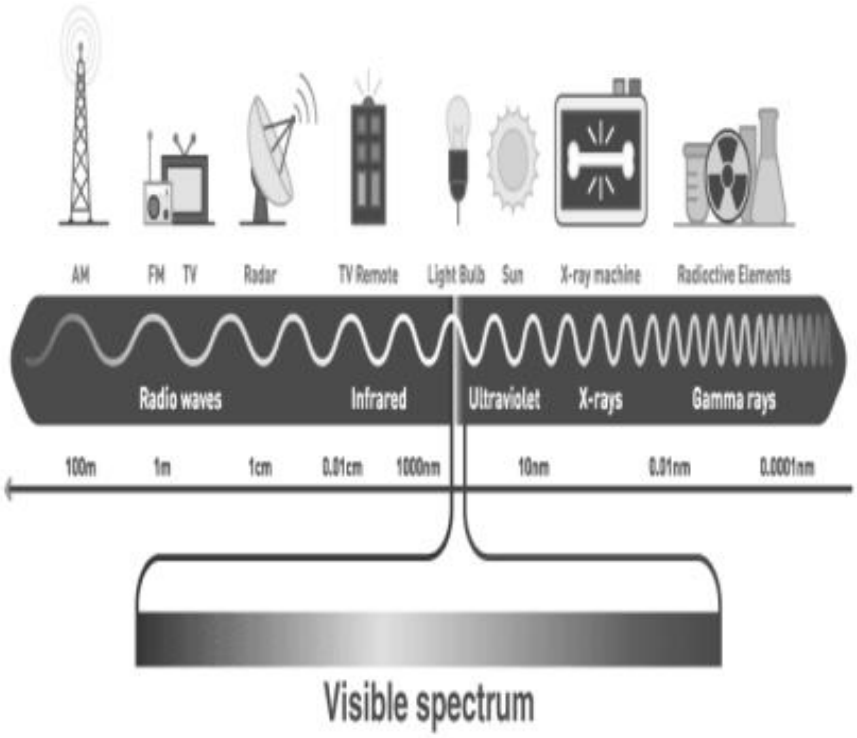


Table 6.2 Properties of alpha, beta and gamma rays

Properties	α rays	β rays	γ rays
What are they?	Helium nucleus ($_2He^4$) consisting of two protons and two neutrons.	They are electrons ($_{-1}e^0$), basic elementary particle in all atoms.	They are electromagnetic waves consisting of photons.
Charge	Positively charged particles. Charge of each alpha particle = +2e	Negatively charged particles. Charge of each beta particle = –e	Neutral particles. Charge of each gamma particle = zero
Ionising power	100 time greater than β rays and 10,000 times greater than γ rays	Comparatively low	Very less ionization power
Penetrating power	Low penetrating power (even stopped by a thick paper)	Penetrating power is greater than that of α rays. They can penetrate through a thin metal foil.	They have a very high penetrating power greater than that of β rays. They can penetrate through thick metal blocks.
Effect of electric and magnetic field	Deflected by both the fields. (in accordance with Fleming's left hand rule)	Deflected by both the fields; but the direction of deflection is opposite to that for alpha rays. (in accordance with Fleming's left hand rule)	They are not deflected by both the fields.
Speed	Their speed ranges from 1/10 to 1/20 times the speed of light.	Their speed can go up to 9/10 times the speed of light.	They travel with the speed of light.

Instrumental methods of analysis

Analytical instrumentation plays an important role in the production and evaluation of new products and in the protection of consumers and environment. It is used in checking the quality of raw materials such as substances used in integrated circuit chips, detection and estimation of impurities to assure safe foods, drugs, water and air, process optimization and control, quality check of finished products and research and development. Most of the modern instruments are microprocessor/computer controlled with user friendly software for collection of data, analysis and presentation.

Lecture session 32: Topics: UV-visible and : principles, instrumentation (Block diagram only) and applications.

Spectroscopy

It is the study of interaction of electromagnetic radiation with matter consisting of atoms and molecules. When a substance is irradiated with electromagnetic radiation, the energy of the incident photons may be transferred to atoms and molecules raising their energy from ground state level to excited state. This process is known as absorption and the resultant spectrum is known as absorption spectrum. The process of absorption can occur only when the energy difference between the two levels E is exactly matched by the energy of the incident photons as given by the equation

$E = h\upsilon = hc/\lambda$

where h is Planck's constant(6.63 x 10-34Js), υ is the frequency of incident radiation, c is the velocity of light and λ is the wavelength of the incident radiation. The excited state atoms and molecules then relax to the ground state by spontaneous emission of radiation. The frequency of the radiation emitted depends on E.

UV –Visible spectroscopy

The UV –Visible spectroscopy is also known as electronic absorption spectroscopy as molecules absorb radiation resulting in transitions between electronic energy levels. Absorption of radiation in the UV (wavelength range 190-400nm) and visible (wavelength 400–800nm) regions result in transitions between electronic energy levels.

The principle of electronic transitions and the instruments required to record electronic transitions are common for both the regions. The electronic transition occurs based on Franck Condon principle which states that electronic transition takes place so rapidly that a vibrating molecule does not change its inter-nuclear distance appreciably during the transition.

Polyatomic organic molecules, according to molecular orbital theory, have valence shell electronic energy structure as shown in Fig 3.1.

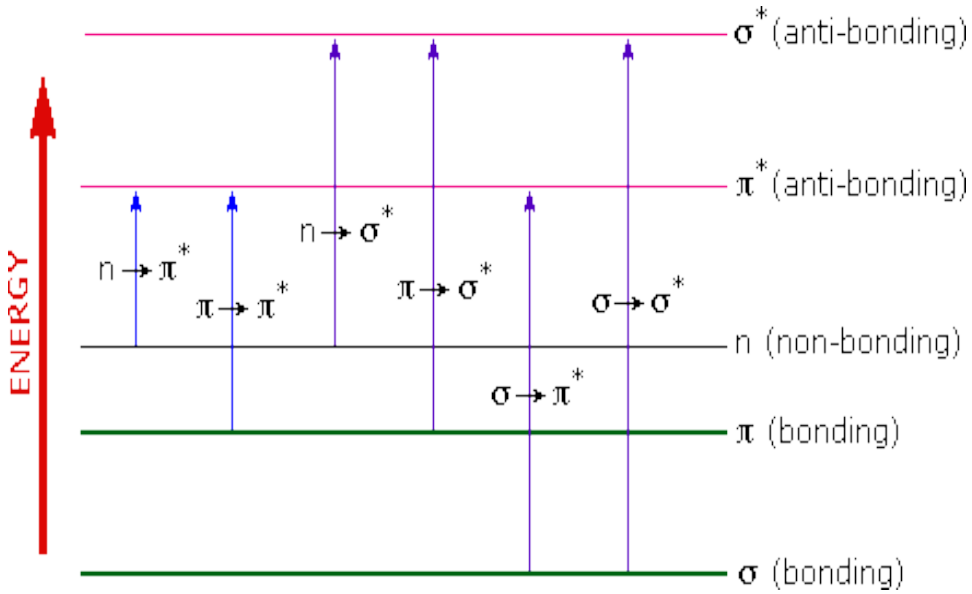
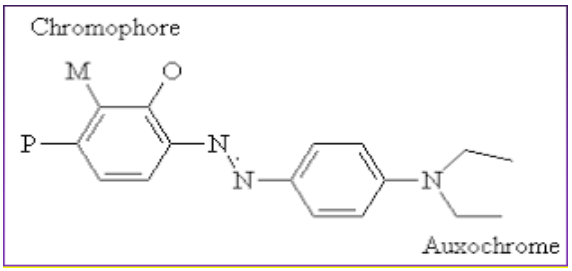


Fig.3.1 Valence shell electronic structure of polyatomic molecules and possible electronic transitions

Molecules or parts of molecules that absorb light strongly in the UV-vis region are called chromophores. These electronic transitions Where UV-vis spectroscopy becomes useful to most organic and biological chemists is in the study of molecules with conjugated π systems.
An auxochrome is a functional group of atoms with one or more lone pairs of electrons when attached to a chromophore, alters both the wavelength and intensity of absorption.



Which electronic transitions are involved in UV Visible spectroscopy?
The transition between a non-bonding and a pi star orbital, and also the transition between a pi bonding and a pi-star anti-bonding. So, if you radiate your molecule with UV visible light then you can induce these transitions. What you find is sigma to sigma transitions, or sigma to pi transitions.

In most of the organic molecules, the bonding and non-bonding molecular orbitals are filled, and the anti-bonding orbitals are vacant. The various electronic transitions that can take place include (i) σ-σ* (ii) n-σ* (iii) π-π*and (iv) n-π*. The relative energy changes involved in these transitions are in the increasing order n-π*< π-π*~ n-σ*<< σ-σ*.n-π*, π-π*and n-σ* transitions account for the absorption in 200 – 800 nm region of the electromagnetic spectrum. On the other hand, σ-σ* transition occur in vacuum UV region below 200 nm.

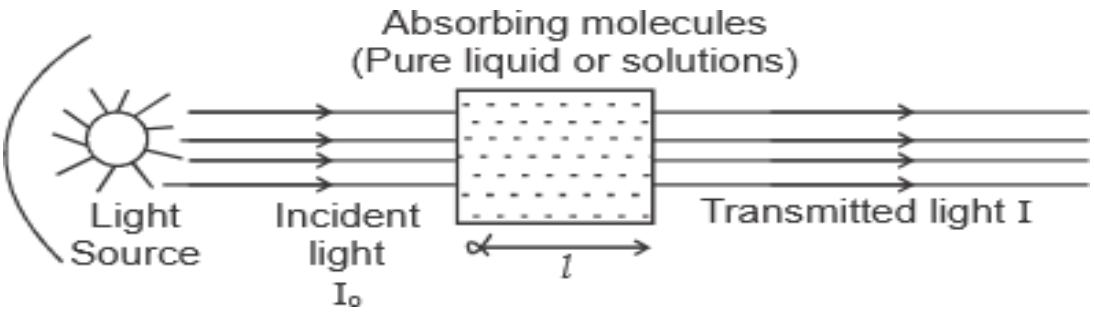
Laws of Absorption

The fraction of the photons absorbed by the molecule at a given frequency depends on

1.The nature of the absorbing molecules

2.The concentration of the molecules (C). The higher the molar concentration, the higher is the absorption of photons.

3.The length of the path of the radiation through the substance or the thickness of the absorbing medium. Larger the path length (in cm), larger is the number of molecules exposed and greater is the probability of photons being absorbed.



Lambert's law

When a monochromatic beam of radiation passes through an absorbing medium, the intensity of the transmitted radiation decreases exponentially with the thickness of the absorbing medium. The law is expressed as

$$It = Io10^{-kx} \quad (1)$$

It and Io are the intensities of the transmitted and incident beams of radiations, x is the thickness of the absorbing medium and k is a constant.

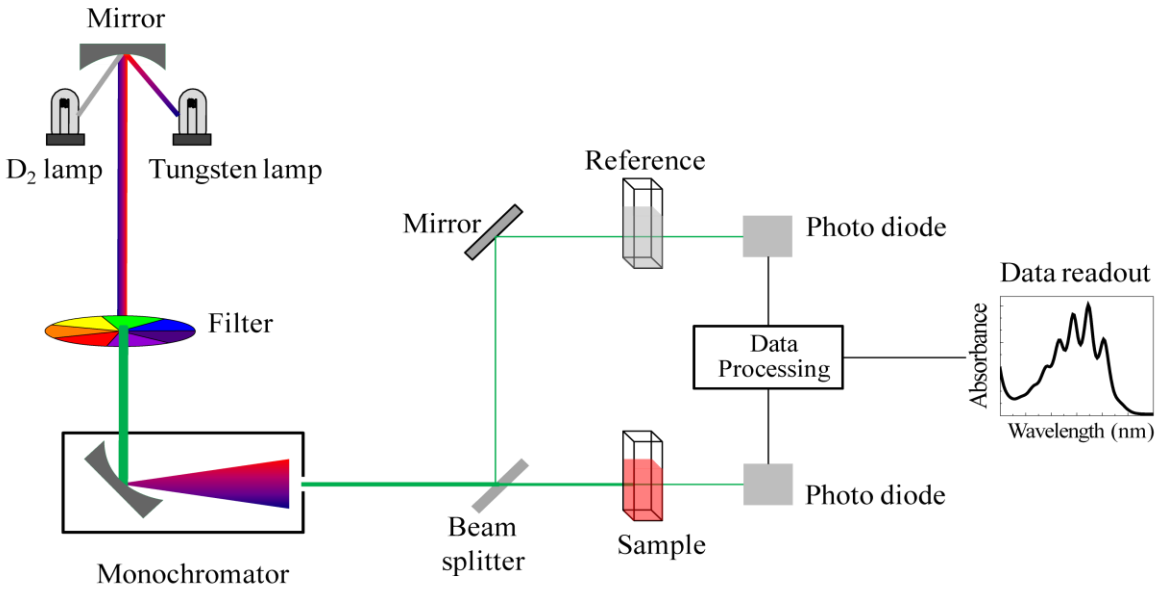
Beer's law

When a monochromatic beam of radiation passes through an absorbing medium, the intensity of the transmitted radiation decreases exponentially with the concentration of the absorbing substance. The law is expressed as

$$It = Io10 – k'C \quad (2)$$

where C is the molar concentration of the absorbing substance and k' is another constant.

Instrumentation of UV-Visible spectrophotometer



The instrument used to record the spectra of molecules is called a spectrometer. The sophisticated double beam recording UV-Visible spectrophotometer covers the entire wavelength range of 190 - 800 nm.

The basic components are

1. Source of radiation
2. Monochromator
3. Sample cell
4. Detector
5. Display/ Recorder

1.Radiation source: Hydrogen discharge lamp or deuterium lamp is used as UV radiation source. For visible light, tungsten filament lamp is used.

2.Monochromator: It disperses the polychromatic radiation from the source to a narrow range of wavelength. For UV and visible light, quartz prism or a grating is used. Two types of prisms, namely 60o Cornu quartz prism and 30o Littro prisms are employed. For visible light, a glass prism can be used.

3.Sample holder (cells or cuvettes): Sample containers should be transparent to UV and visible radiation. Cuvettes made of quartz are used for both UV and Visible region, whereas for visible light, glass cuvettes are used. Standard path length of these cuvettes is usually 1 cm.

4.Sector mirror: The monochromatic beam of radiation is split into two parallel beams by the sector mirrors which pass through the sample and reference cells and reach the detector.

5.Solvents for UV region: Electronic absorption spectra are usually recorded for solutions. Solvent used should absorb in the same region as the solute. Solvents used in the UV and visible region are water, methyl alcohol, ethyl alcohol, chloroform, hexane, etc. 95% ethyl alcohol is the most widely used solvent in UV region since it is a polar solvent, cheaper and transparent up to 210 nm.

6.Detectors: Photovoltaic cells or photo emissive cells or the more sensitive photomultiplier tubes are used to convert the incident photons into electric current.

1.λmax value is the wavelength at which absorption maximum occurs and is different for different molecules.
2.ε value (molar absorptivity) for a given concentration of the compound is related to the height of the absorption band.

The λmax and ε value depend upon the concentration and structure of the molecule and therefore used in characterization and in quantitative estimation of a compound. Unsaturated groups having n or electrons are essentially responsible for absorption and these fragments are known as chromophores. Simple chromophores such as C=C, C≡C, C≡N, N=N, C=O undergo n-π*

transitions in the short wavelength regions of UV light. Saturated groups containing hetero atoms which modify the absorption of the chromophores are called auxochromes - e.g. -OH, -Cl,-OR, NR2, etc. UV visible spectrum of benzene in ethanol is shown below.

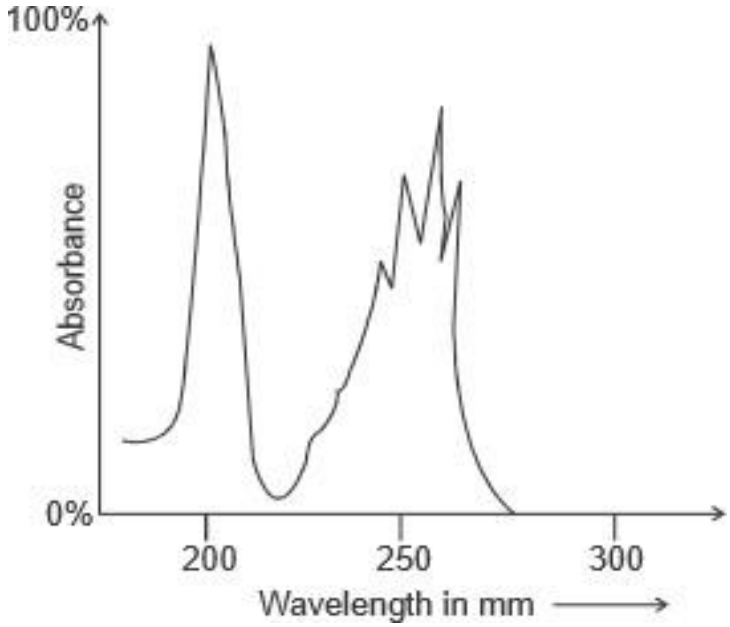


Fig.3.4. Electronic absorption spectrum of a solution of benzene in hexane (λmax = 225 nm)

Applications of UV-Visible Spectrophotometry

1. Detection of Impurities

 It is one of the best methods for determination of impurities in organic molecules. Additional peaks can be observed due to impurities in the sample and it can be compared with that of standard raw material.

 By also measuring the absorbance at specific wavelength, the impurities can be detected.

2. Structure elucidation of organic compounds

 It is useful in the structure elucidation of organic molecules, such as in detecting the presence or absence of unsaturation, the presence of hetero atoms.

3. UV absorption spectroscopy can be used for the quantitative determination of compounds that absorb UV radiation.

4. UV absorption spectroscopy can characterize those types of compounds which absorbs UV radiation thus used in qualitative determination of compounds. Identification is done by comparing the absorption spectrum with the spectra of known compounds.

5. This technique is used to detect the presence or absence of functional group in the compound. Absence of a band at particular wavelength regarded as an evidence for absence of particular group.

6. Kinetics of reaction can also be studied using UV spectroscopy. The UV radiation is passed through the reaction cell and the absorbance changes can be observed.

7. Many drugs are either in the form of raw material or in the form of formulation. They can be assayed by making a suitable solution of the drug in a solvent and measuring the absorbance at specific wavelength.

8. Molecular weights of compounds can be measured spectrophotometrically by preparing the suitable derivatives of these compounds.

9. UV spectrophotometer may be used as a detector for HPLC.

Lecture session 33: Topics: IR spectroscopy:principles, instrumentation (Block diagram only) and applications.

IR Spectroscopy

Defnition

It is the spectroscopy which deals with the infrared region (700 nm to 1000μm) of the electromagnetic spectrum with a longer wave length and lower frequency than visible light**.**

Principle

IR spectra is produced by the absorption of energy by a molecule in the infrared region and the transitions occur between vibrational levels. Hence IR spectroscopy is also known as vibrational spectroscopy
It is divided into three regions.

(i) Near IR – 12500 to 4000 cm-1
(ii) IR – 4000 to 670 cm-1
(iii) Far IR – 670 to 50 cm-1

The most useful IR region lies between 4000 to 670 cm-1

IR radiation does not have sufficient energy to induce electronic transitions like UV-Visible spectroscopy. It causes only vibrational and rotational changes. For a molecule to absorb IR radiation, two conditons must be satisfied.

(i)There must be change in the net dipole moment of the molecule during the vibration.
(ii)The energy of the IR radiation must match th energy difference between two vibrational levels.

The bonds of a molecule experience various types of vibrations. The atoms are not stationary and fluctuate continuously. Vibrational motions are defined by stretching and bending modes. There are two types of vibrations.

(i)Stretching Vibration – Symmetric and Asymmetric
(ii) Bending Vibration – (a) Inplane bending – Rocking, Scissoring,
(b) Outplane bending – Wagging and Twisting.

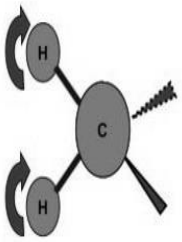
a) Symmetrical stretching:

2 bonds increase or decrease in length

sim

ii. Rocking:

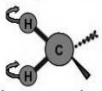
- Movement of atoms take place in the same direction.



b) Out plane bending

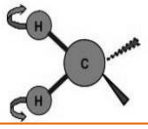
i. Wagging:

- 2 atoms move to one side of the plane. They move up and down the plane.



ii. Twisting:

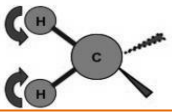
- One atom moves above the plane and another atom moves below the plane.



a) In plane bending

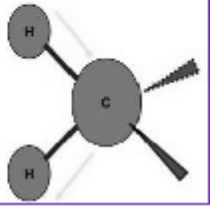
i. Scissoring:

- This is an in plane blending
- 2 atoms approach each other
- Bond angles are decrease



b) Asymmetrical stretching

in this, one bond length is increased and other is decreased.



Instrumentation/Components

The basic components of an infrared spectrophotometer are as follows.

(i) **Source** – The most common sources used are the Nernst glower and th eglobar. The Nernst glower is a tube made up of zirconium, yttrium and thorium.The globar is a cylindrical rod made up of SiC.

(ii) **Sample cells and Sampling techniques** – The sample cells are made up of Nacl and it is transparent to IR light. Gaseous samples are taken in a 10 cm long cell. Liquid samples are placed between two discs of Nacl. Solid samples are made into a mull by grinding with Nujol (mineral oil) or a pellet by grinding with KBr pellets.

(iii) **Solvents** – The solvent should be transparent to IR light and must dissolve the sample completely. Eg., CCl4, CS2, etc.

(iv) **Monochromator** – The monochromator separates polychromatic radiation into individual wavelengths. Eg., NaCl, LiF, CaF2, etc.

(v) **Detectors** – They convert the light signal into electrical signal. Photovoltaic cells, photoconductive cells, bolometers, thermocouples, etc are used as detectors.

(vi)Amplifier / Recorder – The electrical signal is amplified and converted to percentage transmittance as a function of wavenumber and recorded.

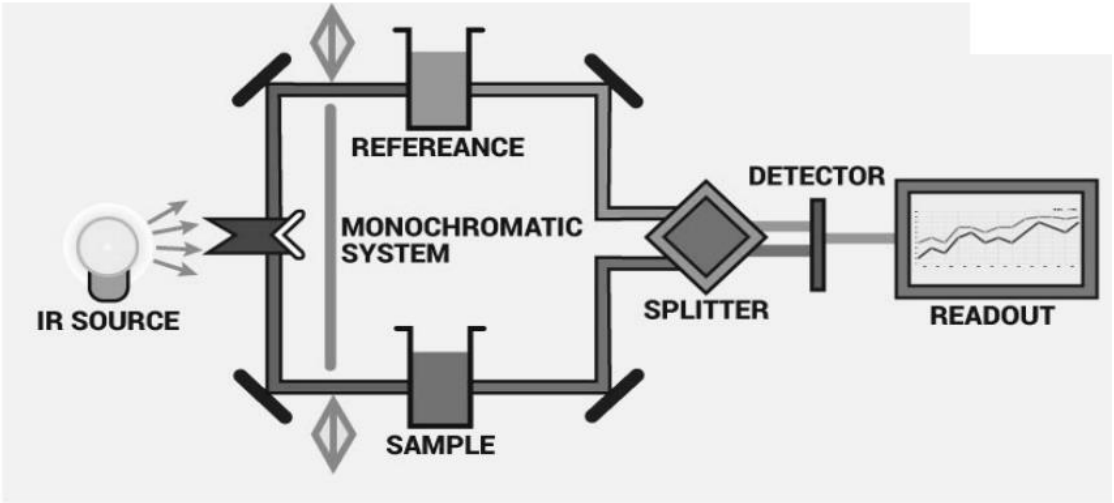


Fig 3.5 Block diagram of IR spectrophotometer

Applications

(i) Identification of functional group and structure elucidation

Entire IR region is divided into group frequency region and fingerprint region. Range of group frequency is 4000-1500 cm-1 while that of finger print region is 1500-400 cm-1.

In group frequency region, the peaks corresponding to different functional groups can be observed. According to corresponding peaks, functional group can be determined.

Each atom of the molecule is connected by bond and each bond requires different IR region so characteristic peaks are observed. This region of IR spectrum is called as finger print region of the molecule. It can be determined by characteristic peaks.

(ii) Identification of substances

IR spectroscopy is used to establish whether a given sample of an organic substance is identical with another or not. This is because large number of absorption bands is observed in the IR spectra of organic molecules and the probability that any two compounds will produce identical spectra is almost zero. So if two compounds have identical IR spectra then both of them must be samples of the same substances.

IR spectra of two enatiomeric compound are identical. So IR spectroscopy fails to distinguish between enantiomers.

For example, an IR spectrum of benzaldehyde is observed as follows. C-H stretching of aromatic ring-3080 cm-1 C-H stretching of aldehyde- 2860 cm-1 and 2775 cm-1 C=O stretching of an aromatic aldehyde 1700 cm-1 C=C stretching of an aromatic ring-1595 cm-1 C-H bending-745 cm-1 and 685 cm-1.

(ii) Studying the progress of the reaction

Progress of chemical reaction can be determined by examining the small portion of the reaction mixure withdrawn from time to time. The rate of disappearance of a characteristic absorption band of the reactant group and/or the rate of appearance of the characteristic absorption band of the product group due to formation of product is observed.

(iii) Detection of impurities

IR spectrum of the test sample to be determined is compared with the standard compound. If any additional peaks are observed in the IR spectrum, then it is due to impurities present in the compound.

(iv) Quantitative analysis

The quantity of the substance can be determined either in pure form or as a mixure of two or more compounds. In this, characteristic peak corresponding to the drug substance is chosen and log I0/It of peaks for standard and test sample is compared. This is called base line technique to determine the quantity of the substance.

Limitation

a.Molecular weight cannot be predicted.

b.It is frequently non- adherence to Beers law of complexity spectra.

c.IR spectroscopy does not provide information of relative position of different functional group on a molecule.

Lecture session 34: Topics: Separation techniques chromatography: Gas chromatography- liquid chromatography-definition, techniques and application.

Chromatography is an essential analytical technique used for separating, identifying, and purifying mixture components for quantitative and qualitative analysis. Chromatography is based on the principle that-
Each element migrates at a different rate through the stationary phase under the influence of the mobile phase. The stationary phase is a porous solid like silica or alumina, whereas the mobile phase is solvent or gas.

Components of Chromatography
Based on the above approach, we can classify chromatography into three components.

Stationary Phase: It is the phase in which the mobile phase passes. It is generally a solid phase or is a layer of liquid adsorbed on the concrete surface.
Mobile Phase: It is either a liquid or gaseous phase chromatography system.
Separated molecules.

What is Liquid Chromatography?

Liquid chromatography (LC) is an analytical technique in which the mobile phase is a liquid.
It is carried out either in a column or a plane.
The sample with the mobile phase is passed through a column or plane, accompanied by the stationary phase. Due to differences in adsorption, size, partitioning and ion exchange, different solutes will interact with the stationary phase to a different extent.Thus, components are separated by utilising these differences.

Liquid Chromatography is an effective technique to separate mixtures. It is especially effective when the mixture is coloured. Even if the mixture is not coloured, we can visualise it using several visualisation methods like irradiating it with ultraviolet light.

We can classify liquid chromatography into four types based on the components of chromatography:

(i) Reversed-Phase Chromatography
(ii) Normal Phase Chromatography
(iii) Ion Exchange Chromatography
(iv) Size Exclusion Chromatography

(i) **Reversed-Phase Chromatography** retains a non-polar stationary phase and polar mobile phase.

Hydrophilic molecules in the polar mobile phase are transported to the column and eluted, whereas hydrophobic molecules of the polar mobile phase are absorbed in the stationary phase.Organic solvents, aqueous buffers, and a mixture of water are used to elute compounds in a reversed-phase column.In it, the alkyl chain is covalently bonded to stationary phase particles.

Charged analytes can be separated through reverse-phase chromatography by ion pairing.

(ii) **Normal Phase Chromatography** retains a polar stationary phase and a non-polar mobile phase.

Silica and organic compounds with cyano and amino groups are commonly used in the stationary phase. Organic solvents like hexane or heptane mixed with polar solvents like chloroform, isopropanol and ethyl acetate are commonly used polar stationary solvents.

Normal Phase Chromatography is generally used to separate chiral compounds, cis-trans isomers, geometric isomers and water-sensitive compounds.

The less polar compounds are eluted first in normal phase chromatography, whereas more polar ones last.

Ion Exchange Chromatography is generally used to separate compounds differing in functional groups.Ion Exchange Chromatography is also used to separate isomers.

(iii) **Ion Exchange Chromatography** retains the ionic stationary phase and aqueous buffer as the mobile phase.

Ion exchanger Chromatography separates ions and polar compounds based on their affinity to the ion exchanger.It can be sub-categorised into two types, ie.

(i) Cation Exchange Chromatography

(ii) Anion Exchange Chromatography

A cation exchange chromatography retains positively charged cations, while an anion exchange chromatography retains negatively charged anions.

Ion Exchange Chromatography is generally used to separate organic and inorganic ions from an aqueous solution.

Ion Exchange Chromatography has the highest matrix tolerance and predictable elution patterns.

A major limitation of ion-exchange chromatography is that it is limited to the ionisable group.

(iv)Size Exclusion Chromatography is also known as Gel Filtration Chromatography.

In Size Exclusion Chromatography, molecules are separated, based on their size and the pore size of the stationary phase.

In some cases, molecules are also separated based on their molecular mass.

In Size Exclusion Chromatography, more giant molecules are eluted first, whereas smaller molecules are last.

Size Exclusion Chromatography is used to separate industrial polymers and proteins.

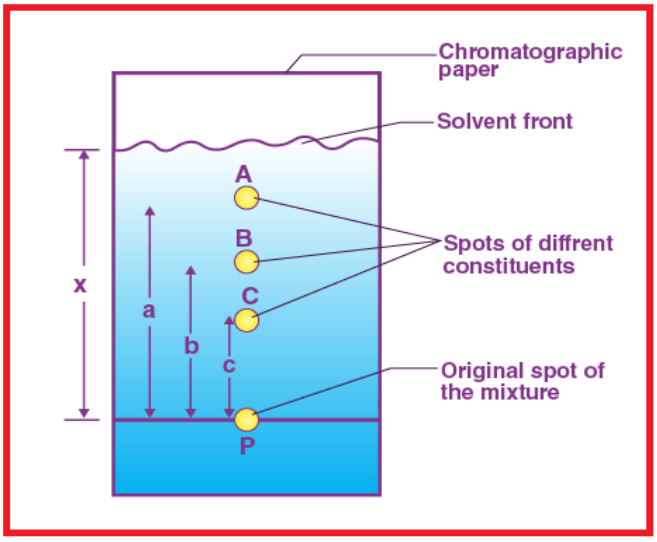
Rf stands for Retention factor.
It is the ratio of distance travelled by the analyte to that of the solvent front.
It is the characteristic identification value of analytes.
Compounds can be analysed and identified based on their Rf value.
Rf = Distance travelled by analyte/ Distance travelled by solvent.
For example,

Rf value of substances A, B, and C will be as given under

Rf value of A= a/X

Rf value of B= b/X

Rf value of C=c/X



High-performance liquid chromatography, formerly referred to as high-pressure liquid chromatography, is a technique in analytical chemistry used to separate, identify, and quantify each component in a mixture.

Principles

Chromatography is used to separate proteins, nucleic acids, or small molecules in complex mixtures. Liquid chromatography (LC) **separates molecules in a liquid mobile phase using a solid stationary phase**. Liquid chromatography can be used for analytical or preparative applications.

Basic function

HPLC separates compounds dissolved in a liquid sample and allows qualitative and quantitative analysis of what components and how much of each component are contained in the sample.

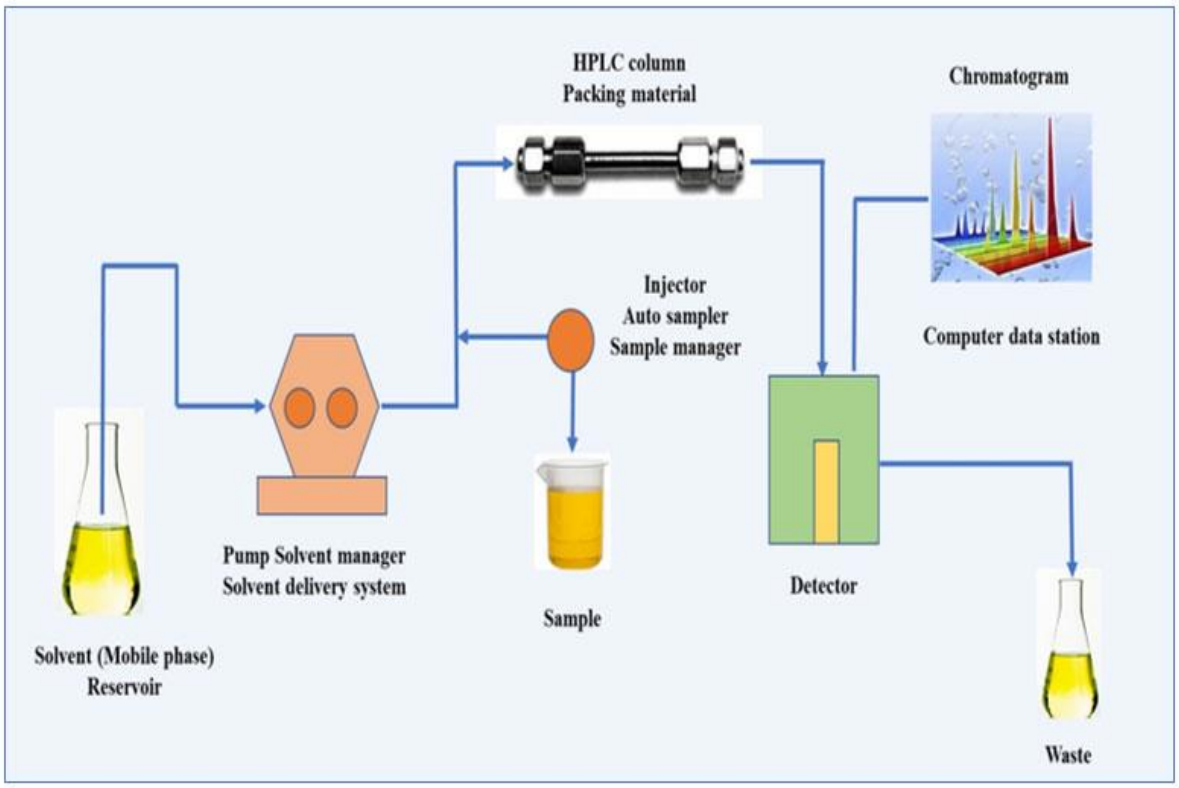


Figure 1: Schematic Representation of High-Performance Liquid Chromatography [15]

Advantages of Liquid Chromatography

Liquid Chromatography is a cheap separatory technique to separate mixtures.
The flow of the mobile phase, detection of separation bands and collection of each component is done manually.
Glass wear used for liquid chromatography is readily available and inexpensive too.

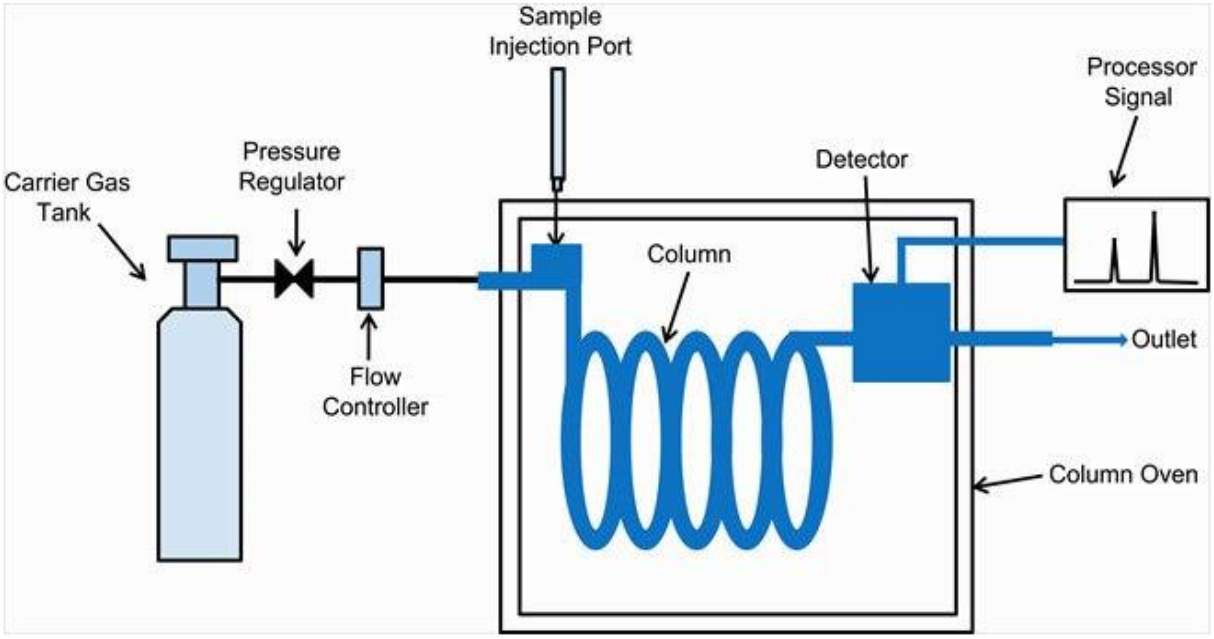
Applications of Liquid Chromatography

Liquid chromatography is used for testing ink samples.
It is used in environmental analysis and cleanliness testing.
It is used in food analysis and quality control
It is used in the pharmaceutical industries and chemical industries.

It is used in forensic science and hospitals.

Gas chromatography is the process of separating compounds in a mixture by injecting a gaseous or liquid sample into a mobile phase, typically called the carrier gas, and passing the gas through a stationary phase. The mobile phase is usually an inert gas or an unreactive gas such as helium, argon, nitrogen or hydrogen.

Principle of gas chromatography: The sample solution injected into the instrument enters a gas stream which transports the sample into a separation tube known as the "column." (Helium or nitrogen is used as the so-called carrier gas.) The various components are separated inside the column.
Working processof GC



How does gas chromatography work?

For having a hold on how does chromatography works, we need to be aware of the individual components of a GC chromatogram or GC Chromatograph.
The main components are:
Mobile phase
In gas chromatography, usually, three types of gases are employed namely –

Carrier gas – This is needed for the transfer of the injected sample to the separation column. They are also responsible for the subsequent transfer of separated components to the detector.Common examples: Nitrogen, helium, or hydrogen
Fuel gas – They support the flame in Flame ionization detector (FID) detector such as Hydrogen.
Zero air – These are the purified air that plays the role of oxidant to support the combustion of flame in the detector. Before being led to the gas chromatographic system, the above three are intermixed in the desired proportion.
Sample injector

The injector is a heated block where the sample is injected. Through the carrier gas stream, the sample is spontaneously vaporized and led to the column.
With the help of a gas-tight syringe, the liquid sample mixtures are injected whereas, with the help of automated injection valves, the gaseous mixtures are injected.
Column
This is filled with the stationary phase or its walls are covered with a liquid adsorbent. This is done for selective absorbance and retention of the sample components.
Commonly used: Packed columns and Capillary columns (More popular)
Component of a Column – Oven
The column is enclosed by a column oven which is responsible for maintaining a constant temperature during isothermal operation. This temperature when temperature programming is needed can be increased in a controlled way for acquiring effective separation of mixture components possessing different volatilities.
Detector
This is employed for the identification and quantification of components.
Here, the regions of individual peaks created relate to their concentrations and their retention times are representative of their identity.
Common examples: Flame ionization detector, Thermal conductivity detector (TCD), and Electron capture detector (ECD).
Data system
It is a set of dedicated software that provides control over many important operational parameters like injection sequence, wash cycles, over-temperature control, the flow rate of gases, detector wavelength, etc. Simultaneously, the data station calculates and displays the parameters.

Applications
Since the discovery of the gas chromatographic system, the areas of Gas chromatography applications is ever-increasing which includes:
(iii) Pharmaceutical industry
(iv) Research
(v) Medical and Forensic
(vi) Environmental monitoring (both inside laboratories, and natural water bodies)
(vii) Petroleum refining and petrochemicals
(viii) Edible oils
(ix) Flavors, beverages, and the food industry
(x) Fragrance industry (Cosmetics)
(xi) Polymers and plastics
(xii) Pesticides

Lecture session 35: Topics: Importance of column technology (packing, capillaries)-working principle and its application.

What is Column Chromatography?
In chemistry, Column chromatography is a technique which is used to separate a single chemical compound from a mixture dissolved in a fluid.

Column chromatography separates substances based on differential adsorption of compounds to the adsorbent as the compounds move through the column at different rates which allows them to get

separated in fractions. This technique can be used on a small scale as well as large scale to purify materials that can be used in future experiments. This method is a type of adsorption chromatography technique.

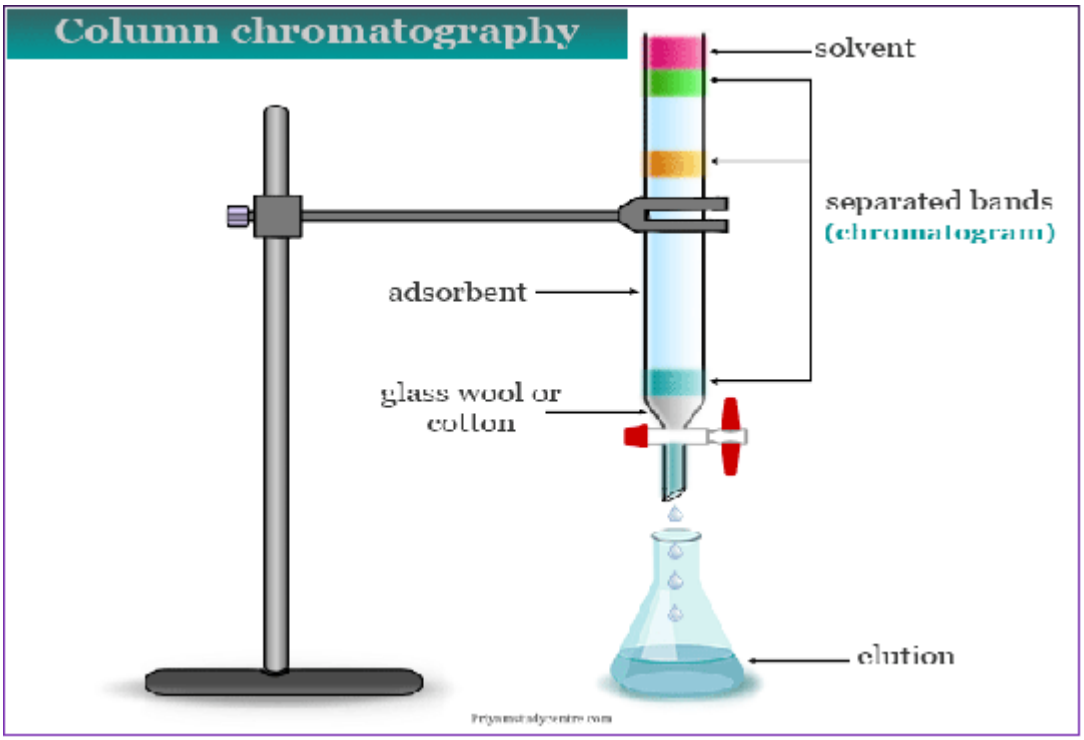
Column Chromatography Procedure
Before starting with the Column Chromatography Experiment let us understand the different phases involved.

Mobile phase – This phase is made up of solvents and it performs the following functions:

It acts as a solvent-sample mixture that can be introduced in the column.
It acts as a developing agent – helps in the separation of components in the sample to form bands.
It acts as an eluting agent – the components that are separated during the experiment are removed from the column
Some examples of solvents used as mobile phases based on their polarity are – ethanol, acetone, water, acetic acid, pyridine, etc.
Stationary phase – It is a solid material which should have good adsorption properties and meet the conditions given below:

Shape and size of particle: Particles should have a uniform shape and size in the range of 60 – 200μ in diameter.
Stability and inertness of particles: high mechanical stability and chemically inert. Also, no reaction with acids or bases or any other solvents was used during the experiment.
It should be colourless, inexpensive and readily available.
Should allow free flow of mobile phase
It should be suitable for the separation of mixtures of various compounds.

Why is column chromatography important?
Image result for column technology importance
Column Chromatography is used to isolate active ingredients. It is very helpful in separating compound mixtures. It is used to determine drug estimation from drug formulations. It is used to remove impurities



Principle

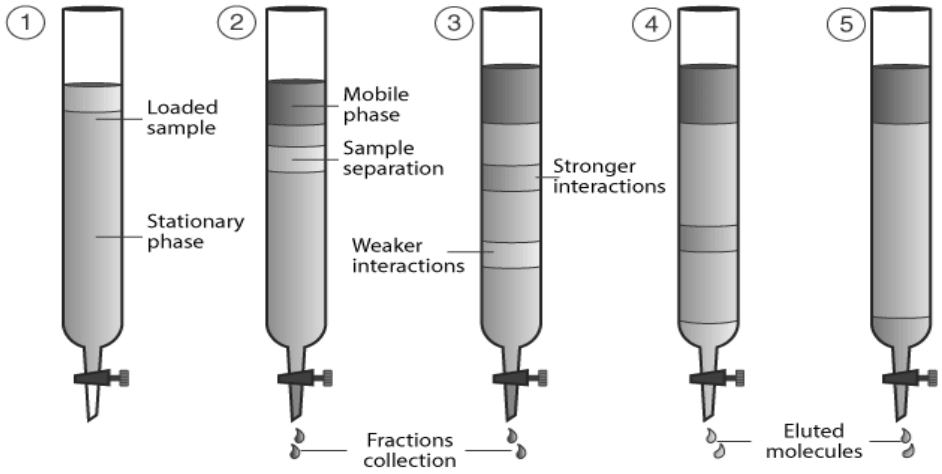
When the mobile phase along with the mixture that needs to be separated is introduced from the top of the column, the movement of the individual components of the mixture is at different rates. The components with lower adsorption and affinity to the stationary phase travel faster when compared to the greater adsorption and affinity with the stationary phase. The components that move fast are removed first whereas the components that move slowly are eluted out last.

The adsorption of solute molecules to the column occurs in a reversible manner. The rate of the movement of the components is expressed as:

Rf = the distance travelled by solute/ the distance travelled by the solvent

Rf is the retardation factor.

COLUMN CHROMATOGRAPHY



Types of Column Chromatography:

1. Adsorption column chromatography – Adsorption chromatography is a technique of separation, in which the components of the mixture are adsorbed on the surface of the adsorbent.

2. Partition column chromatography – The stationary phase, as well as mobile phase, are liquid in partition chromatography.

3. Gel column chromatography – In this method of chromatography, the separation takes place through a column packed with gel. The stationary phase is a solvent held in the gap of a solvent.

4. Ion exchange column chromatography – A chromatography technique in which the stationary phase is always ion exchange resin.

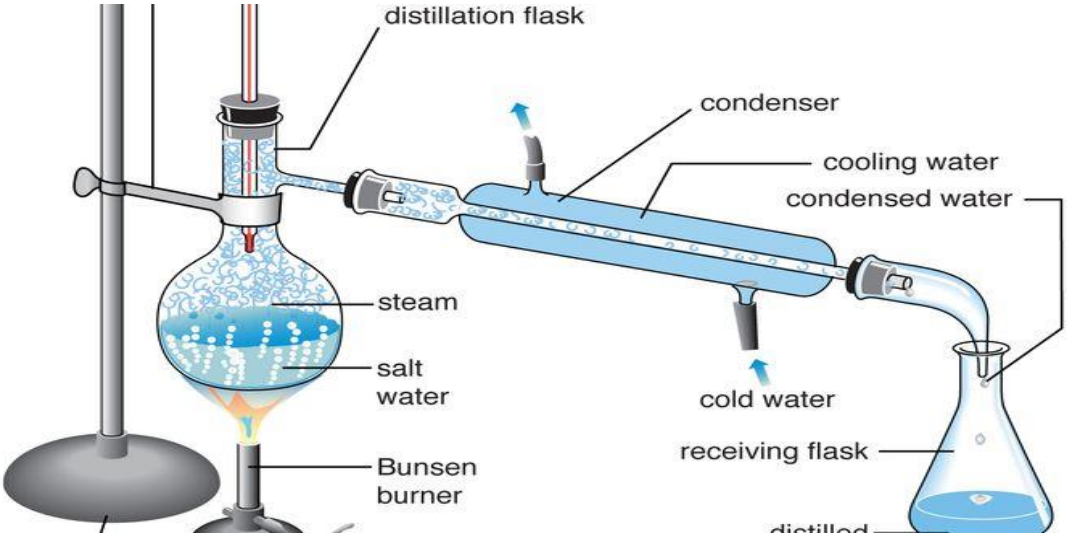
Applications

Column Chromatography is used to isolate active ingredients.
It is very helpful in separating compound mixtures.
It is used to determine drug estimation from drug formulations.
It is used to remove impurities.
Used to isolate metabolites from biological fluids.

Lecture session 36: Topics: Separation based on increasing number of factor (volatility, solubility, interactions with stationary phase, size).

Separation based on Volatility

The solution is heated in the flask. The solvent boils, becoming a vapour, which travels to the condenser. Here it is cooled and condenses, collecting as a pure liquid called the distillate. What remains in the flask is the same mixture, but containing less solvent – a more concentrated solution.



Distillation is a widely used technique in chemical analysis for characterizing materials by establishing an index of purity and for separating selected components from a complete matrix.

The technique is even more widely used in preparative chemistry and throughout manufacturing industry as a means of purifying products and chemical intermediates.
Distillation operations differ enormously in size and complexity from the semimicro scale to the 'thousands of tons per annum' production operations. For analytical purposes the scale employed is usually bench-level.

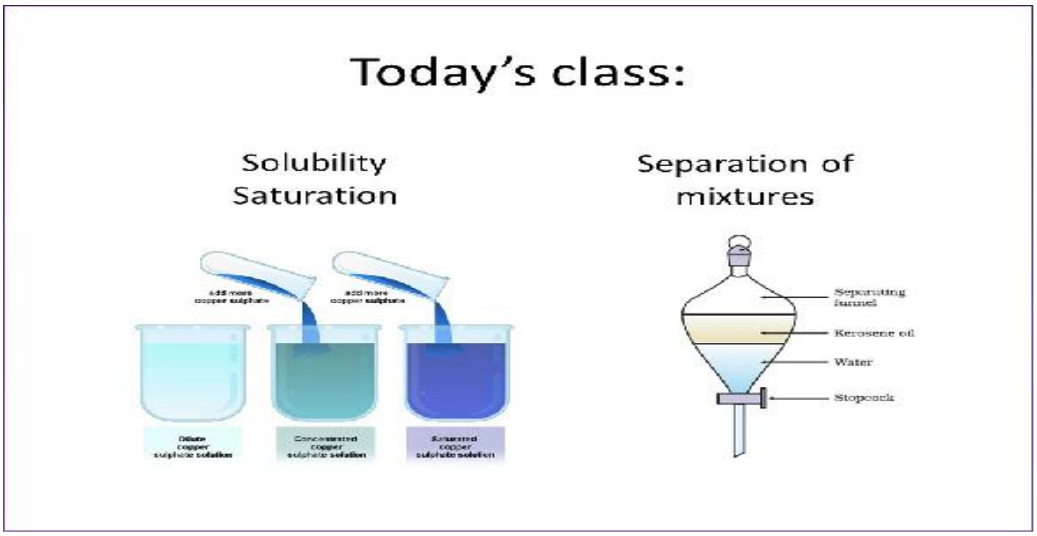
Distillation is the process that occurs when a liquid sample is volatilized to produce a vapor that is subsequently condensed to a liquid richer in the more volatile components of the original sample.
The volatilization process usually involves heating the liquid but it may also be achieved by reducing the pressure or by a combination of both. This can be demonstrated in a simple laboratory distillation apparatus comprising a flask, distillation head, condenser, and sample collector (Figure 1)
. A thermometer is included in the apparatus as shown to monitor the progress of the operation. In its simplest form this procedure results in a separation into a volatile fraction collected in the receiver flask and a nonvolatile residue in the distillation flask.
When a distillation column is incorporated in the equipment (Figure 2), the evaporation and condensation processes occur continuously. This results in a progressive fractionation of the volatiles as they pass up the column.
The most volatile components emerge from the top of the column initially and the less volatile components emerge later. By changing the receivers throughout the course of the distillation a separation or fractionation is effected. Eventually, all the volatiles will have passed over into the sample collectors and any involatile residue present will remain in the distillation flask.

Solubility

Solubility is a good separation technique for different salts. Different salts have different solubility hence they can be separated. pure metals Pure metals are not separated by solubility as they are completely pure.

What separation technique is used for solubility?

Chromatography is a separation technique in which the components of a mixture are separated on the basis of the differences in their solubilities in water.



The concentration of a solution is defined as the amount of solute present in a given amount of the solution. A solution in which some more solute can be dissolved without increasing its temperature is called an unsaturated solution. Whereas a solution in which no more solute can be dissolved at that temperature is called a saturated solution. The maximum quantity of a solute that can be dissolved in 100 grams of a solvent at a particular temperature is known as the solubility of the solute in that solvent at that temperature.

The solubility of a solid in a liquid generally increases on increasing the temperature, and decrease on decreasing the temperature. It remains unaffected by changes in pressure. The solubility of a gas in a liquid generally decreased on increasing the temperature, and increased on decreasing the temperature. In contrast, it increase on increasing the pressure, and decrease on decreasing the pressure. For example, when water is heated, air dissolved in water comes out in the form of tiny bubbles. This shows that solubility of air (gas) in water (liquid) decrease with increase in temperature. When a soda water bottle is opened, the pressure decreased and carbon dioxide gas dissolved in water escapes producing a fizz. This shows that solubility of a gas in a liquid decreases on decreasing the pressure.

A mixture of two solids cab be separated by one of the following methods

(a) Use of suitable solvent: A mixture of sugar and sand can be separated by adding water as the solvent which dissolve sugar but not sand. Filtration of the solution leaves sand the filter paper. Evaporation of water from the filtrate gives sugar.

(b) Sublimation: The process of sublimation is used to separate the component which sublimes on heating from the one which does not. Thus, naphthalene, which sublimes, can be easily separated from sodium chloride by this method.

(c) Use of magnet: Iron is attracted by a magnet. Therefore, it can be separated from other components of a mixture with the help of a magnet. In factories, scrap iron is separated from a heap of waste material with the help of electromagnets fitted to a crane.

A mixture of a solid and a liquid can be separated by one of the following methods

(a) Filtration: Filtration is used to separate insoluble substance from a liquid, e.g., a mixture of sand and water can be separated by filtration. Different kinds of filters can be used. e.g., filter paper, wire-mesh, cotton, muslin cloth or a layer of sand. Used tea leaves are separated from prepared tea by filtration, using a tea strainer. Drinking water is filtered using water filters.
(b) Centrifugation: The method of centrifugation is used to separate suspended particles from a liquid. The mixture is separated by rotating it at high speed in a centrifuge. This process is used in dairies to separate cream from milk.
(c) Evaporation: A solid substance dissolved in a solvent can be separated by the process of evaporation. The dissolved substance is left as a solid residue after the solvent has evaporated. The solvent itself cannot be recovered by this method. Common salt is obtained from sea water by evaporation. Sea water. Trapped in shallow lakes called lagoons, is subjected to the heat of the sun. Water evaporation leaving behind salt as a solid. If any impurities are present in the dissolved solid, they would still be present after it's recovered after its recovery by evaporation.

(d) Crystallisation: When a hot, concentrated solution of a substance is allowed to cool slowly, crystals of pure solid are formed, while impurities remain dissolved in the solvent. This process is called Crystallisation. The crystals can be separated by filtration. An impure sample of compound, like copper sulphate or alum, can be purified by crystallization.

(e) Chromatography: Two or more dissolved solids present in a solution in very small amounts can be separated and identified by chromatography. Though these substances are soluble in the same solvent, yet their solubilities may different. The components of the mixture dissolved in a solvent, move to different extents on an adsorbent material (filter paper, silica gel, etc.) and thus get separated.

Interacts more with the stationary phase?

The solvent acts as the mobile phase along a polar paper stationary phase. Polar compounds will interact more with the paper, travelling slowly, while nonpolar compounds will interact more with the solvent, travelling more quickly.

How does the size of molecules affect chromatography?
Larger molecules take longer to move up the chromatography paper or TLC plate, whereas smaller molecules are more mobile. Likewise, the polarity of the molecules can affect how far the spots travel, depending on the type of solvent used.
How does size affect separation in chromatography?
Column length and particle size of stationary phase play a crucial role in separation efficiency and the column back pressure of HPLC columns. Longer columns and smaller particle size contribute to improved separation efficiency but at cost of increased column backpressure.